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THE PRINCIPLES OF MOTOR FUEL PREPARATION AND APPLICATION

THE PRINCIPLES OF MOTOR FUEL PREPARATION AND APPLICATION

VOLUME II

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THE PRINCIPLES OF MOTOR FUEL PREPARATION & APPLICATION

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VOLUME I

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FOREWORD

I HAVE special pleasure in writing this foreword because I have long known the Authors and have taken a great interest in their publications on petroleum subjects.

It is rather remarkable, in view of the great importance of the subject with which they deal, that so few authoritative text-books have been devoted to it, and indeed this applies broadly to the subject of petroleum technology as a whole. It is very true that the state of flux within the Industry, the astonishing development of new technique and the demand for new and improved products involving the rapid obsolescence of so many processes, make it difficult to get anything but a fleeting glimpse of the march of progress. The authors have presented a work on the subject of motor fuels that contains not only very complete descriptions of present-day technique but includes also discussions of problems that will undoubtedly arise in the future.

The basic attitude of the book is directed to the modern high speed, high efficiency, internal combustion engine which has revolutionised demands for motor fuel. Partly due to the incidence of taxation, partly due to its inherent efficiency, this type of engine has undoubtedly come to stay, and the fuelling of it has set a variety of problems that are by no means solved to-day. Along with this has come a new and improved technique of engine testing, and at the moment of writing it appears that practical unanimity throughout the world has been arrived at in developing a universal engine testing procedure, which is due to the devoted efforts of special committees set up by the Society of Automotive Engineers, the American Petroleum Institute, the American Society for Testing Materials and the Institution of Petroleum Technologists. This achievement is really of the first importance, and it is probably the first time that there has been a world-wide acceptance of a testing method.

The Authors naturally and reasonably give very considerable attention to the compression ignition engine, a type of prime mover that is passing from infancy into a very healthy childhood. The general refining of motor fuels is treated in a thoroughly exhaustive way, and all the ancillary operations are discussed with a degree of completeness that has not hitherto been accorded them.

There is not the slightest doubt but that this work will be invaluable not only to the refiner and the oil industry generally, but to the consumer, and to-day every one of us comes into one or the other category.

A. E. DUNSTAN.

January, 1934.

PREFACE TO FIRST EDITION

THERE are probably few branches of technology which can show so much progress in the past few years as that covering the production of fuels for internal combustion engines. Looking back on old laboratory certificates of tests for petrols it will be seen that the tests determined were: density, distillation characteristics, colour, odour, water content, suspended matter and colour of distillation residue. Such details were considered sufficient for the evaluation of a petrol years ago, but at the present time when automotive engines operate at high efficiencies and high compression ratios such tests are inadequate. Such properties as anti-knock value and gumming tendencies are now of prime importance, while colour and odour have now lost some of their original significance.

The production of Crude Oil in the various parts of the world favoured by Nature with this valuable raw material has a fascination to technologist and layman alike. The team work of geologist, petroleum engineer, refinery chemist, business man and sometimes mathematician, to discover, produce, refine and distribute petroleum and its products may indeed be classed among the great industrial achievements.

This book, because of its length, has been divided into two volumes, of which Volume II will be issued shortly. Volume I deals with the production of motor fuels by methods of distillation, cracking, extraction from natural gas and hydrogenation. It also contains Chapters concerning the production of Benzole, various Synthetic Fuels, including Alcohols, and general Storage and Distribution. Volume II deals with the properties of motor fuels and covers such subjects as Analysis, Sulphur Contents, Gumming Properties, Volatility Requirements and Knock Ratings as well as Motor Fuel and Aviation Spirit Specifications and a Chapter on Automotive Diesel engines and Diesel fuels.

The Chapters on the distillation of petroleum to produce motor spirit, the refining of this to market demands and the development of the cracking and hydrogenation processes, whereby the crude oil is made to yield even more spirit than it originally contains, by conversion of the heavier oils, will serve no small purpose if they only bring home to the layman the vast work and capital expenditure involved in maintaining at each wayside petrol pump a constant, standard and reliable supply of motor fuel.

The Chapters describing the analysis of motor spirit will show clearly the modern trend in this subject. Previously, much painstaking research has been carried out in attempts to provide schemes for the analysis of petrols into the constituent groups of hydrocarbon series such as paraffins, naphthenes, aromatics and olefines. With the recent work on the determination of the anti-knock value of many pure hydrocarbons, it has been found that similar anti-knock value is not a common property to hydrocarbons of one main series, as this property varies with such fundamental properties of hydrocarbon individuals as length of saturated carbon chain and compactness of the molecule. It might then be asked if much of the previous work on the chemical analysis of petrols was not in vain now that the more practical tests, of anti-knock value, volatility and gumming tendency, tell nearly all that is required to be known.

The collection together of motor fuel specifications should prove of considerable value to many, as such information is usually very scattered.

The information on knock-rating and the descriptions of the development and present-day features of test engines should prove a useful portion of this book.

The special requirements of aviation fuels are given the consideration they merit and again much of this information has been collected from widely divergent sources. The position and significance of benzole is not treated at any great length as this subject has been amply treated before.

Alcohol fuels, which derive importance in many countries where intensive nationalism is the order of the day, and synthetic motor fuels, are dealt with somewhat more fully ; and the Authors' researches in this latter field have enabled them to include their own conclusions.

As automotive diesel engines are becoming competitors of petrol engines in heavy lorries and buses, no survey of motor fuels would be complete without an account of diesel engines, their fuel oils and fuel oil evaluation.

In writing this book numerous reference books and other contributions have been used freely, and to the Authors of these we desire to express our indebtedness. We also wish to record our thanks to those who have provided us with hitherto unpublished information and those who have loaned us blocks and illustrations.

The Authors are particularly indebted to Mr. L. V. Woodhouse Clark for his assistance in the Chapters on petroleum storage and on diesel engines, to Mr. T. G. Hunter for calculations on the subject of plant design especially relating to distillation and counter-current refining methods, and to Mr. Reza Fallah for his assistance in the Chapters which include heat transfer and adsorption. The Authors are

also especially indebted to Dr. A. R. Bowen for his help on the subject of possible auxiliary motor fuels, for his valuable criticism of the various Chapters, and for much valuable assistance in the preparation of the book for publication.

In conclusion, we would point out that, while we have made every endeavour to eliminate errors, it is difficult to avoid them entirely in a book of this size covering such a variety of subjects. We shall be very grateful if errors are pointed out to us, and also for any helpful criticisms of the subject matter of the book that will enable us to make the book of greater use to those for whom it is intended.

A. W. NASH,
D. A. HOWES,

Oil Engineering and Refining Department,
University of Birmingham,
July, 1934.

PREFACE TO SECOND EDITION

Since the publication of the First Edition of this book in 1934 rapid advances have been made in the production and utilisation of motor fuels, with the result that some of the material in the First Edition is now out of date and it has been considered necessary to make certain alterations and additions.

A new chapter on Pyrolysis and Polymerisation processes has been added, while the latest developments in other fields have been dealt with in the appropriate chapters.

The authors are indebted to all those who have rendered assistance in the preparation of this edition by pointing out previous errors, by supplying new information, and by loaning blocks and illustrations.

A. W. NASH.
D. A. HOWES.

December, 1937.

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Chapter I

THE PRINCIPLES AND PRACTICE OF DISTILLATION

1. Introduction.—The Base of a Crude Oil.—The object of petroleum distillation is the separation of a number of chemically related liquids of different boiling range, and the difficulty of such separation increases as the boiling points of the various components approach each other.

In describing crude petroleum frequent reference is made to the "base," i.e., basis, of the oil.[1] Many crude oils, when chilled slowly, deposit a waxy material (paraffin) and are hence described as of "paraffin base." Almost all of the petroleums first discovered in the United States were of this nature, and not until the oil industry was extended to California and along the Gulf coast was petroleum found that contained no wax, but apparently did contain certain asphaltic material. Accordingly these oils were known as "asphalt base" oils. The use of this term, however, seems unfortunate, as better grade oils of this type contain little, if any, asphalt; the descriptive term "naphthene base" now seems to be a more desirable term than "asphalt base." The term "intermediate base" is also used commonly in referring to oils intermediate in characteristics between those of paraffin and napthene base.

In a revised classification,[2] the three above classes have been retained but defined more closely. Six additional classes are also added: paraffin-intermediate, intermediate-paraffin, intermediate-naphthene, naphthene-intermediate, paraffin-naphthene and napthene-paraffin, the first term of the compound adjectives referring to the light fractions and the second to the heavy fractions. Analyses of 800 Crude Oils from the principal producing fields show about 85 per cent. to belong to the three main clases—paraffin base, intermediate base and naphthene base.

Paraffin base crudes, although they may contain a small percentage of asphaltic material, are characterised by the presence of some paraffin wax which is normally composed of hydrocarbons of the series $C_n H_{2n+2}$. These crudes often contain a high percentage of the motor spirit fraction, and yield lubricating oils of superior grade.

The asphaltic base crudes usually yield an appreciable percentage of heavy asphalt as residue, which, within recent years, has found considerable and increasing use for road making purposes.

§ 2 MOTOR FUEL PREPARATION AND APPLICATION

A mixed base crude petroleum, containing both paraffin wax and asphalt, may be reduced either to asphalt or worked up into lubricants. Many asphaltic base crudes are made to yield lubricating fractions, but these are often of poorer quality than those obtained from paraffin base oils.

It will be seen, therefore, that each class of crude oil, irrespective of the different grades, may need a different refining technique in order that the more valuable products of each may be preserved.

Paraffin base crudes are usually distilled with every endeavour to avoid overheating so that they may yield a maximum of superior lubricants, while asphaltic base crudes are usually reduced to residual fuel oil, asphalt and/or coke. Mixed base crudes must be handled according to whether a fuel oil residue or lubricants are the more desirable.

Petrol, when it is the first fraction collected in the distillation of the crude, distils between approximately 35° and 200°C. and is known as straight-run spirit. Its proportion varies considerably with the crude oil but an average figure is about 20–25 per cent.

The next main fraction, kerosene (called erroneously in this country by retailers " paraffin oil "), distils over to the limit of about 300°C., and is followed by other products, as shown in the following table.

Oil.	Fraction.	Uses.
Crude Petroleum	Gasolines (i.e., Petrols) Aviation and Motor Grades.	Internal combustion engine fuels. (Spark ignition.)
	Kerosene	
	Gas oil	Diesel or semi-Diesel oil. Compression ignition engine fuels.
	Distillate fuel oil	
	Residual fuel oil	Boiler furnace fuels.

2.—Two general distillation schemes for the separation of crude oil into its various fractions are in use, no matter what type of distillation plant may be employed. They are known as a " topping " process and a full refining process, and the resultant distillates produced in typical schemes are shown in Tables 1 and 2.

The topping scheme is usually employed when the crude yields a suitable fuel oil after the removal of lighter fractions, or where the lighter fractions may be disposed of locally.

The boiling-point diagram is usually plotted in mol fraction or mol percentage units. The employment of such units greatly simplifies the construction and use of these diagrams. The boiling-point diagram is often replaced by a simplified form, called an equilibrium diagram, which gives the relationship between the composition of the vapour and that of the liquid in equilibrium with it. Figure 2 is such a diagram for a system of the type shown in Figure 1. The equilibrium curve is easily constructed from the boiling-point diagram.

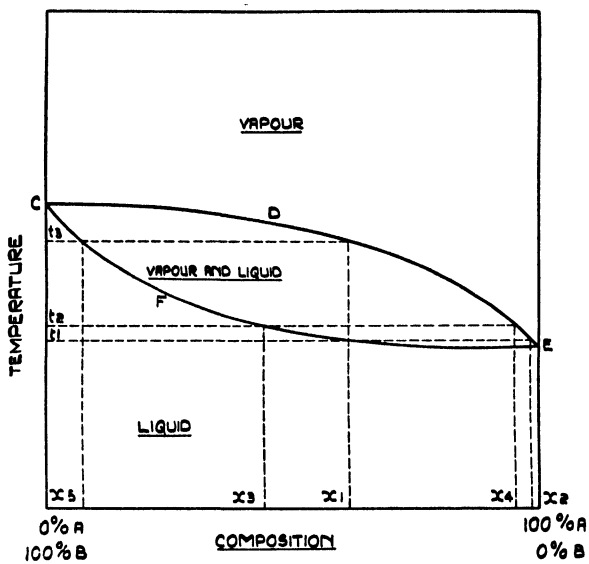


FIG. 1.—BOILING-POINT DIAGRAM

It is possible to construct the boiling-point and equilibrium curves from vapour pressure data of the two pure components A and B. The calculations are based on Raoult's Law.

Raoult's Law states that the partial pressure of a dissolved solute is the product of its vapour pressure and its mol fraction in the solution. For component A, this may be written

$$P_A = V_A x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where P_A = the partial pressure of A over the solution,
V_A = the vapour pressure of A in the pure state at the prevailing temperature
and x = the mol fraction of A in the solution.

Similarly, the partial pressure of component B can be written

$$P_B = V_B(1-x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Now, if P is the total pressure of the system,

$$\begin{aligned} P &= P_A + P_B \\ &= V_A\, x + V_B\,(1 - x) \end{aligned} \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

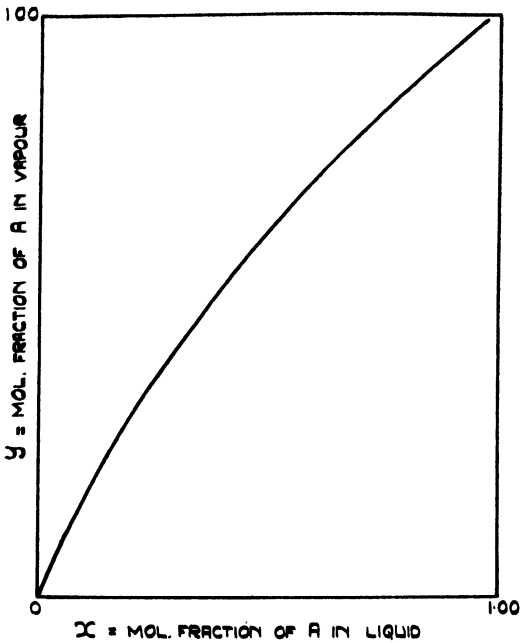


FIG. 2.—EQUILIBRIUM DIAGRAM

If y is the mol fraction of component A in the vapour, then y is equal to the ratio of the partial pressure of A to the total pressure.

$$\begin{aligned} y &= \frac{P_A}{P_A + P_B} \\ &= \frac{V_A x}{V_A x + V_B\,(1 - x)} \\ &= \frac{V_A x}{P} \end{aligned} \quad \ldots\ldots\ldots\ldots\ldots \quad (4)$$

If the mixture obeys Raoult's Law throughout the range of composition considered, and the total pressure (usually atmospheric pressure) and vapour pressures of the components are known, the boiling-point curve can be constructed by means of equations (3) and (4).

Raoult's Law applies to mixtures of chemically similar components which do not interact in any way. In the case of complex hydrocarbon mixtures, such as are met with in petroleum practice, the deviations from the law depend upon the relative composition of the

mixture and upon the similarity and dissimilarity of the components. An accuracy varying between 5–15% may be obtained when the law is applied to such mixtures.

5. The Boiling-point Diagram.—If a mixture of liquid composition x_1 is heated to a temperature t_1, some vapour will be produced. This vapour will have a composition represented on Figure 1 by point x_2 on the vapour curve CDE. This vapour is richer in the more volatile component A than the original liquid, x_1, from which it was produced. Should the temperature be raised to a point t_2, where an appreciable amount of vapour is formed, the composition of the liquid will no longer correspond to x_1, since it has been depleted of the more volatile component A, and the composition of the vapour will also have changed. The liquid will now have a composition x_3 and the vapour in equilibrium with it a composition x_4.

By raising the temperature still further, to the point t_3, the vapour will then have the same composition as the original liquid, and the liquid phase disappears almost entirely. It is obvious from the above discussion that a liquid and a vapour phase in equilibrium with each other can exist only between the temperatures t_1 and t_3. At any temperatures outside these limits one of the phases disappears, to leave only the original mixture as either a vapour or a liquid. In addition, the composition of the liquid phase can only vary between the limits x_1 and x_5. It is evident, therefore, that if the two components A and B are to be separated by distillation, either the system or the equilibrium must be changed in some way. The simplest method is to change the system itself. This can be accomplished by fractional condensation or fractional distillation.

6. Fractional Distillation.—Fractional distillation involves the successive distillation of condensed distillates.

Referring again to Figure 1, we have available a quantity of liquid with a composition represented by the point x_5, which boils under atmospheric pressure at a temperature t_3. At this temperature a certain amount of vapour with a composition x_1 is evolved. If this is condensed and removed from the system, a liquid of the same composition, that is x_1, is obtained. This liquid will begin to evolve vapour under atmospheric pressure at a slightly lower temperature t_1. If it is heated to this temperature, it will evolve a vapour with a composition of x_2. By continuing this operation of successive distillation and condensation, a distillate would eventually be obtained approaching to 100% A in composition. In an exactly similar manner, the residual liquid can undergo successive changes in composition until a product approaching to 100% B is reached.

7. Continuous Fractionation.—Assume an apparatus similar to that illustrated in Figure 3, consisting of a series of distilling vessels, V_1, V_2, V_3, etc., each vessel connected up as shown in the illustration: if vessel V_1 contains a liquid mixture of composition x_5, as in Figure 1, V_2 will contain a mixture of composition x_1: the liquids in these vessels boil at temperatures of t_3 and t_1. Now the vapour leaving V_1 at a temperature t_3, which is higher than the boiling temperature of that in V_2, gives up heat to boil the liquid in V_2, being itself partly condensed by mixing with this liquid. Since the composition of the liquid in V_2 is the same as that of the vapours from V_1 mixing with it, the mixing of the vapours and liquid will not alter the liquid composition in V_2.

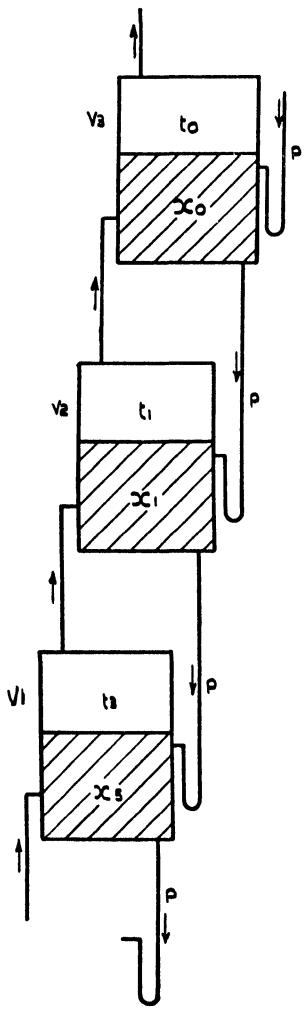


FIG. 3.—CONTINUOUS DISTILLATION DIAGRAM

As the liquid in V_2 distils it will tend to become poorer in the more volatile component A, despite the addition to it of vapour from V_1; if sufficient of it be withdrawn continuously through the pipe P, this tendency towards impoverishment in component A can be prevented, at the same time enriching the contents of V_1. Therefore, if a constant supply of vapour be furnished to the vessel V_1 a continuous fractional distillation may be carried out. This device is the basis of the fractionating column.

A simple fractionating column is illustrated in Figure 4. The column is divided into sections by means of perforated plates, and these sections are equivalent to the distilling vessels in the previous apparatus. The vapour rising from the liquid in S_1 passes through the holes in the perforated plate above it, transferring its heat to the liquid on this plate and causing it to boil. The excess liquid from the plate in the bottom of section S_2 overflows down the pipe P on to the plate in S_1. Theoretically the liquid in S_1 should be in equilibrium with the vapour above it, but, in practice, this ideal condition is never realised. The upcoming vapour passes through the liquid on the plate without coming into complete equilibrium with it. The vapour above the

plate in S_2 is, therefore, a mixture of the vapour coming from the liquid in S_2, and of the vapour passing upwards from S_1.

The fractionating column may be described as a system up which vapours are passing, and down which liquids are travelling, counter-currently to the vapour, both phases being in intimate contact with each other. The liquid in the bottom of the column will be very much richer in the less volatile component than the liquid at the top. Its action is, therefore, analogous to that of a scrubbing column where a vapour is removed from a gas by scrubbing it counter-currently with a liquid in which the vapour is soluble. This scrubbing liquid may be provided by returning a part of the condensate to the column, which returned

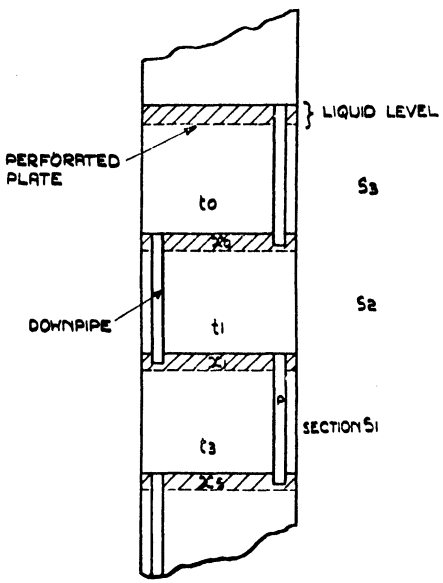


FIG. 4.—SECTION OF SIMPLE FRACTIONATION COLUMN

condensate is called the reflux. The remainder of the condensate, which may be withdrawn to a receiver, is known as the distillate. The ratio of the reflux to the distillate is termed the reflux ratio. By a consideration of the fractionating column on this basis it is possible to predict the most favourable operating conditions by means of the following analysis, due to W. K. Lewis.[3]

Such a system is illustrated in Figure 5. A vaporiser or boiler is fed continuously with a liquid of uniform composition x_o, which delivers V_o mols of vapour per unit time of composition y_o, where x refers to the mol fraction of the more volatile component in the liquid and y to that in the vapour. The liquid residue R_o, from the bottom of the column, is returned to the boiler, and has the composition x_1. V_x mols of vapour

per unit time flow from the top of the column to the condenser and have the composition y_c. R_o mols are returned to the column as reflux and V_c mols withdrawn as distillate. Both the reflux and the distillate have the same composition, $x_c = y_c$.

The input and output of the column must be equal, assuming no leaks or operating losses. Then it may be written:—

$$V_o = V_c + R_o \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

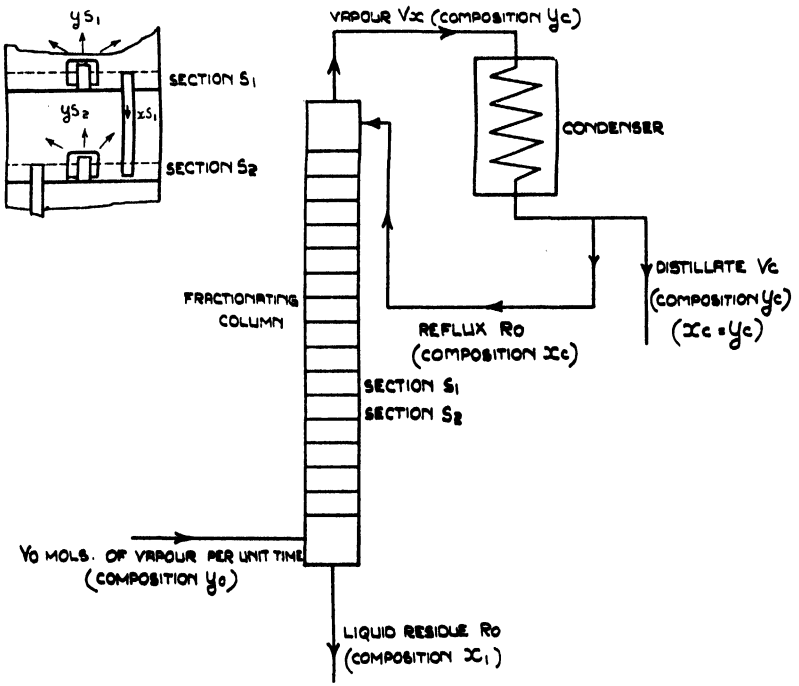


FIG. 5.—FRACTIONATING SYSTEM

Similarly, the input and output of the more volatile component must be equal. Therefore

$$V_oY_o = V_cY_c + R_ox_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

By combining equations (5) and (6), then

$$R_o = \frac{V_c(y_c - y_o)}{(y_o - x_1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The weight of distillate from the still, V_c, will be greatest if $R_o = 0$, when $y_c - y_o$ must equal zero, since V_c is a finite quantity. That is, $y_c = y_o$, or the composition of the distillate is the same as that of the vapour fed to the column. Under these conditions no fractionation occurs in the column.

In any section of the column S_1 (shown enlarged on the left of Figure 5) the composition of the vapour (yS_1) is a function of the composition of the reflux (xS_1) leaving this section and entering a lower section S_2. That is, $yS_1 = f(xS_1)$. The separation in the column between the two sections S_1 and S_2 will be greater, the greater the difference between yS_1 and yS_2. For a given value of yS_2 the value of yS_1 should be as large as possible.

Rewriting equation (7),

$$RS_2 = \frac{V_c(y_c - yS_2)}{yS_2 - xS_1}$$

$$\text{that is, } xS_1 = yS_2 - \frac{V_c(y_c - yS_2)}{RS_2} \quad \ldots\ldots\ldots \quad (8)$$

Since $(y_c - yS_2)$ is always positive, it will be seen that the greater the value of RS_2, the greater will be the value of xS_1: but $yS_1 = f(xS_1)$, so the greater xS_1, the greater will be yS_1, which is the condition specified above for maximum separation. Hence it follows that the fractionation in the column will be greater, the greater the amount of reflux employed.

This analysis has produced several important generalisations with regard to the separation efficiency of a fractionating column.

(1) *When no reflux is used in a fractionating column the fractionating efficiency is a minimum.*

(2) *When maximum reflux is used throughout the entire length of the column the fractionating efficiency is a maximum.*

(3) It follows directly from (2) above, that, in order to maintain the reflux at a maximum throughout the entire column, condensation in the column itself should be prevented. Heat losses to the outside must be avoided. *Other things being equal, a column which is adiabatic, and has its reflux returned entirely to the top of the column, gives the maximum fractionation efficiency.*

8. Fractionation of Complex Mixtures.—Fractionation has been continuously improved in commercial practice until it has become an extremely efficient operation. It was developed originally for the distillation of alcohol mixtures, but in recent years it has been extensively applied to the problems of the petroleum industry. While the separation of binary mixtures into relatively pure components is a comparatively simple problem which may be analysed mathematically, the problem of handling extremely complex hydrocarbon mixtures by similar means is, with our present knowledge or rather lack of knowledge, practically impossible. Nevertheless, methods have been developed by which it is possible to estimate by approximate means the essential requirements for such commercial plants.

§ 9 MOTOR FUEL PREPARATION AND APPLICATION

Petroleum contains a large number of substances with boiling points extending over a wide range, and with very small gaps between the boiling points of individual components. It is extremely difficult to separate, even approximately, individual substances from such a mixture by distillation. The various fractions prepared for commercial use are complex mixtures distilling over a wide temperature range. When a crude petroleum is distilled in a fractionating column, a concentration of low boiling components is obtained at the top of the column and, similarly, a concentration of high boiling constituents is obtained at the bottom: middle fractions are removed at intermediate points. It is evident, therefore, that no real separation of individual components is possible in such a system, and is, indeed, never attempted: only fractions for which there is a ready market demand are prepared. It is impossible, except under very special conditions, to make more than one sharp cut per column, therefore a continuous still should have as many columns less one than there are fractions to be separated. However, several columns may be combined into one shell so that it functions as one column, but the internal arrangements must include all the requirements for separate columns in order to achieve sharp separation. The sharpness of the separation is sometimes improved by passing each intermediate fraction so produced to a small individual column for further fractionation or treatment with steam.

9. Fractionating Devices.—One of the simplest fractionating devices, a perforated plate, has already been described. Such a plate has, however, one great disadvantage. In order to maintain the proper liquid level on each plate, the vapour velocity through the column must never be reduced below a definite value, otherwise the liquid levels on the plates are lost owing to the draining of the liquid through the perforations. This seriously limits the flexibility of the column.

A more effective and convenient device is the bubble-cap plate. In this case, the plates are provided with a number of nipples, on each of which are mounted and secured, by adequate means, a bell-shaped cap. The edge of each cap is either serrated or slotted. Vapour from the plate below rises through the nipples and bubbles out under the serrations or through the slots. A layer of liquid is maintained on the plate, to such a depth that the caps are submerged, by means of an overflow or down pipe. The exit end of this pipe is sealed on the plate below, by being submerged in the level of liquid on the plate so that vapour cannot pass up the downpipe. A diagram of a modern bubble-cap plate is illustrated in Figure 6.

A simple, but less effective, fractionating device is to fill the column shell with lumps or elements of an inert material so providing surface for the contacting of liquid and vapour. A column of this type is known

as a packed column, and is usually much cheaper to construct than a plate column. A variety of types of tower packing have been employed, such as broken quartz, stoneware shapes, Raschig rings (cylindrical rings of equal length and diameter), spirals, etc. The advantages offered by packed over plate columns are cheapness of construction and low pressure drop. With large diameter towers this advantage is lost due to reduced separation efficiency. A limit of about 18 inches diameter is commonly accepted as the maximum for packed columns. With a tower diameter greater than this, channelling of the liquid reflux becomes

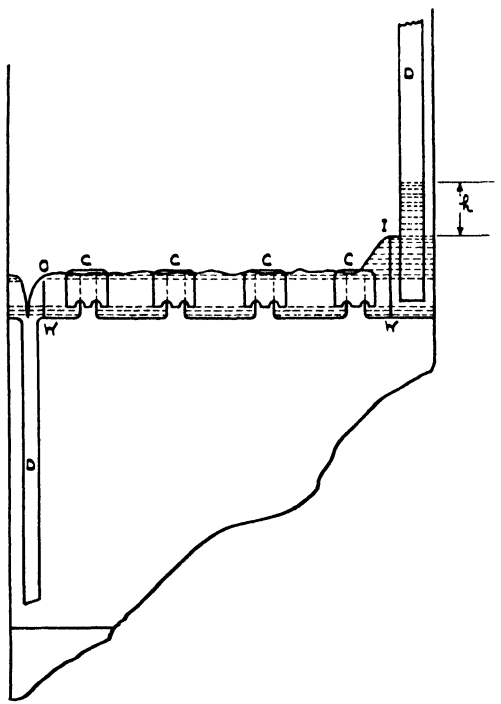


FIG. 6.—DIAGRAM OF BUBBLE-CAP PLATE

appreciable, and the contact area between vapour and liquid is reduced with loss of separation efficiency.

The properties essential to provide a satisfactory tower packing are large surface area combined with low weight.

10. Intermittent Fractionation.—Continuous fractionation has been considered in some detail in the preceding paragraphs. In the method now under consideration, the concentration of the components in the mixture being distilled remains constant at any point in the system. The intermittent process distils the material in batches, the concentra-

tion of the components in the mixture changing progressively with the distillation.

The intermittent still consists of a kettle or boiler for heating and vaporising the charge, and a fractionating column provided with a condenser, a portion of the condensate being returned as reflux to the column. The column holds back the less volatile component of the vapour entering from the kettle, and allows the more volatile component to pass over to the condenser.

The previous generalisations, which were developed with regard to the separation efficiency of the continuous fractionating column, apply equally well to columns operating on an intermittent basis.

The operation is widely employed for the smaller scale refinery operations, such as the preparation of special products and fractions, where both the nature and quantity of the materials are subject to wide fluctuations.

There are also two important types of distillation which do not involve fractionation, namely, equilibrium or flash distillation and simple or differential distillation.

11. Equilibrium Distillation.—Equilibrium distillation or vaporisation comprises the vaporisation of a definite quantity of liquid in such a way that complete equilibrium is maintained between all the vapour formed and the remaining liquid, and at the end of the operation withdrawing the vapour and either condensing it or subjecting it to fractionation.

Pipe-still operation approaches this type of distillation, where petroleum mixtures are heated under pressure and the vapours formed flow through the tubes in contact and approaching equilibrium with the residual liquid. The pressure is finally reduced and the superheated mixture flashed into vapour at the expense of its sensible heat under approximately equilibrium conditions. The temperature and pressure at the coil outlet are called the flash temperature and pressure.

The actual flashing is done in a flash tower which may be either a simple separator, evaporator, or fractionating column. Separators are usually of the simplest construction, being merely drums with provision for the prevention of vapour entrainment, their only function being to effect a separation between the liquid and vapour phases.

An evaporator is a separator where additional vaporisation of the oil is produced by the injection of large quantities of open steam.

When fractionation is carried out in a flash tower, the tower is provided with some form of rectifying device above, and often below, the point of entrance of the feed stream. A reflux is introduced at the top of the tower which latter then operates as a regular fractionating column. Very often additional vaporisation of the liquid phase

separating in the bottom of the flash tower is obtained by the injection of open steam. Unless considerable vaporisation is brought about by this means, the pipe still must be operated at a temperature high enough to supply a sufficient amount of vapour to produce both the amount of distillate and reflux required.

The relationship between the liquid and vapour compositions produced by any such equilibrium distillation process must be that exhibited by the equilibrium diagram. (Figures 1 and 2.)

Consider the simplest case, a binary system of two components A and B, of which component A is the more volatile. Let W_o be the number of mols of the mixture to be processed, and x_o be the mol fraction of the more volatile component A in the mixture. If V mols are vaporised, then $W_o - V$ mols must remain in the liquid phase. Suppose x is the mol fraction of A in this liquid and y is the mol fraction of A in the vapour produced. Assuming no leaks or operating losses, the total mols of A supplied must be equal to the sum of the number of mols present in both the liquid and vapour phases resulting from the process. That is

$$W_o x_o = Vy + (W_o - V)\, x \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Another relationship between x and y obtained from the equilibrium curve, Figure 1, provides the second equation required to solve for the two unknowns x and y, the vapour and liquid phase compositions. Values of x and y must be chosen by trial and error so that they fit both equation (9) and the equilibrium curve.

While this comparatively simple mathematical analysis can be applied to a binary system, when complex petroleum mixtures are considered the necessary mathematical analysis is much more complicated and tedious. Nevertheless, the above equation forms the basis for such computations.

12. Simple or Differential Distillation.—This method of distillation is used in commercial batch distillation. Although the method does not give an effective separation, it finds a wide application where the materials to be separated exhibit wide differences in boiling point. The older type of batch still used in the petroleum industry makes use of this method. Batch operation is a discontinuous, or intermittent, operation, since the material is distilled in batches, the distillation of each batch being completed before the next is commenced.

Sharp separations cannot be obtained by differential distillation, but in cases where a sharp cut is not important the differential batch method possesses several advantages. The plant required is of simple design and construction, cheap to install, and very suitable for small scale processes where the composition of the materials to be handled

may vary widely. It is more adaptable than continuous distillation equipment, which, if designed for a particular quantity of a specified product, may require considerable alteration in order to adapt it to other products.

A simple still consists of a boiler or kettle used for heating and vaporising the liquid to be distilled, a condenser and a distillate receiver. The vapour formed from the boiling liquid is withdrawn and condensed as fast as it is produced.

Assume a quantity of a liquid mixture of A and B in amount W_o mols, has to be distilled, and at any time during the distillation W mols are left as liquid residue in the still kettle, with a composition x and the composition of the vapour above it y, x and y being the mol fractions of the more volatile component A. Now, if a very small amount of liquid dW is vaporised, the composition of the remaining liquid will alter from x to $x - dx$, and its weight will change from W to $W - dW$. Left in the still will be $(x - dx)(W - dW)$ mols of A, while ydW mols will be removed from the kettle. A material balance of component A gives the equation

$$xW = (x-dx)(W-dW) + ydW \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$\text{or } xW = xW - xdW + dxdW - Wdx + ydW.$$

Neglecting the second order differential, $dxdW$, this simplifies to

$$\frac{dW}{W} = \frac{dx}{y-x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

If the left hand side of equation (11) is integrated between the limits W_o and W_1, the initial and final weights, and the right hand side is integrated between the limits x_o and x_1, the initial and final concentrations, then

$$\int_{W_1}^{W_o} \frac{dW}{W} = \int_{x_1}^{x_o} \frac{dx}{y-x}$$

$$\text{Log}_e \frac{W_o}{W_1} = \int_{x_1}^{x_o} \frac{dx}{y-x} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The solution of the problem requiring the value of W_1 when the composition has reached the final value x_1 can be obtained by evaluating the integral in equation (12). This may be done graphically by plotting $\frac{1}{y-x}$ against values of x, the equilibrium curve being used to furnish the relationship between x and y.

13. Steam Distillation.—Consider a system composed of two liquid phases which are mutually insoluble, or immiscible. Each phase will exert its own vapour pressure. In other words, the partial pressure of each liquid will be its vapour pressure at the prevailing temperature of the system. Should heat be applied to such a system the partial pressure exerted by each phase will increase as the temperature rises. When the sum of the two partial pressures becomes equal to the total pressure in the apparatus, the two liquids will start to distil over in the molecular ratio of their vapour pressures. These vapours, when condensed, will form two layers in the receiver from which they may be withdrawn separately. In such a system, if one of the immiscible liquids is water, which is most conveniently introduced in the form of steam, the vapour of the other immiscible liquid passes over along with the steam. This operation is called open steam distillation or wet distillation.

In such an operation, carried out on a mixture of two immiscible components A and B, if

W_A = the weight of component A in the vapour,
W_B = the weight of component B in the vapour,
P_A = the vapour pressure of A,
P_B = the vapour pressure of B,

and M_A and M_B = the molecular weights of A and B respectively, then the ratio by weight of component A to component B in the vapour is

$$\frac{W_A}{W_B} = \frac{P_A M_A}{P_B M_B} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

When steam distillation takes place the temperature of the mixture will be such that the sum of the vapour pressures of the two components equals the total pressure, usually one atmosphere. This means that the materials are vaporised at temperatures considerably lower than their boiling temperature at the total pressure employed.

This method finds a very wide application in the petroleum industry. It is a very important operation in the distillation of heavy oils which undergo thermal decomposition or cracking at temperatures near their boiling points, with the formation of undesirable asphaltic or carbonaceous substances. In both flashing and fractionating equipment handling heavy oils and crudes, considerable quantities of open steam are often required to bring the maximum oil temperature below the cracking range.

14. Vacuum Distillation.—When a liquid is heated to a temperature where its vapour pressure equals the total pressure in the apparatus, it boils and commences to distil over. If the total pressure in the apparatus is reduced, then the liquid will distil at a lower temperature. The reduction of pressure in such a system is most conveniently

brought about through exhausting the vapour space by the use of a suitable pump, which applies a vacuum to the system. A distillation carried out at reduced pressure, that is, at a pressure reduced below atmospheric pressure, is called a vacuum distillation. The ultimate effect is similar to that obtained by a steam distillation, namely, a reduction of the distillation temperature.

In the preparation of lubricating oil fractions of high viscosity from heavy oils, which if distilled at atmospheric pressure undergo partial cracking, thereby resulting in a decreased yield of the desired high viscosity fractions, the employment of high vacua is often essential.

Where sharply cut fractions are required, fractionation under vacuum must be used. Since the vacuum is applied at the condenser a pressure gradient from the source of vapours to the condenser must always exist, owing to the frictional resistance offered to the moving vapours by the pipes, etc., they must traverse. The highest pressure within the apparatus is, therefore, situated at the vapour source, which is also the point of highest temperature. From a purely theoretical point of view this should be the point of lowest pressure, but the practical attainment of this is impossible. Nevertheless, every endeavour is made to keep the pressure at this point as low as possible. In order to do this the frictional resistance to the flow of vapours must be reduced to the minimum. A packed fractionating column with an open filling gives the least frictional resistance to the flow of vapour, and is better than a plate column in this respect. In addition to the pressure set up by the greater vapour velocity head characteristic of a plate column, pressure exerted by the liquid head of oil on each plate will be present.

Owing to the greater vapour volumes produced at the lower pressures in vacuum units, both vapour lines and fractionating columns are much greater in diameter than in plants working at atmospheric pressure.

Flash distillation, differential distillation and steam distillation are employed in conjunction with high vacuum in commercial practice, the latter being known as a wet vacuum. The most important of these is flash distillation under high vacuum. This method is a comparatively new development and is becoming increasingly important in the oil industry. As would be expected, it finds its greatest application in the manufacture of high viscosity lubricating oils.

Usually flash distillation is accomplished by heating the oil in pipe stills under high pump pressures on the inlet side of the still. These high pump pressures are necessary because of the high frictional resistance caused by the volumes of vapour formed at the outlet end of the still. In order that the high vacuum prevailing at the end of the pipe coil can penetrate through the coil the frictional resistance to the flow of the vapours must be reduced to a minimum. This is effected by

increasing at intervals the diameter of the pipes forming the tube bank of the still.

15. Distillation under Pressure.—Whilst the principles of distillation under pressure are applied chiefly to the stabilisation of gasoline, and, indirectly, to the cracking and hydrogenation of oils, both subjects being dealt with in later chapters, nevertheless they are closely related to the general considerations of distillation already discussed, and should form a part of this chapter.

Natural gasoline consists of a mixture of paraffin and other hydrocarbons from methane up to heptane and higher. It often contains such comparatively large amounts of the more volatile lower members that it is dangerous to handle and store, and the evaporation losses encountered during these operations are excessive. It becomes necessary, therefore, to subject it to distillation in order to remove these undesirable volatile constituents. This process, which is explained in detail in Chapter III, is called stabilisation. On account of cooling water temperature limitations it is often essential to operate the stabilisation equipment under pressure. Pressures as high as 25 atmospheres (370 lbs./in.^{2}) are frequently used in practice.

The product from the cracking of oil is a mixture of gaseous and liquid hydrocarbons. When the liquid products are condensed under pressure in contact with the gaseous hydrocarbons, the latter dissolve and the condensate becomes saturated with gas. The amount of gas absorbed is proportional to the pressure prevailing in the condensing equipment. These gases are removed without loss of valuable liquid products by pressure stabilisation of the plant condensate.

Distillation under pressure plays an important part in modern refinery practice. With the development of the hydrogenation process for converting heavy oil and coal into lower boiling oils by the action of hydrogen at elevated pressures, the treatment of the products obtained by distillation under pressure will be utilised to a greater extent in the future.

16. Equilibrium at High Pressures.—It has been shown that in estimating the equilibria between liquid and vapour mixtures of hydrocarbons, Raoult's law and the ideal gas laws may be applied as convenient approximations. Unfortunately Raoult's law is only valid when the vapour approximates to an ideal gas at the total pressure of the equilibrium, and at the vapour pressure corresponding to the equilibrium temperature.

Since the vapour pressure of a pure hydrocarbon is determined under a constant pressure, the effect of pressure upon the vapour pressure is not immediately evident. It is customary to assume that the vapour

pressure depends only on the temperature, being independent of the pressure. If this assumption is employed for calculations on a system operating at pressures substantially above the prevailing normal vapour pressures, large errors are liable to be incurred. Under such conditions a corrected vapour pressure, which is a function both of temperature and pressure, must be employed. The " fugacity " concept of Lewis[4] can be used to replace the vapour pressure.

Fugacity is a measure of the escaping tendency of a component from a phase. It is equal to the vapour pressure when the vapour is an ideal gas, and can be considered as a corrected vapour pressure. At equilibrium, the fugacity of a component in the liquid phase is equal to its fugacity in the vapour phase. In an ideal solution the fugacity of each component is proportional to its mol fraction at every temperature and pressure.

Considering both vapour and liquid mixtures as ideal solutions, the general equation for equilibrium can be written

$$f_L x = f_V y \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where f_L = fugacity of pure component in the liquid phase,
f_V = fugacity of pure component in the vapour phase,
x = mol fraction of pure component in the liquid phase,
y = mol fraction of pure component in the vapour phase.

Since f_L and f_V for each component are functions only of the temperature and pressure, they may be replaced by a single term which is a function of the temperature and pressure, called the equilibrium constant, K. Equation (14) then becomes

$$y = \mathrm{K}x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

K must be numerically equal to the ratio of the fugacities in the liquid and vapour phases. That is

$$\mathrm{K} = \frac{f_L}{f_V} = \frac{y}{x} \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

It is obvious from these considerations that the equilibrium equation (4),

$$\mathrm{V_A}x = \mathrm{P}y$$

derived from Raoult's law, is a special case of the general equilibrium equation and is only valid when

$$\frac{\mathrm{V_A}}{\mathrm{P}} = \mathrm{K} \text{ or } \mathrm{V_A} = f_L \text{ and } \mathrm{P} = f_V$$

that is, when the vapour is an ideal gas at the normal vapour pressure corresponding to the equilibrium temperature and when the vapour is an ideal gas at the total pressure of the system.

The fugacities of the paraffin hydrocarbons in both the liquid and vapour phases have been calculated by Selheimer, Souders and Brown.[5] These authors give values of the equilibrium constant K for the hydrocarbons methane to pentane as functions of temperature and pressure.

The error introduced by the use of Raoult's law under conditions where the total pressure differs greatly from the normal vapour pressure may be as great as 80%. For example, with ethane under a pressure at 100 lbs./in.^{2} and at 85°F., K=3·7, while the value obtained from the equilibrium equation based on Raoult's law $\frac{V_A}{P} = K$ is 6·7.

These principles must, therefore, be used as a basis for arriving at the vapour liquid relationships of a hydrocarbon system under pressure.

By utilising the fugacity concepts for deriving the boiling-point diagram and vapour-liquid curve, calculations for pressure distillation may then be carried out as shown under the headings Fractional Distillation *et seq.*

17. Design of Distillation Equipment.—The process of distillation is one of the most important operations with regard to the determination of refinery costs. In order to maintain these costs as low as possible, efficient equipment is essential. The design of such equipment is a matter for expert and experienced consideration, and it is beyond the scope of this work to examine this problem in detail. A number of references dealing with this subject will be found in the bibliography at the end of this Chapter. The information contained therein is earnestly recommended to the perusal of the student whose inclination lies in this direction. The few supplementary remarks which follow here must only be looked upon as an indication of the order in which such a study should be prosecuted.

The design of equipment to handle binary mixtures such as benzene and toluene is relatively simple. The essential computations are based on the equilibrium diagram and the treatment of the problem is quite precise and straightforward.

The design of plant operating on complex hydrocarbon mixtures is rather more complicated and is necessarily more approximate and empirical in character. Actual experiment with the mixtures to be processed in a semi-technical scale plant is often to be preferred rather than the employment of such methods.

The choice of a plant to carry out a given process must be based upon economic considerations. A balance between the capital cost of the plant and the operating costs must be obtained before the size and type of plant is eventually chosen. For example, in determinating the size of a fractionating column, a balance between the initial cost of the column and the operating charges for steam, power, and water, etc.,

must be obtained. The capital cost of a small column may be low, but a large reflux ratio will be required for such a column and this entails a large steam, power and cooling water consumption. The use of a larger column, on the other hand, involves a large capital cost, but the use of a small reflux ratio and smaller operating costs.

The problems encountered in the design of a continuous fractionating column separating crude petroleum into commercial fractions, the methods employed, and observations on the inclusion of desirable features are perhaps best illustrated by detailing the actual calculations of the principal requirements of such a column.

The method used in the treatment of the example given later in this Chapter is due to Chillas and Weir,[6] while the data employed (distillation range and heat content of fractions) are those quoted in the original paper by the same authors.

THE PRACTICE OF DISTILLATION

18. General.—Whilst the petroleum refining industry, like many other industries, has been developed from old rule of thumb methods, it has now reached a high state of efficiency, particularly in regard to plant control, as the result of the application of accurate and scientific procedure.

In the old days, frequent re-distillation of petroleum fractions was necessary, as sharp fractionation was unknown, whereas to-day commercial separation within close and well-defined limits is possible, despite the complexity of the raw material. The large plant area previously covered by primary stills and re-distillation equipment is now unnecessary as a simple compact unit consisting of a tube still, fractionating column, heat exchangers and condensers is sufficient.

Crude oils vary considerably in their physical and chemical characteristics, and they consist essentially of hydrocarbons of a number of different series in varying proportions, together with smaller amounts of organic substances containing the elements oxygen, nitrogen and sulphur.

In some petroleums the hydrocarbons of one series predominate, particularly in the case of the lighter fractions, while in others the hydrocarbons of many series are mixed in varying proportions.

The structure of the simpler paraffin, naphthene, olefine and aromatic hydrocarbons is fairly well defined, but of other series less rich in hydrogen our knowledge is very incomplete. In fact, it may be said that, of the host of hydrocarbons which come under the first four classes, very little is known, except those present in the petrol fractions. The latter remark applies also to the sulphur compounds.

The dissolved gas, and the water and earthy matter associated

with all crude oils, must be removed before distillation. Dissolved gas constitutes a source of danger since it is inflammable, often poisonous, forms pockets in the pipe-lines and sometimes causes an oil to froth over in the storage tanks. It can be removed almost completely by gradually reducing the pressure on the oil by means of high or low pressure separators, or a combination of both, or by stabilisation.

Water in excess of 2 per cent. should be eliminated, as its removal by distillation is a waste of fuel and cooling water, both of which are

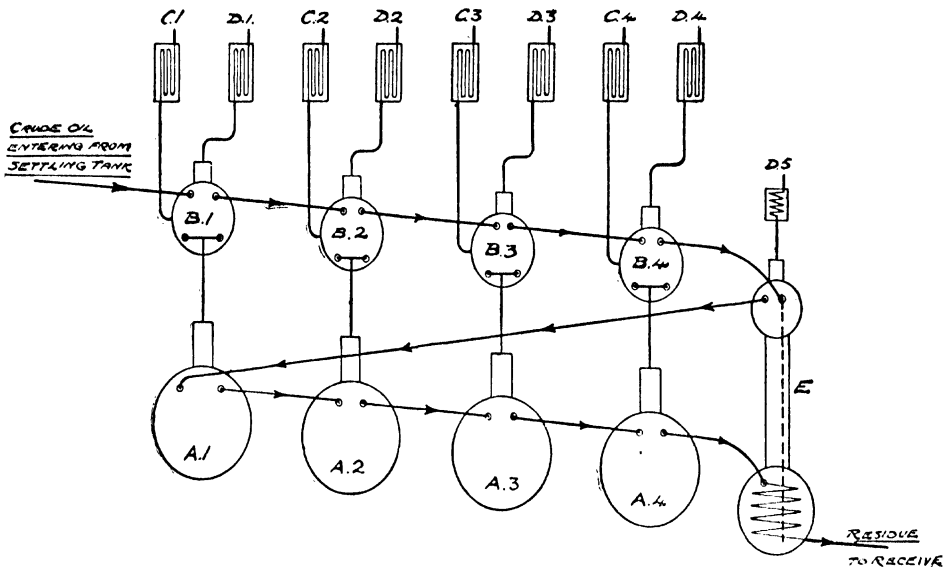


FIG. 7.—DIAGRAM OF METHOD OF CONTINUOUS DISTILLATION BY MEANS OF SHELL STILLS
(*Courtesy of Charles Griffin & Co., Ltd.*)

important items in the cost of manufacture. Where shell stills are used such water can cause frothing which may spoil the distillates: also most oilfield waters contain salts, chiefly chlorides, which, on heating, produce hydrochloric acid with consequent corrosion of the plant. When water is present in the form of an emulsion, the crude oil has to pass through a device for breaking down such emulsions, usually effected by increase in temperature, electrical or chemical treatment; otherwise simple separators will suffice.

Due to the many types of crude oils available, the distillation methods for the production of petrol and other fractions vary considerably; a general method of separation only will be described here. It must be understood, however, that before these fractions reach a standard of purity conforming with market specifications, chemical and physical treatment will be necessary (see Chapter IV).

19. Distillation Methods.—Fractional distillation may be carried out either with shell stills or tube stills. The first method necessitates a number of cylindrical stills each heated progressively to a higher temperature so that each separate distillate has a different and higher boiling range, the process being one of fractional distillation. When pipe stills are used, the oil is heated up to a temperature high enough to vaporise, when it reaches the fractionating column, all but the heaviest residue ; the vapours may then be separated by rectification.

20. Shell Stills. A diagram of an early method of continuous distillation by means of shell stills is shown in Figure 7.

A battery of four shell stills is shown, each set progressively lower in its brickwork setting than the previous one, thereby enabling the crude oil to pass from the first to the last by gravity.

From each still dome, the vapours pass through piping housed in a cylindrical shell, known as a vapour preheater or heat exchanger, through which the oil to be distilled passes between the piping and the shell, and heat is thus transferred from the vapours to the raw oil.

In this manner, a certain amount of distillation of the lighter fractions of the raw oil may occur at the expense of part of the sensible heat of the vapours entering the exchanger ; the bulk of the vapours pass to the condenser, but a certain amount of condensation of the heavier vapours in the preheaters may also result, and this condensate is cooled separately in the condensers. The vapours from the stills which have not condensed in the heat exchanger also pass to the condensers where each fraction is condensed and collected separately. From the condensers the various fractions are led to a building called the tail house, where certain of the fractions may be blended together according to requirements before passing to the intermediate storage tanks.

In the diagram the oil to be distilled passes into the first vapour heat exchanger and is raised to a certain temperature, the gain in heat being the loss in sensible heat of the vapours and the latent heat of any heavier vapours which are condensed. As these preheaters are also set progressively lower, the crude flows by gravity through each heat exchanger in turn, gradually increasing in temperature ; when it reaches the residue preheater it takes up further heat from the hot residue flowing from the last still. The crude oil then passes to the first still, through the remaining stills and through the residue preheater, to the cooler.

Where the amount of residue is small, that is where the percentage of overhead distillate is large, sufficient heat units may not be available in the residue to raise the crude above the temperature at which it leaves the last vapour preheater. It then becomes necessary to pass the raw

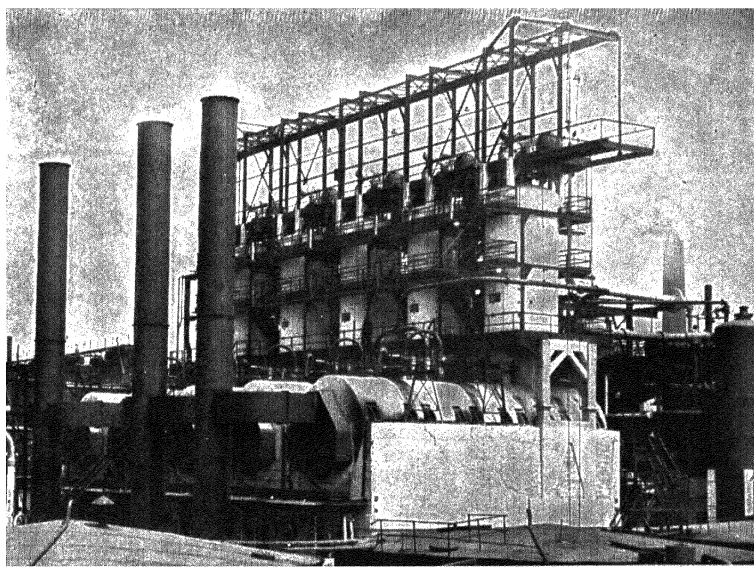


FIG. 8.—MODERN CONTINUOUS BATTERY OF SHELL STILLS
(Courtesy of D. Van Nostrand Company, Inc.)

[*Facing p.* 24

oil through the residue preheater first before it enters the battery of vapour preheaters.

The use and sequence of heat exchangers and preheaters depends entirely on the type of crude oil being distilled and the quantity and nature of the fractions required as distillate. Consequently, the distillation of a number of different types of crude in turn through one battery of stills would need a continual rearrangement of the preheating system, whereas a bench of stills designed for and continually running on one crude would work satisfactorily for a long period with normal supervision, maintenance and repairs.

21. A recent improvement in shell still operation has been the introduction of forced circulation, whereby greater heat absorption may result, with less danger of superheating the oil than was the case with the old method. The throughput of the stills has thus been increased as much as six times for the same proportion of distillate.

This circulating system comprises a centrifugal pump within the shell, driven by a vertical motor mounted above the shell, through a shaft working in a stuffing-box and gland. The suction is taken from within the body of the oil, and the pump discharges through a series of pipes running from a circular shaped manifold in such a manner that the jets, fitted along the horizontal pipes, impinge on the hot shell along the bottom and cause a high sweeping velocity along its surface, circulation being at such a rate that each particle of oil passes through the system at least once every 15 minutes.

Another improvement has been the introduction of return tubes, similar to a horizontal return tube boiler, to those shell stills not fitted with internal flues, whereby the products of combustion after passing along the bottom of the shell may return through the tubes to a smoke box at the front end.

These devices, by increasing the heating surface and the rate of heat transfer, have greatly increased still capacities. This has necessitated the development of high capacity fractionating towers, heat exchangers, condensers, coolers and pumping equipment, and has resulted in a considerably increased firing rate in the combustion chamber; in fact, the firing rate may be said to be the main factor limiting the throughput.

22. The more common shell stills in use in Europe have either one or two corrugated flues running through them similar to a Cornish or Lancashire boiler. Where only one internal flue is used it is usually placed off the centre line of the still to increase convection.

Fractions close enough in boiling range to meet market specifications cannot usually be obtained from shell stills, consequently rectification of the distillate is necessary. This rectification is merely the redistillation of the once-run petrol or kerosene, through one or more shell stills

worked either separately or on the continuous principle, and usually heated internally by means of steam coils, instead of being externally fired as in the first case, to avoid overheating of the distillate. The closeness of fractionation depends largely on the lagged fractionating column, or still head, attached to the still, where the vapour temperature is controlled. This enables products of any required boiling range to be taken off as vapour while those components of higher boiling range are condensed and returned to the still.

The earliest type of unit used for this purpose was the Heckmann still and column, which latter was fitted with a series of perforated baffle plates, each opening holding a piece of pipe projecting upwards and covered with a cap. In this way, the vapours were constrained to travel upwards and then deflected downwards by the cap, to pass through the liquid held on each tray. By this means equilibrium between the vapours and the liquid on each tray tends to be established, and the vapours which pass out at the top of the column are rectified. The Heckmann column is similar in principle to modern bubble towers.

23. Pipe Stills.—These first came into use as a means of dehydrating crude oils which contained emulsified water, to obviate the danger of frothing in shell stills. Later they were used to distil off the lighter fractions from heavy crude oils in order to raise their flash point to liquid fuel requirements, and it was in this manner the term " topping," now in general use, was derived.

The pipe still has since been developed until it is now used to distil all fractions down to asphalt. The principle of such plant is extremely simple, but the numerous variations in design and construction, rendered necessary by the diversity of crude oils undergoing treatment, requires a sound and highly specialised knowledge of physical-chemistry in design and operation.

As in the case of the shell still method of distillation, the raw oil flows first through a series of preheaters, after which it enters the pipe still where it is heated progressively, whilst flowing through the tubes, up to a temperature sufficient to vaporise completely the heaviest fraction required as a distillate. The heated oil and vapour pass into a fractionating column where the distillate is either separated from the residue as one overhead, to be subsequently fractionated by condensation in separate dephlegmators, or separated in and drawn fractionally from the column by means of refluxing. The latter method is the more modern and efficient.

24. The Trumble Pipe Still.—One of the earliest plants using pipe stills was that known as the Trumble, and quite a number of these are still in use in different refineries throughout the world.

The pipe stills, or retorts as they are called in this process, are usually made up of 4-inch diameter steel pipe arranged in rows each of 12 pipes, 16 feet long, placed one above the other, the ends being connected by flanged return bends exposed outside the brickwork, but insulated with asbestos lagging, so that they may be removed for cleaning purposes. There is a continuous run throughout the pipe and the oil to be distilled flows through counter-currently to the flue gases.

Heated oil leaves the retorts in the form of a foamy mixture of vapour and oil, and passes to the top of an evaporator, which consists of a vertical steel cylinder, about 6 feet in diameter and 25 feet high, enclosed in a brickwork stack so that the flue gases from the retorts can pass through the annular space separating the brickwork from the evaporator. This evaporator is the distillation chamber proper, in that the hot oil and vapour entering at the top pass over and through two perforated umbrella plates, and then on to an inclined solid umbrella plate which sends the oil to the heated sides from whence it runs down in a thin film. A number of these solid umbrella plates are held in position by a central pipe, having open ports; the vapours collect under these and pass through the ports to a manifold. Any condensate which falls to the top of the solid umbrella plate below is carried to the heated sides again. Live steam is introduced into the bottom of the evaporator which assists the distillation, by lowering the partial pressure of the vapours and, consequently, their boiling temperature.

The vapours are then led through dephlegmators or fractionating condensers, a number being in series; the heaviest vapours are condensed first, and the lightest vapours pass through the last dephlegmator to the cooler. These dephlegmators have water coils fitted at the top to aid refluxing and restrict the boiling range of the product, and open steam coils at the bottom.

The principle of the dephlegmator is similar to that of the modern bubble tower, except that the saucer plates in use are not nearly so efficient as the plates in a bubble tower, because they do not give such intimate contact between descending liquid and ascending vapour as the bubble cap: they possess, however, higher throughput capacity and a lower pressure drop.

Nevertheless, as a result of this rather crude method of refluxing, and the effect of the open steam, much cleaner separation is effected than with shell stills; also, the efficiency is considerably higher.

Figure 9 shows a diagram of a Trumble plant in operation at Vera Cruz.

Where redistillation of any of the fractions may be necessary in order to get sharper cuts, the crude fractions may be passed through separators using the hot residuum as the heating medium. In this way,

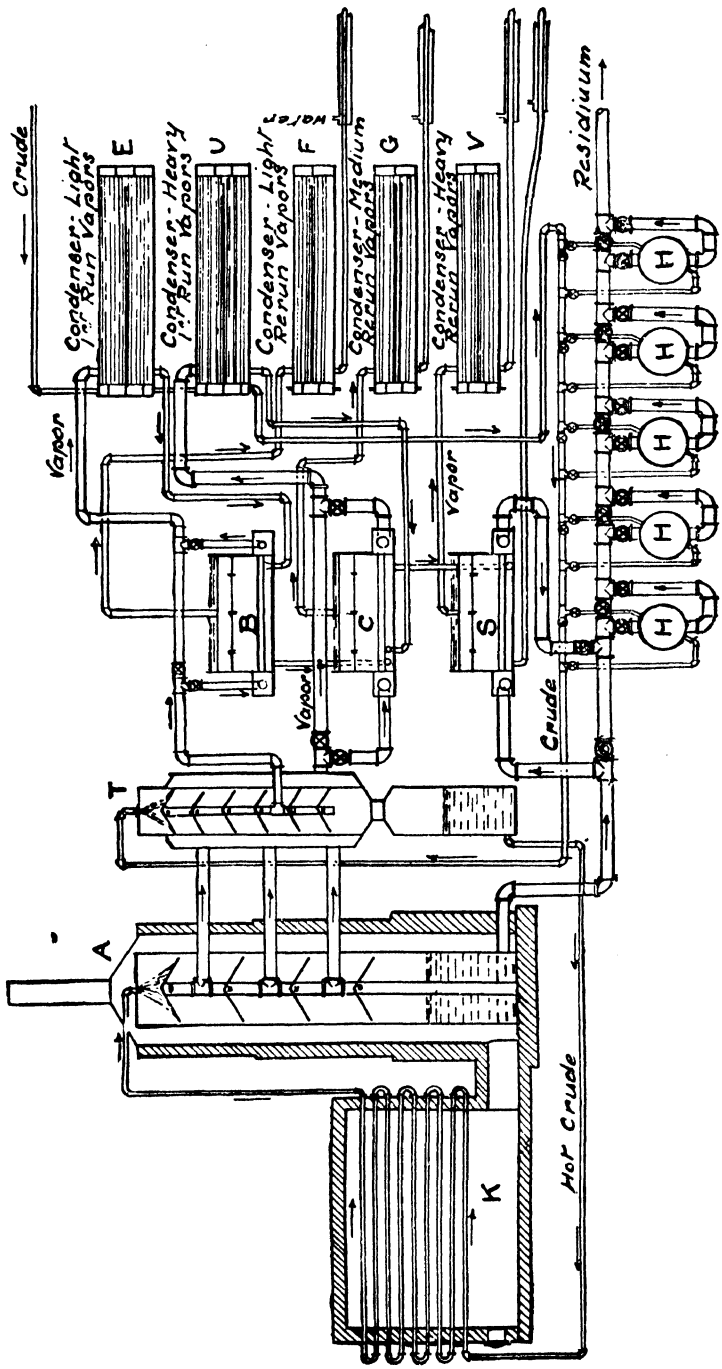


FIG. 9.—DIAGRAM OF TRUMBLE PLANT
(Courtesy of Charles Griffin & Co., Ltd.)

the thermal efficiency of the Trumble still, which must not be confused with the overall efficiency of the distillation unit as a whole, may reach a figure of 60 per cent., as compared with a maximum of 30 per cent. for the ordinary shell still, without forced circulation, working under ideal conditions.

With forced circulation in shell stills, thermal efficiences as high as 60 per cent. are attainable, as considerable turbulence of the oil is produced.

25. The Modern Pipe Still.—Whilst the fundamental principles of this still do not differ from those of the Trumble plant, nevertheless, the design of the furnace and fractionating equipment involves many new features.

The oil-stream passes through the still at a very high velocity in a turbulent condition, which condition is materially accentuated by the presence of bubbles of vapour continually being formed in the stream. High velocity is essential not only to ensure uniform heating as a result of induced turbulence, but also to obtain the maximum rate of heat transfer to avoid cracking at the hot tube surface, and to prevent molecular rearrangements which occur at temperatures lower than those required for actual cracking, and which result in the formation of compounds which increase the difficulty of subsequent refining.

26. The advantages of the pipe still over a shell still are as follows :

1. Higher overall heat transfer giving a higher thermal efficiency. The shell still has a thermal efficiency of *ca.* 30 per cent., whereas a pipe still may reach a figure of 75 per cent. A pipe-still thermal efficiency of 60–70 per cent. is usual.
2. Much less risk of overheating. By proper attention to oil velocity through the tubes, skin temperatures, etc., no overheating is obtained in pipe still operation. In shell stills overheating occurs at the bottom of the still and causes decomposition, lower yields and often depreciated quality. The heating time in a pipe still is incomparably shorter than in a shell still.
3. Much reduced fire risk. In normal-sized pipe stills the total amount of oil present in the tubes at any given moment rarely exceeds 70–80 barrels, compared with several hundred barrels in a shell still. Moreover the headers in pipe stills are enclosed in header boxes outside the combustion zones which are fitted with steam lines.
4. A pipe still is capable of very flexible operation. It has a very wide range of throughput capacity, i.e., 50–200 per

cent. of the rated throughput. Moreover one unit is suitable for the distillation of stocks of widely different characteristics, e.g., gasolines to residues.

5. A pipe still fractionating unit is very compact and occupies little ground area. One 10,000 bbl/day unit can be installed in a 50-yard by 50-yard area, and replaces up to 12 shell stills.

The adoption of pipe stills has also allowed flash vaporisation to be applied with advantage and has also rendered continuous vacuum fractionation possible. Without the use of pipe stills accurate and closely controlled fractionation on a large scale could not have been developed to its present high standard of efficiency.

27. Types of Pipe Stills.—All modern pipe stills are built with both convection and radiant heat sections, and these are usually

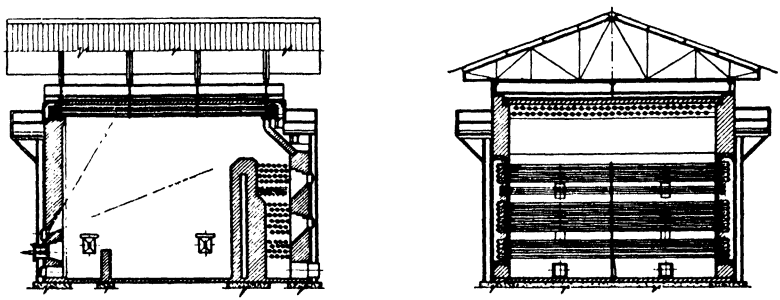


FIG. 10.—TOPPING UNIT TUBE STILL
(Courtesy Alco Products Incorporated)

separated by a wall. The convection tubes are placed on the side of the wall away from the burners and the flue gases pass over these on their way to the stack. The radiant tubes are in close proximity to the burner but are placed in such a manner that they do not suffer flame impingement. Oil flow through the furnace tubes is usually counter-current to the flue gases, i.e., the cold oil passes through the convection tubes first and then through the radiant tubes. An arrangement of a tube still employed on a topping unit is shown in Fig. 10, while Fig. 11 is a photograph of a battery of pipe stills and fractionating columns erected by Alco Products Incorporated.

In Fig. 10 the radiant tubes are situated under the suspended roof and the convection tubes are separated from the combustion space by a bridge wall. Several arrangements are, however, in use. In the De-Florez radiant pipe still, radiant tubes are also placed on the furnace front wall above the burners, while in the Alcorn all-radiant type heaters the arrangement is as shown in Fig. 12, the burners being guarded by carborundum muffles to prevent flame impinge-

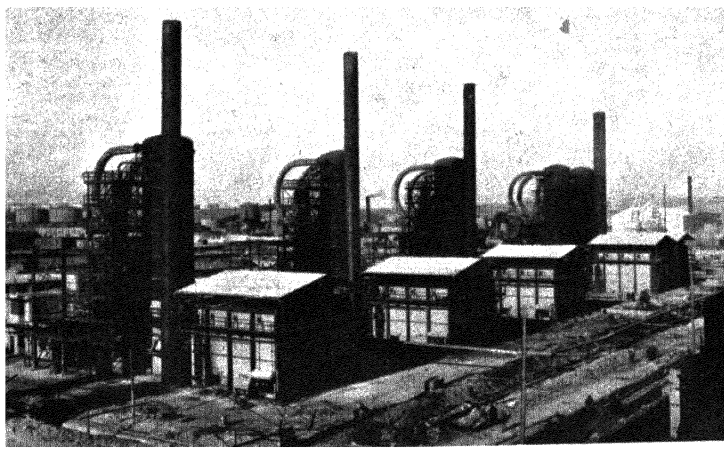


FIG. 11.—BATTERY OF TUBE STILLS AND FRACTIONATING COLUMNS

(Courtesy of Alco Products Incorporated)

[*Facing p.* 30

ment on the tubes. A recent development is the Alcorn duplex furnace, a diagram of which is given in Fig. 13.

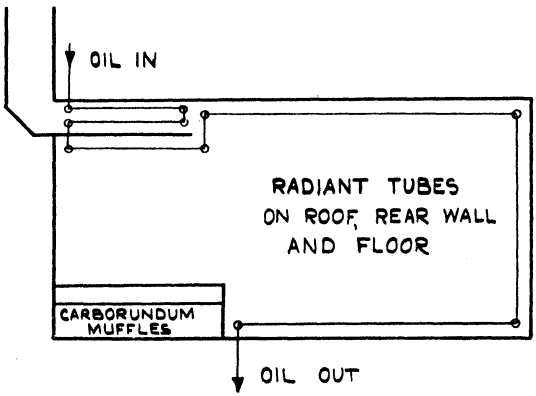


FIG. 12.—ALCORN ALL-RADIANT TYPE HEATER

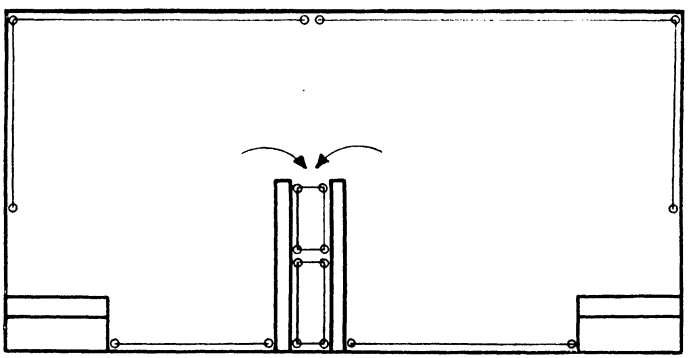


FIG. 13.—ALCORN DUPLEX OPERATION PIPE STILL

28. An important consideration when heating oil is the intensity of heat in a furnace because of the limited capacity of oil to absorb heat, as the specific heat of oil is less than half that of water and the latent heat of oil vapour about one-seventh that of steam. The rate at which heat is absorbed by a fluid is a function of its mass velocity, and the difference in temperature between the metal of the heating surface and the fluid. This is explained at the end of this Chapter under Heat Exchangers. So long as a sufficient weight of fluid is passing at a sufficient speed, the temperature of the metal can be kept below a point where the fluid would become overheated or the heating surface destroyed.

Heat, in a modern tubular still, is conveyed to the oil in three different ways ; by radiation, convection and conduction.

Radiation is the flow of heat by wave motion and this form of radiant energy flowing from one body to another, according to the Stefan-

Boltzmann law, is proportional to the difference between the fourth power of the absolute temperature of the radiating body and the fourth power of the absolute temperature of the receiving body.

Convection involves the migration of streams of a fluid of different temperatures, whereby heat is conveyed by fluid motion.

Conduction is the passage of heat through a body by transference of energy from one molecule to another.

29. All three of these systems of heat transmission are of importance when considering the heat transfer problems of a pipe-still furnace. The heat from the burning fuel, and the incandescent refractories, reaches a portion of the heating surface by radiation. The heat from the products of combustion is transferred by convection whilst the heat received by the oil passes through the pipe walls by conduction.

The usual formula for heat units absorbed per square foot of surface per hour for radiant heat is :—

$$H_R = 1600\left[\left(\frac{T_1}{1000}\right)^4 - \left(\frac{T_2}{1000}\right)^4\right]. \quad . \quad . \quad . \quad (17)$$

where H_R = B.Th.U. per hour per square foot,
T_1 = Temperature of radiating surface in degrees Rankine (°F. + 460),
T_2 = Temperature of absorbing surface in degrees Rankine.

The absorption of heat by convection takes place at a much slower rate and being proportional to the temperature difference between the hot gases and the metal of the heating surface, may be expressed as :—

$$H_c = (T_1 - T_2)\rho \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where H_c = B.Th. U. absorbed per square foot per hour,
T_1 = Temperature of hot gases,
T_2 = Temperature of absorbing surface,
ρ = Rate at which heat is absorbed per degree difference of temperature which varies with the mass flow of the gas over the heating surface.

30. In all pipe stills, highly turbulent flow of the oil and vapours being heated is essential, otherwise cracking takes place and carbon deposition results. Highly turbulent flow is also necessary to obtain high rates of heat transfer—typical values of which, in normal crude distillation and re-running operations, are as follows :—

Convection Sections 3,000–10,000 B.T.U. /sq. foot /hour.
Radiation Sections 10,000–20,000 B.T.U. /sq. foot /hour.

or alternatively, overall transfer rates for pipe stills are approximately 3–4·5 B.T.U. /sq. foot /hour /°F.

In lubricating oil distilling units where oil temperatures are necessarily high and the danger of cracking more pronounced, lower overall heat transfer figures, about half the above, are obtained.

31. Fluid Flow.—Flow within a pipe may be either of the *streamline* or *turbulent* type, depending upon the conditions and the latter type of flow only occurs at fluid velocities above the *critical velocity*, as defined below. Below the critical velocity, the fluid moves as though it were made up of an infinite number of cylindrical shells, sliding past one another at different speeds, so that the fluid cylinder nearest the pipe wall remains stationary with respect to the pipe, and the others travel at a progressively faster rate until the centre cylinder, which possesses the highest velocity, is reached. The velocity of this centre portion is twice the average velocity of flow. This type of flow is known as streamline flow.

The equation of streamline flow is given by Poiseuille's law which may be expressed as :—

$$p = \frac{32\mu L v}{gd^2} \quad \ldots\ldots\ldots \quad (18a)$$

where p = total pressure drop in lbs. per square foot.
L = length of straight pipe in feet. (In practice, "equivalent length" due to bends, etc., must be added.)
v = average velocity of fluid in feet per second.
d = inside diameter of pipe in feet.
μ = absolute viscosity in English units.

When the pressure is increased gradually, thereby increasing the fluid velocity, a point is at length reached where the streamline flow gradually breaks down and the fluid becomes turbulent. At this point, considerable increase in pressure produces only slight increase in velocity. The fluid has now reached a point of unstable flow at which the whirls and eddies formed do not take on any systematic conformation. This is known as the *critical velocity* of the fluid.

Reynolds has shown that the critical velocity depends on the diameter of the tube, the velocity of the fluid, its density and its absolute viscosity. These four factors must be combined in one way only, namely, $\frac{vd\rho}{\mu}$, where d is the inside diameter of the pipe, v the average velocity of the fluid, ρ its density, and μ its absolute viscosity. This function is known as *Reynold's criterion.*

32. On further increasing the pressure, the discharge is found to increase a proportionate amount, and the fluid is now in a new state of equilibrium, not flowing in an orderly manner parallel to the

long axis of the tube but in an erratic manner so that there is complete mixing of the adjacent layers. This is known as turbulent flow, when pressure and velocity remain constant throughout the system for any given set of conditions.

Fanning's equation for turbulent motion is given by

$$p = \frac{f\rho L v^2}{2gm} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where $m = \frac{d}{4}$ or hydraulic mean depth,

ρ = density of fluid in lbs. per cubic foot,

f = friction factor.

Turbulent and streamline flow obey quite definite laws and these laws apply to every fluid whether liquid or gaseous. As further reference will be made to this later, the subject may be dismissed here by stating that resistance increases proportionally with velocity in streamline flow, whereas, with turbulent flow, resistance increases nearly proportionally to the square of the velocity.

In pipe-still design turbulent flow is essential, as it produces a nearly constant oil temperature throughout the cross section of the pipe, and the heated outer layers of the oil are carried continuously into the relatively cooler core of the pipe, thus obviating superheating at the tube walls.

As already explained, the critical velocity of a fluid is determined from Reynold's criterion, which, for the purpose of pipe-still design, may be expressed as :—

$$V_c = K \frac{\nu}{d} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where V_c = critical velocity in feet per second,

ν = the kinematic viscosity,

d = diameter of pipe in inches,

K = constant.

Streamline flow exists when K is less than 25 and turbulent flow when K is greater than 40, so that the critical velocity range begins when $\frac{dV_c}{\nu} = 25$ and ends when $\frac{dV_c}{\nu} = 40$.

From this equation it will be seen that the critical velocity is directly proportional to the kinematic viscosity, which is the absolute viscosity in poises divided by the specific gravity of the oil at the same temperature. Although both the viscosity and specific gravity of an oil change with temperature, the change in viscosity is very much greater for a given change in temperature than the specific gravity. Consequently,

although the change in critical velocity cannot be said to be directly proportional to the change in viscosity nevertheless it is nearly so, so that for heavy cold oils, V_c becomes so large that an effort to exceed the critical velocity involves very high pumping pressures and excessive pressure losses in the pipe due to friction.

33. Where the kinematic viscosity is small, as in the case of hot oils of low absolute viscosity (consequently low Redwood viscosity), velocities in excess of the critical velocity are possible with small friction losses. Since all modern heaters are equipped with heat exchangers through which the oil passes before entering the pipe still, the viscosity of the oil to be distilled is greatly reduced and pressures rarely above 200 lbs. per square inch are maintained, except in cracking furnaces.

The velocity of the oil is greatly increased during its passage through the still due to the fact that vapours are evolved as the oil is progressively heated, which increases the volume of fluid flowing. Whilst the inlet velocity may be from 2 to 3 feet per second, the outlet velocity of the mixture of vapour and oil may be as high as 500 feet per second, depending upon the type of oil being distilled, and the pressure drop.

34. As mentioned earlier, there are various types of pipe stills but most of them are designed on the principle that the radiant heat elements must be protected from overheating as the result of furnace temperature and flame impingement. For this reason the combustion chamber temperature should not exceed 1,800°F. Another method of controlling furnace temperature is by means of the recirculation furnace where a proportion of the waste products of combustion, instead of passing up the stack, are recirculated before they reach the air preheater and are made to mix with the fresh products of combustion. In this manner, the furnace temperature may be kept down to about 1,500°F., without the admission of excess air in large quantity.

35. Whilst for topping purposes the single-flash method is more economical, nevertheless, as double-flashing offers certain advantages, particularly when a crude must be reduced to a small residue, a brief description may be of interest. In the single-flash method all the required distillates are taken off in one operation, whereas in the " double-flash " system a second pipe still, evaporator and column, is employed to deal with the residue from the first. Until quite recently the single-flash system was more widely employed, the double-flash method being considered less efficient and requiring slightly more heat to remove a given quantity of distillate. The last two years have seen an increased development of two-stage and even three-stage units, not only for topping and the production of lubricating stocks, but also

for re-run units of various kinds, particularly where the oils being treated show a marked tendency to crack at the higher temperatures.

In Fig. 14 will be seen three fractionating columns each fitted with a heat exchanger and refluxing coil at the top, and a reboiler at the bottom. The oil to be distilled may be pumped through the three heat exchangers and the residue preheater to the first pipe-heater, and after fractionation in tower No. 1, the refluxed oil passes to the second pipe still through the evaporator and third tower. The second tower gives

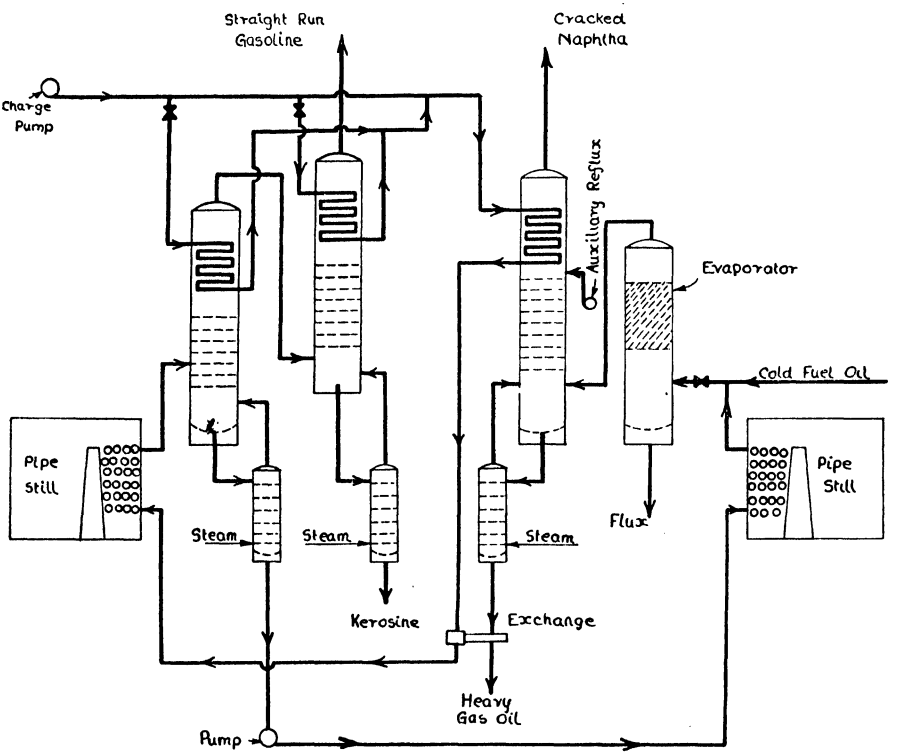


FIG. 14.—DIAGRAM OF THE DOUBLE-FLASH SYSTEM

straight-run petrol as overhead and kerosene as bottoms, whilst the third tower gives cracked petrol as overhead and heavy gas oil as reflux and the evaporator separates the residue.

The advantage of the double-flash system, from the point of view of petrol manufacture, is that straight-run petrol and kerosene are removed at a lower temperature than that required to flash the entire distillate in a single-flash still and, therefore, may need less refining.

A compromise may often be made between the shell-still system and the method of bubble tower fractionation. By employing a single fractionating tower common to a number of shell stills, it is

possible to fractionate the vapours from them all simultaneously, and if forced circulation is installed in the stills the efficiency should approach that of the pipe still and column.

36. The coefficient of heat transfer, K, for any distillate by means of pipe stills may be calculated from the following expression :

$$K = \frac{[(W_v \times S_v) + (W_L \times S_L)] \times [(t_f^\circ - t_i^\circ) + (h_v \times W_v)]}{A \times \theta_m} \quad . \quad (21)$$

where K = B.Th.U. per square foot, per hour, per 1°F. mean temperature difference,
W_v = Weight of oil vapour heated per hour in lbs.,
W_L = ,, ,, undistilled oil ,, ,, ,, ,,
S_v = Specific heat of oil vapours,
S_L = ,, ,, ,, liquid,
t_i° = Initial temperature of oil,
t_f° = Final temperature of oil,
t_i^G = Initial temperature of flue gas,
t_f^G = Final ,, ,, ,, ,,
θ_i = Temperature difference of the hot entering flue-gas and hot effluent oil,
θ_f = Temperature difference of cold incoming oil and exit flue gas,
θ_m = Mean temperature difference between the two fluids,
h_v = Heat required to form 1 lb. of oil vapour at the temperature of hot effluent oil,
A = Area of heating surface.

The mean temperature difference may be found from

$$\theta_m = \frac{\theta_i - \theta_f}{\log_e \frac{\theta_i}{\theta_f}} = \frac{(t_i^G - t_f^\circ) - (t_f^G - t_i^\circ)}{\log_e \frac{t_i^G - t_f^\circ}{t_f^G - t_i^\circ}} \quad . \quad . \quad . \quad (22)$$

The approximate fuel consumption for a pipe still may be determined by the equation :—

$$x = \frac{W h_d}{h_f \left(1 - \frac{L_R}{100}\right) - h_g} \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where x = Fuel consumption, lbs. per hour,
h_g = Heat content in B.Th.U. of flue gas formed per lb. of fuel burned,
h_d = Theoretical heat required, in B.Th.U. per lb., to remove the percentage of distillate in the fractions desired,

h_f = Calorific value of fuel in B.Th.U. per lb.,
L_R = Radiation loss, expressed in percentage of total heat supplied, which should not exceed 10 per cent. in a modern pipe still,
W = Weight of oil passing through the heater in lbs. per hour.

The usual calculation for the quantity of flue gas, in lbs., formed per lb. of fuel used, may be taken, and this, plus the amount of excess air in lbs. (which should not exceed 50 per cent. over theoretical requirements), multiplied by the difference in temperature of the flue gas and cold air in °F., will give h_g.

37. A formula for the size and draught of flues and chimneys is as follows :—

$$D = \left[0{\cdot}52 \text{ PH} \left(\frac{1}{T} - \frac{1}{T_1} \right) \right] - \left[\frac{2W^2H}{rA^2 \times K} \right] \quad . \quad . \quad . \quad (24)$$

where D = Draught in inches of water,
H = Height of stack above furnace, or length of flue, in feet,
P = Absolute pressure, lbs. per square inch,
T = Temperature of atmosphere, degrees Rankine,
T_1 = ,, ,, flue gas, degrees Rankine,
W = Weight of flue gas per second in lbs.,
A = Cross-sectional area of stack or flue in square feet,
K = 550 for steel stacks and 770 for brick-lined stacks,
r = Radius of stack in feet.

38. Bubble Towers.—The design of bubble towers is based on the principle of the Heckmann column, which, in turn, was derived from the earlier developments of rectifying towers used in the alcohol industry. Bubble towers are fitted with trays containing either a number of small holes or long slots, each provided with a lip projecting upwards beyond the tray proper and covered by a cap, in such a manner that there is always a certain depth of liquid on each tray through which the vapours are constrained to pass so that substantial equilibrium between vapour and liquid at each point is established. These towers may also be fitted with special chimneys for rising vapours at various points in order that they may be out of direct contact with the liquid where necessary, and open steam coils and reboilers may be introduced at these stages, as well as downcomers which deliver the condensed liquid to the plate below.

The temperature difference between trays should be small and uniform and the more vapour which is condensed and the more repeated the condensation and distillations which take place, the

more effective will be the fractionation. In practice, reflux ratios vary from $\frac{1}{4}$ to 1, in the case of topping units taking over gasoline only, up to 6 to 1 where a maximum of fractionation is required with a number of side streams.

The temperatures required in a bubble tower depend entirely on the partial pressures of the constituents of the vapours. In the production of gasoline an average boiling point must be selected and the top of the column set at such a temperature as to give the maximum saleable quantity of spirit, which necessitates close regulation and automatic control.

The control of temperature, pressure, and amount of reflux is very important and for recording pipe-still temperatures electrical pyrometers are the most suitable. For tower temperatures, both electrical pyrometers, and air-, gas- and mercury-filled thermometers are in common use. These are usually combined with a compressed air or electrically actuated valve which controls the amount of pump-back reflux, thus maintaining the desired temperature at the top of the tower and at any point of take-off.

Orifice recording meters on the crude charging line are also combined with automatic air-operated control valves which regulate the steam pressure to the charging pump, maintaining the throughput at any predetermined rate.

Plates are placed at such distances as to allow plenty of disengaging space for the vapour and a minimum of 24 inches should be aimed at where possible to allow working space for repairs. The velocity of vapours through the spaces between the plates for columns working at atmospheric pressure should not exceed $2\frac{1}{2}$ feet per second, and for columns under a high vacuum, 5 feet per second. The number of plates depends entirely on the process requirements, but for one overhead cut, say of gasoline, 12 plates may be allowed.

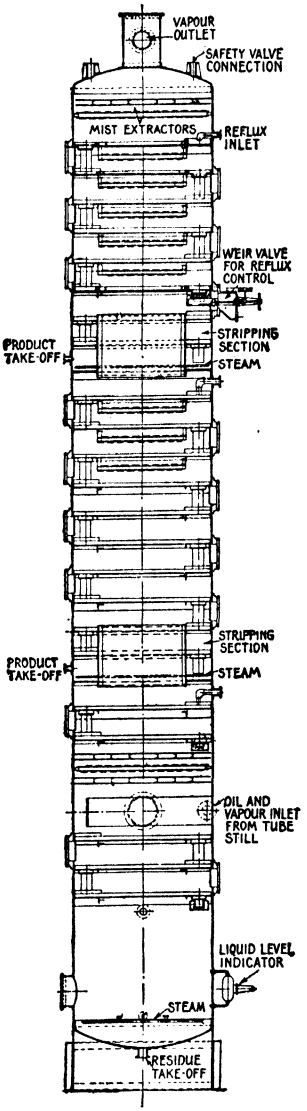


FIG. 15.—BUBBLE TOWER

39. Design of Bubble Towers.—The rudiments of the design of a bubble tower may be briefly indicated as follows :—Let it be assumed that crude oil, after heating in a pipe still, is to be separated by continuous fractionation into 4 distillate cuts, and a residue removed continuously from the bottom of the distillation column. The petrol fraction is to be taken as vapour from the top of the column, condensed in a suitable condensing system and a portion of this is to be returned to the top of the column as reflux. The higher boiling distillates are to be removed as liquid " side streams."

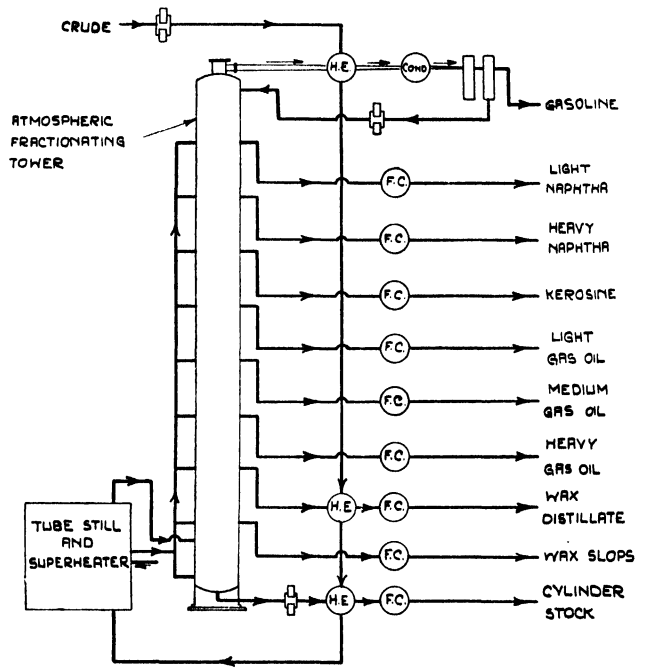


FIG. 16.—DIAGRAM OF PIPE STILL, BUBBLE TOWER AND A NUMBER OF SIDE STREAMS

The column is required to treat 10,000 U.S. gallons per hour (70,000 lbs.) of crude oil available from storage at 60°F. and possessing the distillation range shown in Fig. 17. Analysis of the crude in a True Boiling-point Column gives the four distillate cuts shown in Fig. 18, in the following yields. This figure shows the I.P.T. distillations of the cuts from the T.B. column.

It is required to design a column to reproduce these results.

TABLE 3

Cut.	% by Weight.
Petrol	25
Kerosene	20
Gas Oil	10
Paraffin Distillate	25
Residue	20

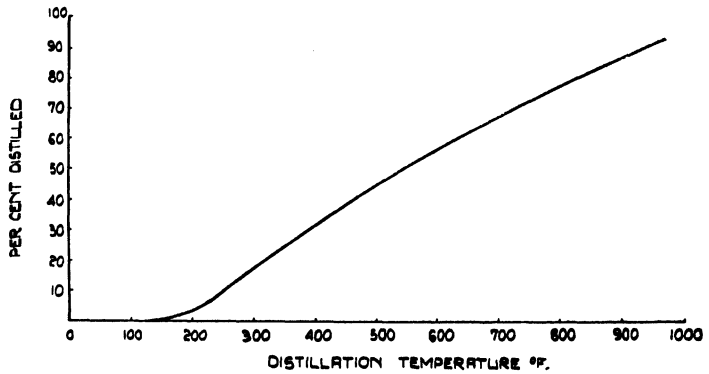


FIG. 17.—DISTILLATION CURVE

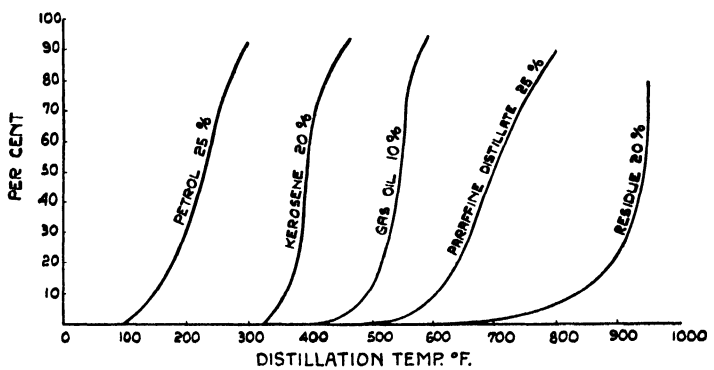


FIG. 18.—TRUE BOILING-POINT CURVES

40. True Boiling-point Column.—The T. B. Column used in the laboratory to produce the True Boiling-point curves shown in Fig. 18, consists of a distilling flask, of 2 litres capacity, attached to a column, 2 inches in diameter and 4 feet high, packed with rings and well lagged. The column is fitted with a reflux condenser and the ratio of reflux to distillate should be not less than 30 to 1. This apparatus is suitable for the distillation of a 1 litre sample. (See also Chapter XI, Vol. II.)

41. Heat Data Suitable for the Calculations.—The heat data which will be used in the following calculations are illustrated in Fig. 19. They represent the average of both laboratory test and practical plant

data, and heat content is plotted against temperature. The liquid curve gives the sensible heat in 1 lb. of liquid at t°F., and the vapour curve gives the total heat (i.e., sensible heat + latent heat) in the vapour at t°F. The difference between the two curves represents the latent heat of vaporisation.

42. Heat Required for Vaporisation.—Sufficient heat must be supplied to the crude in the pipe still to vaporise 80% of it when it is discharged into the bottom of the column at atmospheric pressure.

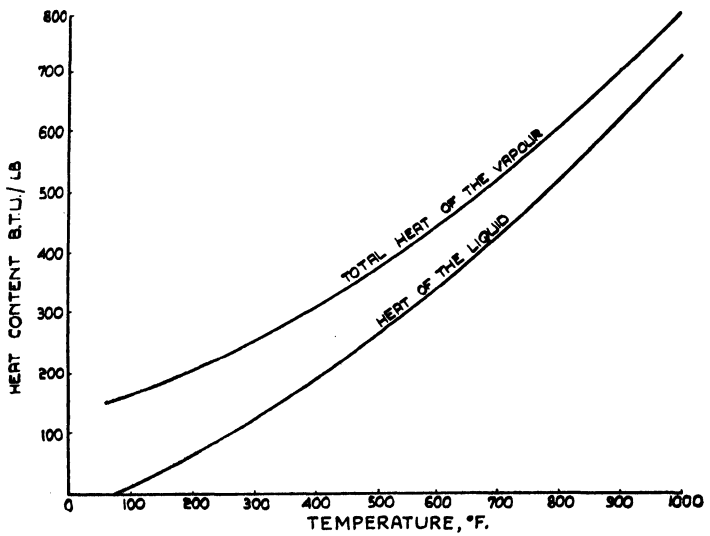


FIG. 19.—HEAT CONTENT CURVES

In order to do this the oil must be heated to the final boiling point of the heaviest distillate, and then the latent heat of evaporation supplied. That is, vaporisation is assumed to take place at the highest temperature. This is not quite correct. During the rise from storage temperature, 60°F., to some temperature t_v, where vaporisation begins, the only heat effect is that of adding sensible heat to the liquid. After vaporisation commences, three heat effects occur simultaneously. Sensible heat is added to both liquid and vapour and latent heat is absorbed. If these effects are taken into consideration, the total heat requirement obtained by calculation is correct. If this requirement is calculated in the simpler manner indicated above, however, the value obtained is only 4% in excess of the correct figure, an accuracy sufficient for general design work.

Temperature to which crude must be raised = 800°F.
Liquid heat at 800°F. = 518 B.Th.U./lb.
Vapour heat at 800°F. = 608 B.Th.U./lb.

$\therefore$ Total heat required
$= (70{,}000 \times 0{\cdot}8 \times 608) + (70{,}000 \times 0{\cdot}2 \times 518)$
$= 70{,}000\,(486{\cdot}4 + 103{\cdot}6)$
$= 41{,}300{,}000$ B.Th.U. per hour.

43. Side-stream Temperatures.—When previous plant or semi-technical plant figures are not available for these temperatures, they can be approximated from laboratory data as follows.

(1) The temperatures of the liquid side streams correspond closely to the 5 per cent. off points on the I.P.T. distillation curve, provided steam is not present in excess of 1 lb. per gallon of charge.

(2) The temperature of the residue leaving the bottom of the column is always less than the temperature of the heaviest side stream. It is also materially affected if steam is used to strip the residue. If the percentage residue is small, considerable error in estimating this temperature will not affect the heat balance of the column.

(3) The temperature of the petrol vapours leaving at the top of the column (at atmospheric pressure) corresponds to the 75 per cent. off point of the I.P.T. distillation curve of this fraction. Where steam is present in practical amounts, assumption of a top vapour temperature equal to the 60 per cent. off point on the I.P.T. curve meets all the requirements of a heat balance.

44. Heat Balance.—The first step in the design of the column is to arrive at a heat balance, as follows.

TABLE 4

Material	*Quantity.* Lbs. per hour	*Temp.* °F.	*Heat Content* B.Th.U. per lb.	*Heat above 60°F.* Million B.Th.U. per hour.	
Input—					
Crude oil	70,000	800	Vapour 608 Liquid 518	41·3	
Output—					
Residue	14,000	500	Liquid 260	3·640	
Paraffin dist.	17,500	600	,, 335	5·863	
Gas oil	7,000	470	,, 235	1·645	Total
Kerosene	14,000	355	,, 155	2·170	
Petrol	17,500	228	Vapour 215	3·763	18·1
*Heat loss by radiation	—	—	—	1·015	

* Heat loss by radiation is approximately 2·5% of the total heat output.

45. Reflux Ratio.—The difference between the heat input and output in the above balance represents the heat carried away from the top of

the column by the petrol fraction vapours which are condensed and returned to the top of the column as reflux.

Assume this is cooled in the condensers to 100°F. The heat returned per lb. of cold reflux at 100°F. is, from Fig. 19, 15 B.Th.U. per lb.

$$\therefore \text{ Reflux rate } = \frac{(41{\cdot}3 - 18{\cdot}1) \times 10^6}{(215 - 15)} \text{ lbs. per hour}$$

$$= \frac{23{,}200{,}000}{200}$$

$$= 116{,}000 \text{ lbs. per hour.}$$

$$\text{Petrol distillate removed } = 17{,}500 \text{ lbs. per hour,}$$

$$\therefore \text{ Reflux ratio required } = \frac{116{,}000}{17{,}500}$$

$$= 6{\cdot}63$$

46. Internal Reflux.—When the comparatively cool reflux is introduced into the top of the column, it must condense some of the vapour present there giving an " internal " reflux greater than the " external " as calculated from the reflux ratio. It is important to know the amount of " internal " reflux, as the liquid down pipes in the top plates of the column must be made of sufficient size to handle this quantity of liquid.

Since the top vapour temperature remains constant, in our case 228°F., the liquid " external " reflux must be heated to this temperature.

The heat in this liquid at 100°F. from Fig. 19 = 15 B.Th.U. per lb.
The heat in this liquid at 228°F. from Fig. 19 = 80 B.Th.U. per lb.
The heat supplied = (80 − 15) B.Th.U. per lb.
∴ Total heat supplied = 116,000 × (80 − 15) B.Th.U. per hour.

Again, since the top column temperature must remain constant at 228°F., the only heat lost by the vapours in this section of the column must be their latent heat, which, from Fig. 19, is (215 − 80) B.Th.U. per lb., and the total heat lost will be this quantity multiplied by the weight of condensate.

Let this be x.

∴ Total heat lost = $(215 - 80)x$ B.Th.U. per hour. By equating these two quantities we can solve for x

$$\therefore (80 - 15)\,116{,}000 = (215 - 80)\,x$$

$$x = 116{,}000\,\frac{(80 - 15)}{(215 - 80)}$$

And the total " internal " reflux must equal the " external " reflux + x.

$$\therefore \text{Total "internal" reflux} = 116{,}000 + 116{,}000\,\frac{(80-15)}{(215-80)}$$

$$= \frac{116{,}000\,(215-15)}{(215-80)}$$

$$= 171{,}850 \text{ lbs. per hour.}$$

47. Vapour Volume at Top of Column.—It is customary to assume that the specific volume of the petrol vapours at the top of the column is 4 cubic feet per lb. It can, of course, be calculated with more accuracy if the actual molecular weight of the petrol is known. However, the figure given is usually sufficiently accurate for design purposes.

TABLE 5

	Weight of vapour. Lbs. per hour.	Specific Volume. Cubic feet per lb.	Total Volume. Cubic feet per hour.
Petrol distillate	17,500	4	70,000
Total internal reflux	171,850	4	687,400
	189,350		757,400

48. Vapour Velocity.—Unless unusual attention is paid to levelling the plate of a large diameter column, uniform bubbling of vapour from all caps will not occur until a vapour velocity of 12 feet per second through the notches in the bubble caps is obtained. For a well-designed plate this velocity corresponds to 1·4 feet per second through the free space of the column. A maximum free-space velocity of between 2–3 feet per second is customary. This velocity ensures that entrainment from the top of the column will not be greater than 1 per cent.

In this case assume a vapour velocity of 2·5 feet per second.

49. Column Diameter.—This is obtained from the vapour velocity and the vapour volume in the top of the column.

$$\text{Cross sectional area} = \frac{757{,}400 \text{ cubic feet per hour}}{2{\cdot}5 \text{ feet per second} \times 3{,}600}$$

$$= 84{\cdot}2 \text{ square feet.}$$

$$\therefore \text{Diameter of column required} = 10 \text{ ft. } 2\tfrac{1}{2} \text{ ins.}$$

50. Height of Column.—The height of the column is dependent on the number of plates required to effect the separation desired. Satisfactory methods exist for determining the number of plates required to separate complex mixtures, but these are tedious. Actual experiment with the crude in a works or semi-works column is of value in finding the number of plates in columns of the type discussed above.

51. Caps and Overflow Weirs.—A plate is illustrated diagrammatically in Fig. 6, where C is the caps, D is the downcomer pipe from the plate above, and IW and OW are the inlet and overflow weirs ensuring that the caps are properly immersed in the oil.

The overflow weir should be about $2\frac{3}{4}$" high and the caps $2\frac{1}{4}$" to $2\frac{1}{2}$".

52. Vapour Density at Top of Column.

From Table 5,

$$\begin{aligned} \text{Weight of vapour} &= 189{,}350 \text{ lbs.} \\ \text{Volume of vapour} &= 757{,}400 \text{ cubic feet.} \\ \therefore \text{ Vapour density} &= \frac{189{,}350}{757{,}400} \text{ lbs. per cubic foot.} \\ &= 0{\cdot}25 \text{ lbs. per cubic foot.} \end{aligned}$$

53. Vapour Velocity through Cap Uptakes.—The total cap uptake area should be about 10–11 per cent. of the plate area. Assume 10 per cent.

$\therefore$ Vapour velocity through the uptakes

$$V = \frac{757{,}400}{\cdot 10 \times 81{\cdot}1 \text{ sq. ft.} \times 3{,}600} \text{ feet per second}$$
$$= 26 \text{ feet per second.}$$

54. Velocity Head of Vapour through the Plate.—The liquid oil equivalent of the vapour velocity head is the height h to which the oil will rise in the downcomer D in Fig. 6.

The velocity head is given by the formula $h = \frac{V^2}{2gc^2}$, where c = discharge coefficient.

c usually varies between 0·38 and 0·54, according to the design of the plate. Taking the figure of 0·45,

$$h = \frac{(26)^2}{2 \times 32{\cdot}16 \times (0{\cdot}45)^2}$$
$$= 52 \text{ feet.}$$

Taking the specific gravity of the hot oil at its boiling point as 0·6, we get the liquid oil equivalent to 52 feet vapour velocity head as

$$\frac{52 \text{ ft.} \times 0{\cdot}25 \text{ lbs. per cubic ft.} \times 12 \text{ in. per ft.}}{(62{\cdot}4 \times 0{\cdot}6) \text{ lbs. per cubic ft.}} = 4{\cdot}2 \text{ ins.}$$

That is, the height to which the hot oil will rise in the downcomer D, Fig. 6, is $h = 4{\cdot}2$ ins.

55. Area of Down Pipes.—The area of the downcomers must be sufficient to pass the maximum volume of reflux.

The volume per minute to be passed is

$$\frac{\text{171,850 lbs. per hour.}}{\text{5 lbs. per U.S. gall.} \times \text{60 mins. per hr.}} = 573 \text{ gallons per minute.}$$

The gravity has been taken as 5 lbs. per U.S. gallon.

The area required is given by the orifice formula

$$a = \frac{Q}{4{\cdot}4\sqrt{h}}$$

where a = area in square inches,
Q = quantity in U.S. gallons per minute,
and h = liquid head equal to the height of the overflow weir, 2·75 inches.

$$\therefore a = \frac{573}{4{\cdot}4 \times 2{\cdot}75} \text{ sq. ins.}$$
$$= 47{\cdot}4 \text{ sq. ins.}$$

$\therefore$ Area of downcomers = 47·4 square inches.
Diameter of ,, = 7·8 inches, say 8 inches.

56. Heat Exchangers and Condensers.—The use of heat exchangers in a distillation plant of any type results not only in a lower fuel consumption, but also in a considerable reduction in the quantity of water required for condensing and cooling the products. The provision of cooling water adds materially to the cost of manufacture in most refineries.

Both heat exchangers and condensers serve the same purpose, in principle, of extracting heat from one fluid through absorption by another. In vapour heat exchangers sensible heat is usually only extracted, but with condensers and residue preheaters the vapours are not only cooled and condensed but the distillates are cooled to a reasonable temperature.

When condensing water is used, the amount required varies considerably with the method of distillation, in other words, whether the distillation is dry or wet. As an example of this, a lubricating oil, if distilled fairly dry, might require 3,000 B.Th.U. per gallon to be absorbed to cool the distillate to a temperature of 150°F., whereas the same fraction, distilled with open steam, would need to have 30,000 B.Th.U. extracted to cool an equal quantity of distillate down to the same temperature, taking into consideration a drop of say 60°F. in the final temperature of distillation, due to the lowering of the partial pressure of the vapours owing to the presence of the steam.

Students should consult the literature quoted in the bibliography at the end of the Chapter, for the design of condensing units and heat

exchanging plant, the most modern of which is the shell and tube type as shown in Fig. 20.

This comprises a number of tubes running between end plates into different compartments, so that the cooling medium is compelled to pass backwards and forwards a number of times through the tubes, and the fluid to be cooled may pass horizontally along the tube surfaces, or be caused to travel across the tubes, several times, by means of baffling.

Heat exchangers may also be of the shell and tube type or of the double-pipe type. In the latter case, the oil to be cooled may pass from one end of the coil to the other through the annular space and the oil to be heated will pass through the inner pipe.

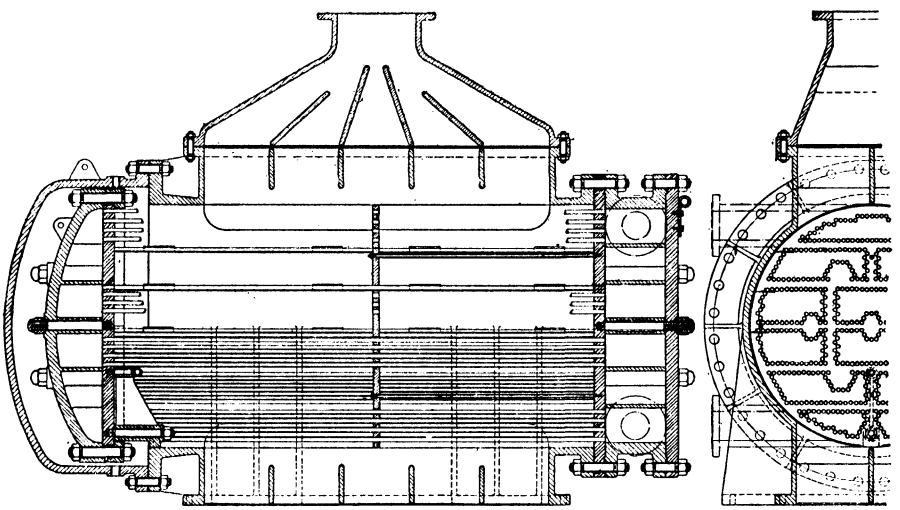


FIG. 20.—DIAGRAM OF FOSTER-WHEELER TYPE I HEAT EXCHANGER SHOWING THE DISTRIBUTING BAFFLES WITHIN THE VAPOUR DISTRIBUTING DOME, THE WATERBOX CONSTRUCTION AND SPLIT RING FLOATING HEAD CONSTRUCTION

The theory of heat exchange is similar in both cases, excepting that when the cooling liquid is oil there is a variation in the physical properties of the cooling medium as well as in the oil being cooled, which tends to complicate the calculations, as will be shown later. For example, not only do increases and decreases in viscosity, specific gravity and volume occur, but, in some instances, vaporisation also takes place.

With the various methods of heat exchange the fluids may be either in parallel flow or counterflow.

In the parallel flow of the two fluids, the transfer of heat will be rapid at the commencement but slow at the finish, and the temperature of the cold fluid cannot be raised above the temperature at which the warmer fluid leaves the apparatus. In the counter-current method, the

cold fluid may be heated well above the temperature to which the warmer fluid is cooled.

It will be apparent, therefore, that counter-current flow should be used when it is desired to transfer as much heat as possible from the warmer fluid and/or to raise the temperature of the colder fluid as much as possible. On the other hand, if it is desired to extract a part of the heat only from the warm fluid, the flow of the fluids should be parallel as, for example, in cooling a heavy residuum, where, if too much heat were extracted, it would become too viscous to flow readily.

57. Heat transfer is not exactly proportional to the difference in inlet and outlet temperatures of the two fluids involved, but is more nearly proportional to the logarithmic mean temperature difference, which is explained more fully later.

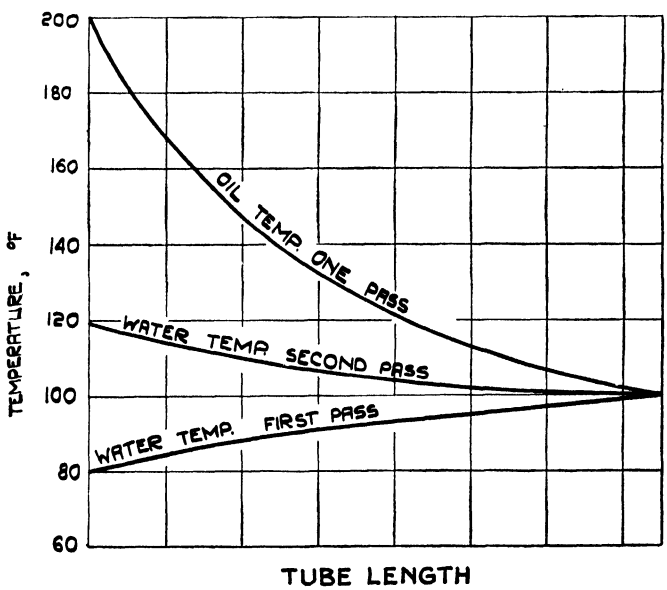


FIG. 21.—CURVES SHOWING MAXIMUM COOLING OBTAINED WITH SINGLE PASS FLOW IN SHELL OF HEAT EXCHANGER

The general equation for the transmission of heat is :—

$$T_T = H A t_m$$

where T_T = total quantity of heat transferred per hour in B.Th.U.
A = area of heat exchange surface in square feet.
H = overall coefficient of heat transfer in B.Th.U. per hour per square foot of heating surface per °F. mean temperature difference.
t_m = mean temperature difference °F.

The constant H is dependent upon the nature of the fluids concerned, condition of surfaces and the mass velocities of the fluids.

In hot climates, where the cooling water is warm, or for any operation involving low terminal temperature differences, multiple passes in both the shell and the tube may be resorted to.

In Fig. 21 a curve is shown giving the maximum cooling which may be obtained in a heat exchanger with an infinite amount of cooling surface with single pass flow in the shell and double pass in the tube bundle, with an entering oil temperature of 200°, an inlet water temperature of 80° and an exit water temperature of 120°F.

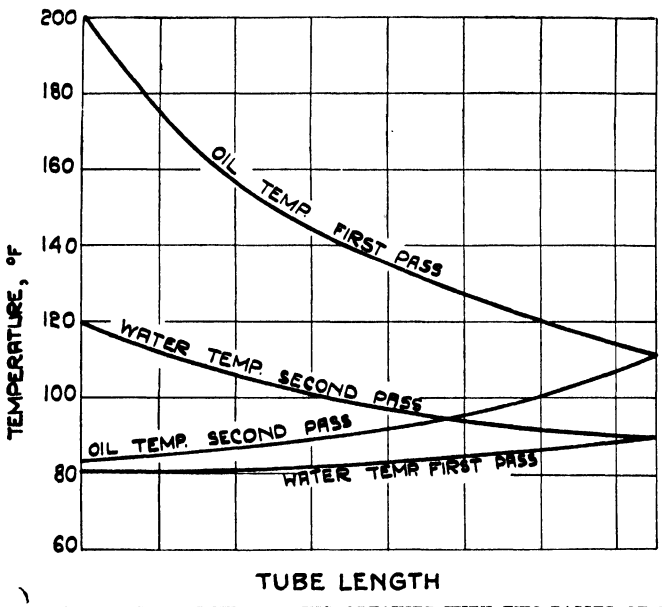


FIG. 22.—CURVES SHOWING MAXIMUM COOLING OBTAINED WITH TWO PASSES OF LIQUID TO BE COOLED IN HEAT EXCHANGER

The curve for two passes of the liquid to be cooled is shown in Fig. 22, other conditions being the same. With the same inlet and exit water temperatures a much greater degree of cooling is possible.

Owing to the high rates of heat transfer obtained in shell and tube units and their small size and weight, these heat exchangers can be mounted on a light steel structure.

58. The Principles of Heat Transfer.—It has been mentioned earlier in this Chapter that the overall coefficient of heat transfer, H, is a complicated function of the velocity, or, more truly, the mass velocity, of each fluid, the nature of the apparatus, the conductivity of the fluids and the metal, and the condition of the heating surface.

This will now be briefly explained.

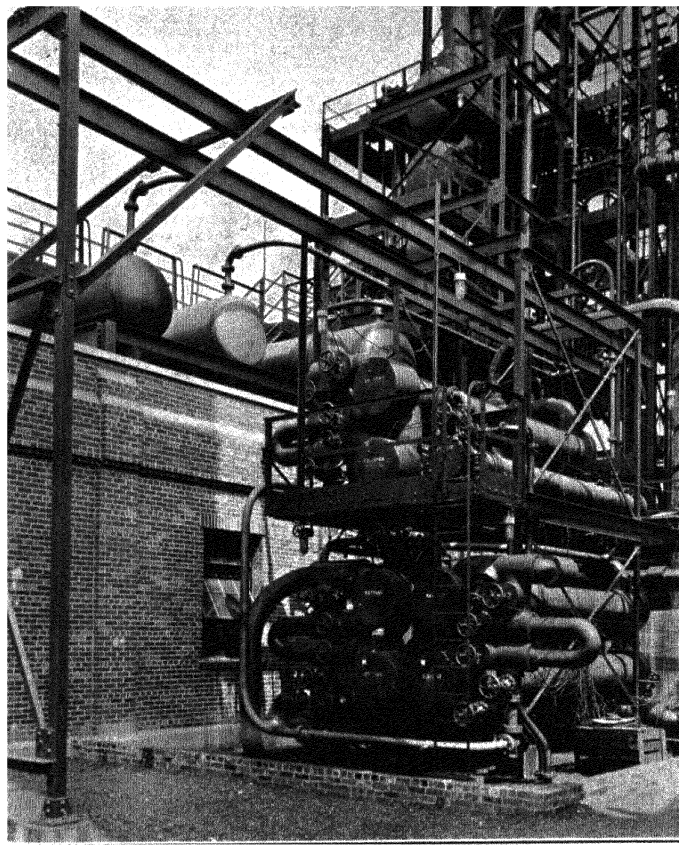


FIG. 23.—SHELL AND TUBE HEAT RECOVERY APPARATUS MOUNTED ON STEEL FRAMEWORK

(Courtesy of Foster Wheeler, Ltd., London)

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59. Newton's Law.—This law states that the quantity of heat passing a given section at right angles to the direction of heat flow is directly proportional to the area of this section, A, to the difference of temperature between the two faces of the section, dt, to the time, $d\theta$, and inversely proportional to the thickness, dL.

Thus

$$\frac{dQ}{d\theta} = -kA\frac{dt}{dL} \quad \ldots\ldots\ldots \quad (25)$$

where k = coefficient of heat conductivity in B.Th.U. per hour, per square foot, per °F., per foot thickness.

If the quantity of heat crossing the unit area per unit time is constant, then

$$\frac{Q}{\theta} = -kA\frac{dt}{dL} = kA\frac{(t_1 - t_2)}{L_2 - L_1} = kA\frac{\Delta t}{L} \quad \ldots\ldots\ldots \quad (26)$$

where Δt = mean difference of temperature between the two faces of the section.

L = thickness.

Heat flowing through several bodies in series. Equation (26) may be re-written as follows :—

$$\frac{Q}{\theta} = \frac{\Delta t}{L/kA} = \frac{\Delta t}{R} \text{ B.Th.U. per hour} \quad \ldots\ldots \quad (27)$$

where " R " represents the resistance of the body to heat flow. If there are several resistances in series, then the following equation is obtained :—

$$\frac{Q}{\theta} = \frac{\Delta t}{R} = \frac{\Delta t_1 + \Delta t_2 + \ldots + \Delta t_n}{R_1 + R_2 + \ldots + R_n} = \frac{\Delta t}{\frac{L_1}{k_1A_1} + \frac{L_2}{k_2A_2} + \ldots + \frac{L_n}{k_nA_n}} \quad \ldots \quad (28)$$

60. The Interfacial Film Concept.—Whenever a moving fluid comes in contact with a solid, there exists a comparatively stagnant thin film of the fluid adhering to the surface of the solid in which motion by convection is very slight, and through which heat can only be transferred by conduction. A temperature gradient is set up across this interfacial film, while in the main body of the fluid the temperature is assumed to be practically uniform due to convection currents.

Since most fluids are very bad conductors of heat, the resistance of such a film to heat flow is considerable and this is the most important factor in designing heat exchange equipment.

Fig. 24 shows the heat exchange between two fluids separated by a solid wall. It will be seen that the temperature gradient in the two fluid films is steep, whereas it is negligible across the solid retaining wall

on account of the latter having a good heat conductivity compared to that of the fluids.

It would be an easy matter to design heat exchange equipment if the effective fluid film thicknesses were known, since

$$\frac{Q}{\theta} = kA \frac{\triangle t}{L} \text{ B.Th.U. per hour.}$$

The effective thickness of the fluid film, L, however, is unknown and it is usual in such cases to replace $\frac{k}{L}$ by h, i.e.,

$$\frac{Q}{\theta} = hA \triangle t \text{ B.Th.U. per hour} \quad . \quad . \quad . \quad . \quad (29)$$

where h = film coefficient in B.Th.U. per hour, per square foot, per °F. mean temperature difference.

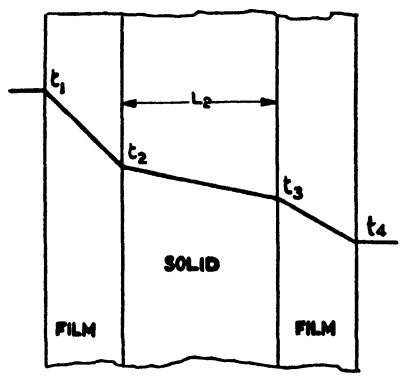


FIG. 24.—HEAT EXCHANGE BETWEEN TWO FLUIDS SEPARATED BY A SOLID WALL

Thus, knowing the film coefficient, h, the need for ascertaining the film thickness disappears. Then equation (28) applied to the case in Fig. 24 becomes :—

$$\frac{Q}{\theta} = \frac{\triangle t}{\frac{1}{h_1 A_1} + \frac{L_2}{k_2 A_2} + \frac{1}{h_3 A_3}} = \frac{\triangle t}{R} = H.A_{av} \triangle t \quad . \quad . \quad . \quad (30)$$

Therefore,

$$H.A_{av} = \frac{1}{\frac{1}{h_1 A_1} + \frac{L}{k_2 A_2} + \frac{1}{h_3 A_3}} \quad . \quad . \quad . \quad . \quad . \quad (31)$$

where A_{av} = average of the areas,
H = overall coefficient of heat transfer.

If the retaining wall is of metal, its resistance can usually be neglected in practice except where the heat transfer coefficients through the fluid films are very high, or where thick tubes are used.

61. Formula (31) applies to clean pipes only, and where a scale or deposit forms on the pipe wall a further resistance to heat flow is introduced, which in some cases can exceed the resistance of the fluid films; thus the final form of equation (31) becomes

$$\text{H. A}_{av} = \frac{1}{\frac{1}{h_1 A_1} + \frac{L_2}{k_2 A_2} + \frac{L'_2}{k'_2 A'_2} + \frac{1}{h_3 A_3}} \quad \ldots \quad (32)$$

where $\frac{L'_2}{k'_2 A'_2}$, represents the resistance of the deposit or scale.

The resistance due to this scale will be increased by its combination with oil, the oil being absorbed in the pores of the scale and forming a coating which offers a much higher resistance to heat flow.

The practical difficulty in determining the resistance of such scales is obvious and nearly all the data so far obtained have been for clean tubes.

The method usually adopted is to calculate the overall coefficient of heat transfer from equation (31), and multiply the result by a " cleanliness factor," which depends largely on the type of fluid, the nature of the plant, the allowable cleaning intervals, etc., and with our present state of knowledge must be left to the experience and judgment of the designer. The value of this factor may vary between 0·3 and 0·9.[7]

The heat transfer per unit area is very low when fluid flow is viscous, thus whenever possible the heat exchange apparatus should be proportioned to give turbulent flow.

62. Calculation of Thermal Conductivity.—The thermal conductivity of petroleum oils can be calculated approximately from the following equation[8]:—

$$k = \frac{\cdot 06775}{\delta} \{1 - 0{\cdot}0003\,(t - 32)\},$$

where k = thermal conductivity in B.Th.U. per hour, per square foot per °F. per foot thickness.
δ = specific gravity of liquid at 60°/60°F.
t = temperature in °F.

This equation is based on the experimental results obtained at atmospheric pressure on a total of 18 petroleum oils by seven different observers and is fairly consistent with most of the available experimental data on petroleum oils.

The values of k at any temperature and gravity can be readily found from the chart, Fig. 25.

63. Calculation of Film Coefficients.—In order to calculate the overall heat transfer coefficient, the values of the individual film co-

efficients are first determined. These coefficients, however, are not constant, even for a given fluid, and are complex functions of many

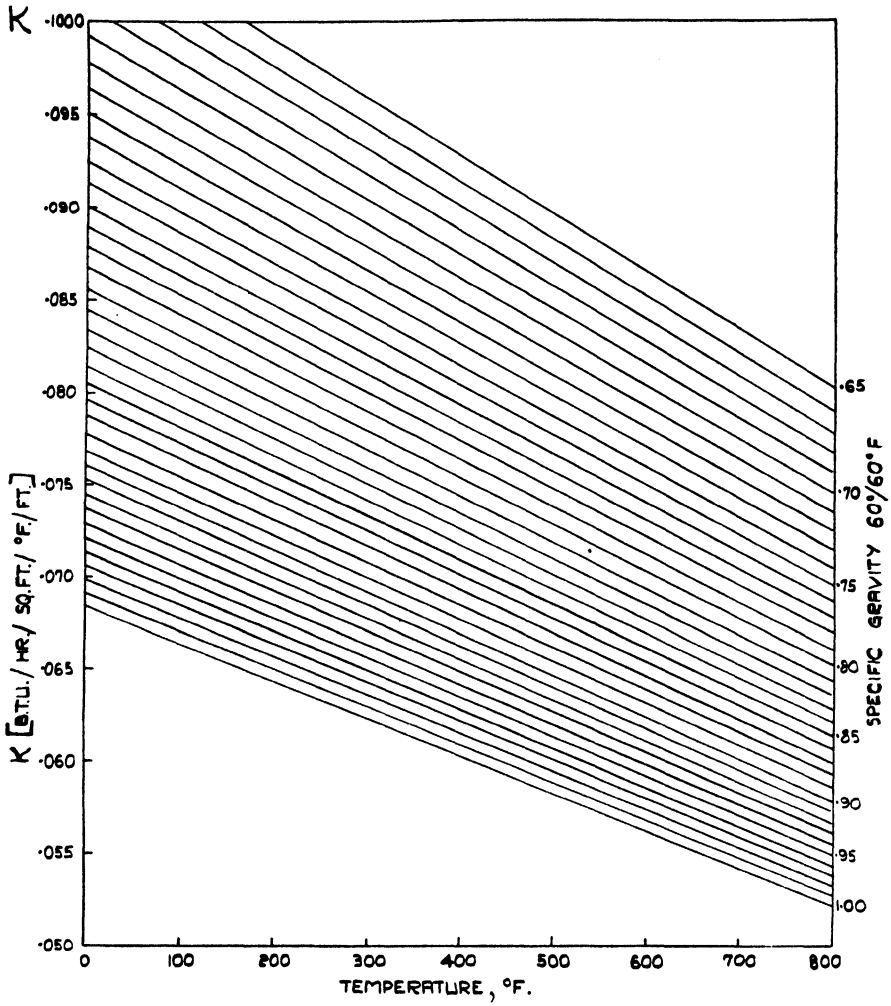


FIG. 25.—CHART SHOWING VALUES OF k AT VARIOUS TEMPERATURES AND GRAVITIES

Instructions for reading the chart: From the point of intersection of the inclined lines representing the specific gravity δ, and vertical lines passing through the temperatures, draw a horizontal line to read the value of k.

Example: Find "k" for a petroleum oil having a specific gravity of ·8 and at a temperature of 400°F. The intersection of specific gravity and temperature lines (·8 and 400 respectively) is at a point which gives k = ·0754.

variables such as the physical properties of the fluids, their velocity, and the nature and shape of the retaining surface.

From the principles of dimensional analysis, Nusselt proposed the following equation for liquids flowing in pipes:

$$\frac{hd}{k} = \phi_1\left(\frac{du\rho}{\mu}\right)\phi_2\left(\frac{C\mu}{k}\right) \quad . \quad . \quad . \quad . \quad . \quad (33)$$

where d = diameter of the pipe,
k = thermal conductivity of fluid,
C = specific heat of fluid,
μ = viscosity of fluid,
ρ = density of fluid,
u = average velocity of fluid,
ϕ_1 and ϕ_2 = functions to be determined.

Nusselt[9] assumed power functions, writing

$$\frac{hd}{k} = a\left(\frac{du\rho}{\mu}\right)^n\left(\frac{C\mu}{k}\right)^m \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

McAdams and Frost[10] deduced a formula from data obtained from heating water in pipes, in which they neglected any variation in $\frac{C\mu}{k}$, but introduced a factor r which is equal to the ratio of length to diameter of pipe, so :—

$$\frac{hd}{k} = 0{\cdot}0272\left(1 + \frac{50}{r}\right)\left(\frac{du\rho}{\mu_f}\right)^{0{\cdot}8} \quad . \quad . \quad . \quad . \quad (35)$$

where h = average film coefficient of heat transfer between the surface and the fluid in B.Th.U. per hour per square foot per °F. mean temperature difference.
k = thermal conductivity in B.Th.U. per hour per square foot per °F. per foot.
d = inside diameter of tube in feet.
$u\rho$ = mass velocity of fluid through tube in pounds per hour per square foot of cross section.
μ_f = fluid viscosity at the mean film temperature.

The mean film temperature was taken as the mean temperature of the inner surface of the tube, less half the logarithmic mean temperature difference between the tube surface and the average fluid temperature.

The factor r allows for end effects. Obviously, when the pipe length is short compared with its diameter, the favourable effect of extra turbulence set up in the fluid at the inlet will be appreciable.

64. Numerous equations have been proposed by different investigators for film coefficients.

Probably the best equations proposed so far are those of Dittus and Boelter,[11] who studied the data of several investigators on both air and

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water, and also the data of Morris and Whitman,[12] on heating and cooling oils. These are

$$\frac{hd}{k} = 0{\cdot}024\left(\frac{du\,\rho}{\mu}\right)^{0.8}\left(\frac{C\,\mu}{k}\right)^{0.4} \text{ for heating} \quad . \quad . \quad . \quad . \quad (36)$$

$$\frac{hd}{k} = 0{\cdot}026\left(\frac{du\,\rho}{\mu}\right)^{0.8}\left(\frac{C\,\mu}{k}\right)^{0.3} \text{ for cooling} \quad . \quad . \quad . \quad . \quad (37)$$

where μ = fluid viscosity at main body average temperature $\left(\text{i.e., at } \frac{t_1 + t_2}{2}\right)$.

C = specific heat, B.Th.U. per pound per °F.

The remaining symbols have the same significance as those in equation (35).

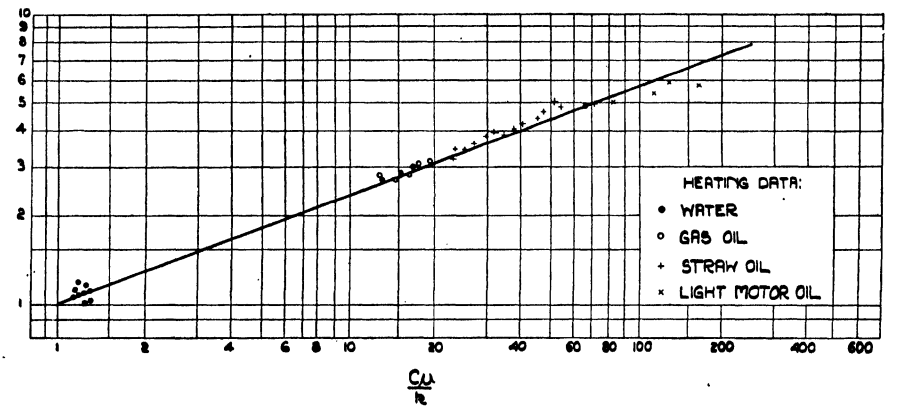


FIG. 26
(After Morris & Whitman)

The equations of Dittus and Boelter given above were later confirmed by Sherwood,[13] who carried out a series of experiments on water, acetone, benzene, kerosene and *n*-butyl alcohol. His results for turbulent flow are in good agreement with the equations of Dittus and Boelter.

65. From the data of Morris and Whitman, where main stream properties have been used, an easy method of determining h is obtained. As stated before :

$$\frac{hd}{k} = \phi_1\left(\frac{du\,\rho}{\mu}\right)\phi_2\left(\frac{C\,\mu}{k}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

where, using mixed but convenient units

d = diameter of pipe in inches.

h = coefficient of heat transfer in B.Th.U. per hour per square foot per °F. mean temperature difference.
k = thermal conductivity in B.Th.U. per hour per square foot per °F. per foot of thickness.
ρ = density of fluid in lbs. per cubic foot.
u = average velocity in feet per second.
μ = viscosity in centipoises.
C = specific heat.

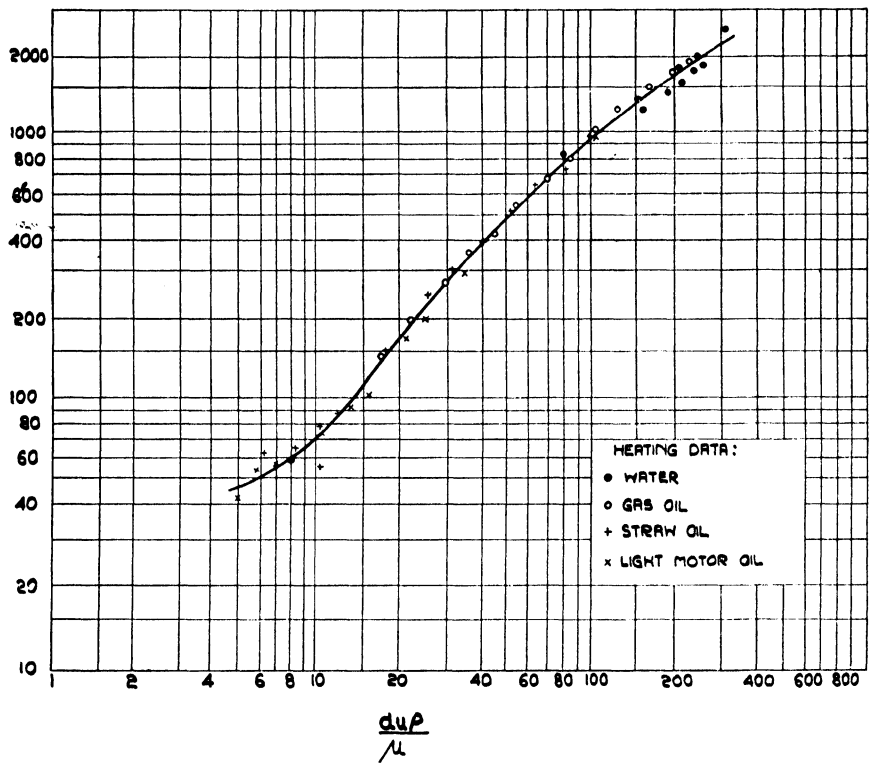


FIG. 27
(After Morris & Whitman)

Fig. 26 is a plot of $\phi_2\left(\frac{C\mu}{k}\right)$ against $\frac{C\mu}{k}$ and Figures 27 and 28 are plots of $\phi_1\left(\frac{du\rho}{\mu}\right)$ against $\frac{du\rho}{\mu}$ for heating and cooling runs respectively, $\frac{C\mu}{k}$ and $\frac{du\rho}{\mu}$ being in the mixed units defined above. It should be noted that equations (36) and (37) must be used with consistent

units, whereas the units employed in connection with Figs. 26, 27 and 28 are mixed units.

For a given set of conditions h is calculated as follows :

Calculate $\frac{C\mu}{k}$ and $\frac{du\rho}{\mu}$ and read $\phi_2\left(\frac{C\mu}{k}\right)$ and $\phi_1\left(\frac{du\rho}{\mu}\right)$ from Figs. 26 and 27, or 28. Then calculate $\frac{hd}{k}$ from equation (33) when h is readily found.

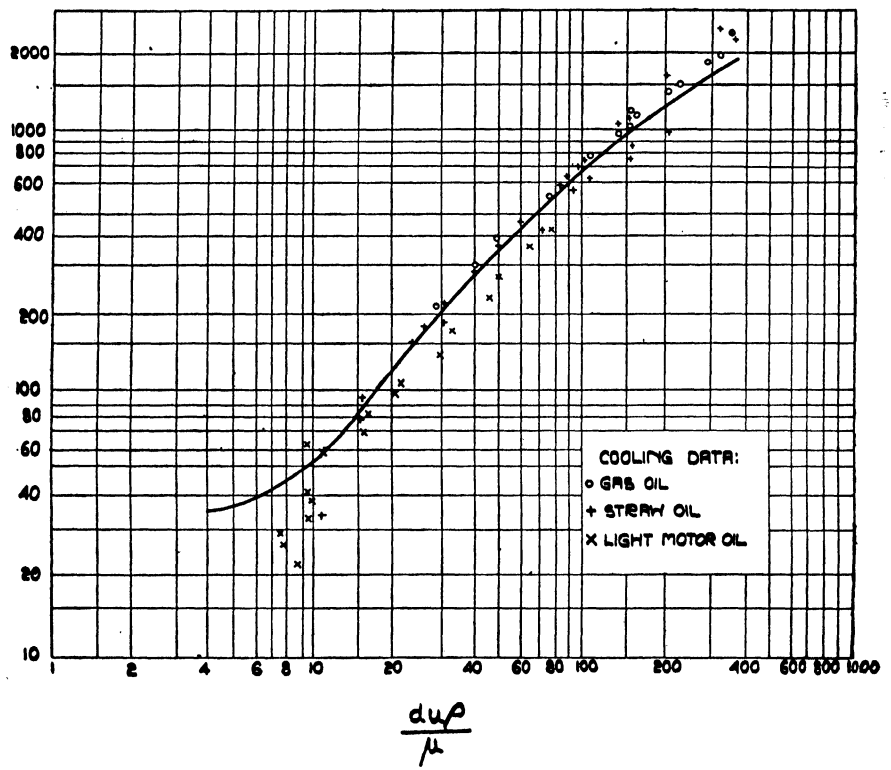


FIG. 28
(After Morris & Whitman)

For instance, suppose a crude oil is being heated in a long pipe 3·07″ diameter, the oil is at 150°F., and at that temperature its density is 50 pounds per cubic foot, its viscosity 1·5 centipoises and its specific heat 0·51. It is flowing with a linear velocity of 2 feet per second, then

$$\left(\frac{du\rho}{\mu}\right) = \frac{3{\cdot}07 \times 2 \times 50}{1{\cdot}5} = 205$$

$$\left(\frac{C\mu}{k}\right) = \frac{0{\cdot}51 \times 1{\cdot}5}{0{\cdot}078} = 9{\cdot}8$$

From Fig. 27 (since heating is being considered)

$$\phi_1\left(\frac{du\,\rho}{\mu}\right) = 1{,}600$$

From Fig. 26, $\phi_2\left(\frac{C\,\mu}{k}\right) = 2{\cdot}3$

Therefore, $\frac{hd}{k} = \phi_1\left(\frac{du\,\rho}{\mu}\right)\phi_2\left(\frac{C\,\mu}{k}\right) = 1{,}600 \times 2{\cdot}3 = 3{,}700$

and $h = \frac{3{,}700 \times 0{\cdot}078}{3{\cdot}07} =$ 94 B.Th.U. per hour per square foot per °F. mean temperature difference.

If the oil changes greatly in temperature while flowing through a pipe, it is not permissible to take its average temperature and from this calculate an average coefficient, since the temperature-viscosity curves are not straight lines.

Where the viscosity change is great, it is suggested that for calculation purposes the pipe be broken up into sections in which the viscosity does not change more than say threefold.

66. Optimum Velocity of the Fluid inside the Pipe.—It will be seen from the foregoing that when fluids are flowing in turbulent motion high velocity gives good heat transfer, and, therefore, reduces equipment expense, but causes high power consumption.

In designing heat transfer equipment, the fluid velocity should be chosen to secure a proper economic balance between installation and operation costs.

If the diameter of the pipe is known, the optimum velocity which makes the total costs a minimum can be calculated from the following formula.[14]

$$G'_{opt} = 2{\cdot}75\sqrt{\frac{12{,}700\,\gamma\,\rho^2(D')^{0{\cdot}25}\,n}{(Z)^{0{\cdot}25}\,B^{(2{\cdot}75-n)}}} \quad \ldots\ldots \quad (38)$$

where G'_{opt} = optimum weight velocity of fluid in tubes, lb. per second per square foot of cross sectional area.

ρ = density of fluid, in lbs. per cubic foot.

D′ = diameter of pipe, in inches.

Z = viscosity of fluid, in centipoises.

B = correction factor for end effects, ratio of equivalent frictional length to actual length.

n = exponent in the formula $h = a(G')^n$, in which h, the individual coefficient of heat transfer, varies as the nth power of the weight velocity of the fluid, G′.

The normal value of n is 0·8, but for cases where $\frac{d\ u\ \rho}{\mu}$ is less than 50, n changes rapidly from this normal value, and in such cases the actual value of n should be employed.

$\gamma = be/ac$ where

b = total installed cost of pipe, in currency units per square foot of inside surface.

e = per cent. annual charges on equipment, including fixed charges, maintenance and depreciation, etc.

a = cost of energy, in currency units per horse power-hour delivered to the fluid, allowing for efficiencies of motors and pumps and maintenance and operation of pumping equipment.

c = total hours operation per year.

Having fixed the diameter and the velocity, the film coefficient is readily calculated as shown before, from which the overall coefficient of heat transfer is derived.

The next step is to calculate the area of the heat exchanger for

$$\frac{Q}{\theta} = \text{H.A. } \triangle t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

67. Mean Temperature Difference.—In a heat exchange apparatus whether employing counter-current or parallel flow, the temperature of the fluid varies from the inlet to the exit and a mean temperature difference tm, should be used instead of $\triangle t$.

$$\text{i.e., } \frac{Q}{\theta} = \text{H.A. } tm \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

Parallel Flow.	Counter-Current Flow.
Fluid No. 1	Fluid No. 1
$t_1 \longrightarrow t'_1$	$t_1 \longrightarrow t'_1$
$t_2 \longrightarrow t'_2$	$t_2 \longleftarrow t'_2$
Fluid No. 2	Fluid No. 2

The mean temperature difference is given by :

$$tm = \frac{(t_1 - t_2) - (t'_1 - t'_2)}{\log_e (t_1 - t_2) - \log_e (t'_1 - t'_2)} \quad . \quad . \quad . \quad . \quad (41)$$

If $t_1 - t_2 = t$
and $t'_1 - t'_2 = t'$

$$\text{then } tm = \frac{t - t'}{\log_e t - \log_e t'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

Fig. 29 is an alignment chart[15] for determining tm in which the values of tm, t and t' satisfying the above equation fall on the same straight line, thus for example :

if $t = 24$ degrees
and $t' = 90$

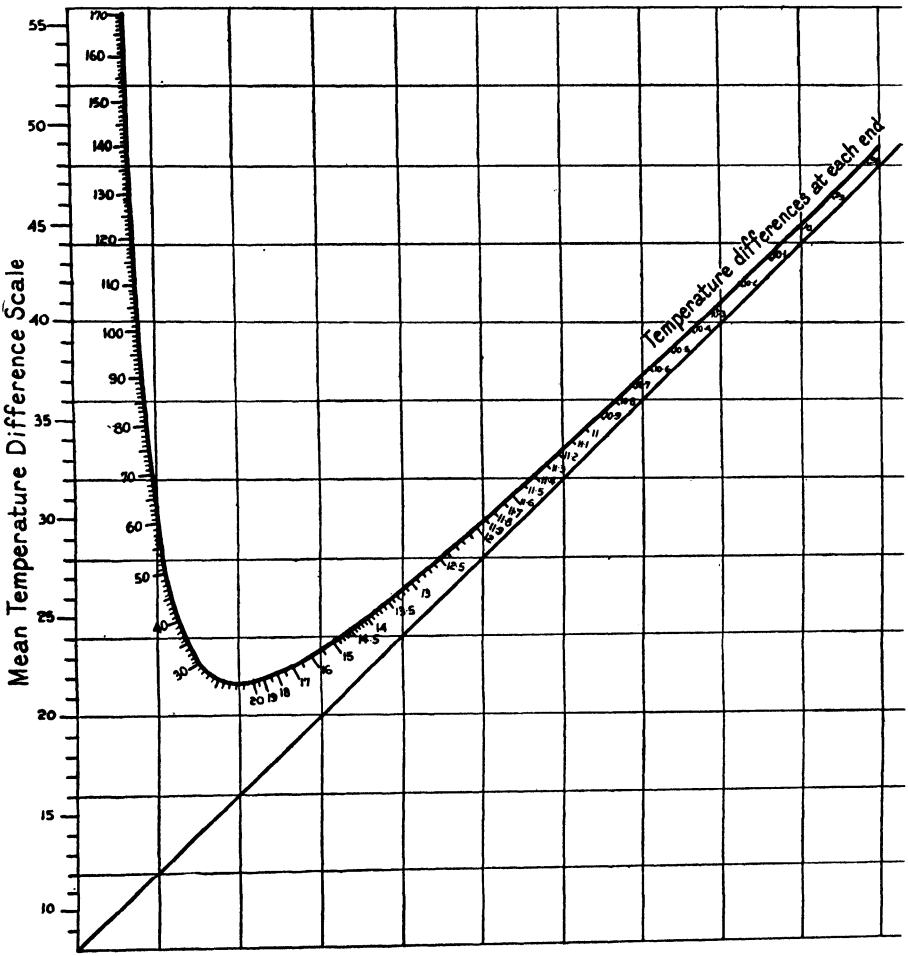


FIG. 29.—CHART FOR DETERMINATION OF MEAN TEMPERATURE DIFFERENCES
(After Roulleux)

we can read $tm = 49{\cdot}8$ degrees at the intersection of the straight line passing through the points 24 and 90 of the curved scale with the straight scale along the ordinate axis, but we can also read $\frac{tm}{2} = 24{\cdot}9$ at the intersection of the straight line passing the points $\frac{t}{2} = 12$ and $\frac{t'}{2}$

= 45 of the curved scale with the ordinate axis. This latter method may be used when the figures do not come within the scope of the diagram.

Where the overall coefficient of heat transfer (H) varies throughout a heat exchanger the calculation of heat transfer by use of the logarithmic temperature difference as above may lead to considerable error. For the case where H is a linear function of temperature Colburn[18] derived the simple relationship that the heat transfer rate is equal to the logarithmic mean of H_1t_2 and H_2t_1, the subscripts indicating terminal conditions.

$$\text{Hence } \frac{Q}{\theta A} = \frac{H_1t_2 - H_2t_1}{\log_e H_1t_2 - \log_e H_2t_1} \quad \ldots\ldots (43)$$

68. Calculation of the Surface of the Heat Transfer Apparatus.— From equation (40),

$$A = \frac{Q}{\theta} \times \frac{1}{H} \times \frac{1}{tm} \quad \ldots\ldots (44)$$

Figure 30 furnishes a graphical method of determining A, as follows: *Example.* Calculate the surface of a heat transfer apparatus to transfer 1,000,000 B.Th.U. per hour under conditions corresponding to the following diagram, with a heat transfer coefficient H = 150 B.Th.U. per hour per square foot per degree F. mean temperature difference.

194°F. ——————→ 80°F.
140°F. ←—————— 65°F.

The temperature differences at the two ends are 54°F. and 15°F., respectively.

Using Fig. 30, the straight line passing through the points 15° and 54° of the curved scale intersects the ordinate axis at a certain point corresponding to the mean temperature difference 30·4. The horizontal line drawn from this last point intersects the straight line marked H = 15 (which is $\frac{1}{10}$ of the given value 150) at a point, the abscissa of which, read on the horizontal scale, gives 0·00219. Before taking the reading we have divided the given heat exchange coefficient H by 10; therefore, the last reading must also be divided by 10, giving 0·000219 as the value of $\frac{1}{H} \times \frac{1}{tm}$. This figure multiplied by the number of B.Th.U. to be transferred per hour, i.e., 1,000,000, gives 219 square feet as the area of the heat transfer surface required.

In the foregoing the mean temperature difference has been calculated for a single-pass heat exchanger. Nagle[16] has shown that serious errors arise if the logarithmic mean formula is used for multi-pass heat exchangers and Underwood[17] gives the following formula for such cases.

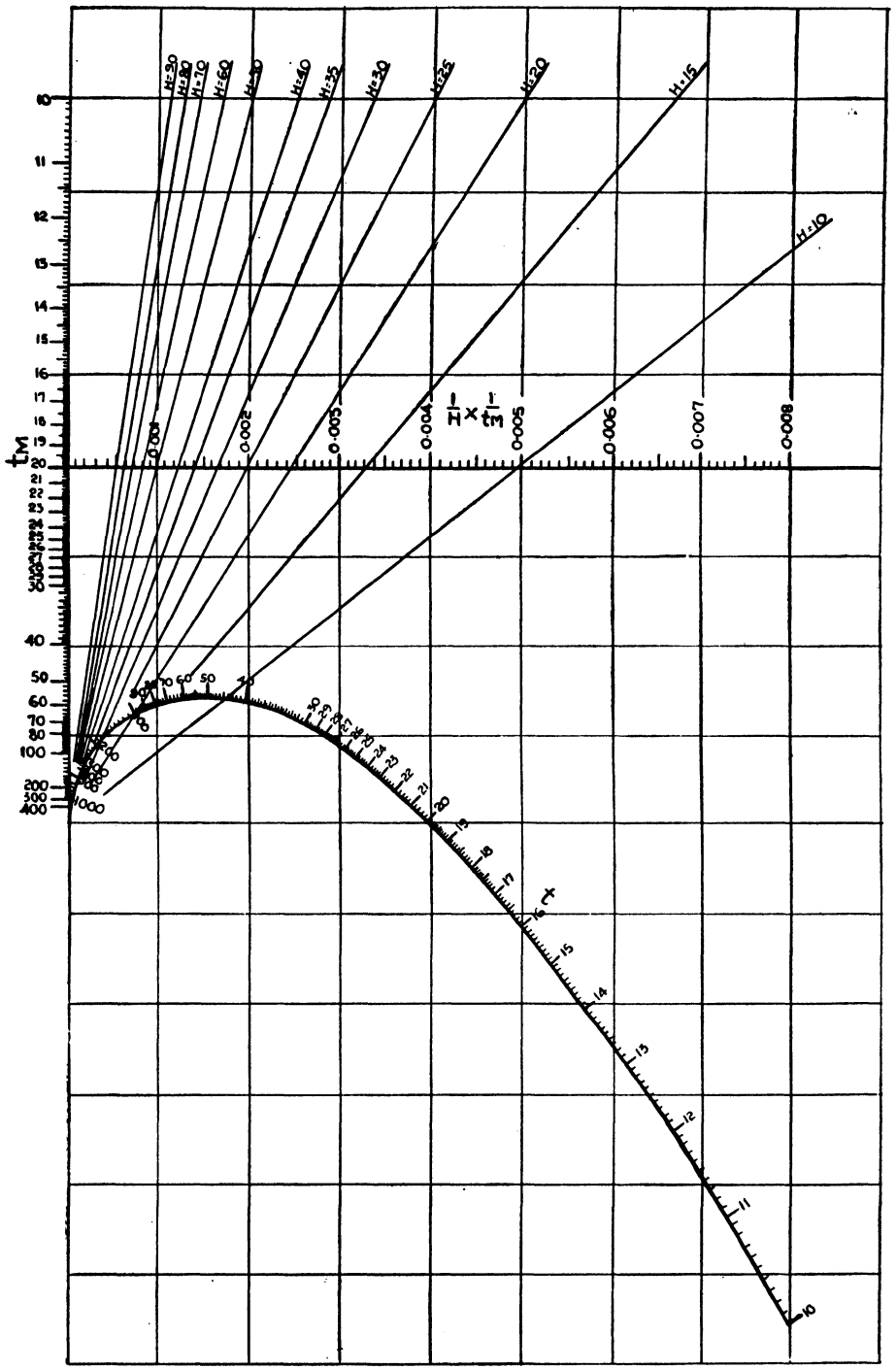


FIG. 30
(After Roulleux)

$$t_m = \frac{\sqrt{(t_1 - t'_1)^2 + (t_2 - t'_2)^2}}{\log_e \left[\frac{(t_1 + t'_1) - (t_2 + t'_2) + \sqrt{(t_1 - t'_1)^2 + (t_2 - t'_2)^2}}{(t_1 + t'_1) - (t_2 + t'_2) - \sqrt{(t_1 - t'_1)^2 + (t_2 - t'_2)^2}} \right]} \quad . \quad (45)$$

The symbols used are the same as for equation (41).

69. Viscous Flow.—In practice, true viscous flow is very rarely obtained in heat transfer apparatus owing to cross currents set up by temperature differences in various parts of the fluid, and the film coefficient calculated from published formulæ for viscous flow usually falls below that obtained in practice.

70. Pressure Drop across Banks of Tubes.—The pressure drop due to the flow across banks of staggered tubes is of importance in the design of heat exchangers. It depends upon the disposition and dimensions of the heating surface and the velocity, density and viscosity of the fluid. A well-designed heat exchanger will show an economic pressure drop per unit of heat transfer.

Chilton and Genereaux[19] have correlated all the existing data and recommend that the value of the fraction factor f, to be introduced into the Fanning equation, be

$$f = 0{\cdot}75 \left[\frac{\mu}{d_s \, \mu_{max} \, \rho} \right]^{0{\cdot}2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

for staggered tubes.

where d_s = clearance between tubes in a row,
μ_{max} = velocity in narrowest cross section.

The Fanning equation for pressure drop, in self-consistent units, then becomes

$$\Delta p = \frac{1{\cdot}5 \rho^{0{\cdot}8} \, \mu_{max}{}^{1{\cdot}8} \, \mu^{0{\cdot}2} \, N}{g \, d_s{}^{0{\cdot}2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

where N = number of rows of tubes.

For rectangular spacing the equation recommended is

$$\Delta p = \frac{4f \, \rho \, \mu^2_{max} \, N}{2 \, g} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (48)$$

where $f = 0{\cdot}33 \left[\frac{\mu}{d_s \, \mu_{max} \, \rho} \right]^{0{\cdot}2}$ . . . . . (49)

This is identical with the equation for staggered tubes except that the friction factor is only 44 per cent. as great.

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Chapter II

THE PRODUCTION OF MOTOR FUELS FROM PETROLEUM BY CRACKING

74. Introduction.—Cracking and Pyrolysis are terms used to denote the thermal decomposition of hydrocarbons, whereby low boiling substances are produced by breaking down the larger molecules present in higher boiling oils.

This pyrolysis of complex hydrocarbons gives, besides simpler hydrocarbons, smaller amounts of hydrocarbons of considerably greater complexity than the original material.

The heavier products of cracking, which are formed in industrial processes in varying amounts depending on the type of original charging stock used, conditions of cracking, and the method employed, are due to secondary reactions, such as the polymerisation of highly unsaturated light products. By such polymerisation or condensation, hydrocarbons much higher in molecular weight than any present in the original stock are formed.

If oil is heated to very high temperatures, then the final products are carbon and hydrogen, but if the temperature be moderated to suit the requisite end-products, then for each particular oil there is an optimum yield of spirit.

A simple example of such cracking is

$$C_{20}H_{42} \xrightarrow{\text{Heat}} C_{10}H_{22} + C_{10}H_{20}$$

in which a paraffin hydrocarbon splits up into a paraffin and an olefine both of lower molecular weight than the original paraffin.

A case of cracking to completion is :

$$C_4H_{10} = 4C + 5H_2$$

in which butane is decomposed to carbon and hydrogen. In commercial cracking for gasoline production this type of reaction must be prevented as far as possible.

The commercial cracking of heavy oils into petrol is of comparatively recent development brought about largely by the growth of the motor industry.

Some forty years ago petrol was in little demand and in many

fields was burned to waste. The development of the motor industry has caused an ever increasing demand for motor fuel, and, had it not been for the introduction of the cracking process, this industry could not have expanded to its present size, as the price of petrol would have been prohibitive.

It has been explained in Chapter I that a crude oil can produce only a given amount of petrol by straight-run distillation, consequently, had all the petrol at present in use been derived by this method, it would have necessitated raising an amount of crude petroleum out of all proportion to the existing consumption of other products. This would have resulted in waste which the cost of the straight-run spirit would have had to bear.

Cracking may be said to be the most effective force in oil conservation to-day, as about one-third of the world's petrol supply is derived from cracking; consequently, far less crude oil is required to meet the motor fuel demand.

Although the chemistry of cracking is complicated and imperfectly understood, it may be said that the fundamental controlling factors are concerned with the rate of reaction and equilibrium phenomena.

Cracking is a sequence of decomposition and polymerisation reactions, the character of the final products being governed by conditions which, apart from the nature of the hydrocarbons present in the original stock, are the working temperature and pressure, and the time of exposure to cracking conditions. Temperature not only influences the rate of molecular decomposition, dehydrogenation being a special case, but also influences the rate of polymerisation.

The development of the cracking process, particularly from the point of view of control of operating conditions and general flexibility, has enabled the range of cracking stocks to be extended considerably.

Stocks for cracking now include petroleum oils ranging from the heaviest distillation residues, e.g., reduced crudes and residues from cracking, over the whole range of distillates from gas oil and kerosene to the lightest gasolines. It has also been found economic, in some cases, to use the whole of the crude oil as the cracking stock, to produce a yield of cracked gasoline comparable to the combined yields of straight-run gasoline and the cracked gasoline from the topped crude. In this manner, the throughput capacity for a given charge is increased considerably over that of the two separate processes, and the anti-knock value of the product is also improved.

With increase in boiling point, the hydrogen-carbon ratio of petroleum oils decreases, and this fact has an important bearing on the cracking and hydrogenation of petroleum.

75. The Principles of Cracking.—Thorpe and Young[1] found that

whilst olefines and paraffins were produced by the decomposition of paraffins at moderate temperatures, no coke was formed. In the higher fractions of the cracked product paraffins predominated, whereas the lower fractions contained practically equal amounts of olefines and paraffins.

At high temperatures, or when heating was continued for a long period, secondary reactions were found to occur, so that the final product was not merely the result of primary dissociation, but was also affected by the action of heat on the substances formed thereby. Aromatic charging stocks were found to be responsible for heavy coke formation.

76. Hague and Wheeler[2] subjected to pyrolysis the unbranched paraffins from methane to hexane, and suggested as typical primary reactions the following:

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

$$C_3H_8 \begin{cases} \longrightarrow CH_4 + C_2H_4 \\ \longrightarrow H_2 + C_3H_6 \end{cases}$$

$$C_4H_{10} \begin{cases} \longrightarrow C_2H_6 + C_2H_4 \\ \longrightarrow CH_4 + C_3H_6 \\ \longrightarrow H_2 + C_4H_8 \end{cases}$$

$$C_6H_{14} \longrightarrow CH_4 + C_5H_{10}$$

Their general conclusions were :—

(*a*) The temperatures 700° to 750°C. represent a transition stage from primary to secondary reactions for all paraffin hydrocarbons. Below 700°C. each hydrocarbon was found to undergo its own characteristic transformation, whereas at higher temperatures secondary reactions were considered to be common to all.

(*b*) Aromatic hydrocarbons are formed between the temperature range 650° to 1000°C., the course of the reaction being primarily the formation of a simple olefine from the paraffin, then the production of a higher olefine containing a conjugated double bond, followed by aromatic hydrocarbon formation.

(*c*) Primary decomposition of all the hydrocarbons investigated indicated rupture of the chain at any position, with the production of an olefine and the complementary lower paraffin, or hydrogen.

(*d*) As the series is ascended, the tendency for hydrogen to be eliminated, leaving an olefine with the same number of carbon atoms as the original paraffin, rapidly diminishes.

77. Sachanen and Tillicheev[3] are also among the more important workers in this field. The results of their investigations may be summarised as follows :—

(*a*) The tendency for the paraffins to decompose at the middle of the chain increases with increase in molecular weight of the parent hydrocarbon.

(*b*) The decomposition reactions of the olefines are more complicated than in the case of the paraffins, and the conversion of olefines into corresponding naphthenes is possible but the reaction velocity is slow.

(*c*) Of the substituted aromatic and naphthene hydrocarbons, the methyl substituted benzenes, and, to a lesser extent, the ethyl substituted benzenes, are the most resistant to heat and have not so great a tendency to decompose. The substituted benzenes with longer side chains, on the other hand, decompose easily, splitting off side chains and forming either olefines or paraffins.

(*d*) The napthenes with side chains decompose to about the same extent as aromatic hydrocarbons with the formation of olefines.

(*e*) The naphthenes may be dehydrogenated with the formation of aromatic hydrocarbons.

78. Of the work of Francis[4] the following conclusions are of importance on this subject.

(*a*) Acetylene is not formed in cracking reactions below a temperature of 850°C.

(*b*) The synthesis of benzene from acetylene is possible except at very high temperatures.

(*c*) At low temperatures the paraffins are more stable than olefines with the same number of carbon atoms, while at high temperatures the olefines are the more stable.

(*d*) The production of aromatics from olefines requires a temperature of from 550° to 900°C.

(*e*) The formation of an olefine, with the same number of carbon atoms, from a paraffin by the removal of hydrogen, is possible only at high temperatures and to a very limited extent.

These investigators have experimented mostly with simpler hydrocarbons, which are the easiest to obtain in a reasonable state of purity. It is the behaviour of the heavier fractions in which the refiner is more interested, however.

Nevertheless, from the results obtained, it may be stated, generally, that :—

At the cracking temperatures used in industry the paraffin hydrocarbons decompose most readily, followed by the higher olefines and the naphthenes while the aromatics are the most stable. The aromatics are the principal constituents giving rise to coke.

Frolich[5] suggests that all petroleum hydrocarbons, with the exception of methane, are inherently unstable thermodynamically above a temperature about 200°C., but as the rate of reaction is so slow below this temperature practically no decomposition occurs even in the case of the most complex and unstable compounds.

As the temperature increases, the hydrocarbon stability decreases and the temperature coefficients of the reaction vary for the different series. For example, from 400°C., there is an increasing tendency towards the formation of aromatics from paraffins, although these aromatics tend to decompose further into methane, carbon and hydrogen at higher temperatures.

79. Thermodynamic considerations lead to the conclusion that, under the conditions of temperature and pressure ordinarily employed in practice, the cracking of a hydrocarbon into two smaller hydrocarbon molecules is a non-reversible process. On the other hand, reactions involving liberation of hydrogen are frequently of the reversible type, such as the formation of aromatics by the removal of hydrogen from naphthenes, and the liberation of hydrogen from a paraffin to form an olefine with the same number of carbon atoms.

Because of this not only may paraffins yield olefines, but olefines may be hydrogenated to paraffins : naphthenes may be dehydrogenated to aromatics and vice versa.

Although the splitting off of hydrogen from a hydrocarbon is favoured by an increase in temperature, and the necessary temperature decreases with increase in molecular weight in a given series, pressure tends to retard dehydrogenation.

In the temperature range 400° to 600°C., Frolich lists the various series of hydrocarbons in the following order of decreasing tendency to crack, the comparison being based on compounds of equal molecular weight.

Paraffins
Diolefines
Aromatics
Olefines
Naphthenes

In other words, the stability of the various hydrocarbons increases with decrease in the ratio of hydrogen to carbon in the molecule, naphthenes being excepted. It was further found that side chains were, in general, more stable than the ends of straight-chain hydrocarbons, and that at temperatures higher than 600°C., diolefines became more stable than the naphthenes.

In this way, it would be possible, by cracking at sufficiently high temperatures, to convert naphthenes into diolefines, which, in turn,

might give aromatics by condensation and polymerisation and subsequent dehydrogenation. As the temperature increases above 700°C. more or less complete breakdown of the larger sized molecules occurs, resulting in the formation of hydrogen and of coke.

It is in this manner that many progressive secondary reactions occur, which cause the formation of new compounds whose molecular weight exceeds, and whose ratio of hydrogen to carbon is smaller than, that of the original stock, resulting in the production of material which becomes more and more resistant to heat.

In this manner gaseous and low boiling liquid compounds with relatively high hydrogen content may be produced together with liquids of high molecular weight, asphaltic material and coke, possessing a low ratio of hydrogen to carbon.

80. The Thermodynamics of Cracking.—The state of equilibrium in a reversible chemical reaction is influenced in general by the temperature, the pressure, and the proportion of the substances present. The Le-Chatelier theorem states that *if a change occurs in one or more of the factors determining a condition of equilibrium, the equilibrium becomes displaced in such a way as to tend to neutralise the effect of the change.* Other factors remaining constant, the effect of an increase of temperature or pressure would be to shift an equilibrium in the direction in which absorption of heat occurs or in which a decrease in volume occurs, respectively, as each change would tend to annul the effect of the increase in either heat or pressure. An increase in the concentration of one of the substances present at equilibrium, will shift the equilibrium in such a way as will tend to decrease the concentration of that substance.

By the use of the Nernst approximation formula for the calculation of equilibria from thermal data, it is possible to predict which reactions are most likely to proceed when cracking pure hydrocarbons.

The equilibrium constant for a cracking reaction proceeding at a constant pressure is Kp, where

Kp = equilibrium constant with the active mass of each component expressed in terms of partial pressures,

and $= \dfrac{\text{product of partial pressure of resultants raised to required power}}{\text{product of partial pressure of reactants raised to required power.}}$

For example, in the following reaction,

$$C_6H_{14} \rightleftharpoons C_3H_8 + C_3H_6$$

$$Kp = \frac{p_{C_3H_8} \cdot p_{C_3H_6}}{p_{C_6H_{14}}}$$

For the reaction,

$$2CO + 2H_2 \rightleftharpoons CH_4 + CO_2$$

this may be considered to be

$$CO + CO + H_2 + H_2 \rightleftharpoons CH_4 + CO_2$$

$$\text{and } Kp = \frac{p_{CH_4} \cdot p_{CO_2}}{p_{CO} \cdot p_{CO} \cdot p_{H_2} \cdot p_{H_2}}$$

$$= \frac{p_{CH_4} \cdot p_{CO_2}}{p^2_{CO} \cdot p^2_{H_2}}$$

With Kp so expressed the Nernst approximation formula becomes

$$\log_{10} Kp = \frac{Q}{4{\cdot}571\,T} + \Sigma\gamma\ 1{\cdot}75 \log_{10} T + \Sigma\gamma\ C_o$$

Q being the heat of reaction at ordinary temperature and constant pressure, and

γ = number of molecules of resultants less the number of molecules of reactants,

T = absolute temperature,

C_o = chemical constant of any particular compound,

($H_2 = 1{\cdot}6$; $CH_4 = 2{\cdot}5$; all other hydrocarbons $= 3{\cdot}0$),

Σ = summation sign showing that all the molecules in the reaction must be included.

The use of this expression may best be shown by an example. Take the dehydrogenation of hexahydro-benzene :—

$$C_6H_{12} \rightleftharpoons C_6H_6 + 3H_2 - 43{,}000 \text{ cals.}$$

$$Kp = \frac{p_{C_6H_6} \cdot p^3_{H_2}}{p_{C_6H_{12}}}$$

$\Sigma\gamma$ = (1 mol C_6H_6 + 3 mols H_2 − 1 mol C_6H_{12}) = 3

The chemical constant C_0 per mol of $H_2 = 1{\cdot}6$.

Therefore for three mols, $3C_0 = 4{\cdot}8$.

C_0 per mol of $C_6H_6 = 3{\cdot}0$

C_0 per mol of $C_6H_{12} = 3{\cdot}0$

Therefore $\Sigma\gamma\, C_0 = 4{\cdot}8 + 3{\cdot}0 - 3{\cdot}0 = 4{\cdot}8$

and the expression for Kp becomes

$$\log_{10} Kp = \frac{-43{,}000}{4{\cdot}571\,T} + 3\,(1{\cdot}75 \log_{10} T) + 4{\cdot}8$$

If log Kp is plotted against the temperature, the following are some of the results obtained.

T°C.	0	27	200	227	527
$\log_{10}Kp$	−16·91	−13·85	−1·21	−0·03	+8·17

As $\log_{10} Kp$ increases with rise in temperature, then

$$Kp = \frac{p_{C_6H_6} \cdot p^3_{H_2}}{p_{C_6H_{12}}}$$ will also increase.

In other words, the reaction is favoured by a rise in temperature.

Taking as a second example the decomposition of $C_{12}H_{26}$, two of the possible reactions are as follows :—

$$C_{12}H_{26} \rightleftharpoons CH_4 + C_{11}H_{22} - 24{,}000$$
$$C_{12}H_{26} \rightleftharpoons C_2H_4 + C_{10}H_{22} - 32{,}000$$

Calculation of $\log_{10} Kp$ at 477°C., a typical cracking temperature, gives values of +0·5 and −1·2 for the two reactions respectively. The greater Kp, as in the first case in the above example, the more likely is the reaction to proceed. These results show that the former reaction is the more likely of the two to take place.

81. Reaction Velocity and Distillate Yield in Cracking. When dealing with the velocity of reaction, it is noteworthy that practically all chemical reactions start off rapidly under certain given conditions, and become slower as the time is increased. The quantity of the substance transformed divided by the time taken, does not, therefore, give a true indication of the reaction velocity, since the latter varies continuously.

To form a clear idea as to the velocity of reaction, the quantity transformed divided by the time should be considered over an infinitesimal period of time, that is to say, $\frac{dx}{dt}$ should be determined, where x is the amount of substance transformed in time t.

The rate at which a body takes part in a chemical reaction is proportional to its active mass. The most general form of the law of mass action may be expressed thus :—the rate at which a substance takes part in a chemical reaction is proportional to its concentration raised to a certain power, this power being numerically identical with the number of molecules of the substance required to satisfy the chemical equation which represents the reaction.

Chemical reactions are divided into classes, mono-molecular, bi-molecular, ter-molecular, etc., and consist of one, two, three or more molecules giving rise to any number of resultants.

Mono-molecular reactions are those in which only one molecular species suffers an essential change of concentration.

Those reactions in the course of which there is a change in the concentration of n-molecular species are termed n-molecular reactions.

Most reactions, however, are of mono- or bi-molecular type, tri- and higher being rare.

In mono-molecular reactions where $A = B + C + \ldots\ldots$

we can write $\frac{dx}{dt} = k(a - x)$ . . . . . (1)

where a = original amount of the substance A,
x = amount of substance A which has been transformed in time t,
$(a - x)$ = amount of A left at any time t,
k = a constant termed the reaction velocity constant.

Integrating equation (1),

$$k = \frac{1}{t} \log_e \frac{a}{a - x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Similarly, for bi-molecular reactions,

$$\frac{dx}{dt} = k(a - x)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\text{and } k = \frac{1}{t} \cdot \frac{x}{a(a - x)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Generally for n-molecular reactions :

$$\frac{dx}{dt} = k(a - x)^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Integrating :

$$k = \frac{1}{t} \cdot \frac{1}{n - 1} \cdot \frac{1}{(a - x)^{n-1}} + C \quad . \quad . \quad . \quad (6)$$

since when $t = 0$, $x = 0$ then,

$$k = \frac{1}{t} \cdot \frac{1}{n - 1} \left[\frac{1}{(a - x)^{n-1}} - \frac{1}{a^{n-1}} \right] \quad . \quad . \quad (7)$$

82. Method of Determining the Order of a Reaction.—The most direct method is to measure the rate of the reaction by suitable means at given intervals of time, and to work out the values of k which are given by the different expressions for mono-, bi- and ter-molecular reactions ; the order which agrees best is the order assigned to the reaction.

J. C. Geniesse and R. Reuter[7] have shown that the mono-molecular reaction equation $k = \frac{1}{t} \log_e \frac{a}{a - x}$ is applicable to the cracking of petroleum oils.

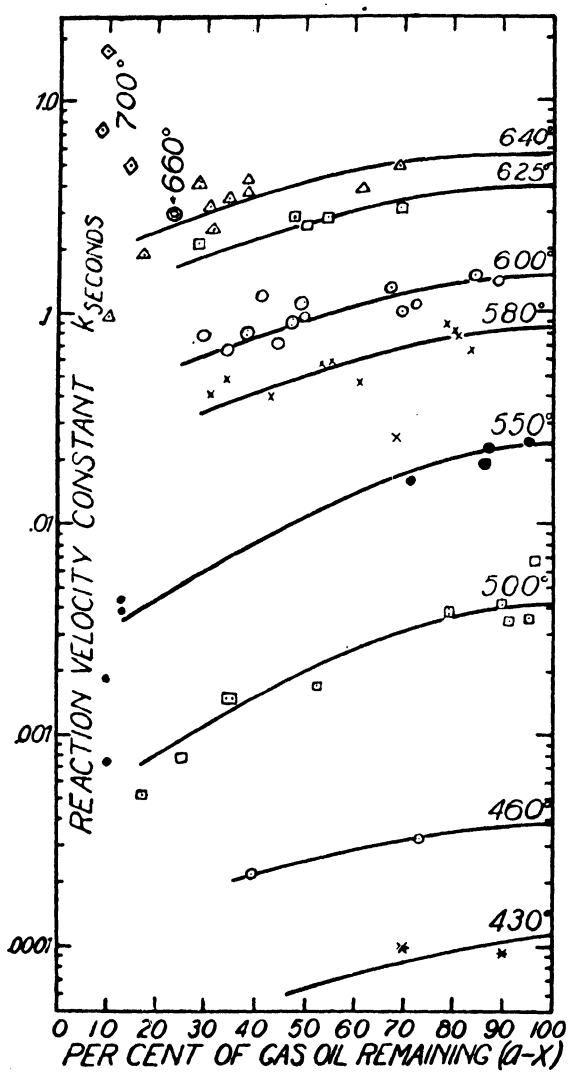


FIG. 1.—VARIATION OF REACTION VELOCITY WITH PERCENTAGE DECOMPOSITION
(After Geniesse & Reuter)

By the use of data obtained on the cracking of a Mid-Continent type gas oil under atmospheric pressure, they have shown that the reaction velocity does not remain constant but decreases as the amount of decomposition increases. This is due to two factors: first the recycle

stock is produced by the polymerisation of some of the products of the initial reaction and, secondly, the cracking stock becomes more stable thermally owing to molecular rearrangements.

The following table shows the reaction velocities obtained in the cracking of a gas oil.

TABLE 1

Temperature	Time (seconds)	$a-x$	k
500°C.	5·9	0·96	·0066
,,	13·5	0·95	·0036
,,	26·9	0·91	·0035
,,	27	0·89	·0042
,,	62·8	0·79	·0038
,,	65·4	0·79	·0037

Similar determinations were made for a number of temperatures, and isothermal curves were obtained, as given in Fig. 1, showing the variation of the reaction velocity constant with percentage decomposition.

The intersections of these curves with the zero decomposition line represent the initial reaction rates at the temperatures indicated.

Fig. 2 is a plot of the log of the initial reaction velocity constant against the reciprocal of absolute temperature.

The relation between the temperature and the rate of reaction according to the Marcelin and Rice[6] equation is

$$\log k = \frac{-E}{RT} + C \quad \ldots\ldots\ldots \quad (8)$$

where E = energy of activation,
T = absolute temperature,
R = gas law constant,
C = a constant.

According to the above equation, the slopes of the curves in Fig. 2 are equal to $-\frac{E}{R}$. It will be seen that the lines representing straight-run naphthas, pressure distillates, and also pure hydrocarbons, are parallel to the gas oil line, which shows that the activation energy is approximately constant for all the hydrocarbons as well as the petroleum fractions, that is to say, E = 53,400 calories per gram mol decomposed. The equation for the curve for gas oil is :

$$k = 28{\cdot}8\, e^{-53{,}400/RT}$$

83. Distillate Yield.—From the foregoing it may be assumed, with reasonable accuracy, that cracking consists primarily in the decomposition of heavy hydrocarbon molecules into lighter ones in accordance with the law of mono-molecular reaction velocity. This assumption, in conjunction with some empirical facts, is sufficient to

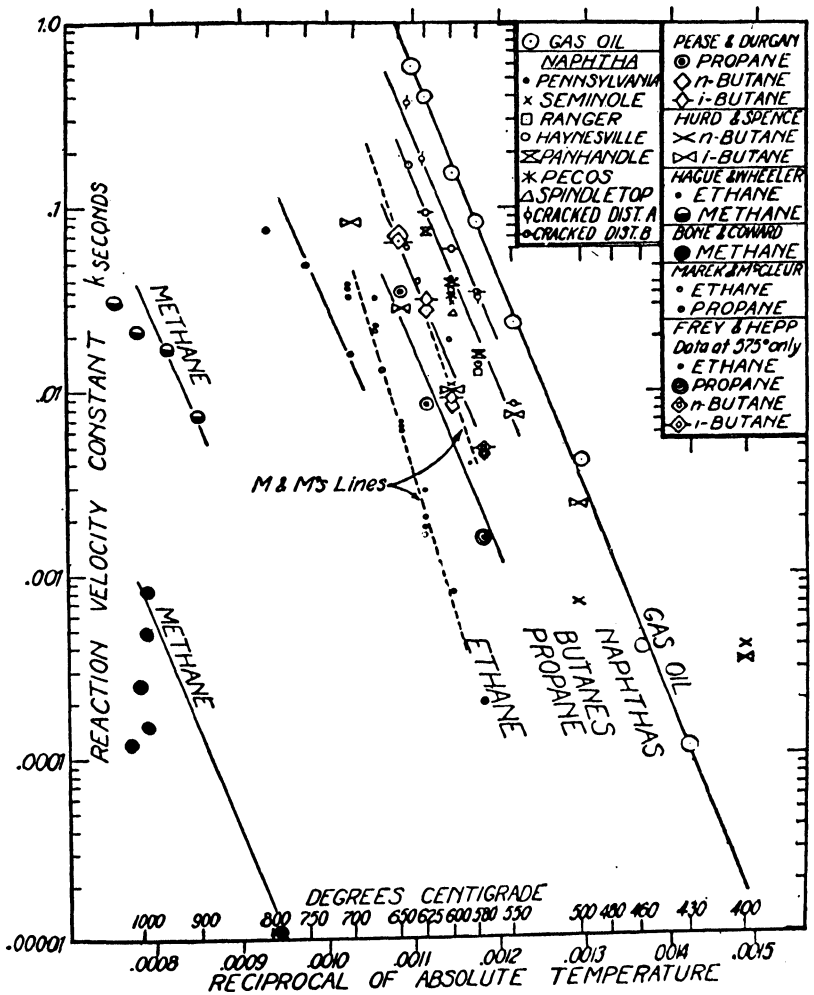


FIG. 2.—VARIATION OF REACTION VELOCITY CONSTANT WITH TEMPERATURE
(After Geniesse & Reuter)

enable a calculation of the distillate yields in cracking to be made. In what follows below three cases of cracking have been considered, cracking with and without by-product formation, and cracking with by-product formation and secondary decomposition.

From equation (2), the following expression may be written :[8]

$$x = a(1 - e^{-kt}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where x = the amount of distillate

and $$y = a - x = ae^{-kt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where y = the amount of original stock undecomposed.

Equations (9) and (10) serve to calculate the distillate yield and residue in cracking, when there are no by-products. In actual practice, however, a whole series of products are formed. Assuming the products of cracking to consist of gas, distillate and residue, and that x_1 represents the amount of gas, the quantity of original stock left will be $a - (x + x_1)$ and formula (1) then becomes :—

$$dx = k[a - (x + x_1)]\,dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Similarly $$dx_1 = k_1[a - (x + x_1)]\,dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Adding these two, then :—

$$dx + dx_1 = d(x + x_1) = (k + k_1)[a - (x + x_1)]\,dt \quad . \quad . \quad . \quad . \quad (13)$$

therefore $$x + x_1 = a(1 - e^{-(k+k_1)t}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Substituting this in equation (11).

$$dx = ake^{-(k+k_1)t}\,dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Integrating :

$$x = -\frac{ka}{k + k_1} e^{-(k+k_1)t} + C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

when $t = 0$, $x = 0$, therefore, $C = a\,\dfrac{k}{k + k_1}$

and $$x = a\,\frac{k}{k + k_1}(1 - e^{-(k+k_1)t}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

This formula holds good provided the distillate and gas are removed as soon as they are formed. Theoretically, when $t = \infty$ the yield of distillate approaches a maximum value of $a\,\dfrac{k}{k + k_1}$, since $e^{-(k+k_1)t}$ approaches zero.

If distillates are not removed as they are formed, they will decompose in turn, so that the yield first increases with time, reaches a maximum and then gradually decreases. If the amount of petrol decomposed in time dt is $k_2\,x\,dt$ then equation (15) becomes

$$dx = (ake^{-(k+k_1)t} - k_2x)\,dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Integrating :

$$x = e^{-k_2t}\left(-\frac{ka}{k + k_1 - k_2} e^{-(k+k_1-k_2)t} + C\right) \quad . \quad . \quad . \quad (19)$$

when $t = 0$, $x = 0$, therefore, $C = a \frac{k}{k + k_1 - k_2}$ and

$$x = a \frac{k}{k + k_1 - k_2} (e^{-k_2 t} - e^{-(k+k_1)t}) \quad \ldots \ldots \ldots \quad (20)$$

This formula therefore applies to cracking when there are by-products and secondary reactions.

84. Waterman and Perquin[9] subjected paraffin wax to cracking in an autoclave at 450°C., and measured the percentage of gas, gasoline (to 220°C.), kerosene (220–300°C.), and residue (above 300°C.) formed. Their experimental results agree fairly closely with those calculated by the above equations, but the deviation increases as the time of cracking is increased owing to the formation of coke and also highly unsaturated products in the gasoline range, as shown in the following table.

TABLE 2. PER CENT. BY WEIGHT OF PRODUCTS FROM CRACKING OF PARAFFIN WAX

Duration of Cracking	Residue		Gas and Gasoline	
	Found	Calculated	Found	Calculated
		k res = 0·02173		$kg + g$ = 0·01076
Minutes	Per cent.	Per cent.	Per cent.	Per cent.
3	93·6	93·7	2·54	3·18
17	69·1	69·1	16·72	16·72
32	48·8	49·9	30·38	29·11
47	35·2	36·0	41·35	39·67
62	25·3	25·9	53·01	48·68
122	10·2	7·1	70·13	73·07
242	6·7	0·5	74·82	92·59

It will be seen from equation (20) that the distillate yield passes through a maximum and then drops as the time increases, due to decomposition of the distillate. This fact was confirmed by the experimental results of Waterman and Perquin. In order to calculate the cracking time corresponding to the maximum yield, equation (20) may be differentiated, made equal to zero and solved for t as follows :—

$$(k + k_1) e^{-(k+k_1)t} - k e^{-k_2 t} = 0 \quad \ldots \ldots \ldots \quad (21)$$

$$t = \frac{1}{k + k_1 - k_2} \log_e \frac{k + k_1}{k_2} \quad \ldots \ldots \ldots \quad (22)$$

85. Recycle Ratio.—Where the products of cracking are fractionated and the recycle stock is mixed with the fresh feed and so cracked

again, the recycle ratio may be expressed as $r = \frac{\text{mixed feed}}{\text{fresh feed.}}$

With a greater recycle ratio, the original hydrocarbons are passed a greater number of times through the system and the average number of passes for hydrocarbons of the original stock is equal to the recycle ratio r. Therefore, we can write :—

$$(k + k_1)\, t = (k + k_1)\, t_1 r = nr \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where r = recycle ratio,
t_1 = time in minutes for which the stock is held under cracking condition in one pass,
$n = (k + k_1)\, t_1$ is a characteristic constant for each unit as long as temperature and pressure remain constant in that unit.

Formula (17) therefore becomes :—

$$x = xm\,(1 - e^{-nr}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

where xm = the maximum distillate yield obtainable on total cracking ($r = \infty$).

Since mixed feed equals r times the fresh feed, the distillate yield on the mixed feed will be :—

$$x_p = \frac{xm}{r}\,(1 - e^{-nr}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

After computing the constants xm and n for two runs with different values of r, x_p (the conversion per pass) can then be calculated for any recycle ratio.

86. The Practice of Cracking.—Of the various types of hydrocarbon oils, aromatic stocks are in general the most resistant to cracking and are characterised by greater coke formation besides being the principal source of heavy residuum in cracking plants.

Besides hydrocarbons, in certain oils there are oxygen, nitrogen, and sulphur compounds which undergo decomposition when the oil is cracked. Only the behaviour of the sulphur compounds has been investigated in any detail. The condition in which sulphur occurs is important from the point of view of corrosion in cracking equipment because hydrogen sulphide is very corrosive while stable sulphur compounds like thiophene are non-corrosive.

It has been established in practice that within the usual cracking range of temperatures there is a definite time-temperature relationship. Within this range, the yield of spirit is a function of the temperature, if the time is constant. Thus work on a typical gas oil showed

that the petrol yield was doubled for approximately each 10°C. rise in temperature within certain limits. At constant temperature, the yield, in the early stages, is a linear function of the time, but this relation ceases to hold after material decomposition has taken place.

Again, if an optimum yield at a given pressure is exceeded, then cracking proceeds at an excessive rate, resulting in a rapid deposition of coke and an excess of permanent gas. Increase of pressure has been found to diminish the quantity of unsaturated compounds in the cracked product.

From a practical standpoint, the effect of raising the pressure in a cracking system is to increase the throughput, decrease the degree of unsaturation, and increase the quantity of liquid products as the result of diminishing the gas formation.

So far as pressure is concerned, only those molecules in the vapour state can be affected by this influence, since those in the liquid state are practically incompressible. The Le-Chatelier theorem states that pressure aids reversible reactions accompanied by a reduction in volume.

As already stated, in the primary stage in cracking, decomposition is roughly proportional to the time, but when the cracked products are re-cracked one or more times they become more resistant to heat and this relationship does not hold. It is for this reason that in some plants the recycle stock is cracked separately at a higher temperature.

The velocity of cracking also depends on the chemical character of the original stock, as well as its boiling range; for instance, kerosene requires a longer time, or higher temperature, than gas oil, to yield the same quantity of gasoline.

In vapour-phase cracking, the character of the original oil is changed completely, and a gasoline of very different chemical composition is produced which is far superior, in anti-knock value, to that usually obtained from liquid-phase systems.

In order to produce a liquid-phase cracked spirit of high anti-knock value, it is usually necessary to use a raw material of aromatic or naphthenic type, and it is for this reason that the petrol from cracked recycle oil is superior to that obtained from primary cracking of the original stock.

87. The modern cracking unit must necessarily be so flexible and adaptable that it can be operated on various types of raw stock for maximum yields of petrol, furnace or Diesel oil, residual oil having a higher calorific value and lower setting point than the original charging stock, coke or gas, according to requirements.

Sometimes the plant is used to crack highly viscous oils in order to increase their fluidity, and lower their setting point.

One of the products of cracking which is finding increasing favour amongst consumers in the U.S.A. is pressure distillate bottoms, which is the residual oil remaining after the fractionation of the cracked product (pressure distillate). This oil is usually of narrow boiling range, has a low setting point and viscosity, and makes a satisfactory cold weather liquid fuel for slow speed Diesel engines.

The following table[10] shows the percentage yields, based on the charging stock, of pressure distillate, gasoline of high end-point, and other products obtained by cracking in Dubbs Units.

These petrols have end points of about 225°C., and are generally acceptable as blending stocks.

Normally, liquid-phase cracked spirits produced at high pressures and low temperatures are deficient in low-boiling fractions. By suitably blending these cracked spirits with a casinghead gasoline or a straight-run spirit, a marketable product is available.

Vapour-phase cracking processes were the first in the field. These were worked at high temperature and at about atmospheric pressure, and produced a spirit difficult to refine, having various objectionable features such as high gumming properties, bad colour and disagreeable odour.

Attention was then turned towards cracking at lower temperatures, when products of a more saturated character were obtained, and liquid-phase cracking processes were developed. These are now being replaced by higher temperature processes.

88. Commercial Cracking Processes.—Some time ago it was customary to classify cracking processes as " Liquid Phase " or " Vapour Phase," but these designations are no longer correct because, depending upon the feed stock, nearly all existing processes operate under such conditions of temperature and pressure that both liquid and vapour states must exist in the cracking zone. The older Dubbs and Cross processes were referred to as liquid-phase processes and the Gyro process as a vapour-phase operation, but the modern tendency is to divide a feed stock into fractions of different boiling range, and to crack these separately under the temperature and pressure conditions found most suitable for the production of the optimum quantity of gasoline of the required properties. In addition to the production of gasoline from heavier oils, cracking is also employed for " viscosity-breaking," i.e., reducing the viscosity of asphalts and fuel oils and also for wax destruction, e.g., reducing the setting point of fuel oils and other residual oils. A recent development is the reforming operation in which light distillates such as straight-run gasolines and naphthas are subjected to cracking conditions of temperature and pressure in order to effect considerable improvement in octane number. In this operation gas and higher boiling residue is

TABLE 3. YIELDS, PER CENT. BASED ON THE CHARGING OIL

Sample. Charging Stock.	S. G.	Cracked Distillate	U.S. Motor Gasoline	Furnace or Diesel Oil	Residuum	Gas. Cu. ft. Per Bbl.	Operating Pressure of System	Liquid Temperature
		%	%	%	%		lb.	°C.
1. Mid-Continent gas oil	0·8468	79·90	44·3	34·0	7·1	303	120	461
2. Mid-Continent kerosene distillate	0·8328	90·86	52·6	34·3	0·0	266	135	454
3. North Texas kerosene distillate	0·8275	96·61	41·9	53·2	2·6	69	135	458
4. Mid-Continent fuel oil	0·8933	51·25	36·8	12·0	45·6	170	120	454
5. Mid-Continent topped crude ..	0·8822	60·01	41·6	15·9	34·1	189	120	452
6. Ranger topped crude	0·8939	59·75	41·5	14·0	39·7	166	120	—
7. Healdton crude	0·8783	65·19	45·1	18·1	26·8	119	120	451
8. Montana topped crude ..	0·8328	83·95	48·2	8·4	14·5	52	135	438
9. Kentucky fuel	0·9013	59·7	43·9	12·0	34·5	185	120	463
10. Mexican distillate	0·8967	60·19	39·6	19·6	35·3	145	120	436
11. Mexican gas oil	0·9279	54·95	41·7	9·7	38·5	236	120	466
12. Panuco residuum (Mexico) ..	1·0020	21·86	18·9	1·9	73·1	124	120	444
13. ,, ,, ,, ..	1·0020	26·32	21·1	3·9	66·5	139	120	439
14. ,, ,, ,, ..	1·0020	22·09	18·2	2·8	66·0	141	120	428
15. ,, ,, ,, ..	1·0020	23·5	18·5	4·0	70·6	110	115	451
16. Panuco crude (Mexico) ..	0·9820	30·8	23·7	6·0	62·9	110	110	439
17. ,, ,, ,, ..	0·9820	34·1	28·2	4·5	64·2	173	110	441
18. Venezuela fuel	0·9765	30·9	23·2	5·7	61·0	111	110	448
19. ,, ,, ...	0·9765	38·5	26·9	10·0	52·2	137	105	444
20. Tarakan crude (Borneo) ..	0·9452	60·62	32·4	25·6	28·8	314	130	458
21. ,, ,, ,, ..	0·9452	61·69	30·6	27·8	26·6	348	125	464

produced in varying amounts but chemical isomerisation occurs in addition to cracking, and naphthene and aromatic hydrocarbons are formed from paraffins and olefines.

89. The Tube and Tank Cracking Process.—This process has been employed extensively for the production of cracked gasolines from heavier stocks and has been developed and applied particularly by the Standard Oil Co. of New Jersey interests. The process is one in which the cracking reactions take place at 750–1,000 lbs. pressure and fractionation and separation of products at 60–100 lbs. pressure. It is applied chiefly to the cracking of distillates, although reduced crudes are often handled. It employs indirect heat exchange at both high and low pressures. A typical flow diagram is given in Fig. 3.

The fresh feed is discharged through a series of low pressure exchangers or partial condensers on the overhead streams from the fractionating towers, to attain heat before entering the accumulator. Into this is also directed the heavy and light recycle stocks from the primary and secondary towers. A high-pressure hot-oil pump discharges fresh feed plus recycle from the accumulator through a series of high-pressure exchangers, or partial condensers, on the vapour stream from the separator to the primary tower. The stock then enters the furnace where it is heated to 900–925°F. at approx. 1,000 lbs. pressure. The furnace discharge is subsequently retained in a high-pressure vertical soaker, where the conversion of the charge continues. After pressure reduction the cracked products from the soaking drum are directed to the base of the tar separator in which cracked gasoline and recycle stock vapours are flashed from the tar. The overhead vapours from the separators are cooled and partially condensed when passing through the high pressure exchangers. The greater portion of the condensate formed in the exchangers gravitates to the accumulator as heavy recycle stock, while a small portion is returned to the head of the separator as reflux.

The uncondensed portion of the recycle and the cracked gasoline vapours from the high pressure exchangers enter the base of the primary tower where a great portion of the recycle stock vapours are condensed and withdrawn from the base of the tower to the accumulator tank. The cooling necessary to reduce the temperature of the feed to this column and to condense the recycle is accomplished in the overhead low-pressure exchangers where the fresh feed absorbs the heat from the tower vapours. The condensate resulting gravitates back over the top bubble tray as reflux. Such a temperature is maintained in the vapour outlet from the low-pressure exchangers on this tower as to allow pressure distillate vapours to proceed to the secondary tower, where the final fractionation of end-point gasoline

from a light gas oil is effected. The light gas oil condensed in the secondary tower may be withdrawn from the system if desired, or else returned to the accumulator as light charging stock.

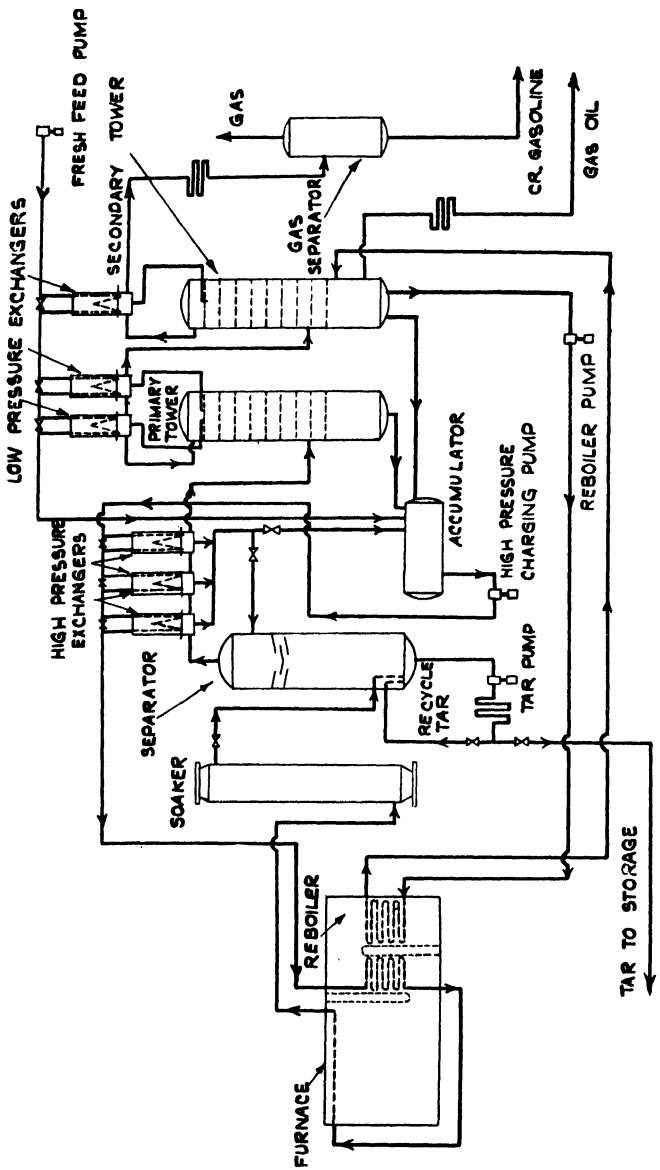


FIG. 3.—FLOW DIAGRAM OF TUBE AND TANK CRACKING PROCESS

90. The Cross Process.—The Cross process differs from other commercial processes in that it more nearly approaches true liquid-

phase cracking on account of the comparatively high pressure under which the plant is operated.

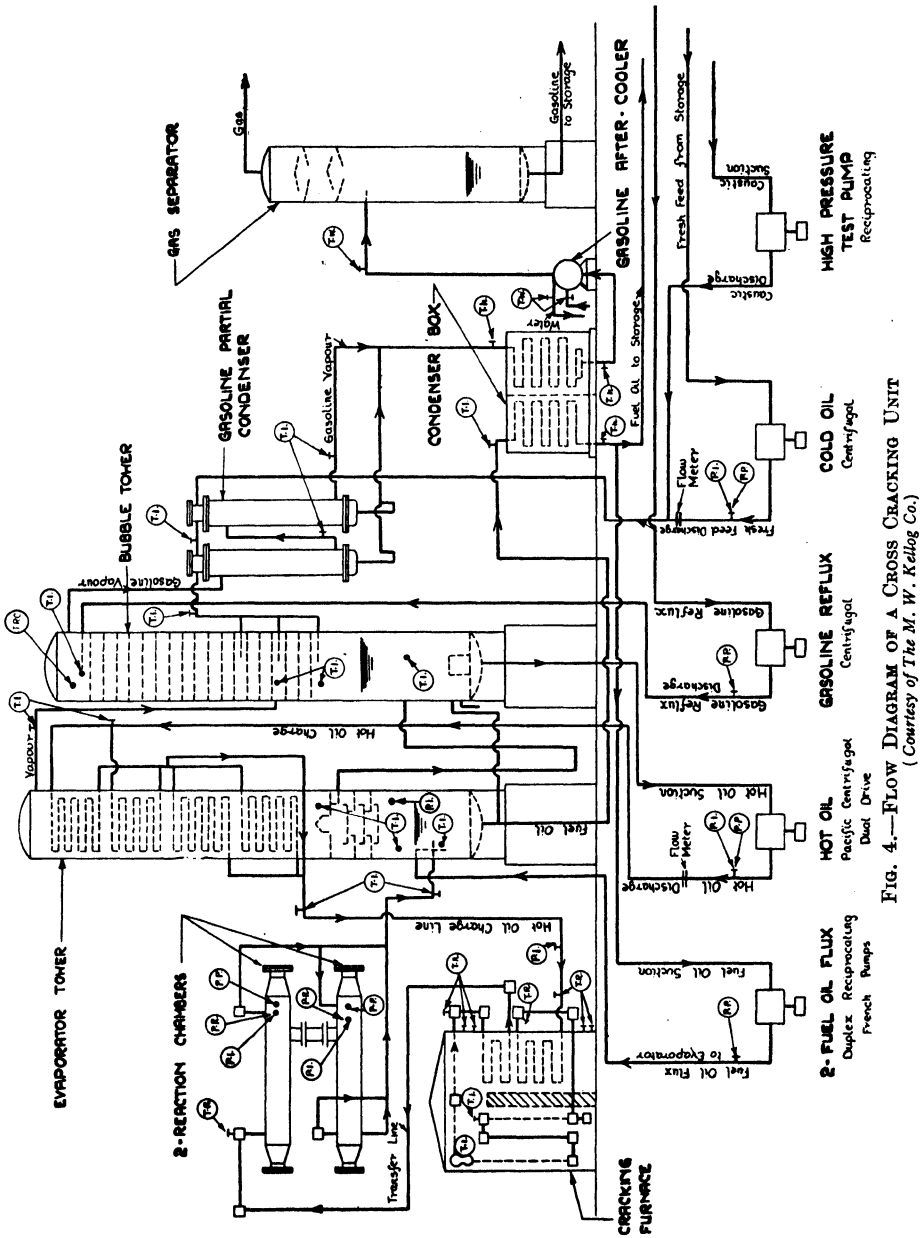


FIG. 4.—FLOW DIAGRAM OF A CROSS CRACKING UNIT
(*Courtesy of The M. W. Kellog Co.*)

The charging stock is fed by cold-oil charging pumps into heat exchangers, which act as partial condensers of gasoline, thence into the

bubble tower and to the hot-oil charging pumps. It is then passed through heating coils to the cracking furnace at a pressure of from 600 to 850 lbs. per square inch, and discharged from there into the reaction chambers at a temperature varying from 450° to 480°C. These chambers are heavily lagged but not heated.

The synthetic crude oil formed leaves the reaction chambers through a piston-type slide valve, at which point practically all the pressure is released, and is then discharged into the evaporator, where the heavy ends are withdrawn as fuel oil, the vapours passing into the fractionating tower.

The bottoms from this bubble tower, which comprise both reflux oil and fresh feed, are withdrawn hot and charged continuously through the heating coils to the cracking furnace.

By following the diagram in Fig. 4, it will be seen that the vapour leaves the bubble tower at the top and enters the partial condensers, and the condensate together with the uncondensed vapours then passes to the condenser proper. After cooling the gasoline is held in the gas separator under reduced pressure until the gas is released, and the spirit is then sent to storage.

All control of the plant is from one control house, which contains the high and low pressure pumps, the steam valves controlling their operation, the wheels of the vapour outlet valves of the reaction chambers, and an indicator board upon which the recording dials and gauges connected to the pyrometers and pressure instruments are mounted.

There are many arrangements of this type of plant, but the principle, in all cases, is the same, and the fundamentals of refluxing and fractionation are similar to those explained in the last Chapter.

In this method of cracking practically no vaporisation takes place in the *cracking zone.* The oil is maintained, substantially, in a liquid-phase, not only during the period in which it is brought to cracking temperature in the pipe still, but also during the completion of the cracking reaction in the reaction chambers.

This does not mean that there is no gas in the reaction chamber, on the contrary, a certain amount of gas must be formed, but the higher the pressure which is maintained, the smaller the amount of gas made and the lower the losses.

The coke made in the Cross process varies with the type of cracking stock, e.g., from 3 lbs. per ton throughput when cracking kerosene, up to 18 lbs. per ton of fresh stock charged in the case of Smackover topped crude oil.

The average yields from the Cross process, based on fresh stock charged, are :—

	Charging Stock		
	Kerosene Per cent.	Gas Oil Per cent.	Fuel Oil Per cent.
Gasoline 225°C. End Point	78–80	65–70	45–55
Fuel Oil	15–20	20–25	37–55
Coke, Gas and Loss	9	9	8

The percentage of working time which Cross units are on stream, when operated normally, is about 93% with kerosene, 90% with gas oil and 85% with fuel oil charging stocks. This period naturally depends on the degree of cracking undertaken ; the more severe the cracking, the greater the loss due to coke formation and the shorter the length of time before a shut-down is necessitated for cleaning purposes.

91. Several interesting engineering and metallurgical problems, concerned chiefly with the effect of temperature on the properties of metals, present themselves in the construction of cracking equipment, and as the conditions in the Cross process are among the most severe they will be considered very briefly in relation to this process.

It is inadvisable to pay much attention to tests at ordinary temperatures when specifying materials which have to withstand high temperatures, as it has been proved that metals and alloys which are stronger than others at ordinary temperatures may be much weaker at higher temperatures. There is, at each temperature, a breaking strength that depends upon the time under load, and there is a limiting creep stress at that temperature.

A stress at a given temperature above which a metal becomes progressively viscous is known as the limiting creep stress. There is a stress below which creep will cease but above which it will be continuous for all metals, and this varies with temperature.

At temperatures above 350°C., the difference between the breaking stress and the limiting creep stress may be very great, a fact of considerable importance in all industrial operations involving the use of vessels at high temperatures.

At stresses only a little greater than the limiting creep stress, creep may be very slow, and only small movements can be noticed over short periods, but, if sufficient time be given, the rate of creep increases and, finally, leads very rapidly to fracture.

It should be mentioned here that Hooke's law, which states that strains, when they do not exceed the elastic limit, are proportional to the load, no longer applies when certain temperatures are exceeded.

For vessels subjected to given stresses, the limiting factor of safety at any stress and temperature can be determined when the "limiting creep stress " under these conditions is known. At ordinary tempera-

tures the limiting creep stress only differs from the " breaking stress " by 1 or 2 tons per square inch for most metals, and the material is permanently hardened by the cold work done during creep ; whereas, at higher temperatures, there is much greater divergence, and the form of load-strain diagram is not continuous over a long period but consists of a series of steps growing wider and wider and having less and less rise ; hysteresis also occurs.

Reference to this " creep stress " in metals, and its importance in cracking practice, is made by Rogers,[11] who gives as an example one test-piece which was found to withstand, at ordinary temperature, a maximum stress of 35 tons per square inch with a yield point of 25 tons per square inch. At 400°C., the maximum stress and yield points were only some 3 tons per square inch less in each case ; nevertheless, it was found that when the load was applied and maintained at this temperature, extension of the test-piece commenced at 9 tons per square inch. At a temperature of 475°C., the " creep stress " was found to be about 7 tons per square inch and as it is necessary that all calculations of diameter and thickness of a Cross reaction chamber should be based on this " creep stress," this figure was taken and a factor of safety of 4½ allowed for.

Sulphur corrosion has also to be considered, but it has been found that when the scale is left upon the interior of the forging, sulphiding ceases at the surface skin. As an extra precaution, however, it is suggested that the steel tubes and reaction chambers may be coated with chromium.

The steel tubes in the pipe heater are usually seamless, being cold drawn, about 5 inches outside diameter, 3 inches inside diameter, 18–30 feet long, and are annealed dead soft before being rolled into the header boxes. The headers, or return bends, are often made from cast steel, having a carbon content not exceeding 0·25 per cent., thoroughly annealed.

Until recently, the reaction chambers were made from a single ingot of open hearth steel weighing about 100 tons and containing 0·25 per cent. carbon and not more than 0·06 per cent. phosphorus. This was forged down to a finished chamber, typical dimensions being 3 feet 10 inches external diameter, 3 feet 2 inches internal diameter, by 41 feet 2½ inches overall length from face to face of flanges, and weighing between 42 and 45 tons. Now these chambers are made in cylindrical segments which are electrically welded, and this has resulted in a considerable reduction in cost.

92. The Dubbs Cracking Process.—This process is widely known and extensively used in the petroleum industry. Early methods of

operation are known as the " non-residuum " and " flashing " processes, in the first of which the oil charged to the system is converted entirely to pressure distillate, gas and coke, and in the second process fuel oil is produced instead of coke. This latter method of operation gives a lower yield of gasoline, but the time on stream is much longer.

In recent years the Dubbs full-flashing selective cracking unit has been developed. This type of operation produces the maximum yield of high anti-knock gasoline and either a residual fuel oil or a petroleum coke, both of good quality. The Dubbs process has from its inception been associated with the cracking of heavy residual oils, and with the recent developments it is one of a few processes which can cope with the many types of cracking stock available. These stocks include crude oils, naphthas, kerosenes, gas oils, fuel oils, light and heavy reduced crudes and even asphalts. The following is a description of a typical Dubbs full-flashing selective cracking unit, shown in Fig. 5 :—

The raw oil charging stock is pumped from storage into a fractionating column which it enters above a few plates located in the bottom section of the column. This raw oil flows downward counter-current to the incoming hot vapours and effects condensation of the heavy vapours. The mixture of heavy condensate and the heavy constituents of the raw charging stock accumulates in the bottom of the column and is pumped from here through a heating coil located in a furnace, known as the " heavy oil coil," wherein it is subjected to those temperatures and pressures most suitable for cracking the mixture without encountering difficulties with excessive coke formation. The oil on leaving this coil passes to an unfired reaction chamber. The light oil fraction is withdrawn from the fractionating column and pumped through a second heating coil located in a furnace, known as the " light oil coil " in which more severe conditions than those in the " heavy oil coil," obtain. On leaving the light oil coil the oil enters the same reaction chamber at the top, together with the heavy oil stream. The vapours and the heavy residual fraction are drawn off from the bottom of the reaction chamber through a pressure reducing valve to the flash chamber. In the flash chamber the vapours are separated from the heavy residual fraction and pass to the fractionating tower where they are fractionated into end-point distillate vapours, light oil, and heavy condensate. The end-point distillate vapours pass from the top of the fractionating column to a condenser where they are condensed and then pass to a distillate receiver from which a portion is returned to the column as reflux, and thence passes either direct to storage or to a conventional stabiliser. The gases from the receiver pass direct to a fuel system or to an absorption plant for the recovery of light gasoline.

The residual fraction from the flash chamber is withdrawn and either pumped through a cooler to storage and marketed as fuel oil

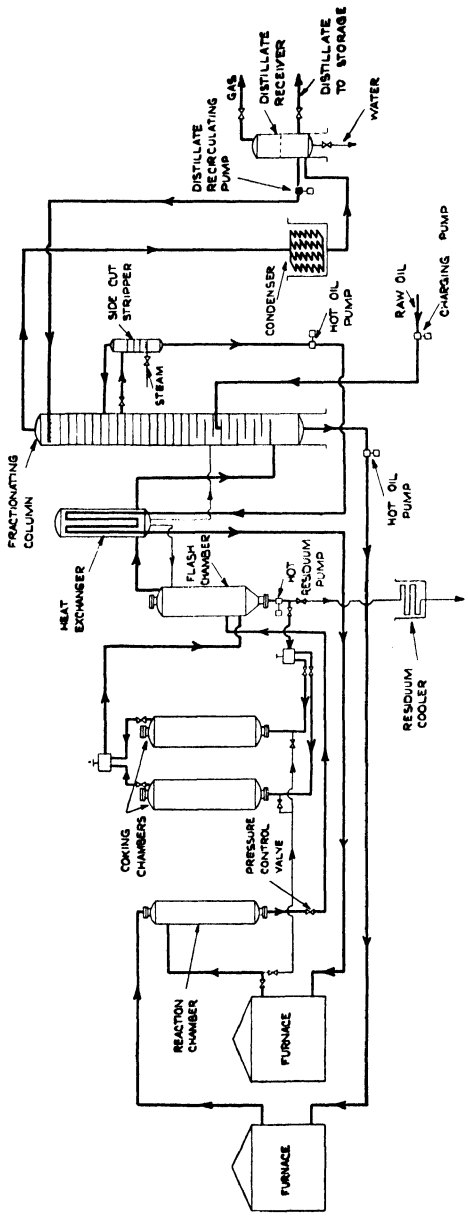


FIG. 5.—FLOW DIAGRAM OF A SELECTIVE CRACKING UNIT FOR COKING OPERATION—DUBBS PROCESS
(Courtesy Universal Oil Products Co.)

or pumped while hot into coking chambers wherein a good grade petroleum coke may be produced. Additional heat for the coking

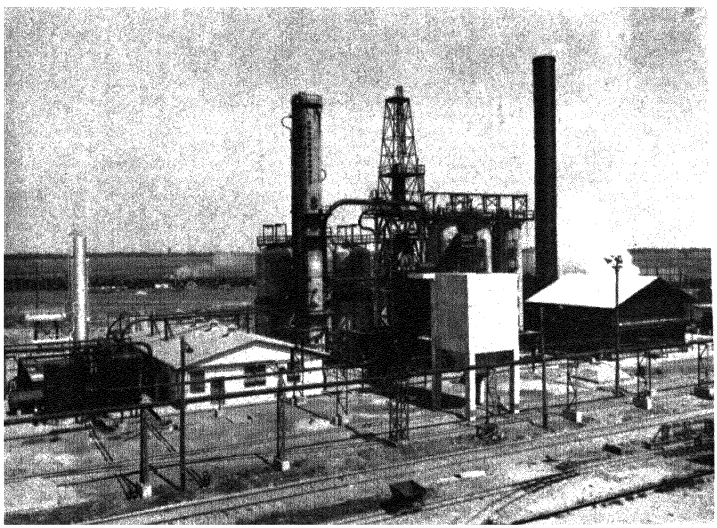


FIG. 6.—TYPICAL MODERN DUBBS CRACKING UNIT
(*Courtesy of Universal Oil Products Co.*)

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operation, if required, may be supplied by introducing a portion of the material from the light oil coil into the coking chambers.

The Dubbs process possesses marked flexibility for the satisfactory treatment of a wide range of feed stocks and gives high on-stream time efficiencies. A photograph of a typical Dubbs cracking unit is shown in Fig. 6.

93. The De Florez Cracking Process.—This process is also suitable for the production of anti-knock cracked gasoline from an almost unlimited variety of charge stocks. It employs temperatures up to 1,080°F. (582°C.) and pressures generally above 200 lbs./sq. in. and handles residual as well as distillate feed stocks under these conditions.

Numerous installations of the process have been put in use during the past few years in the U.S.A. and elsewhere. These have been used for cracking stocks ranging from light gas oil to pressure tar and producing either fuel oil or solid coke as the final product with cracked gasoline. In some cases naphtha reforming has been operated in conjunction. The process is licensed by Gasoline Products Inc., of Newark, New Jersey, and by The M. W. Kellogg Co. of New York.

The manner of preparation of the feed stock for "super-clean circulation" through the heating coil is a noteworthy feature of the process. The fresh feed is contacted with highly heated vapours from the cracking zone, vaporising the lighter fractions. The resultant vapours are then fractionated to produce a gas oil condensate made up of both fresh and recycle constituents, which comprises the heater feed. By proper control of the boiling range, colour and other properties of this stock, it may be subjected to cracking temperatures in excess of 1,050°F. (565°C.) without coke formation in the heater. Thus a high range of temperatures may be employed to secure increased cracking rates and anti-knock value gasoline production, while allowing long continuous operation through elimination of coke deposition.

A flow diagram of a typical de Florez unit operating on 24° A.P.I. (Sp. gr. = 0·91) Mid-Continent reduced crude to give gasoline and fuel oil is given in Fig. 7. The reduced crude feed is first introduced to the flash tower where it is preheated by contact with the flashed vapours. It passes thence to the primary fractionator where it is contacted with the hot vapours entering from the soaking drum. Here, a substantial part of the gas oil in the feed is vaporised and passes over with the cracked vapours into the secondary fractionator. Unvaporised fresh feed and heavier cracked fractions collecting in the primary fractionator are passed to the heater discharge line entering the soaker.

In the secondary fractionator, reflux is supplied to the top in

amount sufficient to produce the desired quality of cracked gasoline overhead. The gas oil condensate formed thereby comprises the heater feed and is passed directly to the heater inlet by a hot-oil pump.

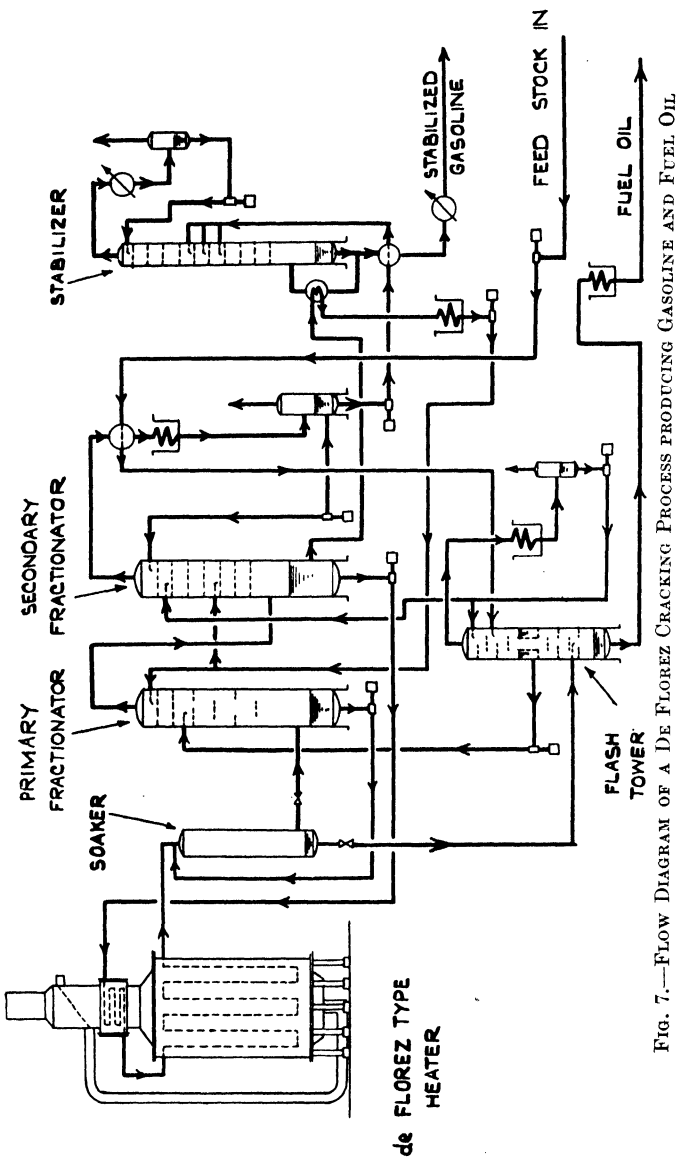


FIG. 7.—FLOW DIAGRAM OF A DE FLOREZ CRACKING PROCESS PRODUCING GASOLINE AND FUEL OIL

In the heater the oil is raised to temperatures which may be as high as 1,080°F. and upon leaving co-mingles with the residuum from the primary fractionator and enters the soaker. Vapour and liquid are withdrawn separately from the soaker, the regulating valves on the

draw-off lines being used to hold a minimum level of liquid in its base and to maintain the back pressure of 200 or more lbs./sq. in. upon the soaker and heating coil.

The vapours from the soaker enter the primary fractionator where they contact with the fresh feed as above mentioned. The liquid from the soaker passes to the fuel oil flash tower where the lighter portion is flashed off at or near atmospheric pressure. The flashed fractions are returned to the cracking cycle and the unvaporised portion comprises the final fuel oil product.

The cylindrical de Florez heater has been widely used in connection with this as well as other processes. These heaters are employed in both up-fired and down-fired form. When coke is to be the final residual product of the de Florez process, a large coke-collecting vessel may be substituted for the soaking drum in the fuel oil unit described above and the fuel flashing system is eliminated. Fresh feed is introduced direct to the primary fractionator, the residuum therefrom being passed to the coke drum in which a temperature of 800–900°F. produces a dry and dense coke. Two or more coking vessels are used alternately to permit continuous operation. This type of operation is shown in Fig. 8.

The wide range of heater outlet temperatures permitted by this process is reflected in a correspondingly broad operating flexibility. The anti-knock value of the cracked gasoline is largely controlled by the heater outlet temperature and by this means it is possible to adjust the throughput capacity, yield and other important variables. This serves not only to adapt a given unit to the handling of greatly dissimilar feed stocks but permits each stock to be handled in accordance with market requirements.

94. The Gyro Cracking Process.—The Gyro Vapour-Phase Cracking Process operates under relatively low pressure but at comparatively high temperatures for the production of high octane number gasolines. Fig. 9 indicates the essential features of the process. The charging stock consists of a reduced crude or a gas oil of wide boiling range and is pumped through heat exchangers into the heavy oil fractionating tower. The feed is further preheated by contact with hot vapours in the tower and the lighter fractions are evaporated. The heavy ends plus condensed recycle stock accumulate in the pan in the centre of the tower and are fed to the heavy oil cracking coil where light gas oil, and small amounts of gas and gasoline, are produced. The oil and vapours leaving the cracking coil are returned to the lower portion of the fractionating tower. The bottoms from the tower pass to a primary fuel flash tower operating at a lower pressure where steam is introduced and the fuel oil reduced

to specification flash point, before being pumped to storage. The overhead vapours from the heavy oil fractionating tower pass to a light oil fractionator from which any gasoline present goes overhead

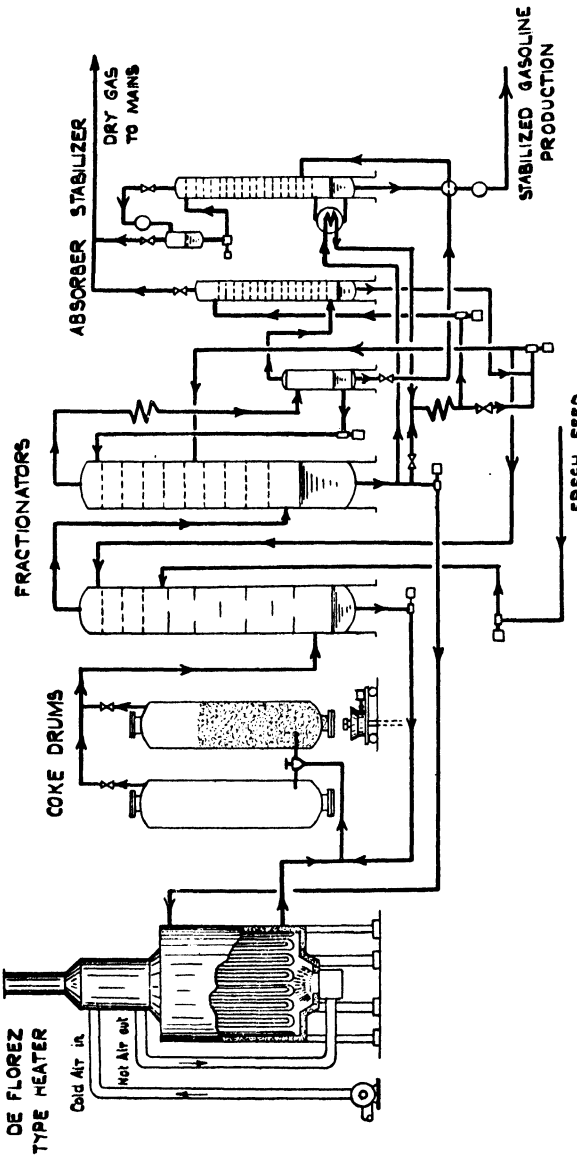


FIG. 8.—FLOW DIAGRAM OF DE FLOREZ CRACKING PROCESS. COKING OPERATION

and the gas oil is condensed and accumulates with light oil cycle stock in the pan. The light gas oil is then charged to a vaporising coil and thence to an evaporator. From the latter, heavy ends are returned to the heavy oil fractionator for further reduction and gas

oil and recycle oil pass to the vapour-phase cracking coil where the major part of the cracking is effected. After leaving the cracking coil the vapours are suddenly reduced in temperature to halt the cracking reaction by the introduction of a quenching oil and then all the vapours return to the base of the light oil fractionating tower.

The refractory fuel oil produced is collected in the base of the tower where it may be stripped by steam prior to passing to storage. The gas and gasoline pass up the tower and a heavy gasoline is removed as a side stream. A low end-point gasoline passes overhead and is condensed, a part being returned to the tower as reflux. Gas from the separator passes to an absorber for the recovery of gasoline which is then stabilised. Stabilised gasoline is taken from the bottom of the stabiliser through heat exchangers to coolers and storage.

In the Gyro process, which successfully employs high cracking temperatures for the production of gasolines of high octane number, the oil is raised to full reaction temperature very rapidly so that substantially no cracking takes place at lower temperatures. To achieve this the oil is introduced into the cracking furnace in the vapour state at high velocities. Careful furnace design permits the maintenance of these vapours at the cracking temperature for an exact and predetermined time which is definitely controlled by rapidly cooling the oil to below cracking temperatures when the reaction is completed. In order to obtain the best results from the heavy oil, it is handled separately in an individually controlled coil in the furnace, thus ensuring a high grade of fuel oil and the maximum yields obtainable from any given charging stock.

An additional advantage of the Gyro process is the high olefine content of the gas produced; this enables the overall yield of gasoline to be considerably augmented by polymerisation processes.

The main advantages of the Gyro process are :—

1. The gasoline produced is about 70 per cent. more volatile than that obtained by other processes. This eliminates, in most cases, the need for blending with natural gasoline.
2. The gasoline produced is of high anti-knock value and therefore permits the utilisation of larger amounts of straight-run gasoline (of lower octane number) in marketed blends.
3. The fuel oil produced can be completely disposed of as fuel oil (Bunker C grade).
4. The gas produced is a very valuable polymerisation feed stock—or raw material for chemical synthesis.

The following figures indicate the yields and quality of products obtained from a Gyro unit operating on East Texas Reduced Crude.

Yields	% volume
Gasoline	43·5
Fuel oil	38·0
Gas	19·5 (by difference)

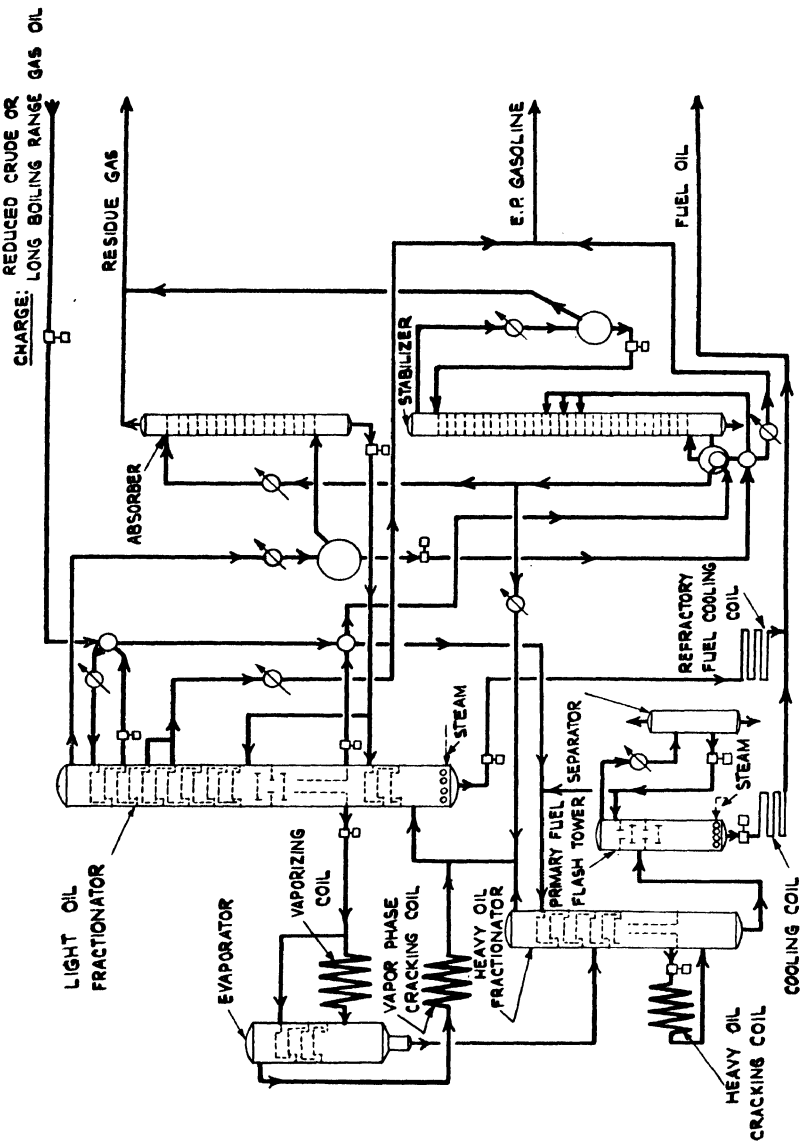


FIG. 9.—FLOW DIAGRAM OF GYRO CRACKING PROCESS

Quality of Products.

Gasoline. Sp. gr. = 0·752 (A.P.I. gravity = 56·7)
Reid Vapour Pressure 10·7 lbs. /sq. in.
Octane No. (C.F.R. Motor method) 71·7

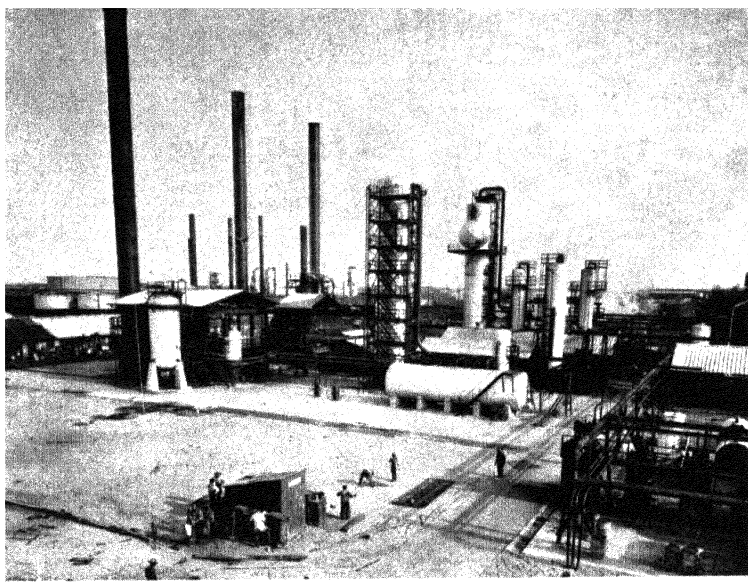


FIG. 10.—PHOTOGRAPH OF A TYPICAL GYRO CRACKING UNIT INSTALLATION

(Courtesy of Alco Products Incorporated)

Facing p. 99]

I.B.P.	..	30°C.
5%	..	43°C.
10%	..	52°C.
20%	..	70°C.
30%	..	85°C.
40%	..	100°C.
50%	..	120°C.
60%	..	138°C.
70%	..	155°C.
80%	..	175°C.
90%	..	190°C.
F.B.P.	..	201°C.
Res.	..	0·9%
Loss	..	2·6%

Fuel Oil.

Sp. gr.	=	0·9986 (A.P.I. gravity = 10·2)
B.S. & W.	=	0·4%
Flash Point	=	125°C. (253°F.)
Furol Viscosity at 122°F.	=	219 sec.

Gas. 850 cubic feet per barrel of charge.

Methane and Hydrogen	29·0% vol.
Ethane	17·0% „
Propane	14·8% „
Butane	1·9% „
Ethylene	14·1% „
Propylene	18·0% „
Butylene	5·2% „

A photograph of a typical Gyro installation is reproduced in Fig. 10.

94a. The True Vapour-Phase Cracking Process.—As the name implies, the T.V.P. (True Vapour-Phase) Cracking Process operates entirely in the vapour phase. The process has its origin in the work of Knox in the U.S.A., and development has aimed at the avoidance of the difficulties which arise from heating vaporised oils through tube walls. It is for this reason that the heating of the oil vapour from a point 20–100°F. below the cracking temperature of the charging stock is accomplished by physically mingling the oil vapour with a heat-carrier gas heated to a temperature somewhat above that of cracking. The gas employed for this purpose is that produced from cracking within the system.

In the cracking operation the oil is vaporised and the oil vapours normally superheated to about 950°F., the cracking temperature of approximately 1,000°F. being attained by subsequently mingling this oil vapour with the heat-carrier gas at about 1,100°F. This "inert" gas, apart from its use as a heat-carrying medium, exerts a moderating influence on the course of the cracking reaction. Polymerisation reactions proceed concurrently with the decomposi-

tion of the larger molecules. As unsaturated compounds are formed they are subjected to conditions of low pressure and high temperature favourable to the production of aromatic compounds.

The raw charge, after passing through the vaporiser coil, is reduced to a low per cent. bottom in a flash drum and the overhead vapours passing through the reaction zone are subjected to effective viscosity breaking, the combined cracked and natural residues consequently having a low viscosity and a low pour-point. The products from the reaction chamber pass into a scrubber into which the flash drum bottoms are also discharged. Under the partial pressure conditions existing in the system the accumulated residue in the scrubber may be reduced to any desired gravity at comparatively low temperatures.

The operation of a T.V.P. cracking unit can be followed by referring to the flow diagram (Fig. 11). The charge combined with recycle stock enters the system through heat exchange with the vapours from the scrubber. The preheated feed is then raised to the required temperature in the vaporiser coil and discharged into the flash drum. The gas circulated round the system, and known as cycle gas, is split into two streams, namely, heat-carrier gas and flash gas. The latter is heated to a suitable temperature and injected into the flash drum to assist vaporisation and to dry the vapours going to the super-heater coil. The cycle gas is preheated by heat interchange with scrubber vapours before entering the cycle gas coil.

Leaving the respective heating elements the super-heated vapours and cycle gas are combined to produce a predetermined cracking temperature and flow through a common line into the reaction chamber where, under suitable conditions of time and temperature, the de-composition and polymerisation reactions proceed simultaneously. The reaction products then enter the scrubber, from the bottom of which the fuel oil residue is withdrawn and the overhead vapours pass through the heat exchangers into the fractionator. Recycle stock is pumped from the bottom of the fractionator and joins the raw charge as feed to the vaporiser coil. The overhead from the fractionator passes through a condenser into the heavy distillate accumulator, from which the cracked heavy gasoline is withdrawn.

Wet gas from the top of this accumulator is compressed and passes through a cooler into the light distillate accumulator where cracked light gasoline is collected. Gas from the top of this accumulator is returned to the cycle-gas heater coil. Excess gas leaving the system through the automatic pressure-control valve may be handled by absorption, compression or fractionation, and the propylene fraction may be returned to the system for further polymerisation.

The heating of the cycle gas was originally performed in hot blast stoves, familiar to the steel industry, but to-day pipe heaters are

employed for each of the above heating operations. These heaters are of the double-end-fired type with a central convection section.

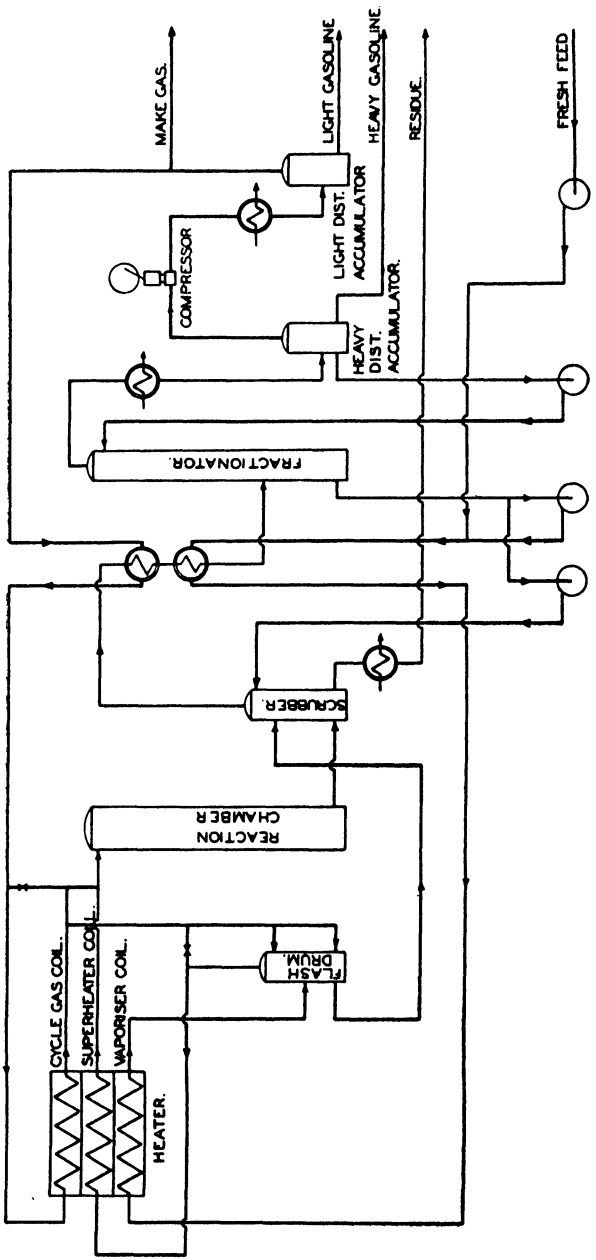


FIG. 11.—FLOW DIAGRAM OF TRUE VAPOUR-PHASE CRACKING PROCESS
(Courtesy of T.V.P., Ltd.)

Generally, the vaporiser coil is located in one furnace and the superheater and cycle-gas coils in the other, but in the case of small units,

the coils may all be installed in one heater. The arrangement described permits of the necessary control of temperature to suit the particular charging stock.

In the vaporiser and superheater coils heat is applied so rapidly in the short time involved that practically no cracking takes place in the tubes. The superheated vapour is then intimately mixed with the highly heated cycle gas, so that uniform heat distribution is obtained. This instantaneous rise in temperature from a point at which practically no cracking has occurred to the full intensity of the predetermined cracking temperature has been found to minimise such skin temperature effects as are usually accompanied by undercracking or overcracking. Further, it would appear that the partial pressure conditions existing, due to the presence of the cycle gas, in the distilling units of the system, are favourable to effective vaporisation.

Any grade of charging stock ranging from naphthas to reduced crudes may be handled in a single T.V.P. unit. It is adapted to either reforming or cracking operations, simultaneously or separately, without the necessity of mechanical changes.

The noteworthy features of the process are the high octane rating and the high yield of finished gasoline, regardless of the character of the charging stock. The following are examples of results obtained from the cracking of various charging stocks by the T.V.P. Process:—

Type of Stock	E. Texas Reduced Crude	Michigan Crude	E. Texas Gas Oil	Naphtha Blend (W. Texas and Mid-Continent)
Gravity A.P.I.	26·3	28·9	31·2	51·4
Yields.				
Gasoline % vol.	56·1	57·0	49·7	84·18
Fuel Oil % vol.	35·4	27·3	29·0	2·49
Gas and Loss % vol. ..	8·5	15·7	21·3	13·33
Gasoline.				
Gravity A.P.I.	56·7	59·0	56·8	54·2
End Point °F.	430·0	425·0	392·0	425·0
Octane Number .. .. (C.F.R. Motor Method)	71·6	74·6	75·0	73·0
Fuel Oil.				
Gravity A.P.I.	8·0	6·5	11·2	3·3

It is also believed that good results have been obtained from cracking crude oils produced by the synthetic treatment of gases. Figures

relating to these are not yet available, but it would be reasonable to expect that the process as described would be well suited to cracking high-paraffinic stocks of that type.

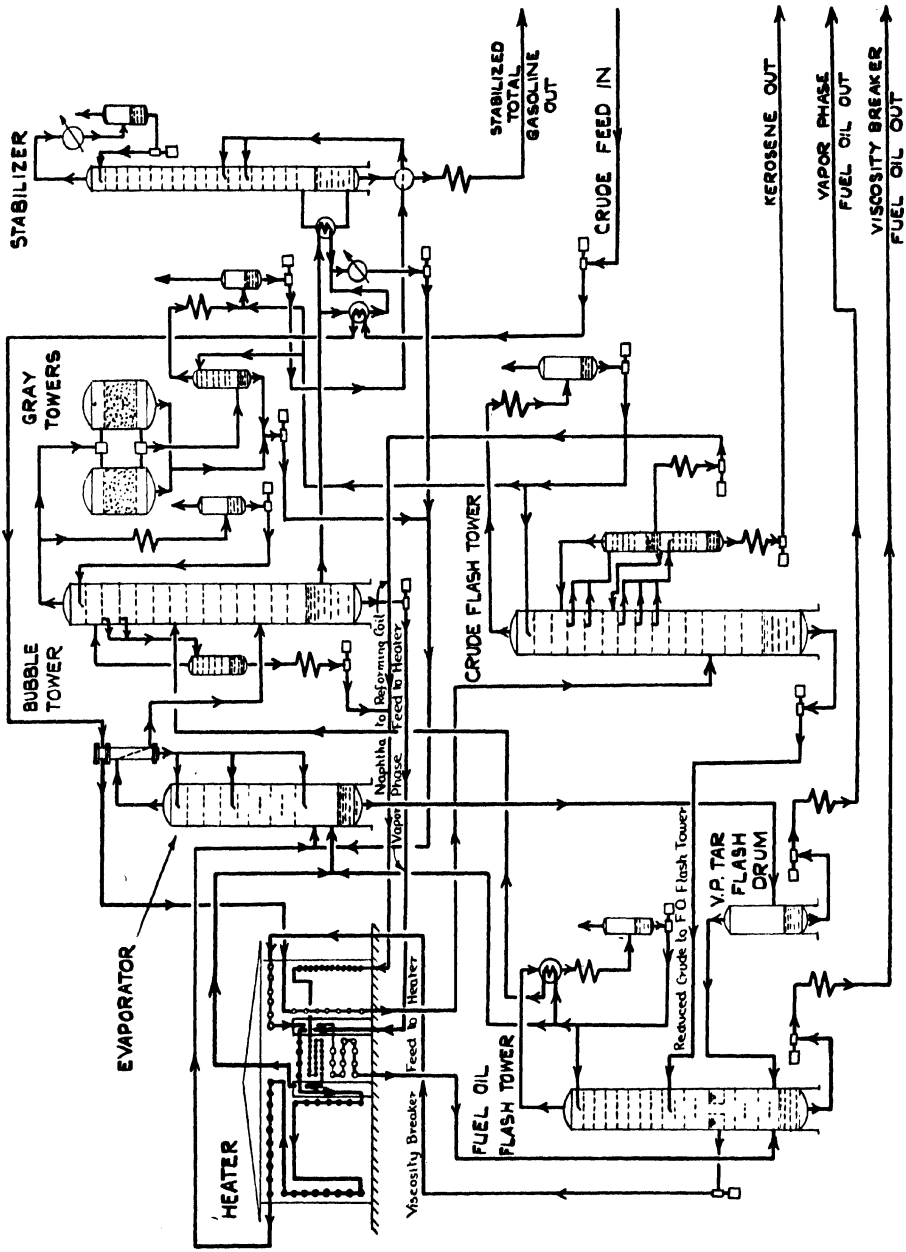


FIG. 12.—FLOW DIAGRAM OF A TYPICAL COMBINATION CRACKING UNIT

The authors are indebted to T.V.P. Limited for the above information relating to this process.

95. Combination Cracking Units.—Prominent among the recent developments in refining practice has been the trend towards the close association of cracking with distillation operations and so-called "combination" units are now in vogue for initial distillation of crude, viscosity breaking, and naphtha reforming in self-contained units. A typical flow diagram of such a unit is reproduced in Fig. 12. Crude oil is fed, after heating in the furnace, into the crude flash tower, from which may be taken kerosene (if required), a heavy naphtha cut for reforming, a light gasoline, and a reduced crude. The latter is flashed to provide feeds for the viscosity breaker coil and the vapour-phase coil. Clay treatment of the finished gasoline and final stabilisation are also allowed for. It will be noted that a single furnace is employed, the duties of which comprise the heating of four separate oil streams. The furnace contains one convection section, but two radiant sections. Units each handling up to 32,000 barrels per day of crude are now in operation, producing 66 per cent. weight yield of 70 octane number gasoline from Mid-Continent crude oil.

96. The processes described above are merely typical of those in use in the petroleum industry, but there are many others which possess peculiar advantages.

The *Knowles* process reduces topped crudes and residuums to a dense coke of unusually high fixed carbon content and of firm gel structure. As overhead streams it produces appreciable quantities of gasoline of high octane number and all the remaining gas oil present in the charging stock—and this gas oil, in turn, is cracked to produce additional gasoline.

The *Holmes-Manley Process* has been adapted chiefly to the processing of gas oils, and operates at 300–400 lbs. pressure, the cracking reaction being influenced more by length of soaking time than in other cracking processes. The cracking temperature employed is 800–900°F. and soaking is allowed to take place in vertical chambers.

In addition, the Pratt, Leamon, Blaine, Jenkins and Donnelly cracking processes are well known.

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Chapter III

THE PRODUCTION OF MOTOR FUELS BY THE EXTRACTION OF GASOLINE FROM NATURAL GAS

99. Introduction.—" Natural gasoline " or " casinghead gasoline " is a term applied to petrol recovered from natural gas by scrubbing, adsorption or condensation, as distinct from " straight-run spirit " obtained in the refinery by means of distillation of crude oil, or " cracked spirit " by the pyrolysis of heavier oils.

The use of casinghead gasoline has been much increased during the last five years and this has led to a general improvement in the anti-knock values of motor spirits on account of the high knock ratings of the low boiling paraffin hydrocarbons. The limiting factor to the amount of light hydrocarbons which can be added to a fuel is the danger of vapour-locks being formed in the fuel-pipe or carburettor of a petrol engine. Propane being extremely volatile is usually removed from the gasoline before blending with straight-run spirit, for this reason.

Owing to the enormous production of gas in many oilfields, and the beneficial properties of natural gasoline, methods of recovery were quickly developed, and nowadays natural gasoline is recovered even from gases containing small percentages of this constituent.

Natural gases are termed " wet " gases or " dry " gases, according to the amount of petrol they contain. A " wet " or rich gas is one which contains more than one gallon of petrol per 1,000 cubic feet, whereas if the petrol content falls below this limit the gas is usually termed " dry."

There are many factors which influence the petrol or gasoline content of a natural gas. Gas in intimate contact with crude oil is saturated with the different constituents of the latter. In general, if the crude oil contains a high percentage of spirit, the gases will be rich, while with heavy gravity crudes the percentage of gasoline will be small.

The percentage of petrol in a crude oil may vary from a trace to as much as 60 per cent. in special cases, consequently the petrol content of a crude is an important variable in determining the richness of a gas which accompanies it. Other factors influencing the gasoline content of natural gas are the intimacy of contact between the gas and the crude oil and more important still the gas pressure in the oil sand.

In wells flowing naturally under very high pressures, natural gas may consist solely of methane, nitrogen and carbon dioxide. As the wells continue producing oil, and the pressure consequently diminishes, the percentage of gasoline in the gas increases. It should be realised, however, that the change of pressure merely alters the percentage of vapour in the gas and not the total quantity of gasoline existing in the state of vapour.

100. Henry's law states that in a two-phase system, i.e., a liquid and a vapour in equilibrium, the partial pressure of a certain component of the gaseous mixture is proportional to the mol fraction of this component in the liquid.

Expressed mathematically

$$P_A = Kx \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where P_A = partial pressure of component considered.
x = mol fraction of the same component in the liquid state, and
K = constant.

The value of the constant K is, for most hydrocarbons, equal to the vapour pressure of the pure component under consideration, corresponding to the equilibrium temperature.

Expression (1) may therefore be rewritten

$$P_A = V_A x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where V_A = vapour pressure of pure component corresponding to the equilibrium temperature.

This second law is a special case of Henry's law, known as Raoult's law, and is explained in Chapter I.

According to Dalton's law of partial pressures, the partial pressure of a certain component of a gaseous mixture is equal to its mol fraction in the gas (or its volumetric fraction), multiplied by the total pressure :—

$$P_A = Py \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where P_A = partial pressure of component of the gas,
y = mol fraction of the component in the gas,
P = total pressure of the gas.

Combining equations (2) and (3), the following expression is obtained :—

$$P_A = V_A x = Py \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

i.e., the mol fraction of a component in the liquid phase, times the vapour pressure of this component in the pure state (corresponding to the equili-

brium temperature), is equal to the mol fraction of the same component in the vapour phase multiplied by the total pressure exerted on the system, provided that the vapour is perfectly soluble in the liquid.

For a definite temperature and a crude oil of fixed composition, V_A and x will have constant values, hence

$$P_A = Py = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

i.e., the mol fraction of petrol in natural gas will be a hyperbolic function of total pressure. It will increase with decrease of pressure but the total quantity of gasoline in a state of vapour will remain constant, as this is proportional to the partial pressure.

Therefore, with a reduction in pressure the quantity of dry gas diminishes and since the quantity of vaporised petrol remains constant, a richer gas is produced.

101. The mechanism of evaporation of the light constituents of crude oil, with change of pressure, can be explained simply.

Assuming a cylinder enclosed by a piston has a volume of two cubic feet and that one cubic foot of this volume is occupied by a liquid such as benzene, the other half containing air and benzene vapour at atmospheric pressure in equilibrium with the liquid, the temperature being 70°F., then

Vapour pressure of benzene at 70°F. $= 75$ mm.

Mol fraction of benzene in vapour $= \frac{75}{760} = \frac{15}{152}$

The volume of benzene vapour present, calculated at atmospheric pressure and 70°F. $= \frac{75}{760} \times 1 = \frac{15}{152}$ cubic feet.

Assume first that the piston is lifted until the volume in the cylinder is 3 cubic feet. Neglecting small changes in the volume of liquid and assuming that the system is isothermally expanded, we have :—

Total pressure $= \frac{760}{2} = 380$ mm.

Mol fraction of benzene vapour $= \frac{75}{380} = \frac{15}{76}$

The volume of benzene vapour present, calculated at atmospheric pressure and 70°F. $= \frac{75}{760} \times 2 = \frac{15}{76}$ cubic feet.

In this case, when the pressure is halved both the mol fraction and the quantity of benzene in a state of vapour are doubled.

A reduction in original pressure could also be obtained by withdrawing the vapours until the pressure is reduced to 0·5 atmospheres : again neglecting any change in volume of liquid and assuming that temperature has remained constant, we have

Total pressure = 380 mm.

Mol fraction of benzene vapour $= \frac{75}{380} = \frac{15}{76}$

The volume of benzene vapour present, calculated at atmospheric pressure and 70°F. $= \frac{75}{760} \times 1 = \frac{15}{152}$ cubic feet.

In this case the mol fraction is doubled but the total amount of vaporised benzene remains the same as in the original case.

This last case is analogous to the decline of pressure in an oil well.

102. Composition of Natural Gas.—Natural gas is composed chiefly of hydrocarbons of the paraffin series, ranging from methane to octane, the percentage of each constituent present being governed by the factors already described. The percentage of each of the constituent hydrocarbons usually decreases with increase of molecular weight, due to the fact that heavier hydrocarbons, although existing in a greater proportion in crude oil, have much lower vapour pressures.

A characteristic analysis of four natural gases associated with crude oils of different gravities is shown in the following table.[1] As is to be expected the percentage of heavier hydrocarbons in the gasoline increases with decrease in specific gravity of the crude oil.

TABLE 1

Specific Gravity of Crude Oil at 60°F.	0·9333	0·9032	0·8750	0·8485
Methane per cent.	96·19	89·80	87·76	81·28
Ethane ,, ,, ...	1·84	5·00	5·30	8·58
Propane ,, ,, ...	1·46	2·80	3·20	4·75
Butane ,, ,, ...	0·13	0·80	1·90	2·79
Pentane and heavier per cent.	0·38	1·60	1·84	2·60

Carbon dioxide and nitrogen are nearly always present in natural gas in varying amounts, and helium is also present in some gases from a trace up to 2 per cent. Whenever water is associated with oil or gas, water vapour will also be present. Sulphuretted hydrogen is often found in natural gas.

The hydrocarbons which constitute the main part of natural gasoline range from butane upwards, the first three members of the paraffin

series, viz. methane, ethane, and propane, being undesirable, are usually eliminated by pressure distillation.

The presence of propane raises the vapour pressure of the gasoline, thus making it unstable and greatly increasing the losses in storage and handling. The producer always aims to make a petrol free from propane and containing as much butane as his seasonal specification will allow.

103. Methods of Recovery.—There are three principal methods in general use for the recovery of petrol from casinghead gas.

(1) Compression, where the gases are compressed and then cooled; in this manner the hydrocarbons whose partial pressures are in excess of their corresponding vapour pressures at the temperature of the condenser are liquefied until equilibrium is established between the liquid and the vapour.

(2) Oil absorption, where the gases are scrubbed counter-currently with a suitable oil distillate. The casinghead gasoline is thus removed by solution and recovered from the scrubbing oil by distillation.

(3) Charcoal adsorption.—Charcoal adsorbs the heavier components of natural gas when the latter is passed through it and the adsorbed gasoline is then removed from the charcoal by treatment with steam.

The total available quantity of natural gasoline which a gas contains can be calculated from an analysis of the gas.

For example, a gas having the following composition, methane 48·8 per cent., ethane 18·5 per cent., propane 15·2 per cent., *n*-butane 10·3 per cent., *n*-pentane and heavier hydrocarbons 7·2 per cent., would yield as useful components of natural gasoline the butane, pentane, etc., and their volumes per 1,000 cubic feet of gas when liquefied would be determined as follows :—

	Volume in 1,000 cubic feet	Cubic feet per gallon	Gallons per 1,000 cubic feet
Butane	103	31·6	3·26
Pentane, etc. ..	72	27·5	2·25
			5·51

The total theoretical quantity of recoverable gasoline would be, therefore, 5½ gallons per 1,000 cubic feet of gas. In practice, the total amount cannot be recovered, however, as the percentage recoverable depends on

the efficiency with which the plant is operating and, to some extent, on the particular type of plant used.

Natural gas containing 0·75 gallon of gasoline per 1,000 cubic feet is at present the driest gas which will yield commercial gasoline economically by compression: oil absorption can be used economically down to a concentration of 0·125 gallon per 1,000 cubic feet while with charcoal adsorption gas of any kind can be treated.

104. Compression Method.—From the compression standpoint it is known that all gases and vapours can be liquefied at definite conditions of temperature and pressure. For a gas to be liquefied by the application of pressure the temperature must be lowered at least to a certain point peculiar to each gas, which is known as the critical temperature.

No matter how great the pressure applied, a gas will not pass into the liquid state until its temperature is reduced to the critical temperature; the pressure required to change a gas to the liquid state at the critical temperature is called the critical pressure. It has also been shown that each gas in a mixture of gases, which do not chemically react with each other, exerts the same pressure as it would if it alone were present, and that the sum of the partial pressures of each constituent of a mixture of gases equals the total pressure.

In the case of a mixture of gases, therefore, the total pressure required to liquefy any component at its critical temperature is that at which the partial pressure of such a component is equal to its critical pressure.

Critical data of some of the lighter paraffin hydrocarbons are given in the following table.

TABLE 2

Hydrocarbon	Formula	State at 60°F. and 30 inches Hg.	Molecular Weight	Critical Temperature °F.	Critical Pressure. Lbs. per sq. in. absolute
Methane	CH_4	Gas	16·03	115·8	773
Ethane	C_2H_6	do.	30·05	90·0	708
Propane ..	C_3H_8	do.	44·06	207·5	661
Butane	C_4H_{10}	do.	58·08	272·7	532
Iso-butane ..	C_4H_{10}	do.	58·08	307·8	524
Pentane	C_5H_{12}	Liquid	72·09	387·0	485
Iso-pentane ..	C_5H_{12}	do.	72·09	370·0	483
Hexane	C_6H_{14}	do.	86·11	454·6	435
Heptane	C_7H_{16}	do.	100·13	512·6	396
Octane	C_8H_{18}	do.	114·14	565·5	371

Pentane, one of the principal constituents of natural gas gasoline, is easily kept in the liquid state due to its low vapour pressure. Its

vapour pressure at the usual temperature of cooling in compression plants, approximately 70°F., is about half an atmosphere, so that pure pentane can be kept liquid at normal temperature and pressure. Where it is a constituent of a mixture of hydrocarbons in the gaseous state the application of pressure is necessary in order to liquefy it.

The total pressure necessary to liquefy these hydrocarbons can be calculated from a knowledge of the percentage of each component present, together with the vapour pressure at the prevailing temperature. Whilst it would be expected that those hydrocarbons would first liquefy whose vapour pressures were first exceeded, it is found in practice that they do not liquefy singly, but at any given pressure some of the more volatile fractions are condensed along with those more readily liquefied. Consequently, in determining the pressure necessary for the liquefaction of the heavier components of any particular gas, practical experience is a useful guide.

This is shown by the following example of a gas containing methane 36·8 per cent., ethane 32·6 per cent., propane 21·1 per cent., butane 3·6 per cent., pentane 2·2 per cent., hexane, etc., 3·7 per cent., which by theory would require a pressure of about 300 lbs. per square inch to liquefy the pentane and higher hydrocarbons. In actual practice, it was found that a pressure of 150 lbs. per square inch liquefied about 15 per cent. of the total volume, which meant that some of the propane was also liquefied. This problem is further complicated by the fact that hydrocarbon gases depart, very markedly, from the gas laws, the extent of such deviation increasing with the molecular weight of each component.

105. The simplest type of compression plant consists of gas-engine driven single-stage compressors, and their auxiliary apparatus such as cooling coils, storage plant, etc. These plants are suitable for the treatment of small volumes of gas of high gasoline content.

In the more modern plants the gas is first compressed to about 35 lbs. per square inch and then cooled, when some of the heavier vapours are condensed. The gas is then compressed a second time to a much higher pressure, say 150 lbs. per square inch, and cooled once more, when all the vapours liquefiable at that pressure are condensed.

The compression condensates are invariably stabilised before they are blended. This is referred to in detail later.

106. The Oil Absorption Process.—This process, as used in the petroleum industry, is an adaptation of the older method employed for many years to extract benzole and toluole from gas made by carbonising coal. Young used the process first for extracting petrol from gas obtained in the distillation of oil shale and patented the process in 1776.

When a constituent of a gas is removed from it by treatment with a liquid the constituent is dissolved in an amount proportional to its solubility. The solubility is determined by the gas-liquid equilibrium relationships involved. A solution of a gas in a liquid exerts, at a fixed temperature and concentration, a definite partial pressure of dissolved gas. A given quantity of liquid will dissolve an amount of gas proportional to the partial pressure of the dissolved gas. In the case of a slightly soluble gas, a higher partial pressure of the gas in contact with the liquid will be required to yield a solution of given concentration : while a very soluble gas will give rise to a similar concentration at a much lower partial pressure.

In a gas absorption process which has attained equilibrium, the partial pressure of the soluble constituent in the gas phase must be equal to the partial pressure that is equivalent to the concentration in the liquid phase. The most concentrated solution that can possibly be produced, even if equilibrium is reached in the operation, is that in which the equivalent partial pressure of the dissolved constituent is equal to its highest partial pressure in the gas phase. This has already been explained.

In absorption problems an equilibrium diagram, showing the relationship between the amount of soluble constituent in the two phases, is often of great use. In natural gasoline absorption processes where a hydrocarbon mixture is being treated at low pressures Raoult's law can be used to calculate the equilibrium curve.

The amounts of the soluble constituents in the two phases may be expressed as

$$y = \frac{V_A x}{P} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5a)$$

This expression was derived in Chapter I.

107. Bubble-plate Absorption Towers.—The most common type of absorption equipment employed for the recovery of gasoline from natural gas is the bubble-plate absorption tower. Except in cases of high pressure absorption the packed tower is nowadays very seldom used. The theory of bubble-plate absorption will, therefore, be dealt with here exclusively.

Assume that it is desired to extract by absorption in an absorbent oil, certain desirable products from natural gas. Usually the volume of methane and ethane present is very great compared with the volume of the remaining constituents. Since these two constituents are not absorbed to any appreciable extent, a negligible volume of gas compared with the initial volume will be absorbed. If the methane and ethane are considered together as inert gas absorbed only in negligible amounts

then at constant rate of input into the absorber, the inert gas rate at all points in the column will be the same.

In a bubble-plate absorption tower it is obvious that the maximum attainable extraction would be reached if each separate plate unit of the system was ideal, that is, if the oil on each plate extracted its maximum quota of soluble constituents. Such a plate is illustrated in Fig. 1,

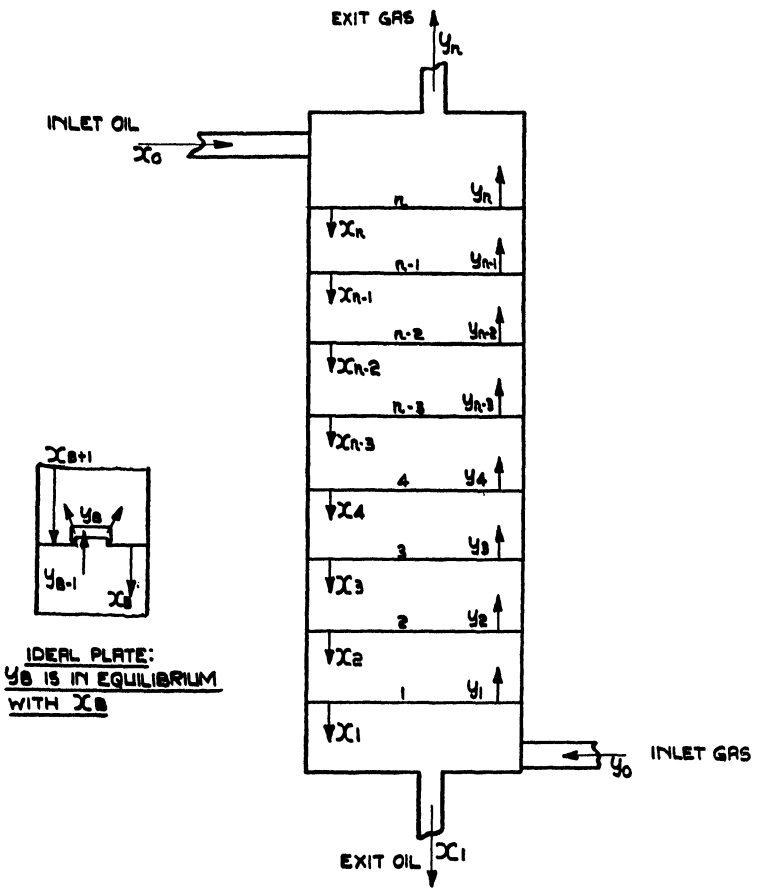


FIG. 1.—DIAGRAM OF IDEAL PLATE AND BUBBLE-PLATE ABSORPTION TOWER

where the overflowing oil of solute concentration x is in equilibrium with the upgoing gas of concentration y. Alongside this is drawn a diagram of a scrubber consisting of n plates.

In such a system it has been already shown that the quantity of inert gas is constant at all points. Similarly the quantity of absorbing liquid may be considered to remain constant throughout the apparatus. Since the volume of absorbed components is very small compared with the

total volume of absorbent, unless a very rich gas is being treated, the error introduced by these assumptions is negligible. When employing the above assumptions it becomes more convenient to express the concentration of the soluble components in the gas and liquid phases as mols per mol of inert gas and mols per mol of scrubbing oil respectively.

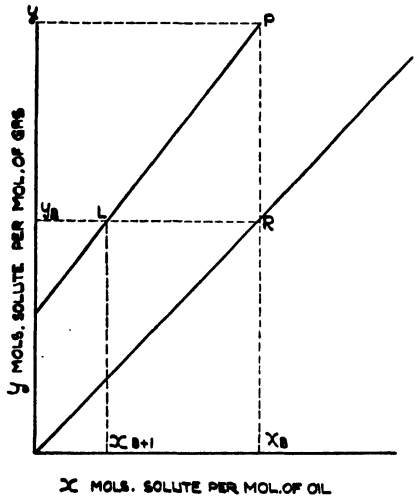


FIG. 2.—OPERATING LINE—EQUILIBRIUM CURVE DIAGRAM

If

Q = mols extracted per unit time,
G = inert gas rate, mols per unit time,
L = scrubbing oil rate, mols per unit time,
y = gas phase concentration of soluble component,
x = liquid phase concentration of soluble component,

and the subscripts refer to position in the apparatus shown in Figure 1, then for the total amount extracted

$$Q = G(y_o - y_n) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$\text{also } Q = L(x_1 - x_o) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and since the amount given up by the gas must equal the amount absorbed by the oil

$$G(y_0 - y_n) = L(x_1 - x_0)$$

$$y_0 - y_n = \frac{L}{G}(x_1 - x_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Since for any given set of conditions y_0 and x_1 are constants, equation (8) resolves itself into a linear equation with y and x as the variables. Concentration relationships in the two phases can, therefore, be repre-

sented by a straight line whose slope is $\frac{L}{G}$, the ratio of scrubbing oil to inert gas passing through the equipment per unit of time. This line is called the "operating line." Plotting the "operating line" and the equilibrium curve in similar units then results in a graphical representation of conditions within the absorber. The vertical distance between the operating line and the equilibrium curve represents the change in solute concentration of the gas rising from one ideal plate to the next. Similarly, the horizontal distance between the two lines represents the change in solute concentration of the oil overflowing from one ideal plate to the one below.

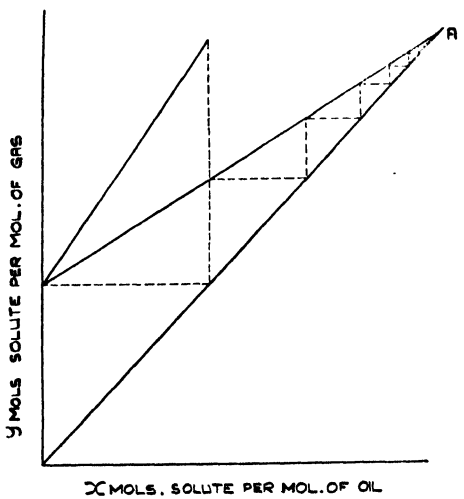


FIG. 3.—OPERATING LINE—EQUILIBRIUM CURVE DIAGRAM FOR DEFINING THE NUMBER OF PLATES

In Fig. 2, the operating line and equilibrium curve are drawn for a hypothetical plate tower composed of ideal plates. The inlet gas and exit oil concentrations, that is, the concentrations prevailing at the bottom plate, are obtained from point P on the operating line, as y and x_B respectively. By definition the overflowing oil from this bottom plate x_B must be in equilibrium with the gas rising from the bottom on to the second plate y_B. Obviously the point R on the equilibrium curve which is in equilibrium with x_B will give y_B. Further, the point L on the operating line must give the concentration of the oil entering the bottom plate, namely $x_B + 1$. Therefore, the step PRL is equivalent to one ideal plate, and the number of ideal plates required to give any desired extraction may be stepped off on the combined operating line—equilibrium curve diagram.

In Fig. 3 a special case is illustrated where the $\frac{L}{G}$ ratio employed is such that the operating line and equilibrium curve meet at point A. Near this point the exit oil and inlet gas are in equilibrium; the driving force is infinitely small and the plate tower will have an infinitely small capacity in this section. That is to say, the apparatus necessary to give the desired extraction would have to be of infinite length. This figure then gives the $\frac{L}{G}$ ratio required for a scrubber composed of an infinite number of ideal plates, and is obviously the smallest ratio which can be employed for the required solute removal, since the exit oil is completely saturated with solute.

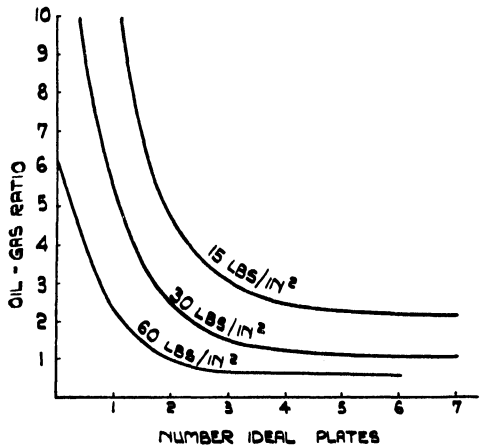


FIG. 4.—THE EFFECT OF PRESSURE ON THE OIL-GAS RATIO REQUIRED BY ABSORBERS OF DIFFERENT HEIGHTS

In this figure also a single ideal plate scrubber is illustrated. Here the $\frac{L}{G}$ ratio required can be considered as the theoretical maximum which must be employed for the necessary degree of extraction. Obviously, the amount of scrubbing oil required to give the desired solute removal, for an extractor of any height equivalent to from one to an infinite number of plates, must lie between these two extreme values.

108. Effect of Temperature and Pressure.—The effect of temperature, pressure and oil-gas ratio on the size of the absorber required and on the extraction of the individual constituents of natural gas, namely, propane, butane, pentane, etc., may now be examined.

Assume for this purpose that a gas with the composition shown in Table 8 is available.

TABLE 3

Hydrocarbon	% by Volume	Mol/Mol of Inerts
Methane	50·0	Inerts.
Ethane	30·7	
Propane	13·5	·167
Butane	4·2	·052
Pentanes, etc. ..	1·6	·020

Since it is desirable for an absorption plant to remove as much butane, pentane and higher hydrocarbons from the gas with as little propane as possible, let us assume that the butane content is to be reduced to 0·84% by volume (Fig. 4). Employing the methods

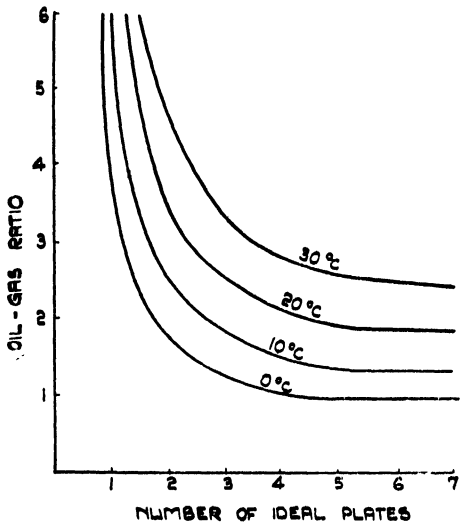


FIG. 5.—THE EFFECT OF TEMPERATURE ON THE OIL-GAS RATIO REQUIRED BY ABSORBERS OF DIFFERENT HEIGHTS

outlined above, the oil-gas ratios required to remove the desired amount of butane with absorbers varying in size from one up to an infinite number of ideal plates may be obtained. By inserting different values for the total pressure P, and the vapour pressure V_A for the different components absorbed (butane, propane, etc.) corresponding to the required working temperatures and pressures in equation (5a), the effect of pressure and temperature can be determined.

In Figs. 4 and 5 the effect of pressure and temperature on the oil-gas ratio required by absorbers of different heights is illustrated. It will be seen that with an absorber of constant height, equivalent to a given number of ideal plates, a decrease of temperature and an increase of pressure will decrease the amount of scrubbing oil required.

In Fig. 6, the percentage of the total propane and pentane removed at constant temperature and pressure by different-sized absorbers, all removing the required amount of butane, is shown. This illustrates the effect of the number of plates on the selectivity of the system. With an increasing number of plates more pentane and higher hydrocarbons and less propane is absorbed.

When both the size of the absorber and the pressure are kept constant, the effect of temperature variation on the amounts of the

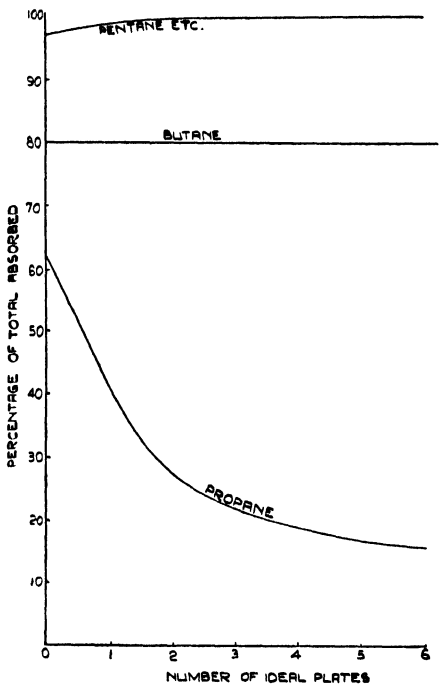


FIG. 6.—CURVE SHOWING VARIATION IN PROPANE AND PENTANE REMOVAL AT CONSTANT TEMPERATURE AND PRESSURE BY DIFFERENT-SIZED ABSORBERS

different constituents absorbed is as shown in Fig. 7. This shows that temperature reduction is also advantageous from the point of view of selectivity, since the percentage of the total propane removed decreases while the percentage petrol removal increases.

In Fig. 8 the same effect has been examined for rather a different case. In this instance nearly complete extraction of pentane and higher hydrocarbons, in a gas of the composition shown in Table 4, was assumed to occur at 15 lbs. per square inch as a basis for calculation.

TABLE 4

Hydrocarbon	Volume %	Mol/Mol of Inerts
Methane	50	Inerts.
Ethane	30	
Propane	10	·125
Butane	6	·075
Pentane	4	·050

Here the selectivity effect exhibited by temperature reduction is not so favourable, since both the butane and propane extracted are reduced,

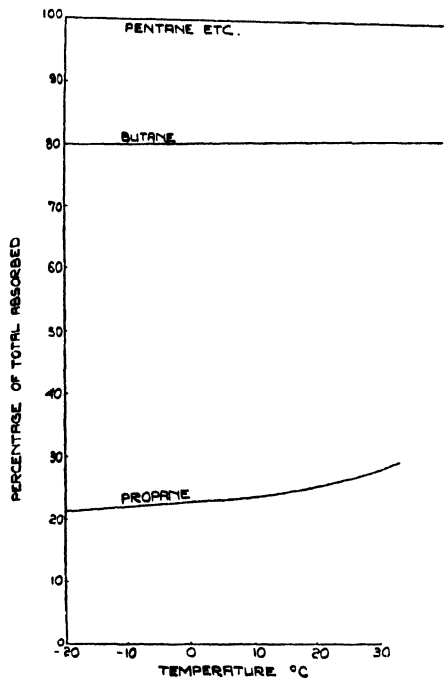


FIG. 7.—CURVES SHOWING THE ADVANTAGE OF TEMPERATURE REDUCTION FOR PROMOTING SELECTIVE ABSORPTION

the propane by a greater percentage than the butane. Reduction in propane absorption has been obtained only by sacrificing the recovery of some of the available butane.

109. Details of Plant.—An oil absorption plant may consist of a number of towers constructed in such a manner that the absorbent oil is led in at the top and allowed to flow downwards, usually over some form of baffling, while the gas flows in at the bottom and passes upwards, both being brought into contact with each other in order that the gasoline in the gas may dissolve in the oil. The stripped gas

then passes on to the consumer, after purification if necessary, if it is being sold as domestic gas, or is burned either as fuel or to waste.

The enriched oil passes through a heat exchanger in counter-current flow to the hot denuded oil leaving the stripping still and thence into the still. Here the gasoline vapours are distilled and pass through a column, to reflux any absorbent oil which might be carried over, into a cooler and through water separators to storage. The denuded oil, or "lean oil," after it leaves the heat exchanger, passes through cooling coils and back to the absorbers to be used over again.

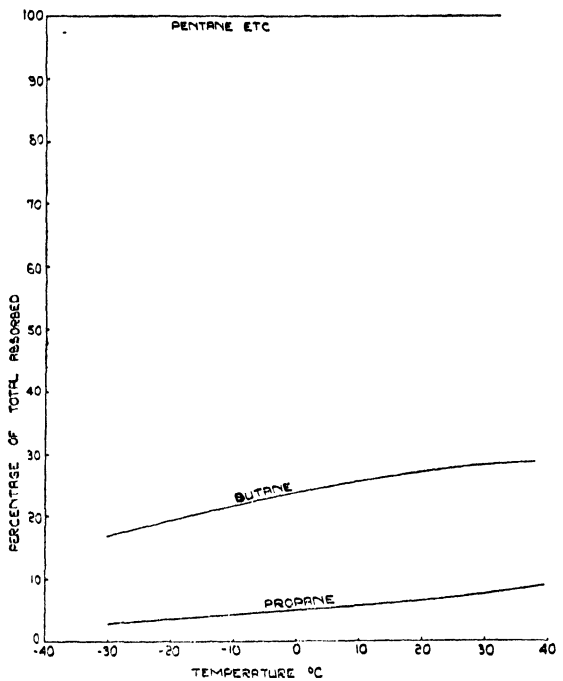


FIG. 8.—CURVE SHOWING A SPECIAL CASE OF SELECTIVE ABSORPTION BY TEMPERATURE REDUCTION

The gas to be treated is usually cooled before it enters the towers and it is then compressed to a pressure depending on the richness of the gas: with rich gases the pressure is usually about 30 lbs. per square inch although many plants work at pressures as low as 5 to 10 lbs. With dry gas pressures up to 450 lbs. per square inch may be used in order that the size of the plant and its cost may be kept down to a minimum.

As an indication of the size of the units required, a typical plant, owned by the Phillips Petroleum Co., in Oklahoma, circulates 400,000 U.S. gallons of gas oil per 24 hours, and has a throughput of 18 million cubic feet of gas daily, yielding about 1½ U.S. gallons per 1,000 cubic feet.

This represents about 22 U.S. gallons of gas oil per 1,000 cubic feet throughput, which is circulated through 24 absorbers, 3 feet diameter by 48 feet high, connected in series and operating under a pressure of 30 lbs. per square inch. These towers are baffled with steel shavings. Four horizontal stills, 7 feet diameter by 30 feet long, are used for separation, three 150 horse-power boilers supplying the steam. In the more modern plants special scrubbers involving solid plate baffling or a special design of bubble plate, are used as absorption towers.

The oil used for absorption is usually that known as Mineral Seal Oil, a light gas oil fraction, being a cut between kerosene and gas oil. It is a highly refined product obtained by reducing the kerosene distillate and treating the residue. Its initial boiling point must be well above the end boiling point of the gasoline to effect sharp separation on distillation; its viscosity must be low in order that it may flow freely and widely over the baffling at atmospheric temperature, it should have a low cold test, and no tendency to emulsify.

Efficient operation of absorption towers in the casinghead gasoline industry is dependent on the temperature of the lean oil entering and the enriched oil leaving the absorber, as there are two outlet equilibria to be considered, the one at the top and the other at the bottom of the tower. The top point of equilibrium is between the dry gas and lean oil which partly determines the amount of petrol leaving the tower with the gas, while the lower equilibrium point determines the amount leaving the tower in the enriched oil.

As the temperature of the lean oil entering the absorber is lowered, the equilibrium concentration which can be approached by the gas leaving the tower is reduced. As the oil passes down the column its temperature rises owing to the evolution of the latent heat of the absorbed hydrocarbons. The higher the temperature attained by the enriched oil leaving the tower, the smaller becomes the equilibrium petrol concentration which it attains. It is evident, therefore, that the temperature of the enriched oil leaving the bottom of the tower is an important controlling factor in absorption efficiency.

Fig. 9 shows the construction of an absorption tower fitted with internal coolers in a number of sections.

In the more modern plants the enriched oil is first led to a high pressure still, fitted with a reflux column operating at a pressure of about 80 lbs. per square inch, where the light gasoline fractions are distilled over separately. In operating at this pressure it is possible to condense and recover all valuable fractions of the overhead, thus obviating the necessity of recompressing or reabsorbing the more volatile spirit. The gasoline fractions remaining in the absorption oil are then distilled over in a low pressure still and reflux column operating at about 5 lbs. per square inch pressure. In this manner, the major part of the gasoline

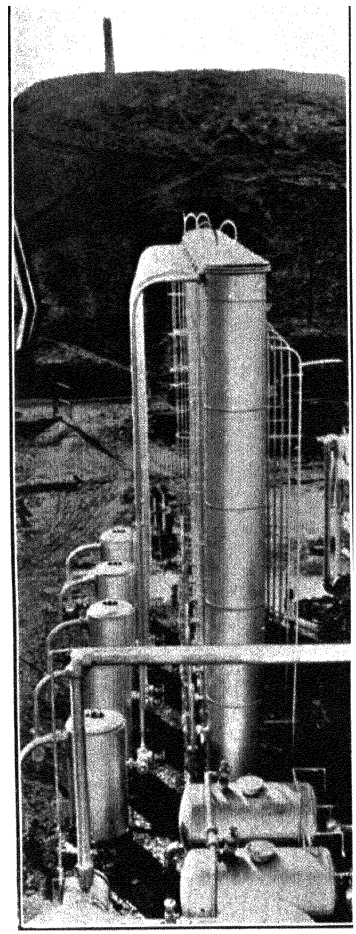


FIG. 10.—BATTERY OF NINE ABSORBERS
(*Courtesy of Foster Wheeler, Ltd., London*)

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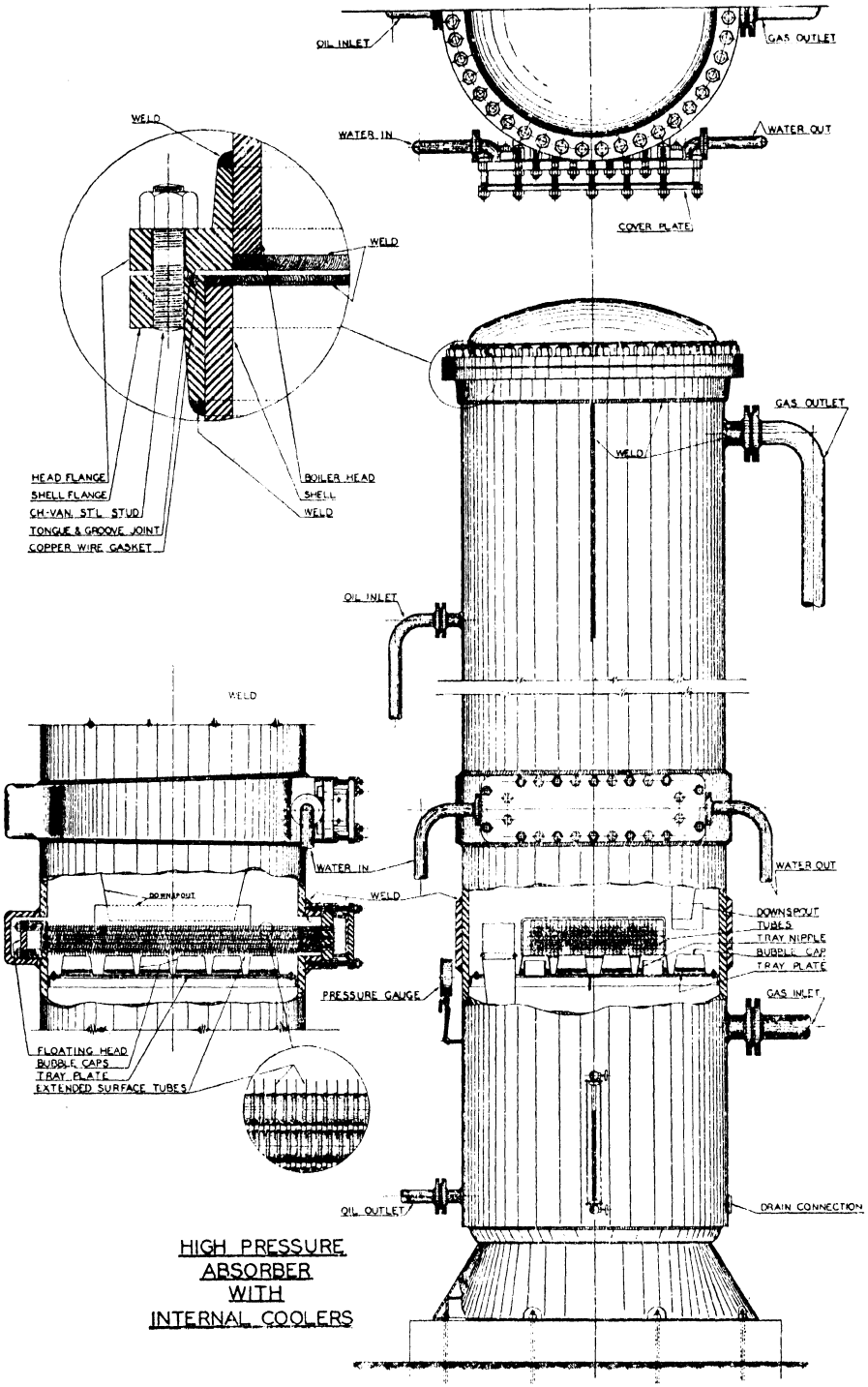


FIG. 9
(Courtesy of Foster Wheeler, Ltd., London)

is stripped from the oil under the most economical conditions with regard to steam consumption, and the lean oil is then cooled and returned to the absorbers while the two fractions of gasoline are sent to the stabiliser to be treated in a manner which is described later.

Similar plant is also used in refineries to deal with the evaporation products from petrol tanks and processing equipment, which previously had been allowed to vent into the atmosphere. This has resulted in a considerable saving of the commercial products which hitherto had been lost.

A photograph of a typical absorption unit erected by Messrs. Alco Products, Inc., is reproduced in Fig. 11.

110. Charcoal Adsorption Process.—Considering any two-phase system, there always exists at the interface a force called the surface tension. Surface tension and internal pressure will oppose any force trying to increase the surface area and the system will tend to minimise its free surface energy. This energy is the product of surface tension and the area of surface and a reduction in either of these two factors will cause a reduction in the free surface energy.

In dealing with a pure substance, therefore, where the surface tension remains constant, the system will tend to reduce its surface area. As an example of this, drops of water assume a spherical shape due to the fact that the sphere is a geometrical figure having a minimum surface area for a given volume. Where the surface area of a pure substance cannot be reduced the surface energy must remain constant.

Where, however, the substance is not pure but is a liquid mixture, the concentration of the solution will not be the same at the interface as in the body of the solution and change of concentration will be such that the interfacial or surface tension will be lowered, which will reduce the free surface energy. Therefore, if an increase in the concentration of the solute results in a lowering of surface tension of the solvent, the molecules of the solute will have a higher concentration at the interface, while if an increase in the concentration of the solute results in an increase in surface tension, the concentration at the interface will be less than the concentration in the bulk of the solution. Any concentration at the interface is called *adsorption.*

The foregoing statements apply to a two-phase system, where one phase consists of a solution, the other phase being solid or gas.

In the liquid-gas phase, assuming the liquid to be a pure substance while the gas is a mixture, similar phenomena will occur but in a different phase, that is to say, the concentration of one of the gaseous components will be altered at the interface or, in other words, the gases will be adsorbed at the liquid surface.

Adsorption of a component of a mixture of gases follows an increase



FIG. 11.—TYPICAL OIL ABSORPTION INSTALLATION
(Courtesy of Alco Products Incorporated)

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in partial pressure of this component at the interface, hence the following law. Should an increase in partial pressure of a component of a gaseous mixture at the interface result in a decrease of surface tension, such component will be positively adsorbed, but if an increase in partial pressure results in an increase of surface tension, negative adsorption will take place which will mean that the partial pressure at the interface will be less than the partial pressure in the bulk of the gas.

These phenomena were first mathematically expressed by Gibbs.[2]

$$a = -\frac{C}{RT} \times \frac{\delta\sigma}{\delta C} \quad \ldots\ldots\ldots \quad (9)$$

where a = excess of substance in surface layer,
C = concentration of substance in the bulk of solution,
R = gas constant,
T = absolute temperature,
σ = surface tension.

It will be seen from the formula that if σ and C change in the same direction, $\frac{\delta\sigma}{\delta C}$ will be positive and a will be negative as already explained.

Replacing concentration by partial pressure the following formula is obtained :—

$$a = -\frac{P}{RT} \times \frac{\delta\sigma}{\delta p} \quad \ldots\ldots\ldots \quad (10)$$

where P = partial pressure.

The phenomenon taking place at a solid-gas interface is similar to those already mentioned and also follows Gibb's formula of adsorption, but the calculation of the expression $\frac{\delta\sigma}{\delta p}$ becomes difficult due to the rigidity of the solid phase. In simple terms, the adsorption in this case could be expressed as the condensation of gases at the solid surface. Adsorption of gases will take place whether the gas is a simple gas or a mixture, but in the latter case some of the constituents will be more readily adsorbed than others.

Langmuir[3] offers an explanation of the above phenomena, by suggesting that molecules of the adsorbing medium have their internal valencies neutralised by other molecules of the same substance, while their external valencies remain free, producing a force of attraction at the solid surface. Gas molecules within the boundary are attracted and held at the surface by these free valencies.

In adsorption, a film of gas covers the surface of the adsorbent but the process does not end here as further gas is absorbed by this fluid film, until the partial pressure of the gas equals the vapour pressure of

the adsorbed film. It is possible, of course, that a certain amount of gas diffuses into the solid adsorbent, which could be regarded as the absorption of the gas by the solid body.

A common term to cover the phenomena referred to is "sorption," the reverse of these processes being termed "desorption."

111. Adsorption Equilibrium.—In the following discussion on adsorption equilibrium a pure gas will be considered. As already stated, adsorption is due to the attraction of the free valencies of the solid molecules; on the other hand, some of the gas molecules are released again, owing to the kinetic energy of the gas acting in the opposite direction. Equilibrium is established after a certain interval of time.

This adsorbed layer of gas will have a vapour pressure depending on the temperature of the system, and if the partial pressure of gas exceeds this vapour pressure it will be absorbed by the liquid, until equilibrium is reached.

When the adsorbent has a porous structure, with capillaries of colloidal dimensions, the condensed layer of gas will exert a lower vapour pressure than it otherwise would if it were exposed to a large area. Therefore, gases in the capillaries will be adsorbed to a greater extent, finally filling up the capillaries, when the solid adsorbent may be said to be saturated.

The following formula shows the relation between the radius of the capillaries and the change in the vapour pressure.

$$\nu = \frac{2\delta d}{d_o \mathrm{P}_o \log_e \frac{\mathrm{P}_o}{\mathrm{P}}} \quad \ldots\ldots\ldots \quad (11)$$

where ν = the radius of the capillary,
δ = surface tension of liquid,
d = density of vapour,
d_o = density of liquid,
P_o = ordinary vapour pressure of the liquid at the temperature considered,
P = actual vapour pressure of the liquid in the capillary.

It will be seen from this that with a decrease in ν, the value of P decreases, provided the other factors remain constant. Water rising in a capillary is an example, the rise increasing as the diameter of the capillary is reduced.

As already explained, two main processes take place when the capillaries of a solid adsorbent are filled, namely, adsorption and absorption.

Absorption is the more important quantitatively, as bigger quantities of gas are condensed by this process : it is limited, however, as the gas

pressure must be high enough to cause absorption, while adsorption takes place even at low pressures.

112. Factors which influence the Adsorption Equilibrium.—For a definite adsorbing medium, the equilibrium depends on two factors, pressure and temperature.

Pressure.—The amount of gas adsorbed varies directly as its pressure.

According to Freundlich

$$a = Kp^{\frac{1}{n}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where a = amount of gas adsorbed per unit weight of adsorbent. (In C.G.S. units, a is the gas volume expressed in cc. reduced to 0°C. and 760 mm., adsorbed by 1 gram of adsorbent.)

p = pressure of gas,

K and $\frac{1}{n}$ are constants.

If adsorption of a component of a gaseous mixture is being considered, the same formula applies, but p will represent the partial pressure or concentration of this component in the gas, and for each pressure there will be a definite amount of gas adsorbed.

The exponent $\frac{1}{n}$ varies between 0·2 and 1, depending on the system.

So long as the temperature is constant, the above formula, which is known as the "adsorption isothermal," holds good, and the amount of gas adsorbed is a parabolic function of its pressure, the curve showing the relation between these two variables being concave to the pressure axis.

Taking the logs of equation (12), the following relation is obtained :—

$$\log_{10} a = \log_{10} K + \frac{1}{n} \log_{10} p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

Therefore, if different quantities of a certain gas adsorbed at varying pressures be plotted logarithmically, a curve should be obtained, whose tangent with the log p gives the value of $\frac{1}{n}$.

As shown in Fig. 12, however, the curves are not straight lines in most cases : if the angle of inclination of the lines passing through every two experimental points with the log p axis are measured, the mean of their tangents will give the mean value of $\frac{1}{n}$. The value of K may be calculated from the log curves, since log a = log K, when log p = 0 :

it can also be experimentally determined by measuring a at unit pressure.

113. Temperature.—This is the second factor influencing the adsorption equilibrium. Again Freundlich's formula holds good but the constants K and $\frac{1}{n}$ are functions of temperature and should be calculated for different temperatures by plotting the corresponding logarithmic isothermals.

Summarising, there are three variables in the adsorption process, the amount adsorbed, the pressure and the temperature. To obtain a clear conception as to the effect of temperature change, one of the two

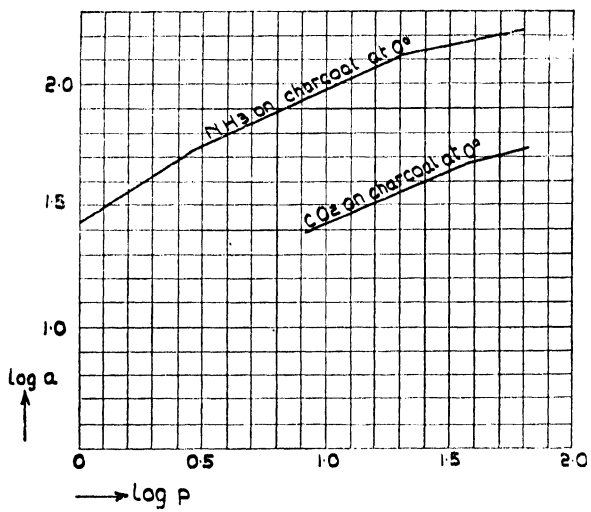


FIG. 12.—ADSORPTION ISOTHERMS OF VARIOUS GASES

other variables should be kept constant. When the pressure is kept constant and the amount adsorbed at different temperatures studied, the curves obtained are termed "isobars": if the amount adsorbed is kept constant and pressure-temperature changes plotted, the curves obtained are termed "isosters."

The effect of temperature change in adsorption is two-fold.

(*a*) It alters the surface tension so that an increase in temperature reduces the surface tension, causing a lesser tendency to adsorption.

(*b*) A rise in temperature produces an increase in vapour pressure thereby reducing the amount absorbed by the condensed liquid.

To formulate a relation between the amount adsorbed and the temperature, adsorption isothermals of the gas should be plotted.

Fig. 13 shows adsorption isothermals of carbon monoxide on charcoal plotted logarithmically for a certain number of temperatures above and below 0°C. These logarithmic isothermals are straight lines, diverging as the axes are approached, and divide all the ordinates in lengths nearly proportional to the temperature difference between them. Assuming that the pressure is kept constant at P_0 and that the amounts adsorbed per unit weight of adsorbent at 0°C. and t°C. are A_0 and A_t respectively, the following relation is obtained from the diagram.

$$\log_{10} A_t = \log_{10} A_0 - AB \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

but AB is proportional to the temperature difference, that is to say, proportional to t°C.

$$\therefore \log_{10} A_t = \log_{10} A_0 - \Sigma t \text{ (isobar)} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where $\Sigma = \frac{AB}{t}$, which is constant for a particular pressure.

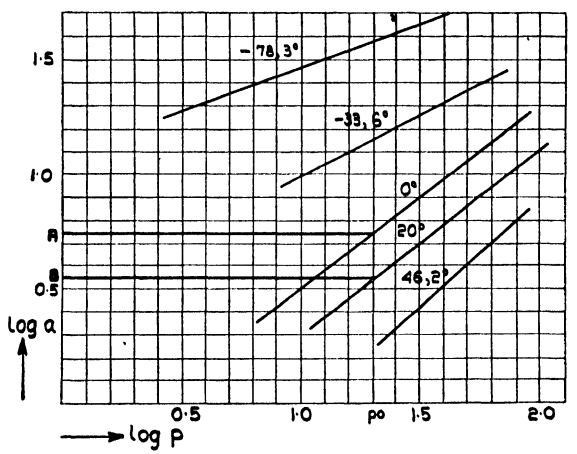


Fig. 13.—Adsorption Isotherms of Carbon Monoxide on Charcoal

As the pressure increases, the isothermals converge and the vertical interval corresponding to AB decreases whilst the temperature difference remains constant: therefore, $\frac{AB}{t}$ decreases with an increase of pressure, in other words, it varies in the opposite direction to p, so that the following expression may now be written :—

$$\Sigma = \Sigma_1 - \Sigma_2 \log_{10} p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where Σ_1 is the value of Σ when p = unity.
Hence the general equation for isobars :—

$$\log_{10} A_t = \log_{10} A_0 - (\Sigma_1 - \Sigma_2 \log_{10} p) \times t \quad . \quad . \quad . \quad . \quad (17)$$

Integrating :—

$$A_t = A_0 e - (\Sigma_1 - \Sigma_2 \log_{10}) t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

The values of constants can be calculated from the above diagram.

By keeping the amount adsorbed constant at say A_0, isosters can be plotted by comparing pressure at different temperatures.

It will be seen from the diagram that pressure increases with increase of temperature, in other words, at higher temperatures a bigger pressure is necessary to cause an equal amount to be absorbed.

As stated previously, the constants $\frac{1}{n}$ and K are functions of the temperature. Logarithmic isothermals get flatter as the temperature falls and consequently $\frac{1}{n}$ becomes smaller since it represents the tangent of the angle between these isothermals and the $\log_{10} p$ axis, but K increases with decrease in temperature.

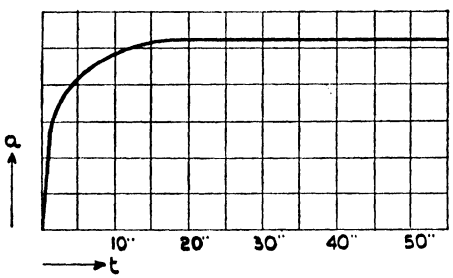


FIG. 14.—CURVE SHOWING THE VELOCITY OF ADSORPTION OF CARBON DIOXIDE BY CHARCOAL

In the isothermal equation $A = Kp^{\frac{1}{n}}$, if p is constant, a fall in temperature increases K and decreases $\frac{1}{n}$ but the expression $Kp^{\frac{1}{n}}$ follows the variation of K.

It should be realised, however, that every system has its own constants depending on the nature of the gas and the adsorbing medium.

114. Velocity of Adsorption.—In most cases the amount adsorbed is nearly a parabolic function of time. For example, if the amounts adsorbed are plotted against time a curve is obtained which rises steeply at first and finally becomes parallel to the time axis when saturation is reached, as in Fig. 14.

The theoretical time required for adsorption equilibrium to be established under favourable conditions does not exceed a few minutes, but in actual practice the time is much longer, as the condensed gases lose their latent heat, thereby heating the adsorbent and causing a retardation of the process. Still more effective is the fact that adsorp-

tion is followed by absorption and diffusion, which obviously require a longer time.

When dealing with a mixture of gases, such as natural gas, some constituents are preferentially adsorbed and a certain amount of time is taken in the process of substitution as the gas molecules have to diffuse through the adsorbed layer in order to reach the surface and replace other molecules previously adsorbed.

115. Reversibility of Adsorption.—In discussing the adsorption equilibrium it has been assumed so far that adsorption is a reversible process. This is only true in certain cases. In the case of charcoal and benzene vapour, the amount adsorbed, as already stated, varies with the pressure. To every pressure and temperature there corresponds a definite amount adsorbed irrespective of whether the pressure is rising or falling, in other words, sorption and desorption curves coincide and such systems are termed "reversible."

With silica gel–water vapour or charcoal–water vapour, however, the adsorption is irreversible. For an equilibrium pressure p, the amount adsorbed is no longer definite; it has two different values according to whether the pressure is rising or falling. Adsorption isothermals for sorption and desorption do not coincide and hysteresis becomes apparent. For the same equilibrium pressure a larger amount is adsorbed than desorbed. Experiments carried out on charcoal–water vapour show that the amount of water retained on desorption is 4 to 5 times as much as the corresponding amount in sorption.

Hysteresis curves of ferric-oxide gel–benzene vapour furnish a peculiar example, as they coincide except for the middle part.

In irreversible systems the same problems have to be dealt with when considering isobars and isosters. When charcoal and water vapour are placed in a closed system and pressure readings taken for a series of falling temperatures and then gradually warmed up, it is found that pressure does not follow the same course and will be smaller, due to the fact that more water vapour is retained in the desorption period.

The time required to reach equilibrium is greater in systems where hysteresis exists and if part of the sorption and desorption curves coincide, this part will be quickly established, while the process will slow down during the hysteresis stage. The time for sorption is comparatively longer than that for desorption.

No satisfactory theory has yet been put forward to explain the irreversibility of some cases of adsorption.

116. Specific Surface.—There are different opinions regarding the thickness of the adsorbed layer and conflicting results have been obtained by different investigators.

Langmuir[4] states that adsorption is complete when the residual valencies of adsorbent molecules are neutralised by gas molecules and he believes that the adsorbed layer is one molecule thick. Others have shown experimentally that in certain cases this layer can be several molecules in thickness.

In the process of adsorption the area of the adsorbent is of great importance as adsorption is primarily a surface phenomenon.

With the adsorption of gases or substances in solution, it is not only necessary to have a large surface area, but a comparatively small volume in order to render the process practicable. Hence, liquids do not form good adsorbing media, because their molecules are mobile, whilst in solid porous substances such as charcoal, there exists a comparatively large area per unit volume and the system cannot reduce its surface owing to the rigidity of the molecules.

The ratio of surface area to volume, termed the specific surface, determines the adsorption capacity.

The specific surface for a cube is represented by

$$\frac{\text{Surface}}{\text{Volume}} = \frac{6L^2}{L^3} = \frac{6}{L} \quad \ldots\ldots\ldots \quad (19)$$

In other words, the specific surface is inversely proportional to L, the length of one side of the cube : if this cube is divided into a number of smaller cubes the surface area increases, while the total volume remains the same, consequently, the specific surface increases. Assuming the cube is divided into cubes of dimensions $\frac{L}{2}$, the specific surface becomes $6 \div \frac{L}{2} = \frac{12}{L}$; the specific surface and the surface area are therefore doubled.

Activated charcoal is a highly porous substance which has a very large specific surface : in one c.c. of charcoal composed of capillaries 1 $\mu\mu$ in dimension, the calculated specific surface is

$$\frac{6}{L \times 10^{-7}} \text{ where } L = 1 \text{ cm.}$$

Therefore, the total surface area = 60,000,000 square cm. = 6,000 square meters per c.c.

As the whole mass of charcoal is not uniform, however, in that it contains capillaries of large sizes, the above figure is too high and usually $\frac{1}{10}$th of this figure is taken to represent the approximate surface area of the charcoal per c.c., that is to say, 600 square meters.

117. Selectivity of Adsorption.—When a mixture of gases is adsorbed, the process is a selective one, that is to say, some gases are

preferentially adsorbed. In general, in a mixture of gases the charcoal adsorbs preferentially that component of the gas which is more strongly adsorbed in a pure state. The heavier hydrocarbons of natural gas having lower vapour pressures are, therefore, preferentially adsorbed.

In passing natural gas upwards through a bed of charcoal, the heaviest constituents of the gasoline are adsorbed in the bottom layer. As the gas passes upwards through the charcoal bed, its different components are retained according to their molecular weights, the heavier ones being adsorbed first, so that in the top layers very light gases are adsorbed and the residual gas passing from the top of the charcoal bed does not contain any heavy constituents. As time goes on, however, and the gas continues to pass through, the top layers of the charcoal become saturated and the lighter constituents previously adsorbed are gradually replaced by the heavier hydrocarbons. In this manner, the whole bed of charcoal eventually becomes saturated with the heaviest constituents of the natural gas.

This selectivity of adsorption gives flexibility to the plant in practice as regards the specification of the petrol recovered, in that the gravity and initial boiling point of the recovered petrol may be controlled by varying the quantity of gas passed through a given quantity of charcoal. In this manner different petrols may be produced to meet different requirements and the conditions may be controlled so that mainly stable spirit is produced by allowing the wilder constituents to be carried out with the residual gas, thus reducing to a great extent the necessity for stabilisation.

118. Details of Plant.—There are two types of plant used in the recovery of casinghead gasoline from natural gas, one designed for treating dry gases, the other for treating rich gases.

Since both plants are similar in principle and design, the latter method only will be described. In this case the temperature of the charcoal is raised considerably, and this rise in temperature, unless counteracted, results in inefficient adsorption. For this reason coils are placed in the adsorbers through which cold water is circulated to assist cooling. These coils may also be used as steam heaters during the removal of the adsorbed petrol.

The operation consists of four cycles.

Charging.—The untreated gas is passed through adsorbers for a length of time sufficient to saturate the charcoal. During this time cold water is passed through the coils to keep the temperature of the charcoal below a certain limit, usually below 50°C.

Steaming.—The charcoal is first heated indirectly by passing steam through the coils at a pressure of 2 to 3 atmospheres and a temperature

of about 127°C. After a certain period scouring steam is admitted direct to the charcoal which drives off the gasoline.

Drying.—At this stage the scouring steam is cut off while indirect steam still continues to flow through the coils. Dry gas is also passed through the adsorber.

Cooling.—When the charcoal is practically free from moisture the indirect steam is cut off, but the dry gas continues to flow through the adsorber, thus cooling the charcoal. The cooling effect of the gas is assisted by circulating cold water through the coils. When the cooling is complete rich gas is admitted once more to the adsorber.

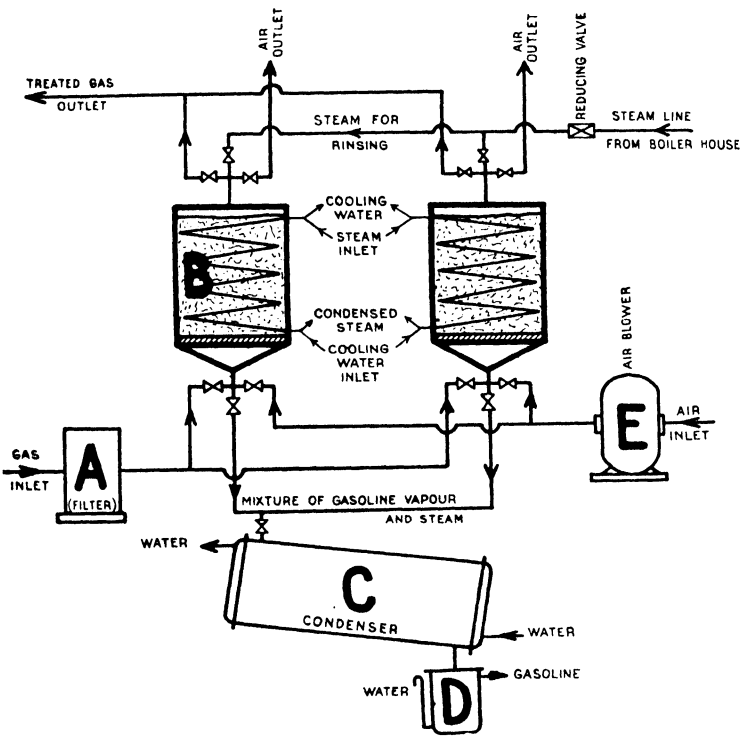


FIG. 15.—DIAGRAM OF A GASOLINE ADSORPTION PLANT
(Courtesy of the Institution of Petroleum Technologists)

Although these plants work on the batch principle, each cycle is continuous as when one adsorber is cut off from charging and put on steaming, another unit is cut off from steaming and put on drying, while a third unit is changed over from drying to cooling and similarly another unit is cut off from cooling and commences adsorption.

119. Stabilisation of Gasoline.—Vaporisation of a gasoline in those passages in an automobile designed to carry motor fuel causes what is

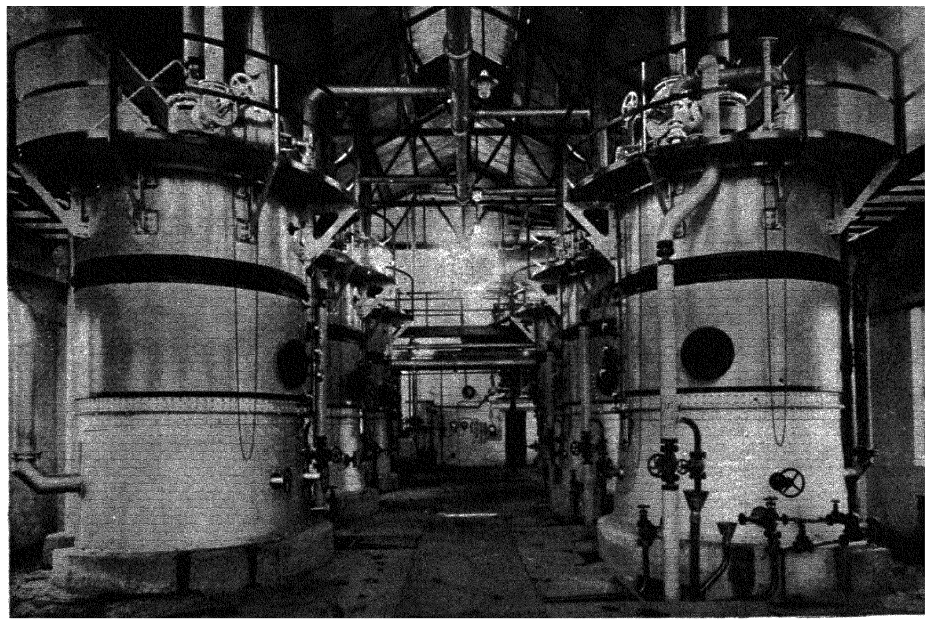


FIG. 16.—VIEW OF GASOLINE ADSORPTION PLANT
(Reproduced by courtesy of the Institution of Chemical Engineers)

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commonly known as vapour lock. A very small quantity of petrol vaporised is sufficient to produce vapour lock since the volume of a unit weight of petrol vapour is approximately 185 times greater than the same quantity in the liquid state under similar conditions of temperature and pressure. When vapour lock occurs it is because the small orifices and passages in the carburettor cannot pass sufficient petrol vapour to maintain an explosive mixture in the engine cylinders.

A liquid tends to form vapour in direct proportion to its vapour pressure. Volatility is the extent to which a fuel will vaporise under specified conditions of time and temperature. This property is not, however, directly proportional to vapour pressure, for example, a motor fuel may possess high volatility and low vapour pressure and vice versa. It may be said that high volatility in a motor spirit is most desirable and useful in that it ensures ease of starting and satisfactory engine performance, whereas a high vapour pressure is undesirable and should be avoided in order to ensure freedom from vapour lock. (See Volume II, Second Edition.)

Natural gasoline contains from a trace to 5 per cent. of propane, up to 40 per cent. of butane, 15 to 40 per cent. of pentane, the remainder consisting of heavier hydrocarbons. Whatever "wildness" natural gasoline possesses is due primarily to its butane content as such gasoline usually contains only very small percentages of propane and lighter hydrocarbons. The aim of the natural gasoline manufacturer is the economical production of a gasoline containing all the pentane and heavier hydrocarbons, with as much butane as his seasonal marketing specifications will allow and a minimum amount of propane and lighter fractions.

The butane fraction of natural gasoline normally has a vapour pressure of 56 lbs. absolute per square inch at 100°F., a boiling point of about 20°F., and a specific gravity of 0·58; its presence in a motor spirit materially raises the anti-knock value.

As butane is available in the average natural gas in quantities equal to or even greater than the amount of pentane and heavier fractions present, the problem of how much butane to incorporate in the finished spirit depends upon seasonal volatility requirements.

Oberfell[5] has shown that the addition of one per cent. of butane to a butane-free gasoline increases the vapour pressure at 100°F. by approximately one half-pound per square inch. This increase in vapour pressure is the factor which limits the markets for natural gasoline as a motor fuel. Hence the need by petroleum refiners for more stable grades of natural gasoline and the removal of the wilder fractions of the raw casinghead gasoline.

120. The oldest methods of separation of the wilder fractions from

natural gasoline were processes of weathering or simple distillation, and resulted in considerable losses. These have been almost entirely replaced by methods of pressure fractionation in efficient units.

121. Fractionation of raw gasoline may be carried out either at high or low pressures, but this classification is not sharp and certain installations may fall into either class.

In low pressure fractionation the natural gasoline condensate is often expanded into the top of a column to give the low reflux temperature necessary when a low column pressure is employed, but this method does not give the sharpness of separation which may be sometimes desired.

More efficient separation may be effected by introducing the natural gasoline condensate as a secondary feed, on a plate containing liquid of a similar composition, which position will be above the primary feed plate. The condensate from the recompression of the vapours from the top of the column may be expanded into the reflux condenser to produce the required low reflux temperature.

In high pressure fractionation, however, the reflux temperature is usually above the temperature of the cooling water available so that water forms a very satisfactory cooling medium for a reflux condenser under these conditions.

122. A few years ago there was a decided move on the part of refiners to instal vapour recovery systems which involved the collection and processing of vapours from tankage, primary distillation units and cracking plants, and the name given to such processes to distinguish them from casinghead gasoline stabilisation was "Debutanisation."

Whilst the functions of debutanisers and stabilisers are different, the principles underlying their design are very similar.

The present practice in refineries is to distil over in a debutaniser all the hydrocarbons up to and including butane before sending the crude oil or pressure distillate to the main distillation benches. The light distillate so obtained is then rectified in a stabiliser before it is used for blending with straight-run or cracked motor fuel; any butane which is not required for blending purposes, the amount varying with the time of year, is taken from the top of the stabiliser column and eventually passes to the refinery gas main.

More recently the controlled removal of propylenes and butylenes, and the corresponding paraffins, from the pressure distillate petrol derived from cracking units, has been effected by means of debutanisers. This is of special interest in view of the fact that vapour-phase cracking is developing rapidly.

The change in characteristics of a raw pressure distillate from a Dubbs unit after debutanising is shown by the following distillation figures.

gasoline produced from a casinghead gasoline absorption plant, in order to reduce both the first cost as well as the operating expense.

These two volatile spirits are mixed together to form the feed to the second rectifier unit or final stabiliser. This unit operates at 180 lbs. per square inch and produces an essentially propane-free product which is excellent for blending purposes because of its high butane content. The process is exactly the same as for the debutanising portion of the plant.

The Engler distillations for the raw feed to the stabilising unit and the product obtained are as follows :—

	Raw Feed to Stabiliser	Product from Stabiliser
Sp. gr. at 60°F.	0·647	0·651
I.B.P. °F.	45	78
10% distilled at °F.	78	87
20% ,, ,, ,, ...	89	92
30% ,, ,, ,, ...	100	95
40% ,, ,, ,, ...	112	100
50% ,, ,, ,, ...	130	106
60% ,, ,, ,, ...	148	112
70% ,, ,, ,, ...	172	120
80% ,, ,, ,, ...	—	136
90% ,, ,, ,, ...	—	188
F.B.P. °F.	347	328
Distillation Recovery per cent.	83	94

A second product is obtained from the stabiliser unit as an overhead product. This liquid has a boiling range of from 18°F. to 46°F. and consists largely of propane. It is stored in high-pressure storage tanks connected directly with the stabilising unit, and may be disposed of in the form of liquefied gas.

Both rectifying units are equipped with steam preheaters between the heat exchangers and the columns to permit the feeds being introduced into the towers at the correct temperatures.

The pumps, with the exception of the stabiliser feed pump which is of the reciprocating type, are centrifugal, each being directly driven by explosion proof-motors equipped with oil-immersed starter gear. Pump capacities are 30 per cent. in excess of the rated unit capacities of 165,000 gallons per day of raw pressure distillate and 39,000 gallons per day of raw stabiliser feed. Both rectifying units are fitted with full automatic control.

124. A typical vapour recovery and stabilising plant, of which a number of units have been erected in various fields in the United States, is shown in Figs. 18 and 19.

The larger plants were designed to process 13 million cubic feet of

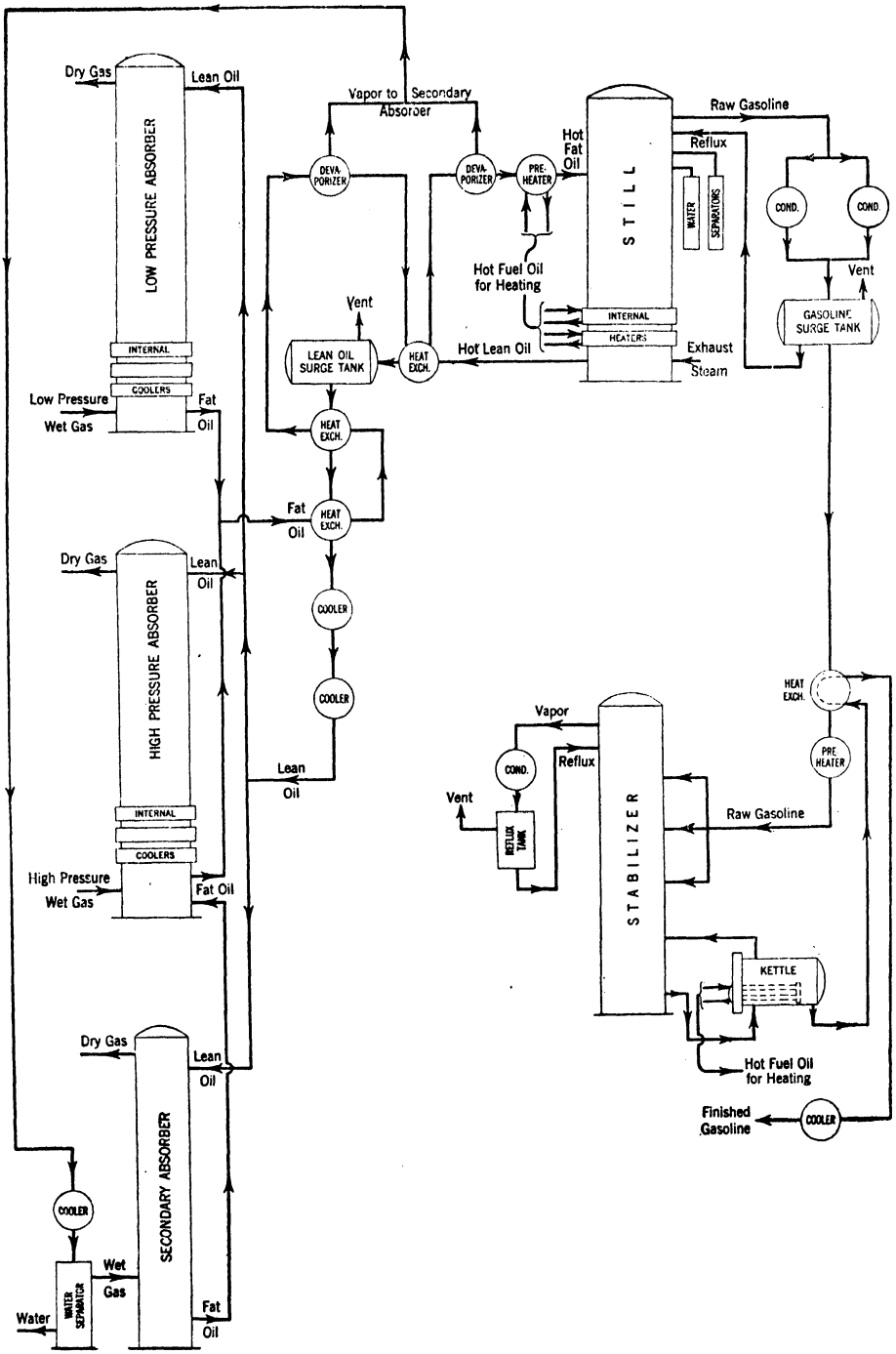


FIG. 19.—FLOW DIAGRAM OF VAPOUR RECOVERY PLANT AND STABILISER

(Courtesy of Foster Wheeler, Ltd., London)

natural gas per day. Wet gas from the fields is supplied at two different operating pressures, namely, 65 lbs. and 35 lbs. per square inch, in practically equal amounts. Two absorbers handle this gas separately in order that advantage may be taken of the lower oil to gas ratio required with the higher pressure gas. Both the high and low pressure absorbers are equipped with internal coolers to maintain the temperature of the enriched oil leaving the bottom of the absorber as low as possible, and thus keep the oil to gas ratio at a minimum : both absorbers are also equipped with an oil to gas ratio controller. These controls maintain a fixed oil to gas ratio regardless of fluctuation in gas flow, thus assuring complete stripping of the gas without danger of a too high total lean oil circulation during periods of minimum gas flow.

Each absorber has a mist extractor above the trays at the top of the column to prevent the carrying over of lean oil during sudden surges in the gas flow.

The enriched oil from the high and low pressure absorbers is combined and passes to the pressure heat exchangers. Devaporiser tanks are fitted between the pressure and gravity heat exchangers and the pre-heater : the function of these is to separate the light vapours, formed during the heating of the oil, from the enriched oil. The vapours thus vented are taken to a re-absorber, while the enriched oil continues on through the preheater to the still. The use of a re-absorber in this way is one of the best methods of eliminating the necessity of recycling and possibly recompressing the non-condensable vapours from the still condensers.

Ridding the enriched oil of these light fractions makes it possible to attain a greater degree of condensation in the gasoline condenser. Distilling the vapours from the enriched oil under comparatively high pressure permits their economical extraction in a high pressure re-absorber : if these vapours were to be recycled from the still they would have to be recompressed to absorb them under an equal pressure.

The enriched oil from the secondary absorber is combined with the enriched oil from the high and low pressure absorbers before entering the pressure heat exchangers.

Internal reheaters using recycle stock as a heating medium are fitted in the still, and the temperature of the oil is maintained as close as possible to its inlet temperature as it passes from the feed plate down through the stripping trays. As the gasoline fractions are vaporised, the oil temperature drops, due to the removal of latent heat of vaporisation, but the internal heaters compensate for this falling temperature and combine the advantages of thorough stripping of the lean oil and maximum steam economy : special dehydrator trays are inserted in the column to remove any of this steam which may condense in the column. A top temperature controller automatically regulates the

amount of reflux to give a constant vapour temperature at the top of the column.

The raw gasoline from the still condensers is passed into a surge tank made large enough to allow a constant rate of feed of the raw gasoline to the stabiliser unit, and an automatic controller maintains the feed to the stabiliser constant as it passes through the heat exchanger and steam preheater before entering the column.

It is just as important to hold the temperature of the feed free from fluctuation as it is to maintain a constant rate of feed; for this reason the steam flow to the preheater is equipped with a back pressure regulator, maintaining a constant pressure of steam in the preheater.

A photograph of a modern stabiliser unit erected by Messrs. Alco Products is reproduced in Fig. 20.

125. Characteristics of Natural Gasoline.—The distillation range is important since natural gasoline is used mostly for blending so as to increase the front end volatility of motor spirit. This blending has to be done with care, however, as too high a percentage of the lower fractions might easily give rise to vapour lock when in use.

Losses in handling can be estimated to a certain extent from the distillation loss obtained in laboratory test distillations, and whilst this loss also gives some indication of the vapour pressure the two are not directly related. For example, a natural gasoline which does not contain any propane or iso-butane, but contains a high percentage of *n*-butane, may have a high vapour pressure whilst showing a distillation loss of 10 per cent. On the other hand, a natural gasoline containing smaller percentages of *n*-butane, but also containing some propane and iso-butane, may have a lower vapour pressure but show a higher distillation loss, since propane and iso-butane, having low boiling points, do not condense and may carry off some of the *n*-butane.

Vapour pressure is a most important point in a specification of natural gasoline as it determines the shipping hazards. The standard method adopted for the determination of the vapour pressure is that known as the Reid method which is described in Chapter XI (Volume II).

An approximate figure for the vapour pressure of a petrol can also be obtained by calculation. The partial pressure of each constituent is calculated according to Raoult's law and the sum of the partial pressures gives the vapour pressure.

The following table (6) is an example of such a calculation.

Under the recent system of grading adopted by the National Gasoline Association of America, all grades of natural gasoline should conform to the following general specification.

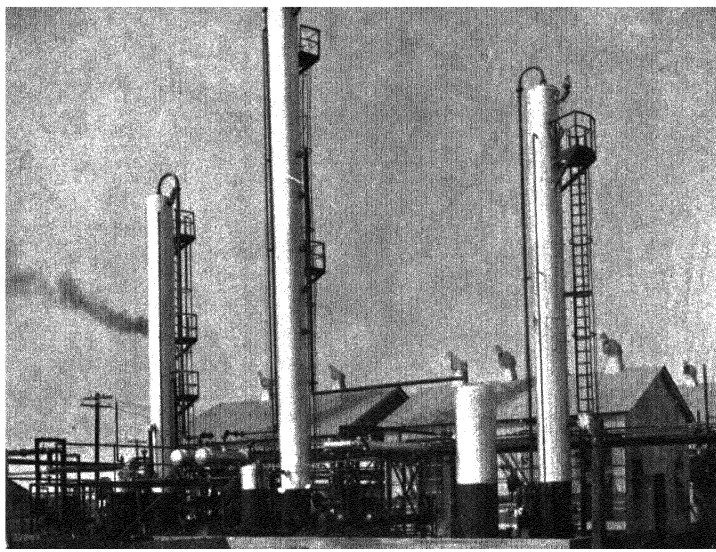


FIG. 20.—TYPICAL STABILISER INSTALLATION
(Courtesy of Alco Products Incorporated)

[*Facing p.* 142

Vapour pressure — 10–34 lbs. per square inch absolute at 100°F. (Reid method).
Percentage evaporated at 140°F. — 25–85 per cent.
,, ,, ,, 275°F. — not less than 90 per cent.
End point — not higher than 375°F.
Corrosion — non-corrosive.
Doctor test — negative.
Colour — not less than 25 (Saybolt).

TABLE 6

Hydrocarbon	Per cent. by weight	Spec. Grav.	Weight in Grams.	Molecular Weight	Mols	Mol fraction	Vapour Press. at 100°F.	Partial Press. lbs. per sq. in.
Propane	1·0	0·515	0·515	44·06	0·0117	0·0139	187·00	2·60
Iso-butane	10·0	0·562	5·62	58·08	0·0969	0·1156	73·70	8·52
N-butane	22·0	0·581	12·782	58·08	0·2200	0·2624	52·20	13·69
Iso-pentane	13·0	0·625	8·125	72·10	0·1127	0·1344	20·27	2·72
N-pentane	14·0	0·632	8·848	72·10	0·1227	0·1464	15·35	2·25
*Hexane, and higher.	40·0	0·687	27·48	100·13	0·2744	0·3273	1·62	0·53
	100·0				0·8384	1·000		30·31

* Calculated as *N*-heptane.

In addition to this general specification natural gasoline is also divided into 24 grades. Each grade has a range in vapour pressure of 4 lbs., and as the limiting vapour pressures are 10 and 34, the maximum vapour pressures of the different grades are 14, 18, 22, 26, 30 and 34 lbs. per square inch.

The range in percentage evaporated at 140°F. for each grade is 15 per cent., hence the maximum percentages distilled at this temperature for different grades are respectively 25, 40, 55 and 70 per cent.

Each grade is designated by its maximum vapour pressure and minimum percentage evaporated at 140°F., and as there are six ranges of vapour pressure and four ranges of distillation, there are altogether 24 grades.

It should be noted, however, that the distillation point of 140°F. applies to a barometric pressure of 740 mm.: for higher pressures, the distillation temperatures should be corrected accordingly. The correction necessary is R + 1°F. for every 14·5 mm. rise in barometric pressure.

126. Blending of Petroleum Spirits.—A valuable paper on this subject has recently been published by E. W. Zublin,[6] who points out that recent work has correlated the A.S.T.M. distillation test with

certain phases of engine performance. The ease of starting and the 10% point of the A.S.T.M. distillation test are closely related. Other important engine performance factors such as acceleration are also concerned. The latter depends upon effective volatility which is shown by the intermediate, i.e., 35 to 60 per cent. points of the distillation. Knock-rating has been shown to be related to volatility as is explained to some extent under the knock-rating section of this book, where it is shown that in some hydrocarbon series, such as the paraffin series, the knock-rating increases with diminishing length of carbon chain in the molecule. The effect of fuel volatility upon engine operation is dealt with in detail in Chapter XV (Volume II).

It is often found that crude petroleum oils produce straight-run petrols insufficiently volatile to conform with commercial standards and the addition of natural gasoline becomes necessary.

127. Many blending charts that have been evolved do not apply to all grades of petrol and natural gasoline. Zublin has largely overcome this difficulty by expressing all blending data in per cent. of the difference between respective points, and has put forward empirically determined charts which, though not based upon any fundamental principle, are based upon blending data systematically collected over a long period of time. These charts are thus based on the principle of expressing the properties of the blends in per cent. of the difference between equivalent properties of the blending stocks, and this per cent. difference is plotted against the per cent. of natural gasoline. An example is quoted to make this scheme clear.

E.g., two blending stocks have the following 10 per cent. points : a refinery naphtha, 200°F., and a natural gasoline, 70°F., the difference being 130°F. On the addition of 20 per cent. of this natural gasoline to the naphtha, the 10 per cent. point of the latter drops to 144°F., which is 56°F. lower than the original. Fifty-six degrees constitute 43 per cent. of the total difference of 130°. This gives one point for the curve at 20 per cent. of the natural gasoline. On blending any other naphtha with 20 per cent. of any other natural gasoline, the 10 per cent. point of the naphtha will be found to drop 43 per cent. of the total difference within close limits. The largest deviation that has been found and checked amounted to 5 per cent. of the total difference or 5 per cent. of the amount of the natural gasoline added.

The work of Zublin covers the 10 per cent. distillation point, the 50 per cent. point and distillation loss of the A.S.T.M. distillation, the vapour pressure (and vapour lock) and the knock-rating.

When dealing with the results of A.S.T.M. distillation tests, there are two sets of figures to be considered ; those uncorrected and those corrected for distillation loss. It has been the experience of Zublin when

making up blending charts applicable to all grades of refinery naphthas and natural gasolines, that the uncorrected 10 per cent. point and the corrected 50 per cent. or higher points should be used.

According to the Bureau of Standards a deduction of 5·4°F. should be made for every cubic centimetre of distillation loss below 5 c.cs., and this represents a fairly good average correction for normal cases. The distillation curve must be used where the distillation loss exceeds 5 per cent. and where the loss is greater than 8 per cent., the 10 per cent. point cannot be corrected accurately even with the aid of the curve. In the case of the 50 per cent. point, conditions are different and it is necessary to use corrected values in order to obtain a smooth curve applicable to all grades of blending stocks. For most purposes it is sufficient to deduct 2·4°F. for every c.c. distillation loss, even where this loss exceeds 5 c.cs. Uncorrected points above 50% are usually little affected by the addition of small percentages, i.e., less than 30%, of natural gasoline. The corrected points of natural gasoline blends are always lower than those of the original naphtha. There is, however, no simple way such as the deduction of a constant value for every c.c. distillation loss to correct approximately the 90 per cent. point.

Vapour pressure determinations such as are determined in the Reid vapour pressure apparatus are among the best single tests for vapour lock tendencies. In most gasolines the 10 per cent. point and the vapour pressure show a close relation, but exceptions have been found. Brown's empirical formula correlating the 10 per cent. point and vapour lock is subject to similar exceptions. The scale for vapour lock temperatures used by Zublin is based on the assumption that vapour lock occurs, or may occur, at the temperature at which the Reid vapour pressure equals atmospheric pressure, i.e., 14·7 lbs. per square inch. It is interesting to note in this connection that Brown observed that the temperature of gasoline in the average carburettor can reach 100°F., plus half the atmospheric temperature in °F. This gives a temperature figure upon which to base vapour lock estimations. (See also Chapter XV, Vol. II.)

128. The curves, Figures 21–23, by Zublin, show the change of properties of a naphtha with the addition of natural gasoline and are the basis of the blending charts. In the latter the properties of the two blending stocks are evenly distributed on vertical scales, while the horizontal scales for the percentage of natural gasoline have been derived by transcribing on the abscissa the vertical distances of the curves from the abscissa for various percentages of natural gasoline. By using such scales the curves for all properties become straight 45° lines. Thus the blending charts have been brought to a form in which all relations are expressed

by straight lines, and problems can be solved by the mere application of a straight edge.

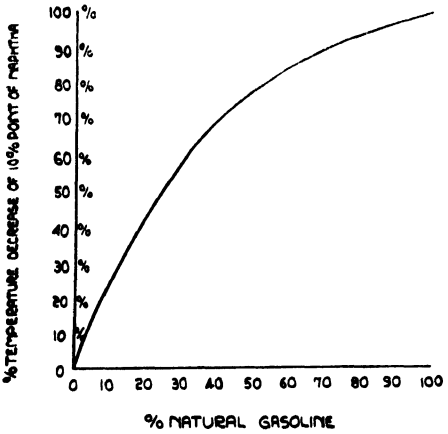


FIG. 21

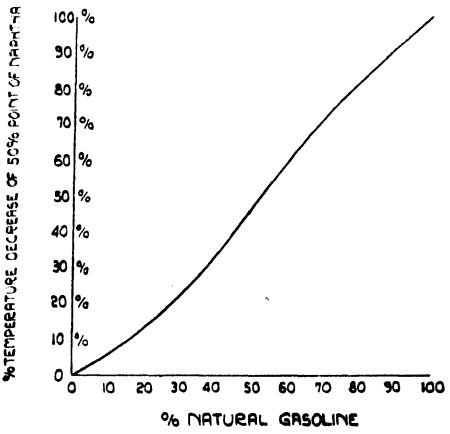


FIG. 22

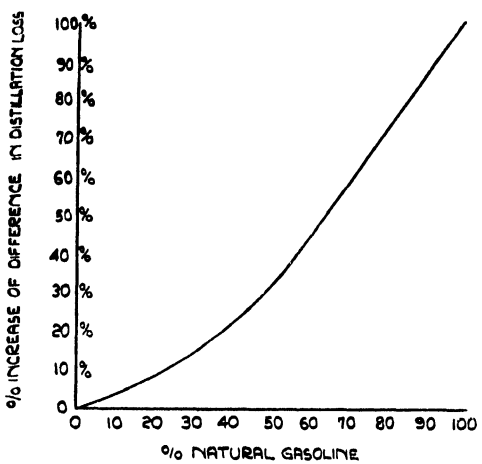


FIG. 23

(Courtesy of E. W. Zublin)

An example may be quoted as follows :—

A certain blend stock has the properties :—

A.S.T.M. distillation 10% at 200°F.
50% at 291°F. uncorrected.
290°F. corrected.

Distillation loss = 0·5%.

Reid vapour pressure at 100°F. = 4·2 lbs.

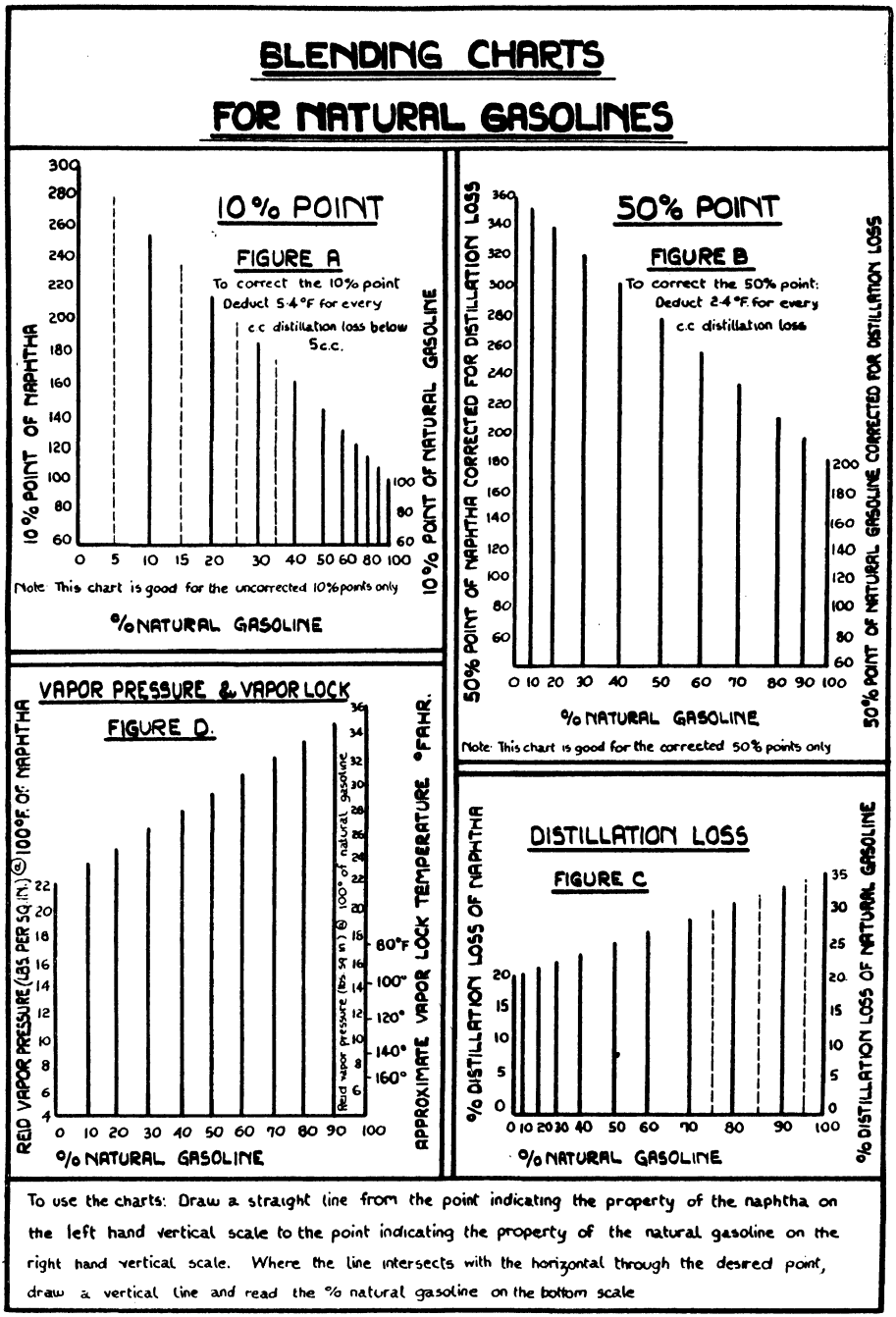


FIG. 24
(Courtesy of E. W. Zublin)

A natural gasoline has the properties :—

A.S.T.M. distillation 10% at 70°F.
50% at 110°F. uncorrected.
95°F. corrected.

Distillation loss = 14%.
Reid vapour pressure at 100°F. = 32 lbs.

It is desired to produce a gasoline having a 10 per cent. point of 150°F. uncorrected. The percentage of natural gasoline to be added is calculated thus :—

Using Figure A, the 200° point on the left hand scale is connected with the 70° point on the right hand scale by means of a straight edge, and where the line intersects with the horizontal through 150°, a vertical line is drawn to the natural gasoline scale. The percentage found is 17½. In order to find the 50 per cent. point of the blend, the corrected data must be used. The 290°F. point on the left hand scale of Figure B is connected with the 95°F. point on the right hand scale by means of a straight edge. At the point of intersection with the vertical line through 18 per cent. of natural gasoline, a horizontal line is drawn. The corrected temperature read in this case is 268°F. The 50 per cent. point as it would be read on the thermometer is estimated as follows :—the distillation loss must be determined in Figure C in a similar manner as described above. For every c.c. distillation loss below 5 c.cs., 2·4°F. must be added. In the example given, 1·5 c.c. distillation loss will be found and an uncorrected 50 per cent. point of 272°F.

The Reid vapour pressure corresponding to 17½ per cent. content of natural gasoline, is found from Figure D to be 9·4 lbs. at 100°F., and the vapour lock temperature is 138°F. This motor spirit is safe as regards vapour lock at atmospheric temperatures up to 76°F.

For further properties of blends, other charts can be made up on the lines of these shown.

129. Valuable experimental work from the point of view of the manufacturer of natural gasoline has been carried out by S. S. Smith.[7] Many charts have been evolved from which the following conclusions are made.

If the Reid vapour pressure, and the percentage distilled off at 100°F., are known for a natural gasoline which is to be used for blending, the specification can be checked and the fact determined whether the vapour pressure is properly in line with the percentage off at 100°F. If it is found to be so, it will be known that the natural gasoline does not contain appreciable amounts of propane nor appreciably reduced amounts of pentane. This being the case, it is safe to assume that the natural gasoline in question could be used to blend to any type

of specification desired in a finished motor fuel and the only criterion that need be observed is that the per cent. off at 100°F., or the volatility, is not excessive for the seasonal blending requirements.

130. An additional series of experiments used to evolve charts for the blending of natural gasoline to volatility specifications has been described by R. C. Alden and M. Gage Blair.[8]

These investigators state that, in the past, the A.S.T.M. distillation data have been used almost entirely as a means of specifying the volatility of motor fuels. With the growing emphasis on Reid vapour pressure as the best safeguard against vapour lock it has become desirable to include this factor as a volatility specification.

From a specification viewpoint the use of vapour pressure greatly simplifies blending, and the calculations involved in blending to a desired vapour pressure are almost as simple as those required in blending to a desired gravity.

The Reid vapour pressure needs no material correction for barometric pressure and is not complicated by such an uncertain variable as is distillation loss in the A.S.T.M. distillation. Furthermore, a vapour pressure specification is in itself a fairly definite measure of vapour-locking tendencies, a quality that has been proved difficult to evaluate in terms of the A.S.T.M. distillation.

Another factor which apparently is not generally realised is that with a Reid vapour pressure specification, it is necessary to specify only one A.S.T.M. distillation point in the middle of the distillation curve to maintain the following items of motor fuel performance within comparatively narrow limits :—

(1) Vapour-locking tendencies,
(2) Ease of starting,
(3) Warming-up ability,
(4) Acceleration.

Thus, with a given Reid vapour pressure and a given A.S.T.M. per cent. evaporated at 212°F., the A.S.T.M. distillation is fixed within narrow limits, particularly those portions which have been proved to be indicative of the four qualities cited above.

The other factors of motor fuel performance which are at least partially dependent on volatility characteristics are power, mileage and crankcase dilution. These can be attributed largely to the heavier materials used in blending. It is taken for granted in this discussion that the characteristics of the naphthas used in blending with natural gasoline will be such as to maintain these qualities of the finished blends within reasonable limits.

131. It has been stated that blending to a vapour pressure speci-

fication is comparatively simple. Likewise, blending to an A.S.T.M. distillation point near the middle of the distillation curve is comparatively simple. It therefore follows that blending natural gasoline to volatility specifications can be reduced to very simple relationships.

For practical purposes, Alden and Blair have developed a very empirical expression of Raoult's law, which appears to yield quite satisfactory results in blending natural gasoline to vapour pressure specifications. The equation is as follows :—

$$\frac{V_n G_n P_n + V_g G_g P_g}{G_n P_n + G_g P_g} = V_b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where V = vapour pressure,
G = A.P.I. gravity,
P = volume per cent.,

Subscript n = naphtha, or heavy gasoline,
,, g = light gasoline,
,, b = blend.

The above empirical equation is based on the fact that the significant numbers of the A.P.I. gravities of the predominant hydrocarbons in motor fuel are roughly proportional to the significant numbers of the quotients of their specific gravities by their molecular weights. Substituting these quotients for A.P.I. gravities restores the empirical equation to the precise expression of Raoult's law.

132. It would be possible to prepare an alignment chart which included all of the seven factors involved in this empirical equation. The chart, however, would be rather complicated. Here again it has been found more practical to eliminate certain of the variables at the expense of accuracy rather than to attempt refinements beyond the limits of actual application. By assuming a definite relationship between the gravities and vapour pressures of the light and heavy components it is possible to prepare a very simple vapour-pressure blending chart. The assumptions made were as follows :—

	Gravity (°A.P.I.)	Reid Vapour Pressure. (Lbs. per square inch at 100°F.)
Refinery Gasoline	52	1·8
	56	5·4
	60	9·0
	64	12·6
Natural Gasoline	74	9
	82	18
	88	27
	94	36

An examination of these assumptions indicates that they are fairly well founded on average conditions. Furthermore, considerable deviations from the assumptions cannot materially influence the results obtained within the limits of accuracy of commercial blending and testing. Alden and Blair state that actual use of the simple vapour-pressure blending chart thus made possible has repeatedly demonstrated its practical accuracy.

A graphical presentation of these relationships is given in Fig. 25, from which it is possible to read the results of any blend combination containing up to 70 per cent. of natural gasoline in the finished product directly. This figure delineates the approximate vapour pressure relationships that exist in blending natural gasoline and refinery naphthas.

The horizontal ordinate is the percentage of natural gasoline in the blend. The vertical ordinate (numerical values on the left in parentheses) is the difference between the vapour pressure of the finished blend and that of the refinery blending stocks in pounds per square inch. The solid curves represent the difference in vapour pressure in pounds per square inch between the natural gasoline and the finished blend as designated by the numbers on the individual curves.

An important factor to remember in the use of the vapour pressure relationships shown in Fig. 25 is that the upper left hand corner (the point of convergence of the solid curves) is the vapour pressure of the finished blend. The vertical ordinate represents deviations of the vapour pressure of the finished blend from the vapour pressure of the naphtha; while the numerical values of the solid curves represent deviations of the vapour pressure of the finished blend from the vapour pressure of the natural gasoline.

133. There are four major variables in any blending problem concerning vapour pressure, in which two components are blended together in varying amounts. These variables are:

Vapour pressure of the heavier component,
Vapour pressure of the lighter component,
Vapour pressure of the finished blend,
Percentage relationship of the components.

Any one of these variables can be determined from Fig. 25 when the other three are known. The following examples will illustrate the use of the chart.

(*a*) *Blending Percentages Unknown.*

The following variables are known.
Vapour pressure of refinery stock :—7·0 pounds.
Vapour pressure of natural gasoline :—16·0 pounds.
Vapour pressure of blend :—10·5 pounds.

The upper left hand corner in this case represents the blend vapour pressure of 10·5 pounds. Since the refinery blending stock has a 7·0 pound vapour pressure, the difference is 3·5 pounds. The difference between the vapour pressure of the finished blend and the natural gasoline is 5·5 pounds.

Starting from 3·5 on the left hand ordinate a horizontal line is drawn to the point of intersection with the 5·5 curve, then a perpendicular to the line at the intersection drawn to the base line of the graph indicates 32 per cent. of natural gasoline, leaving a balance of 68 per cent. of refinery blending stock necessary to make the desired finished product.

(*b*) *Vapour Pressure of Refinery Stock Unknown.*

Vapour pressure of natural gasoline :—18 pounds.

Vapour pressure of blend :—12 pounds.

Blending percentages :—60 per cent. refinery stock, 40 per cent. natural gasoline.

The difference between the vapour pressure of the finished blend and the natural gasoline is 6·0 pounds, consequently the curve governing the case is the one marked 6.

Reversing the procedure of the problem above, a perpendicular from 40 per cent. on the base line is drawn to the No. 6 curve. From this intersection a horizontal is drawn to the left hand ordinate. The horizontal line intersects the left hand ordinate at 5·7, which deducted from 12 pounds indicates 6·3 pounds as the vapour pressure of the refinery blending stock.

(*c*) *Vapour Pressure of Natural Gasoline Unknown.*

Vapour pressure of refinery blending stock :—6·0 pounds.

Vapour pressure of finished blend :—8·5 pounds.

Blending percentages, 35 per cent. natural gasoline, 65 per cent. refinery stock.

Deducting the refinery stock vapour pressure of 6·0 pounds from the 8·5 pounds vapour pressure of the finished blend establishes the point on the left hand ordinate at 2·5. A horizontal line from 2·5 intersects a vertical line from 35 per cent. natural gasoline on the base line at a point 0·4 of the distance from No. 3 to No. 4 curve ; hence 3·4 added to 8·5, the vapour pressure of the finished blend, gives 11·9 as the requisite vapour pressure of the natural gasoline.

(*d*) *Vapour Pressure of Blend Unknown.*

Vapour pressure of refinery blending stock :—6·5 pounds.

Vapour pressure of natural gasoline :—13·0 pounds.

Blending percentages :—45 per cent. natural gasoline, 55 per cent. refinery stock.

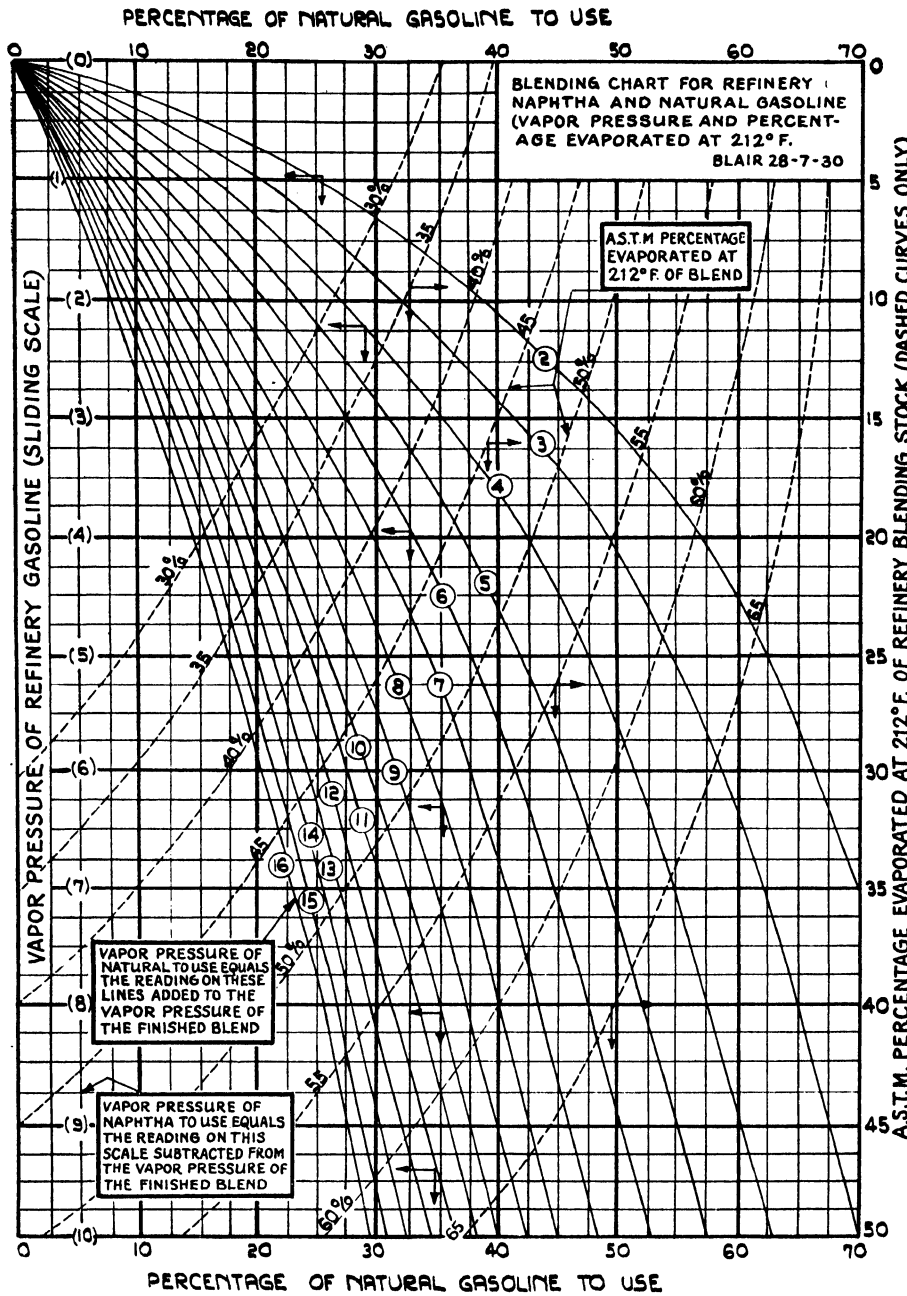


FIG. 25

(Courtesy of R. C. Alden and M. G. Blair)

This example probably represents the least common use of the graph. It is also the most complicated.

Let P^r = vapour pressure of refinery gasoline,
P^n = vapour pressure of natural gasoline,
P^b = vapour pressure of blend.

Then the values represented by the left hand ordinate can be expressed by the expression $P^b - P^r$. Similarly, the numerical values of the solid curves can be represented by the expression $P^n - P^b$. The sum of these two values is $P^n - P^r$ or the difference between the vapour pressures of the natural and refinery gasolines. Hence, the point on the given percentage line, where the sum of the numerical values of the vertical ordinate and the solid curve is equal to the difference between the vapour pressures of the two components, is the point solving this problem.

In the problem stated, the difference between the vapour pressures of the two components is 6·5 pounds (13·0 — 6·5) and the percentage of natural gasoline is 45. Following the line upward from 45 per cent. natural gasoline, noting the sum of the values of the solid curves and the left hand ordinate, it will be found that the sum of these two values is 6·5 at the point where the 45 per cent. perpendicular intersects the solid curve of 2·9 and the value on the left hand scale is 3·6. The vapour pressure of the blend must be, then, 10·1, since 6·5 + 3·6 and 13 — 2·9 both equal 10·1.

In order to make Fig. 25 a complete chart for blending natural gasoline, the dashed curves have been added to provide means of blending to a specified A.S.T.M. per cent. evaporated at 212°F. The right hand axis of Fig. 25 represents the A.S.T.M. per cent. evaporated at 212°F. of the naphtha. The dashed curves represent the same quality of the finished blend plotted against the horizontal scale of "Per Cent. of Natural Gasoline to Use." The dashed curves are based on the assumption that natural gasoline has an A.S.T.M. per cent. evaporated at 212°F. of 89 per cent. This assumption is true within narrow limits for many commercial natural gasolines.

As an example of the use of Fig. 25 as a guide to the selection of the quantity and quality of natural gasoline to use in blending refinery naphthas to volatility specifications, the following illustration may be cited :

Assume that a naphtha is available with a Reid vapour pressure of 6·5 pounds per square inch and an A.S.T.M. per cent. evaporated at 212°F. of 25, and that a finished blend is desired with a Reid vapour pressure of not more than 10·0 pounds per square inch and an A.S.T.M. per cent. evaporated at 212°F. of not less than 40.

The first step in the solution is to determine the *quantity* of natural

gasoline that must be used to assure the desired A.S.T.M. distillation characteristics. On the 25 ordinate of the right hand scale from the dashed curve designated 40, the per cent. of natural gasoline to use, which is 26·5 per cent., can be read.

The next step is to determine the *quality* of natural gasoline to use from the vapour pressure curves. At the intersection of the 26·5 ordinate of the horizontal scale and the 3·5 (10 — 6·5) ordinate of the left hand scale the value of the solid curve, 3, is read. The Reid vapour pressure of the natural gasoline to use for this blend would be 10 + 8, or 18 pounds per square inch. From the conditions assumed, the Reid vapour pressure of the natural gasoline must not be more than 18 pounds per square inch and the per cent. of natural gasoline in the blend must not be less than 26·5.

For practical blending of natural and refinery gasolines to definite volatility specifications, Alden and Blair state that Fig. 25 provides a very simple and convenient graphical relationship.

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Chapter IV

THE REFINING OF MOTOR FUELS

136. Introduction.—Light distillates obtained by the straight distillation of crude oils, by the cracking of higher boiling oils, or by the physical or chemical treatment of natural gases, are not usually suitable for use as motor fuels without purification. The nature and extent of the purification required vary with the nature of these different materials, but, in general, light spirits obtained by the compression, absorption or adsorption of natural gases require the least purification and cracked spirits require the most. There are, however, many exceptions to this general rule. The reasons for purification or refining are many, but may be summarised thus :—(*a*) to remove objectionable sulphur compounds, (*b*) to remove smell and colour, and (*c*) to remove chemically unstable bodies which deteriorate on storage. The methods employed in refining are numerous, but those methods first adopted for the refining of coal oil and shale oil in the early part of the nineteenth century, and adopted by the petroleum industry in its infancy, are still widely used and have not yet been supplanted to any great extent by more modern methods. These methods, recommended by Professor Silliman in 1855[1] and by Selligue[2] in 1838 and independently developed by Young in the beginning of the Scottish shale oil industry, consist of treatment with sulphuric acid for actual refining, followed by caustic alkali for neutralisation. Thus Young refined shale oil in 1850 by stirring it for 6 to 8 hours with what would now be considered an enormous excess of sulphuric acid (10 per cent. by volume), which was emptied into lead-lined rectangular iron tanks from glass carboys. After settling and drawing off the mixture of acid and tarry impurities from the bottom of the vessel (or, originally, drawing off the oil from the top), the oil was stirred with water; this was also run off and the oil was further stirred for 10 hours with an aqueous caustic soda solution. After settling, the "soda-tar" was drawn off, the oil was finally stirred with water and settled and the water run off. The treated oil was redistilled and sometimes retreated and again distilled.[3]

The refining of petroleum in America may be said to date from about the year 1855, when Samuel M. Kier, who introduced "American oil" as a patent medicine, fitted up a small refinery with a five-barrel still, for the treatment of the oil obtained from his father's salt wells. Dis-

tillation, however, was the only refinery operation carried out. In 1859, when the first oil well was drilled by Drake, and in 1861, when the first flowing oil well was struck, the refineries operating on shale oil were provided with crude petroleum, a material which could be worked more profitably than coal or shale, and applied their existing refining methods to the new raw material.

In the early part of the twentieth century, the sulphuric acid–caustic alkali method of refining was established as standard practice in the petroleum industry but it was soon found to have certain disadvantages, particularly when dealing with spirits produced by cracking and containing large amounts of hydrocarbons which reacted readily with the sulphuric acid, causing large refining losses. This led to the development of other processes, among the first of which was the Frasch process,[4] developed as early as 1888, in which objectionable sulphur compounds are removed by distillation of the oil in the presence of finely ground oxides, e.g., copper oxide ; the plumbite process and the aluminium chloride process of McAfee, developed in 1915,[5] of which the latter two are still in wide use. In 1918, Dunstan[6] perfected a method of refining, making use of sodium and calcium hypochlorites as oxidising agents for converting foul-smelling and corrosive sulphur compounds into innocuous sulphur compounds, thereby obviating the need for sulphuric acid refining. Refining methods involving the adsorption and polymerisation of reactive unsaturated hydrocarbons by microporous earths have also been developed, as instanced by the well-known Gray Process. Numerous other refining methods have been adopted.

It is not possible, within the limits of a single chapter, to deal exhaustively with all the refining processes proposed for large scale use ; consequently, only the most important treating methods will be considered.

The Use of Caustic Soda in the Refining of Light Distillates

137. Caustic soda is used in refining processes in two different ways : (*a*) to remove sulphur compounds and other acidic impurities and (*b*) as a neutralising agent after other treatments, e.g., acid washing. These two applications will be dealt with separately.

The Removal of Sulphur Compounds and other Acidic Impurities.—Of the undesirable substances present in petroleum distillates, sulphur and its derivatives are the most widespread and the most costly to remove. Sulphur occurs in the distillates in many different forms, which are of diverse types and which react toward refining agents in various ways. A small proportion of the sulphur occurs in the free or elemental state (generally resulting from aerial oxidation, *vide infra*), a comparatively large proportion is present as hydrogen

sulphide, while the remainder is in the form of organic derivatives of sulphur. These are divisible into two classes, (i) acidic, a property shared with hydrogen sulphide and due to the presence of the ·SH group, and (ii) neutral. The first class includes mercaptans, which with hydrogen sulphide are mainly responsible for the unpleasant odour of unrefined distillates. The second class includes the organic sulphides and disulphides and also the thiophenes.

138. As shown in Chapter XII (Volume II), free sulphur cannot be tolerated in motor fuels because of its corrosive nature. It is usually formed from hydrogen sulphide, which undergoes oxidation with great readiness by the action either of atmospheric oxygen or of reagents commonly used in refining, such as sulphuric acid or hypochlorite. Therefore, it is necessary as the first step in any refining operation to remove hydrogen sulphide completely in order to prevent the formation of elemental sulphur. It is advisable to remove this hydrogen sulphide at the earliest possible moment after the spirit is produced, either immediately after distillation and condensation or, preferably, actually in the condenser coil by injection of caustic soda or other alkali solution. Hydrogen sulphide can be removed by water washing, but this is a lengthy process, due to the lower solubility of the gas in water than in light distillates and large volumes of water are required. It is therefore better to use sodium hydroxide solution for this purpose, although, of late, cheaper alkaline substances have been adopted, e.g., brucite (magnesium hydroxide), ammonia and lime. For this purpose, caustic soda can be used at any reasonable strength, say from 0·1 up to 10 per cent. solution, but it is equally efficient at all concentrations up to 90 per cent.

The chemical reaction involved is

$$H_2S + NaOH \rightarrow NaHS + H_2O$$

and the sodium sulphide so formed can be partially recovered by the Koppers process, which consists essentially of aeration, causing hydrolysis of the sulphide, liberation of the hydrogen sulphide and regeneration of the soda. This recovery is comparatively cheap within limits, being of the order of 20 per cent. of the cost of the fresh soda equivalent to the soda regenerated.[7]

139. Qualitatively, the acidic organic derivatives, namely, the mercaptans (RSH), behave like hydrogen sulphide, but, whereas the latter is dibasic and is a comparatively strong acid, the mercaptans are monobasic and are only weakly acidic.[8] The sodium mercaptides are really hydrolysed by water, that is, the reaction by which they are formed is reversible.

$$RSH + NaOH \rightleftarrows RSNa + H_2O$$

For this reason, the removal of a mercaptan from a light petroleum distillate is never complete and a balance is eventually attained between the concentration of mercaptan in the oil and the concentration of mercaptan (present as alkali mercaptide) in the aqueous solution.

A further reason why mercaptan removal is never complete on agitation with aqueous alkali is that the acidity of the mercaptans, i.e., the ease of replacement of the acidic hydrogen atom by a metal, rapidly falls off as the molecular weight of the hydrocarbon radicle is increased. This is well shown in Table 1.

TABLE 1. REMOVAL OF MERCAPTANS BY TREATMENT WITH SODIUM HYDROXIDE (BIRCH AND NORRIS)[9]

Compound	Boiling Point	Percentage removed from Petroleum Solution by the same quantity of Soda under identical conditions
Hydrogen Sulphide	Gas	100
Ethyl Mercaptan C_2H_5SH	39°C.	97·1
n-Propyl Mercaptan C_3H_7SH	68°C.	88·8
Iso-Propyl Mercaptan C_3H_7SH	59°C.	87·2
n-Butyl Mercaptan C_4H_9SH	98°C.	63·2
Iso-Butyl Mercaptan C_4H_9SH	88°C.	62·8
Iso-Amyl Mercaptan $C_5H_{11}SH$	118°C.	33·0

It will be seen from this table that, under the conditions of experiment employed, which are comparable with usual works batch washing, only 33 per cent. of iso-amyl mercaptan is removed, whereas ethyl mercaptan is removed to the extent of 97·1 per cent. Thus, the lower boiling mercaptans are removed by caustic soda more easily than the higher boiling homologues.

In view of the fact that equilibrium as represented by the equation

$$RSH + NaOH \rightleftarrows RSNa + H_2O$$

is rapidly attained with efficient mixing, it is evident that a multiplicity of washings is advantageous. Counter-current scrubbing, in which the oil being treated is continually brought into contact with fresh soda, is even more efficient, and for this reason is largely employed.

140. Another point of interest in the removal of mercaptans from light distillates by means of aqueous sodium hydroxide solutions is the rather surprising fact that a given weight of soda will remove more of a given mercaptan from oil solution the greater the dilution at which the soda is used. This has been pointed out by Meyer,[10] who arrived at this conclusion by a consideration of the various equilibrium reactions concerned and checked it by experiment. The explanation given for

this phenomenon, which is only true when the weight of alkali is great compared with the total mercaptan present, is as follows :—

When a mercaptan is added to aqueous sodium hydroxide, or when a sodium mercaptide is dissolved in water, the above-mentioned equilibrium is set up and, if water is added to this system, the equilibrium is displaced to the left, that is, more sodium mercaptide is hydrolysed, with the production of free mercaptan. But if, for example, the system consisting of water, sodium hydroxide, sodium mercaptide and mercaptan is diluted to twice its volume, the quantity of free mercaptan in the aqueous solution will not be doubled, but will only be increased by some smaller amount. Thus, the concentration of free mercaptan in the dilute aqueous solution will be less than before. Now if the aqueous solution containing mercaptan is in contact with an oil solution containing mercaptan, there is a constant partition coefficient, i.e.,

$$\frac{\text{Conc. RSH oil}}{\text{Conc. RSH water}} = \text{K}$$

and this partition coefficient is dependent purely on the solubility of the mercaptan in the oil and in the water and is entirely independent of the presence of other materials. If, therefore, the aqueous solution is diluted and the concentration of free mercaptan therein decreased, more mercaptan must pass from the oil to the water to maintain the constant partition. That is to say, the efficiency of a given weight of sodium hydroxide for removing a mercaptan from oil solution is greater the lower the concentration at which it is employed. On the other hand, the use of dilute soda involves the handling of larger volumes of refining agent and increases the costs of recovery. The economic advantages and disadvantages of using dilute soda solutions therefore need to be carefully studied.

141. The ease with which mercaptans undergo oxidation has also an important bearing upon soda washing. Compounds of this type readily become oxidised, either through the agency of elemental sulphur or atmospheric oxygen, with the production of organic disulphides, thus,

$$2\text{RSH} + \text{O} \rightarrow \text{R}_2\text{S}_2 + \text{H}_2\text{O}.$$

The oxidising action of elemental sulphur is pronounced in the presence of aqueous soda. The aerial oxidation of mercaptans is probably slight, but oxidation undoubtedly occurs in the soda solution during soda washing through the agency of alkali polysulphides. These are formed from elemental sulphur in the unrefined oil and sodium sulphide which is derived from hydrogen sulphide. The products of oxidation, namely disulphides, are neutral substances, which, being insoluble in soda, return to the oil during treatment, and if desulphurisation, rather than sweeten-

ing, is aimed at (see later), this return of sulphur to the oil as disulphide entails a heavier subsequent treatment. This formation of disulphides by the oxidising action of elemental sulphur is an additional reason for avoiding the production of free sulphur, by atmospheric oxidation of hydrogen sulphide, as far as possible.

142. In some cases, the same batch of soda is used to remove both hydrogen sulphide and mercaptans in counter-current scubbers, arranged so that the mercaptans are removed in the second stage with fresh soda and the hydrogen sulphide removed in the first stage with spent soda. In such cases, care must be exercised to prevent the hydrogen sulphide displacing the mercaptans out of solution, which it will do, being a stronger acid than mercaptans. Moreover, when caustic soda is used to perform two functions in this way, its recovery is a matter of greater difficulty than is the case when separate quantities of soda are used for the two purposes. Thus, caustic soda used for removing hydrogen sulphide alone may be recovered by air blowing, when the hydrosulphide formed is converted into sodium sulphide and hydrogen sulphide is liberated, thus,

$$2NaHS \rightarrow Na_2S + H_2S$$

The recovery is by no means complete and the recovered material is of no value except for removing hydrogen sulphide and elemental sulphur; it cannot be used for removing mercaptans. Caustic soda which has been kept away from hydrogen sulphide and used to remove mercaptans can only be recovered as far as possible by boiling and distilling off the mercaptans in a current of steam. The degree of recovery depends upon the oil washed, but falls off at each stage so that the soda cannot be used indefinitely. Soda that has been used for both mercaptan and hydrogen sulphide removal cannot be regenerated so conveniently. In any case, recovery is limited by the presence of polysulphides.

143. Mention has already been made of the fact that sodium sulphide reacts with free sulphur in oil solution to give sodium polysulphides. This reaction is used to effect removal of elemental sulphur. Dilute aqueous caustic soda has no action on thiophenes, carbon disulphide, sulphoxides, sulphones, alkyl sulphides or alkyl disulphides.

It has, however, been observed[11] that solid sodium hydroxide or potassium hydroxide or these substances in organic solvent solution (e.g., ethyl alcohol) are capable of reacting with elemental sulphur. Thus, 6 ml. of a 21·8 per cent. solution of potassium hydroxide solution in ethyl alcohol added to 200 ml. of a 0·227 per cent. naphtha solution of elemental sulphur is said to effect complete removal. Caustic soda is

much slower in its action than the corresponding potassium compound. The reactions occurring may be expressed as

$$6KOH + nS = K_2S_2O_3 + 2K_2S_{\frac{n-2}{2}} + 3H_2O$$

but this equation does not express the various intermediate processes. The primary products are claimed to be potassium thiosulphate, potassium monosulphide and water, the higher polysulphides being formed by secondary reactions involving the addition of sulphur to the lower polysulphides. Potassium trisulphide is the highest polysulphide formed if the mixture is not agitated, but if the reagent is brought into intimate contact with the oil, pentasulphides and probably hexasulphides are formed. There is, however, some danger of elemental sulphur being returned to the oil by the action of dissolved air which oxidises the polysulphides and the thiosulphate with the liberation of free sulphur. It is not believed that the use of alkalies dissolved in organic solvents has found large scale application for the removal of elemental sulphur in this way. The main difficulty would appear to be the high cost of the solvents.

144. In the case of benzoles and other light hydrocarbon oils obtained by carbonisation processes from coal, caustic soda is also used to remove phenolic impurities. These bodies are found in very small amounts in some cracked spirits but in the case of benzoles they are present in amounts up to 4 per cent.

145. Neutralisation of Acidity.—A further use of caustic soda in the refining of light distillates is the neutralisation of residual acidity left in these distillates after acid treatment, hypochlorite treatment or liquid sulphur dioxide treatment. Each of these refining agents leaves the oil with an acid reaction, partly due to the incomplete removal of the refining agent and partly to the incomplete removal of acidic reaction products and reaction products which decompose with the formation of acidity on subsequent distillation or in storage.

After either of these treatments, distillates must be treated in order to remove acidic products. Water is used for this purpose wherever possible and is usually employed for removing the major part of the acidic bodies which are soluble in water, in order to reduce refining costs. After sulphuric acid treatment, a water wash is employed to remove the bulk of the finely divided acid particles (" pepper ") left in the oil, and a slight treatment with caustic soda is then employed to remove the last traces. Thus, some of the products obtained in the sulphuric acid refining of cracked distillates are mono-alkyl sulphuric esters, e.g.,

$$R = CH_2 + H_2SO_4 \rightarrow R - CH_3HSO_4$$

These are soluble in water or in caustic soda and may be removed by washing with these materials. On the other hand, di-alkyl sulphuric esters are also formed, e.g.,

$$R{\cdot}CH_3HSO_4 + R{=}CH_2 \rightarrow CH_3{\cdot}R - OSO_2{\cdot}ORCH_3$$

but these bodies cannot be removed by either water or caustic soda. On distillation, however, they decompose with the formation of sulphur dioxide and caustic soda is used to remove this as soon as it is formed, by injecting it into the condenser coils connected to the distillation plant in which the oil is being distilled.

TABLE 2. CONSUMPTION OF CAUSTIC SODA IN U.S.A.

Year	1924	1929	1930	1931
Petroleum Refining (Short tons)	50,000	134,000	117,000	100,000
Per cent. of Total	12·3	17·7	17·95	16·6
Total all Industries (Short tons)	408,000	759,000	652,000	604,000

During the year 1929, the American petroleum refining industry consumed 134,000 tons of caustic soda for the refining of its various products, an amount equivalent to 17·7 per cent. of the country's total consumption. At an average cost of $57 per ton, this amount involved the expenditure of $7,638,000. In view of the high cost of this material, it is not surprising to find that many efforts have been made to find cheaper substitutes and much success has attended the use of ammonia, lime and magnesium hydroxide (" Brucite ") in this direction.

146. Patents.—Numerous patents have appeared dealing with methods of refining with caustic soda solutions. The following are of some interest.

E.P., 364,778. Troniseck. Appl., December 4, 1930.
U.S.P., 1,759,730. Black and McConnell.
U.S.P., 1,774,611. Phillips.
U.S.P., 1,639,531. Phillips and Stratford.
U.S.P., 1,738,518. Axtell. December 10, 1929.
U.S.P., 1,718,375. Petzer (assignor to Sinclair Refining Co.), April 11, 1928.
E.P., 335,952. N. V. Mijnbouw en. Culturmaatschappij, " Boeton." April 5, 1929.
U.S.P., 1,867,908. D. E. Day. July 19, 1932.

The Use of Lime in the Refining of Light Distillates

147. For the removal of acidic sulphur compounds, lime is as effective as caustic soda at equal dilutions, but suffers from the dis-

advantage that its solubility in water is very low. Thus, at a temperature of 80°F. (26·7°C.), its solubility in water is only approximately 5·5 grams per U.S. gallon, i.e., about 1·45 lbs. per 100 Imperial gallons. Furthermore, the solubility of lime in water decreases with rise in temperature, a phenomenon exactly opposite to that observed with most inorganic compounds. It is of interest, however, that the solubility of lime can be increased by the addition of certain proportions of other salts, e.g., ammonium chloride, calcium chloride and sodium chloride (common salt). The latter salt is of the greatest interest because of its lower cost and greater availability, and its effect in raising the solubility of lime is shown in Fig. 1 and Table 3, reproduced from U.S. Bureau of Mines Report of Investigations, No. 3178, by Rue.

TABLE 3. SOLUBILITY OF CALCIUM HYDROXIDE IN WATER

Temperature°F.	Lbs. per U.S. gallon	Grains per U.S. gallon	Grains per Imp. gallon
32	0·019	132·09	158·5
40	0·018	127·95	153·6
50	0·017	121·73	146·1
60	0·0165	115·51	138·7
70	0·0158	110·85	133·1
80	0·0154	107·74	129·6
90	0·0148	103·60	124·4
100	0·0143	99·97	120·0
110	0·0138	96·87	116·3
120	0·0134	93·72	112·5
130	0·0124	86·51	103·9
140	0·0118	82·88	99·5
150	0·0112	78·74	94·5
160	0·0101	70·87	85·1
170	0·0098	68·79	82·6
180	0·0090	63·71	76·5
190	0·0085	59·57	71·5
200	0·0081	56·98	68·4
212	0·0075	52·32	62·8

Thus, the addition of 11 per cent. of common salt raises the solubility of lime at 80°F. from 5·5 grams per U.S. gallon to approximately 9 grams, but greater amounts of common salt decrease the lime solubility. Because of the low solubility of lime, even when increased in this way, handling charges on washing liquors are appreciably increased and recovery is precluded on account of the large bulk of liquor to be treated. These difficulties may be overcome by the use of a lime suspension in water, or by the use of lime slurries if facilities exist for the handling of such materials. On the other hand, lime is much cheaper than caustic soda and may readily be obtained by the calcination of calcium car-

bonate rocks, e.g., chalk and limestone, followed by slaking, i.e., treatment with water. A convenient source of common salt may be oilfield brines.

148. Several reactions take place when lime and hydrogen sulphide are brought together in aqueous solution. One of the reactions is the formation of calcium hydrosulphide ($Ca(SH)_2$)

$$Ca(OH)_2 + 2H_2S = Ca(SH)_2 + 2H_2O,$$

calcium sulphide (CaS) not being precipitated because it is immediately hydrolysed by water, as follows :—

$$2CaS + 2H_2O = Ca(OH)_2 + Ca(SH)_2.$$

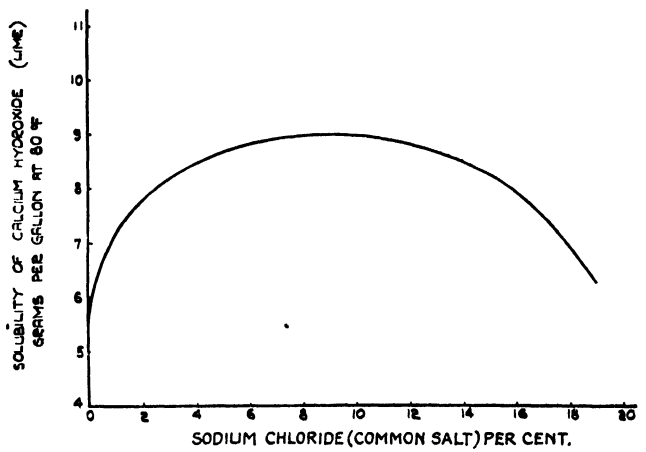


FIG. 1.—THE SOLUBILITY OF LIME IN COMMON SALT SOLUTIONS

However, other reactions can take place. Free sulphur can react with the hydrosulphide formed to give calcium polysulphide and hydrogen polysulphide, the latter decomposing very rapidly with the liberation of hydrogen sulphide and free sulphur.

$$Ca(SH)_2 + 8S = CaS_5 + H_2S_5$$
$$H_2S_5 \rightarrow H_2S + 3S$$

The calcium polysulphide formed may also react with the liberated hydrogen sulphide, as follows :—

$$CaS_5 + 2H_2S = Ca(SH)_2 + H_2S_5$$

Theoretically, an aqueous solution containing calcium hydrosulphide can be regenerated by boiling, when the hydrogen sulphide is expelled. In practice, however, free sulphur is formed by aerial oxidation and recovery is never complete.

Calcium sulphide is insoluble in water but the hydrosulphide is

soluble. By proper contacting and agitation, it has been found possible to exhaust the lime in treatment and obtain an entirely soluble reaction product.

Lime may also be used in the dry form for neutralising hydrogen sulphide in light distillates, thus offering the possibility of avoiding the handling of large volumes of water and eliminating any danger of emulsions.

149. An obvious use for lime is in the neutralisation of excess acidity. The choice between milk of lime and lime slurry will depend upon their relative costs, though, in some cases, it may be undesirable to introduce water into the system, in which case only the slurry is used. Lime is also used extensively for reducing or eliminating the corrosion occurring in cracking coils and condenser tubes, while it is finding application for the removal of hydrogen sulphide from refinery and natural gases.[12,13] Lime is also used for removing mercaptans from light distillates in a modification of the " Doctor " treatment. This is described later (see Paragraph 162).

150. The Use of Ammonia in the Refining of Light Distillates.—The most widespread use of ammonia in refining is in the neutralisation of acidic bodies formed during distillation processes. Iron sulphide formed by the action of evolved hydrogen sulphide appears to act as a protective coating on iron equipment, but this is dissolved by hydrochloric acid formed by the decomposition of any chlorides present and hydrogen sulphide is regenerated. The immediate neutralisation of hydrochloric acid is therefore a matter of much importance. The advantages of ammonia neutralisation are that it is easy to handle, the hazards are small and the injection is cheap, and simple to control. Good contact is immediately obtained between the vapours, resulting in thorough neutralisation. In crude-oil distillation units the ammonia is injected from a bank of cylinders into the vapour line between the top of the tower and the first heat exchanger or into the naphtha section of the tower, if the reflux gasoline contains any condensed acid water. Condenser coils may be protected by injecting ammonia into the line between the heat exchanger and the condenser box. It is not possible to use ammonia for the neutralisation of either hydrochloric acid or hydrogen sulphide at high temperatures, e.g., in cracking coils, because of the low dissociation temperatures of ammonium chloride and ammonium sulphide. On the other hand, sulphur dioxide evolved during the redistillation of acid-treated oils, hydrogen sulphide present in reflux lines, and hydrochloric acid formed in the Lachman zinc chloride refining process are all conveniently neutralised by ammonia. The methods of control, e.g., flow meters and ammonia reducing valves and the use of *p*H

determinations in routine testing, have been recently described by Woodward.[106]

The Use of Magnesium Hydroxide (Brucite) in Refining

151. Magnesium oxide is almost insoluble in water, an approximate value for its solubility at 20°C. being 10 milligrams per litre. This is equivalent to 0·045 grams per Imperial gallon or 0·01 lbs. per 100 Imperial gallons. In the form of the mineral "Brucite," it is found in extensive deposits in many parts of the world.

The salts formed by the reactions of magnesium hydroxide are subject to hydrolysis to a marked degree, owing to the slight solubility of the hydroxide and, in the case of the reaction with hydrogen sulphide, the following equilibrium exists [14] :—

$$2H_2S + Mg(OH)_2 \rightleftarrows Mg(SH)_2 + 2H_2O.$$

Since hydrogen sulphide is feebly dissociated and magnesium hydroxide is almost insoluble in water, this equilibrium should be appreciably to the right at ordinary temperatures. At elevated temperatures, the high vapour pressure of hydrogen sulphide from aqueous solutions should result in a shift of the equilibrium to the left, owing to loss of hydrogen sulphide from the solution as rapidly as hydrolysis occurs. At atmospheric temperatures, several successive extractions should be required to remove substantially all of the hydrogen sulphide from light distillates.

152. Owing to its extremely low solubility in water, brucite can only be employed for neutralisation purposes in the form of a slurry or in granular form. Both methods of application have been recently described in detail by Gardner and Higgins.[15] In employing granular magnesium hydroxide packed into a vertical tower for the removal of weak acids from liquid or gaseous petroleum products, the magnesium salts formed are deposited progressively on the surface of the hydroxide, and thus the acids are removed as passage through the tower occurs, until, after contact with a large number of successive surfaces, the amount of free acid becomes infinitesimally small. Thus, even though the process of salt formation is never complete, the removal of successive increments of acids as salts insoluble in light hydrocarbon distillates results in eventual neutralisation of practically all free acid. If the concentration of the weak acids is appreciably large, it is conceivable that the use of a solid base may not represent the most economical method of application, that is, the surface of magnesium hydroxide becomes coated with a film of reaction products so rapidly that the time of use is too short for effective plant operation. The use of magnesium hydroxide as a thin suspension may be preferred in such cases.

The ease of hydrolysis of magnesium salts makes possible ready recovery of the hydroxide from such salts. Boiling salts of this type for a few minutes results in expulsion of practically all of the acid, leaving the magnesium hydroxide available after cooling for reaction with further weak acid.

153. Gardner and Higgins (*loc. cit.*) have described experiments using both granular magnesium hydroxide and the same substance in water suspension for the removal of hydrogen sulphide from light distillates and gases. In these experiments, effective removal was obtained until the equilibrium between the hydroxide and the hydrosulphide was set up, but, in the use of granular hydroxide, coatings of reaction products soon prevented further action. The use of suspensions in water met with greater success. These investigators also studied the case of hydrolysis of magnesium hydrosulphide at the boiling point of water and found that 81% hydrolysis could be obtained on boiling for two minutes. Thus regeneration may readily be accomplished. The cost of heating the suspension to bring about hydrolysis should not be excessive if well-designed heat exchange equipment is employed in conjunction with continuous operation.

Granular magnesium hydroxide may also be applied in the neutralisation of acid-treated distillates. The product of the reaction is, in this case, magnesium sulphate ($MgSO_4 \cdot 7H_2O$), which is readily soluble in water, so that the hydroxide may be revivified by water washing.[16]

A further use of magnesium hydroxide is in the sweetening of light distillates by a modified " Doctor " treatment. This is described later (see Paragraph 161).

Cadmium hydroxide has also been proposed as a refining agent. Its reactions with sulphur compounds are similar to those of magnesium hydroxide.[17]

Plumbite Treating

154. The plumbite process is used exclusively for the removal of mercaptans from light distillates. It is termed the " Doctor " process and " sweetens " " sour " distillates, so called because of the foul or sour smell which they possess in virtue of their content of these sulphurous materials.

The chemicals used in this process are caustic soda and litharge (lead oxide), which combine to give the effective refining agent, sodium plumbite.

$$2NaOH + PbO \rightarrow Na_2PbO_2 + H_2O$$

Hydrogen sulphide readily reacts with this substance to give lead sulphide, but the use of plumbite solution in this way is unnecessary

and wasteful since a complete removal may be effected by soda washing (*q.v.*). For this reason, a distillate which contains hydrogen sulphide should always be treated with caustic soda or some other reagent for its removal previous to plumbite treatment. The refining action of sodium plumbite solutions is usually explained in the following way :—

Mercaptans react with sodium plumbite to give lead mercaptides, the reaction being accelerated by the solubility of the mercaptans in caustic soda, which brings them into intimate contact with the plumbite.

$$2RSH + Na_2PbO_2 = (RS)_2Pb + 2NaOH \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Mercaptan + plumbite = mercaptide + caustic soda

The reaction mixture is coloured and varies from yellow to red according to the molecular weight of the mercaptan. The lower mercaptides are light in colour and are precipitated from solution, but higher mercaptides are soluble in the oil and impart to it a red colour (which is, however, masked if hydrogen sulphide is present). Thus, treatment with plumbite in this way brings about partial desulphurisation by the precipitation of the lower molecular weight lead mercaptides. The higher members must, however, be removed from solution and this is accomplished by the addition of elemental sulphur which brings about the reaction

$$\begin{matrix} RS \\ RS \end{matrix}\!\!\diagdown\!\!\diagup Pb + S = PbS + \begin{matrix} R{-}S \\ | \\ R{-}S \end{matrix} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Lead mercaptide → disulphide

whereby lead sulphide is precipitated as a black precipitate and organic disulphides are formed. The latter, being oil-soluble, pass back into the oil and, unlike the original mercaptans, are not foul smelling. Therefore they can be tolerated in refined gasolines in very small amounts.

155. Commercial sweetening by means of Doctor solution corresponds, in general, to the two equations given above, but there are, however, two important facts to be considered. Equation (1) calls for 1 mol of lead oxide for every 2 mols of mercaptan; equation (2) calls for 1 atom of sulphur for every 2 mols of mercaptan. In actual practice, however, 1 mol of original lead oxide is capable of sweetening not 2, but from 10 to 20 mols of mercaptan. This suggests either a regeneration of the lead sulphide formed in equation (2) or a catalytic action of the lead sulphide itself. In the event of lead sulphide acting catalytically, two other processes are to be considered.

$$PbS + 2NaOH = PbO + Na_2S + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$2RSH + S + 2NaOH = \begin{matrix} R-S \\ | \\ R-S \end{matrix} + Na_2S + 2H_2O \quad . \quad . \quad (4)$$

one of which shows a regeneration of lead sulphide (equation (3)) and the other a direct oxidation of the mercaptan to disulphide by means of sulphur and sodium hydroxide, lead sulphide acting catalytically. Each of these secondary processes has been defended as giving a proper explanation of the sweetening process as practised on a large scale.

Faragher and Morrell[18] incline strongly to equation (3), with the addition that the conversion of lead sulphide into lead oxide takes place through the intermediate formation of lead sulphate. Wendt and Diggs,[19] on the other hand, view the process according to equation (4). However, these conflicting opinions have been brought together by Lachman,[20] who has shown that both reactions can occur at the same time.

Treatment with sodium plumbite solution alone is termed " plumbite treatment," while treatment with sodium plumbite solution followed by the addition of sulphur to decompose the higher mercaptides is referred to as " Doctor treatment."

156. It will be evident from the above chemical considerations that Doctor treatment does not bring about complete elimination of mercaptan sulphur, because only the lead derivatives of the lower mercaptans are precipitated. In the case of the higher mercaptans, the sulphur content of the disulphides formed in the above reactions is exactly the same as the original mercaptans. If a product of low sulphur content is required, the plumbite process is rarely sufficient treatment and must be followed by some other refining process (e.g., acid washing).

Great care must be exercised in the addition of the free sulphur in Doctor treatment. Enough must be added completely to convert the lead mercaptides into disulphides, but the evils attendant upon the presence of elemental sulphur in refined oils makes it imperative not to add any excess. The addition of elemental sulphur is usually made by preparing a strong solution of it in a small proportion of the oil to be treated, and adding the requisite amount of this solution to the bulk of the oil.

Light distillates which give no reaction with Doctor solution are termed " sweet."

157. A point of some interest in Doctor treatment is that the lead sulphide is precipitated in a form which is capable of adsorbing other sulphur compounds. Consequently, a certain amount of desulphurisation occurs in this way. An important development of this is the lead sulphide method of desulphurisation.[21] This is described later.

158. Recovery of Sodium Plumbite Solutions.— For economic reasons it is necessary to recover refining agents as completely as possible. The lead sulphide in spent Doctor solution is recovered by

various methods. One procedure adopted is to convert lead sulphide to sodium plumbite through the intermediate formation of lead sulphate, by the action of air at elevated temperatures. The spent Doctor solution is run into a regenerating tank which is fitted with a closed steam coil and a pipe through which air can be passed. The solution is then heated to between 175° and 200°F. (79·5° and 93·3°C.), and air is blown through it until the lead sulphide has been converted into lead sulphate. Sufficient caustic soda is then added to dissolve the lead sulphate and convert it into sodium plumbite. The reactions which take place are as follows :—

(1) $PbS + 2O_2 \rightarrow PbSO_4$

(2) $PbSO_4 + 4NaOH \rightarrow Na_2PbO_2 + Na_2SO_4 + 2H_2O.$

159. The Kinsel Process for Sodium Plumbite Recovery. — In this process lead sulphide and spent Doctor solution are withdrawn from the treating plant and run to a settling tank where, by means of a steam coil, the mixture is heated and then allowed to settle, the heating greatly facilitating the separation of the lead sulphide. The clear caustic soda solution is drawn off for further use and the lead sulphide is passed to a filter. Here it is filtered as dry as possible (i.e., to a water content of about 30 per cent.), and then discharged into a tank containing a necessary amount of diluted sludge sulphuric acid for the conversion of the sulphide into lead sulphate. The acid used is sludge acid obtained in sulphuric acid refining, which has been diluted with water to a specific gravity of 1·32–1·38 (35–40° Bé) and allowed to stand for the separation of the tar present.

After complete conversion, the lead sulphate is pumped to a washing tank where it is washed to an acid content of about 0·5 per cent., and is discharged to storage or direct to the solution tanks where it is mixed with caustic soda solution to give fresh Doctor solution. The chemical reactions involved are

(1) $PbS + H_2SO_4 \rightarrow PbSO_4 + H_2S$

(2) $PbSO_4 + 4NaOH \rightarrow Na_2PbO_2 + Na_2SO_4 + 2H_2O.$

The process not only recovers the lead, but also recovers 75–80 per cent. of the caustic soda used in making up the Doctor solution. It also recovers any light distillate which may be drawn from the treating plant in admixture with the lead sulphide. This process is covered by patents,[22] and has been fully described by Fanning.[23]

160. The F. C. Process for Plumbite Recovery.—This process enjoys some measure of popularity at the present time and makes use of liquid chlorine. It is operated as follows :—

Spent plumbite sludge is settled in a tank and the precipitated lead sulphide washed free of caustic soda before it is passed to a conversion

tank. Here it is mixed with sufficient water to produce a heavy suspension and hydrochloric acid (obtained from a previous conversion) is pumped in to accelerate the subsequent reactions. The suspension is then vigorously agitated and a stream of chlorine gas slowly passed into the mixture until approximately 0·3 lbs. of chlorine are present for every pound of lead sulphide. After conversion, which may take as long as three hours for completion, the solid reaction products consist of litharge (PbO), elemental sulphur and a small amount of lead chloride ($PbCl_2$). The liquid product consists of dilute hydrochloric acid and contains some lead chloride in solution and colloidal sulphur in suspension. After allowing to settle for a short time, the contents of the conversion tank separate into three distinct layers; the upper layer being a mass of flocculent elemental sulphur, the middle layer a dilute solution of hydrochloric acid and the bottom layer a mixture of finely divided solid material, consisting principally of litharge, some sulphur and traces of lead chloride. These layers are removed separately and the solid layers washed to free them of acid.

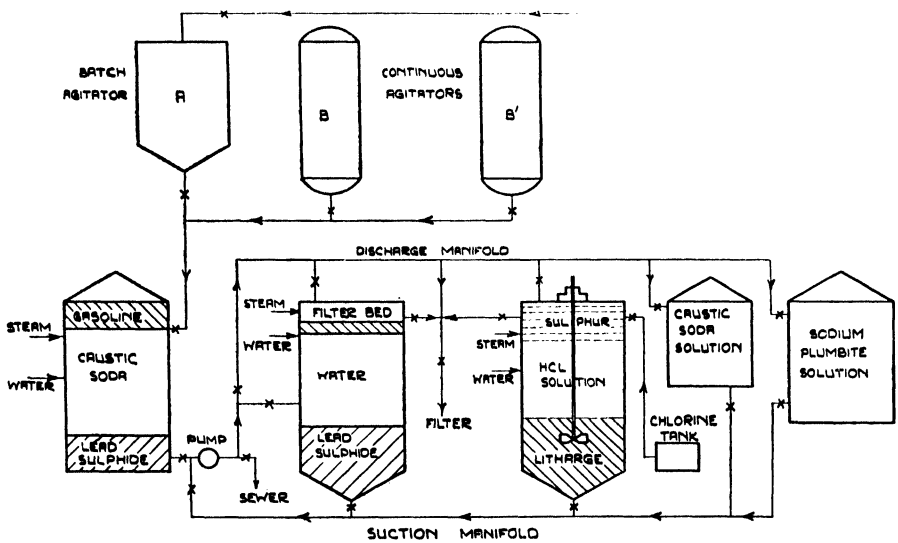


FIG. 2.—THE F.C. SODIUM PLUMBITE RECOVERY PROCESS (GOODE)

The chemical reactions involved are as follows :—The lead sulphide is oxidised to litharge and free sulphur by the action of chlorine. After being freed of hydrochloric acid, the litharge, admixed with a small amount of sulphur, is ready to be used in making up fresh Doctor solution with the caustic soda recovered in the first settling operation. Thus,

$$H_2O + Cl_2 \rightarrow HOCl + HCl$$
$$HOCl + PbS \rightarrow PbO + S + HCl$$
$$PbO + 2NaOH \rightarrow Na_2PbO_2 + H_2O$$

Usually, there is sufficient elemental sulphur entrained in the litharge to obviate the need for further sulphur addition to the plumbite solution.

Some figures relating to the cost of recovering plumbite by this process at the refinery of the American Refining Properties Co. at Wichita Falls, Texas, have been given by Goode.[24]

Claims are made that Doctor solution prepared from recovered reagents gives more efficient sweetening than a similar solution made up from fresh reagents, but no satisfactory explanation of these claims has been made.

161. The Use of Magnesium Hydroxide in the Sweetening of Light Distillates.—A recent development in refining practice is the use of magnesium hydroxide in a modified type of Doctor treatment. This has been fully described by Gardner and Higgins.[25] The method consists of passing sour distillate containing the requisite amount of elemental sulphur in solution through a tower packed with magnesium hydroxide, when the following reactions occur :—

$$(1)\ Mg(OH)_2 + RSH \rightarrow Mg\begin{matrix}SR\\OH\end{matrix} + H_2O$$

$$(2)\ 2Mg\begin{matrix}SR\\OH\end{matrix} + S \rightarrow MgS + Mg(OH)_2 + RS{-}SR$$

The surface of the hydroxide granules gradually becomes covered with a film of magnesium sulphide, so that sweetening is gradually prevented. Eventually, the rate of sweetening becomes so slow that regeneration of the magnesium hydroxide becomes necessary. This is accomplished by hydrolysis with steam or boiling water, or, preferably, with a two per cent. sodium hydroxide solution. Fig. 3 is a flow diagram of the process employed.

Two towers are connected in series and equipped with drying coils having a surface of about 25 square feet per ton of brucite (magnesium hydroxide). Saturated or super-heated steam is used as the heating medium. Steam jets or evacuators are attached to outlets at the top of the towers to facilitate rapid removal of vapour during the drying period after revivification. Brucite is contained in the towers on perforated plates or screens to reduce channelling to a minimum. The distillate to be sweetened is pumped into the bottom of the tower, a portion of it being passed through a smaller tank containing roll sulphur. Commercial operating cycles are governed mainly by the minimum rate which is economically feasible. Runs have been made in which 14,000 to 20,000 barrels of sour spirit have been sweetened by passage through two towers each containing 8 tons of brucite before revivification was

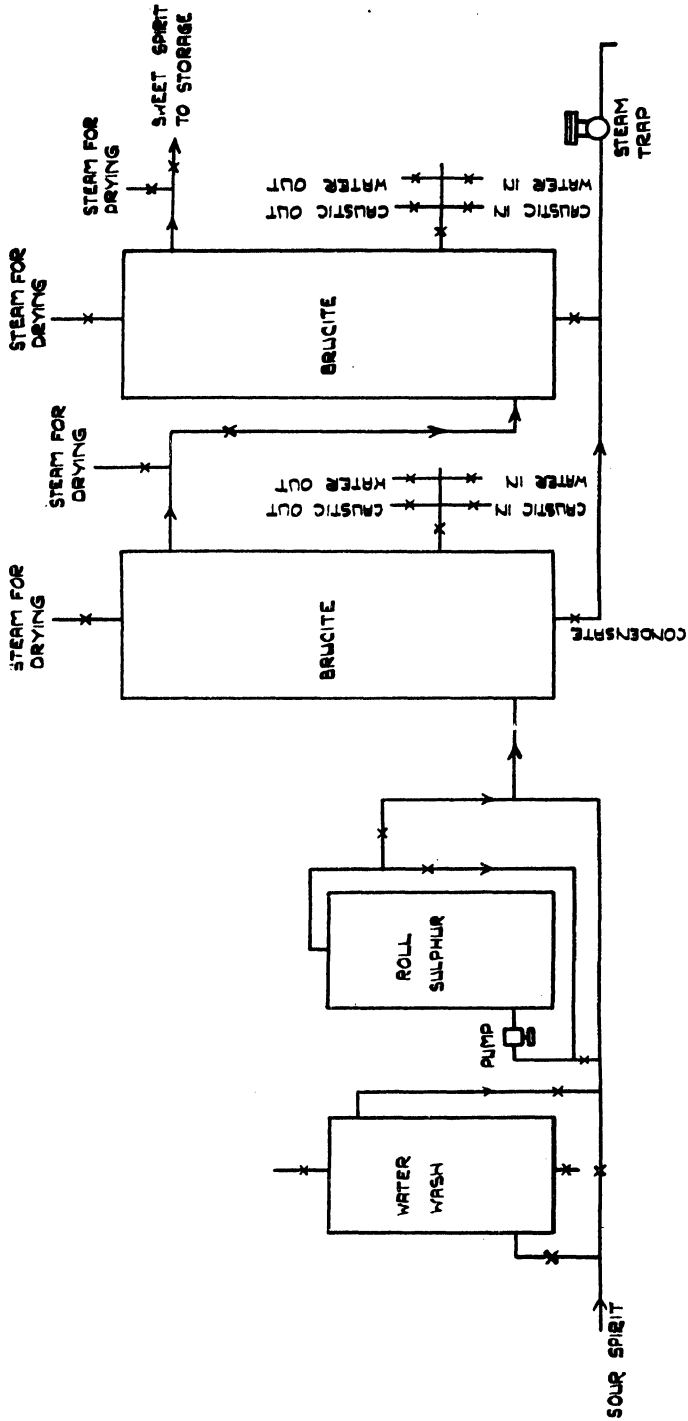


FIG. 3.—FLOW DIAGRAM OF BRUCITE SWEETENING UNIT (GARDNER AND HIGGINS)

necessary. When the spirit is no longer sweetened by the brucite, the latter is boiled with water and then with 2 per cent. sodium hydroxide solution and again with water. The washed material is then dried *in situ* and is used for another cycle. The loss in weight of the brucite is about 1–2 per cent. per cycle and the consumption of caustic soda about 0·004 per cent. of the weight of brucite in operation per cycle.

162. The Use of Lime in a Modified Doctor Treatment.—A mixture of lime and lead oxide (litharge) is used as a sweetening agent in the Cannon Process. These two reagents form the hypothetical calcium plumbite, but are employed in the form of a dry powder instead of in solution. Diatomaceous earth is added to give a larger effective surface and to facilitate the progress of the reaction. The reagent also contains a small amount of water added in the form of a caustic soda solution, but this is completely adsorbed by the adsorbent earth.

In contact with mercaptans, disulphides are formed and the lead is precipitated as lead sulphide and this then reacts with the lime and forms a fresh supply of calcium plumbite, calcium sulphide being formed as the end product. Very little loss of lead occurs. It is claimed that the cost of this method of sweetening is only 15 to 20 per cent. of that of the normal Doctor process. One ton of reagent is said to be capable of sweetening from 20,000 to 100,000 barrels of sour distillate. The process has been fully described in the literature[26,27] and is covered by the following patents.

U.S.P., 1,789,168, *January* 13, 1931. Cannon and Gary.
U.S.P., 1,802,628, *April* 28, 1931. Caldwell (to Celite Corporation).
E.P., 367,969, *March* 3, 1932. Cannon.

The Removal of Mercaptans from Light Distillates by Treatment with Metallic Sulphides

163. An interesting development of the plumbite refining process is that described by Rowsey and Whitehurst[28] and which makes use of a suspension of lead sulphide in aqueous caustic soda as a sweetening agent. The strength of the caustic soda employed may be from 7% to 19% N*a*OH (10–25°Bé, 1·074–1·210 sp. gr.), but it is preferably about 15% N*a*OH (1·16 sp. gr., or 20°Bé). The spirit to be treated is mixed with the lead sulphide suspension and air is blown into the mixture. Mercaptans are adsorbed on to the surface of the lead sulphide and are there oxidised by the air through catalytic action. The reaction is essentially one of sweetening and no appreciable desulphurisation occurs. The catalytic activity of the sulphide is impaired by the presence of sodium sulphide. Sulphur assists the sweetening process but is not required.

The action of various metallic sulphides in this reaction has been studied by Greer,[29] who found that cupric sulphide was particularly effective. Stannic and arsenious sulphides were found to be very slow in their action.

It has recently been observed that the activity of metallic sulphides as refining agents may be increased by deposition on silica gels.[30]

The Hypochlorite Refining Process

164. The successful development of the hypochlorite refining process is due entirely to the Anglo-Iranian Oil Company and, more particularly, to Dr. A. E. Dunstan, the chief chemist of that company, who was the first to use this reagent in such a way that chlorination of the oil was avoided.

Prior to Dunstan's work, various proposals had been made to refine light distillates by means of chlorine. Thus, Watson Smith[31] passed chlorine gas into crude petrol and was able to distil off a spirit of " faint and agreeable odour." Johnson and Johnson prescribed a very similar treatment and completed the refining by filtration through charcoal.[32] Frasch[33] treated oils with a suspension of chloride of lime or bleaching powder and followed this by treatment with sulphuric acid and, finally, with sodium plumbite to remove any chlorine compounds formed. At a later date, Colin and Amend[34] proposed to desulphurise petroleum distillates by means of a hypochlorite in alkaline solution. They claimed a reaction which is principally one of oxidation, carried out in the presence of an oxygen carrier, the excess chlorine being removed by the use of some salt of a heavy metal which is capable of existing in two or more states of oxidation, such as manganous and ferrous salts. They based their principle of oxidation upon the fact that when chlorine gas is passed into a solution of caustic soda containing a so-called oxygen carrier, such as manganese, cobalt, nickel, copper or iron, the hypochlorite is decomposed into the corresponding chloride and oxygen without the production of free chlorine, thus avoiding chlorination. The method of procedure proposed by Colin and Amend was to agitate the distillate with a solution of sodium or calcium hypochlorite to which had been added a small amount of manganous nitrate. Manganese dioxide or, possibly, manganous hydroxide was stated to be formed and give up its oxygen to the sulphur compounds (mercaptans), whereupon it was again oxidised by the hypochlorite. Good results were claimed.

Patents by Dunstan began to appear in 1918, and embodied the novel idea of using alkaline hypochlorite in order to prevent chlorination.[35] These patents are the basis of the hypochlorite treatment as used at the present time and the bulk of our knowledge of this process is due to the published work of Dunstan and his co-workers.[36]

The process is used principally for the desulphurisation or sweetening of light distillates and normally consists of washing distillates with an aqueous alkali or alkaline earth hypochlorite solution under controlled conditions, this treatment being followed by a soda wash to remove traces of hypochlorous acid, etc., dissolved in the oil. It is essential that the hypochlorite solution should contain sufficient free alkali to stabilise it, but insufficient appreciably to retard the interaction of the hypochlorite and the objectionable sulphur compounds present in the oil. The reasons for this are explained later.

165. Preparation of Hypochlorite Solutions.—Both calcium and sodium hypochlorite solutions are readily prepared. The sodium hypochlorite originally employed in the process was manufactured by the electrolysis of brine, the current density being adjusted to give, simultaneously, chlorine and the requisite amount of caustic soda: 0·2 to 0·3N solutions were easily prepared in this way. Alternatively, chlorine may be purchased in tank car lots and the gas passed into 10 per cent. caustic soda solution until the required concentrations of hypochlorite and of free alkali are obtained. Calcium hypochlorite has now replaced sodium hypochlorite because of its lower cost and may be prepared by passing chlorine into well-agitated milk of lime, or may be prepared from bleaching powder. The working strength of the hypochlorite solution is adjusted to 0·2 to 0·3N or even lower, with an alkali content of 0·5 to 1·0 grams per litre.

166. Method of Application.—The hypochlorite treatment is always given after a preliminary alkali wash, which removes acidic sulphur compounds and effects a considerable economy in chlorine. Either batch processes or methods involving continuous operation may be used. In the former, the time of agitation required (which obviously depends upon the efficiency of the mixing) is usually about 30 minutes. The treating operation is usually adjusted in such a way that the hypochlorite becomes completely used up and can be run to waste.

167. The Action of Hypochlorite Solutions on Various Sulphur Compounds.—In order to investigate the action of hypochlorite on the sulphur compounds present in Iranian light distillates, Birch and Norris[36] made a study of the action of aqueous sodium hypochlorite on representative sulphur compounds of the types likely to be present, and examined and identified the reaction products. Their results are reproduced in Table 4 and their conclusions are as follows:—

(1) Whereas hydrogen sulphide, mercaptans and disulphides all react to give, at least, some acid products, no acid products are formed from sulphides or sulphoxides.

(2) Thiophenes and sulphones do not react under the conditions employed (comparable with refinery practice).

(3) Increase in the molecular weight of the sulphur compound (*a*) decreases the rate of oxidation (di-iso-amyl disulphide hardly reacts at all), (*b*) decreases the solubility of the oxidation products in the aqueous liquor and (*c*) increases the solubility of the oxidation products in the oil.

(4) Increase in the free alkali content of the hypochlorite decreases the rate of reaction considerably (and vice versa). This fact is also borne out by works' practice.

(5) Dilution of the hypochlorite increases the rate of reaction.

TABLE 4. THE ACTION OF AQUEOUS SODIUM HYPOCHLORITE ON VARIOUS SULPHUR COMPOUNDS

(BIRCH AND NORRIS)

Sulphur Compound	Reaction Products		
	Soluble in Oil	Soluble in Water	Insoluble
Hydrogen Sulphide	(Sulphur)	Sulphuric acid	Sulphur
Ethyl Mercaptan ..	Ethyl di-sulphide	do. (trace) Ethane sulphonic acid	
Isopropyl Mercaptan ..	Isopropyl disulphide	Sulphuric acid (trace) Isopropane sulphonic acid	
Isobutyl Mercaptan ..	Isobutyl disulphide	Sulphuric acid (trace) Isobutane sulphonic acid	
Ethyl sulphide		Ethyl sulphone	
n-Propyl sulphide ..	(*n*-Propyl sulphone)	*n*-Propyl sulphone	
Isobutyl sulphide ..		Isobutyl sulphone	
Isoamyl sulphide ..	Isoamyl sulphone	(Isoamyl sulphone)	
Pentamethylene sulphide	Sulphone	Sulphone	
Diethyl disulphide ..		Ethane sulphonic acid Sulphuric acid	
Isoamyl sulphoxide ..	Isoamyl sulphone	(Isoamyl sulphone)	
Diethyl sulphone ..		No action	
Thiophene		No action	

The first of these conclusions is of great importance, because the acid products neutralise the free alkali of the reagent as they are formed, and thus progressively render the hypochlorite more reactive. Consequently, if insufficient alkali is originally present, the aqueous solution may actually become acid and then there will be a tendency for chlorina-

tion to occur. The observation that the addition of free alkali stabilises the hypochlorite and that increased dilution increases its reactivity is explained on the assumption that the active oxidising agent is not sodium hypochlorite, but free hypochlorous acid produced by reversible hydrolysis.

$$NaOCl + H_2O \underset{H_2O \rightarrow}{\overset{\leftarrow NaOH}{\rightleftarrows}} NaOH + HOCl$$

Thus, added sodium hydroxide displaces the equilibrium to the left and dilution moves it to the right. These effects respectively stabilise and accelerate the activity of the solution.

168. Organic Sulphides (R_2S).—Organic sulphides are quantitatively oxidised to sulphones by the action of sufficiently active hypochlorite. No intermediate compounds appear to be formed and the hypochlorite is without further action on the resulting sulphones. Four atoms of available chlorine are absorbed for each sulphur atom oxidised, i.e., 32 grams of sulphur oxidised require 142 grams of chlorine. It will be noticed that, in this case, no acidic compounds are formed; consequently the alkalinity of the hypochlorite does not change appreciably during the reaction. The lower sulphones are more soluble in water than in light distillates and are chiefly found in the spent aqueous reagent, but the higher molecular weight sulphides give sulphones which tend to remain in the oil, being more soluble therein, with the result that the sulphur content of the oil remains unchanged. However, the higher molecular weight sulphones have high boiling points and may be removed from the oil by distillation. Sulphones of intermediate molecular weight, e.g., dipropyl and di-isobutyl sulphones, can be gradually removed from the treated spirit by water washing.

The rate of oxidation of the organic sulphides, particularly the lower members, is only slightly affected by the alkalinity of the hypochlorite. Large quantities of free alkali are required to prevent the oxidation occurring within a few minutes.

169. Organic Disulphides. (R_2S_2)—The primary oxidation products formed by the action of hypochlorite on a disulphide, unlike those from a sulphide, are acidic, i.e., the sulphonic acid together with a smaller quantity of sulphuric acid. These react with the free alkali present in the treating agent and appear in the aqueous layer as their sodium salts. The gradual neutralisation of the free alkali by the acidic products makes it necessary, in describing the effect of alkalinity on the reaction, to distinguish between two somewhat different cases: (1) The free alkali is more than equivalent to the total possible acid products; the reagent will always remain alkaline, (2) The free alkali

is less than equivalent to the total possible acid products ; if the reaction is continued long enough the reagent will become acidic. The reaction under the first conditions may be described as the normal one. In Fig. 4 (reproduced from the published work of Dunstan and his co-workers), the number of atoms of available chlorine absorbed per atom of sulphur originally present as diethyl sulphide are plotted as a function of time. Curve (i) refers to a strongly alkaline solution and curve (ii) corresponds to a weakly alkaline solution. These show the marked effect of increased alkali concentration in slowing up the oxidation reaction. If, however, the alkalinity of the reagent is so chosen

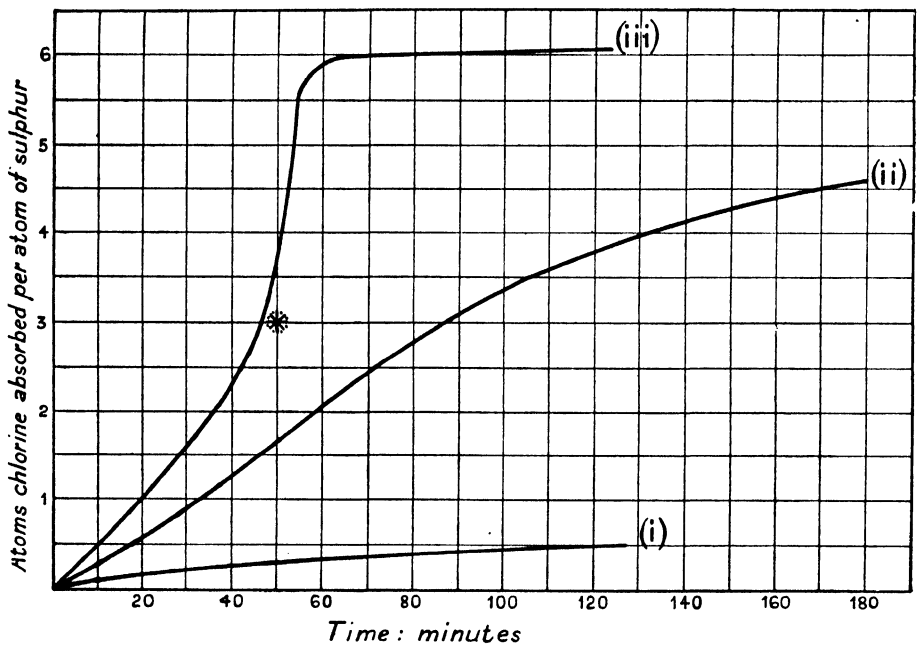
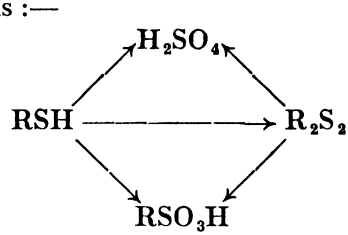


FIG. 4.—DIAGRAM SHOWING THE REACTION BETWEEN HYPOCHLORITE AND ALKYL DISULPHIDES
(Courtesy of Royal Society of Arts)

that the acid products are more than sufficient completely to neutralise the free alkali present, a curve such as curve (iii) is obtained. In this case, the initial point of the reaction follows the normal course until the free alkali present is completely neutralised, but at the point (*) there occurs a very rapid absorption of available chlorine which continues until the sulphur compound is entirely oxidised. The reaction then slows down and, finally, a slow, spontaneous decomposition of the residual dilute acid hypochlorite continues to take place. At the point (*), the reaction proceeds with evolution of heat and is so rapid that it is impossible to isolate any intermediate products. Although the reaction is considerably slowed up by the addition of a little alkali, it

is interesting to note that even 20 per cent. of sodium hydroxide does not completely inhibit the oxidation.

170. Mercaptans.—The apparent course of the reaction between sodium hypochlorite and a mercaptan is dependent to a large extent upon the amount of free alkali present. The first action, as stated above, leads simultaneously to the formation of the corresponding sulphonic acid, sulphuric acid and the corresponding disulphides. The last products are oxidised further if the hypochlorite employed is reactive enough, and their acids as their sodium salts are the only products. With a more stable hypochlorite solution, slower decomposition of the disulphide occurs and this substance then appears as the chief product, accompanied by smaller quantities of the acids which have been formed, for the most part, by direct oxidation of the mercaptan. The first part of the reaction, in which the mercaptan itself takes part, does not appear to be greatly affected by the alkalinity of the reagent, whilst the factors which influence the destruction of the resulting disulphide are those which govern the normal interaction of this type of compound with sodium hypochlorite. The reaction may be represented diagrammatically thus :—



171. Hydrogen Sulphide, Elemental Sulphur and Thiophene.—As already stated, sodium hypochlorite reacts with hydrogen sulphide to form elemental sulphur and traces of sulphuric acid. Part of the elemental sulphur formed dissolves in the distillate being treated. This fact again emphasizes the necessity for a preliminary soda wash on any distillate which is likely to contain hydrogen sulphide and which is to be treated with hypochlorite. Thiophenes are not attacked by hypochlorite and are similar to elemental sulphur in this respect.

172. The hypochlorite refining process was originally developed for the treatment of Iranian light distillates and is now extensively used for this purpose. It is also employed, to a considerable extent, in the desulphurisation of natural gas gasolines in America. On the other hand, it has not been applied, on any scale, for the treatment of cracked spirits of high sulphur content from Mid-Continent crudes. Thus, it has been stated by Morrell[37] that " the use of hypochlorite solutions in the refining of cracked distillates, even though strongly alkaline, has been

generally unsuccessful and cracked distillates are seldom so treated. The resulting products, in most cases, have been unstable and go off colour on storage." Again, the statement has been made by the same authority that "the practice of sweetening cracked spirit with hypochlorite solutions has been practically discontinued, mainly because of poor colour stability of the sweetened spirit."

Refining Processes involving the Use of Oxidising Gases other than Chlorine

173. Various attempts have been made to refine cracked spirits and benzoles by partial oxidation of the more reactive unsaturated hydrocarbons, by means of air, ozone and other oxidising gases.

Recently, Bruzac[38] has patented a process for the refining of light oils, such as benzoles, by a comparatively mild treatment with ozonised air (8–10 grams of ozone per cubic metre), which is passed at atmospheric temperature and pressure through the oil for a period not exceeding an hour. The quantity of ozonised air necessary is said to be about 100 volumes per volume of light oil. The brown precipitate which is formed is filtered off and the treatment completed by washing with 20 per cent. caustic soda solution and distilling. It is claimed that the process is inexpensive and that the treatment reduces the sulphur content and produces a colourless and stable product.

The use of oxidising reagents has also been proposed, as, for example, the process of Michot-Dupont,[39] in which mineral oils are purified by treatment with acid in the presence of substances capable of liberating oxygen, such as per-salts, followed by distillation.

Sulphuric Acid Refining

174. Sulphuric acid is still widely used as a refining agent in the petroleum industry although, as already pointed out, it was first applied as a refining agent in the treatment of shale and coal oils before the petroleum industry came into being. Refining by means of this agent can be most efficient and economical, providing that the process is very carefully controlled, but, on the other hand, if not carried out correctly, can give very high refining losses and also inferior products. Modern modifications of the old acid and soda process are now practised, one of these making dual use of sulphuric acid and diatomaceous earths. Continuously operated plant is now favoured in preference to the old batch methods of treatment. In the U.K. benzole industry, the acid and soda process has been almost exclusively used until two or three years ago, but, at the present time, there is evidence that more economical methods are growing in popularity (see Chapter VI). Sulphuric acid refining is particularly applicable to the production of highly refined naphthas,

such as dry cleaning spirit, and also high boiling, highly purified oils, such as medicinal paraffin. On the other hand, it is not generally applicable to the refining of highly unsaturated spirits, such as those produced by vapour-phase cracking, since it often entails high refining losses and causes an appreciable decrease in anti-knock value, due to the removal of valuable anti-knock constituents.

175. The Action of Sulphuric Acid on Hydrocarbons.—Of the four main classes of hydrocarbons present in light petroleum distillates, namely unsaturateds, aromatics, naphthenes and paraffins, the last two are not attacked at the low temperatures and short reaction times normally employed in sulphuric acid refining, but the solution by the acid sludge (formed by other reactions) of light paraffins and naphthenes has been observed. Prolonged treatment of paraffin hydrocarbons with sulphuric acid at elevated temperatures does, however, result in reaction, for Worstall[40] has reported the formation of the sulphuric esters of *n*-hexane, *n*-heptane and *n*-octane by heating with oleum under a reflux condenser. It has also been observed[41] that when paraffins and naphthenes are in contact with substances which *do* react with sulphuric acid, they may sometimes undergo a change, but whether an actual chemical reaction takes place is unknown. The effect may be a simple absorption in the acid sludge. If naphthenic acids are present in any quantity in the oil being treated these may contribute to this effect, because they are soluble in sulphuric acid and hence enhance the solubility of hydrocarbons therein. In spite of these observations, it may, however, be safely assumed that in normal sulphuric acid refining processes where the temperature of the reaction is kept low, naphthene and paraffin hydrocarbons are not attacked to any measurable extent.

176. Aromatic Hydrocarbons are not appreciably attacked under normal refining conditions, but if fuming sulphuric acid is used or if the temperature is allowed to rise far above normal, sulphonation of these hydrocarbons may occur. This reaction is important in the case of oils containing large amounts of aromatics, for example, benzoles and vapour-phase cracked spirits. When both aromatic and unsaturated hydrocarbons are present together, the acid may bring about a condensation between members of these two types of constituents. Thus, it has been found by Brochet[42] that benzene and hexene, in the presence of small amounts of sulphuric acid of specific gravity 1·84, condense to give hexyl-benzene, methyl-butyl-phenyl-methane and other similar compounds. Styrene is also known to condense with aromatic hydrocarbons, under similar conditions, e.g., styrene condenses with xylene to give β-phenyl α-tolyl propane, a compound boiling at 316–317°C.[43]

177. In the case of benzoles containing fairly large amounts of unsaturated hydrocarbons, e.g., benzoles produced by the pyrolysis of paraffin gases, sulphuric acid refining causes the loss of quite large amounts of aromatics, unless low treating temperatures are employed. In the case of normal light distillates of gasoline boiling range, containing only small amounts of aromatics and unsaturateds, no appreciable loss of aromatics occurs. In the case of kerosenes, however, where the removal of aromatics is definitely desired, because these hydrocarbons burn with a smoky flame, this is effected by using larger amounts of acid or acid of greater strength, e.g., oleum. The higher aromatics are more easily attacked by sulphuric acid than benzene. Thus, Birch and Norris[44] have found that on diluting "acid tar" produced in the acid treatment of kerosene a highly aromatic oil separates. It is of interest to note that these hydrocarbons are present in the tar as such and not as the sulphonic acids, that is, they are soluble in the tar. That sulphonation of aromatic hydrocarbons may be brought about by 98 per cent. acid is, however, shown by the presence of diphenyl sulphone in benzole which has been acid treated.

$$C_6H_6 + H_2SO_4 \rightarrow C_6H_5SO_3H$$
$$C_6H_6 + C_6H_5SO_3H \rightarrow C_6H_5SO_2{\cdot}C_6H_5$$

178. Unsaturated Hydrocarbons are readily attacked by sulphuric acid and the chemical reactions involved are of great importance and significance in the acid refining of cracked spirits. Straight-run spirits do not, normally, contain anything more than a trace of unsaturated hydrocarbons.

Prior to 1914 little was known regarding the mechanism of the reaction of sulphuric acid with unsaturated hydrocarbons, but during that year Brooks and Humphrey[45] inquired into the subject in some detail, with the following results.

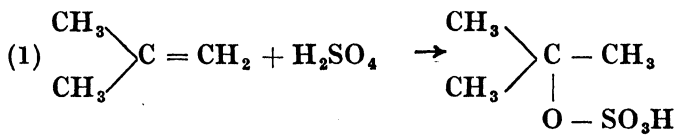
(*a*) The principal effects of acid treatment are polymerisation, formation of secondary and tertiary alcohols, and mono- and di-alkyl esters.

(*b*) The tendency of the unsaturateds to polymerise increases with increasing molecular weight.

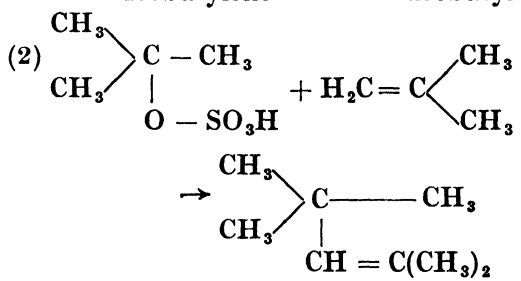
(*c*) The polymerisation products formed are more stable towards sulphuric acid than the parent hydrocarbons and are generally found dissolved in the oil. A polymer formed from two molecules of a mono-olefine contains only one double bond.

(*d*) Di-olefines form tars with sulphuric acid, but the mono-olefines do not react in this way.

The generally accepted theory of the polymerisation of unsaturated hydrocarbons by the action of sulphuric acid is that it proceeds through the intermediate formation of an acid alkyl ester, thus :

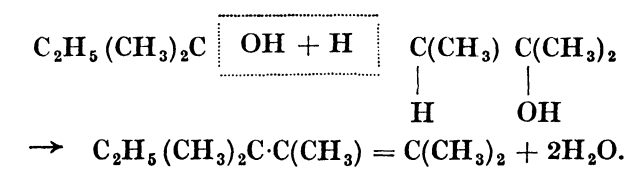


Isobutylene Isobutyl sulphuric acid



Di-isobutylene

but this is not borne out by the results obtained by Norris and Joubert.[46] These authors, working with the five possible pentenes, found that polymerisation takes place with four of the five more readily when the acid ester is not formed, and that it probably results from the removal of water from the alcohol first produced. Four pentenes were found to pass completely into solution either as alcohol or ester before polymerisation began. The formation of the di-polymer from trimethyl ethylene is explained on this basis as follows :—



When a secondary alcohol is formed by the action of the acid, more concentrated acid is required to bring about polymerisation than if a tertiary alcohol is formed. This is not surprising as tertiary alcohols are more easily formed and decomposed than the corresponding secondary alcohols.

179. The extent to which polymerisation occurs is largely dependent upon the concentration of acid employed, concentrated acid giving a higher polymer than acid of lower concentration. Di-olefines polymerise much more rapidly than mono-olefines and the polymerisation occurs to a greater extent. They are, moreover, readily polymerised by dilute acid. Thus, when cracked spirit containing di-olefines is treated with sulphuric acid, they are at once polymerised with the more reactive mono-olefines and are partly eliminated on subsequent distillation.

It is the generally accepted opinion that the removal of di-olefines from cracked spirits is necessary because of their gum-forming properties (see Chapter XIII, Volume II), but, on the other hand, most of these hydrocarbons have valuable anti-knock properties, e.g., butadiene and α-γ-dimethylbutadiene.[36] This, of course, partly explains the fall in anti-knock quality when vapour-phase cracked distillates are acid treated, although the removal of certain mono-olefines, such as tri- and tetra-methyl ethylene, also has this effect.

The common supposition that the polymers of olefines act as pro-knock agents is quite unfounded. Thus, the di-polymers of isobutylene and tri-methyl ethylene have been shown to have valuable anti-knock qualities.[47, 48]

180. The formation of mono- and di-alkyl esters by the action of sulphuric acid on unsaturated hydrocarbons has a special significance. Alkyl sulphuric acids remain in the acid layer, but the alkyl sulphuric esters are partly dissolved in the oil being treated. Of these, the di-alkyl esters $\begin{matrix}RO\\RO\end{matrix}\!\!>SO_2$ are, of course, neutral and are not removed by washing with aqueous alkalies. They become decomposed when the treated spirit is distilled and, in the presence of steam, become hydrolysed to very corrosive free acids. It is therefore essential that a cracked distillate should receive a thorough water wash and soda treatment both prior to and after distillation, in sulphuric acid refining. Mono-alkyl sulphuric esters are removed by water washing and caustic treatment.

181. The Action of Sulphuric Acid on Asphaltic Material and Colouring Matter Present in the Oil, either in Solution or in Colloidal Suspension.—Probably the first action that occurs when sulphuric acid is brought into contact with crude spirits is the flocculation of colloidally dispersed colouring matter. Chemical action with the asphaltic material present in the spirit also occurs. Such chemical and physical actions are of far greater importance in the refining of oils heavier than light distillates and may be dismissed from further consideration.

182. The Action of Sulphuric Acid on Sulphur Compounds.—Perhaps the most useful application of sulphuric acid in the refining of light distillates is in the removal of sulphur compounds.

When spirits containing hydrogen sulphide are treated with concentrated sulphuric acid, the hydrogen sulphide is oxidised to elemental sulphur and water. Sulphuric acid has no action on elemental sulphur. This fact again emphasizes the need for hydrogen sulphide removal as a

preliminary to any refining scheme, as the presence of elemental sulphur renders a spirit very corrosive. Furthermore, it can only be removed with some difficulty and expense.

183. Thiophenes.—Sulphuric acid reacts with most thiophenes to form thiophene sulphuric acids, but tetramethyl thiophene is merely dissolved by this reagent. Thiophenes are unattacked by hypochlorite solutions, by caustic soda, by Fuller's earth or other normal refining agents, and sulphuric acid treatment is the only practical method, excluding hydrogenation, by which they may be removed from light oils.

184. Mercaptans.—It has been shown by Wood, Sheeley and Trusty[49] that 98 per cent. sulphuric acid oxidises mercaptans to disulphides, although acid of lower concentration has no oxidising action. Sulphur dioxide is formed simultaneously. Fuming sulphuric acid has an even greater oxidising effect, chiefly because it does not so soon fall below the concentration at which the acid becomes ineffective. Probably small amounts of disulphoxides are also formed. The action of sulphuric acid on mercaptans has also been studied by Birch and Norris,[50] who have pointed out that with small amounts of sulphuric acid conversion to disulphides is incomplete. If, after refining with small amounts of acid, the spirit is washed with soda, then the total result is a lowering of the sulphur content, since the soda partially removes the residual mercaptans left after the acid wash. When larger amounts of acid are used, the conversion of mercaptan into disulphides is more nearly complete, subsequent soda washing has no effect on the disulphides formed and the net result is that the sulphur content is not appreciably reduced. But when even greater amounts of sulphuric acid are employed, the sulphur content is reduced, because of the solvent action of the sulphuric acid upon the disulphides produced. Birch and Norris also found that in the case of certain mercaptans, sulphuric acid treatment causes the formation of traces of corrosive polysulphides (almost certainly trisulphides). The production of such compounds in normal acid refining processes is, however, very slight, and may be disregarded in the case of distillates sweetened by plumbite prior to acid treatment.

185. Disulphides.—Sulphuric acid dissolves disulphides, but very little chemical reaction takes place. This solvent action decreases rapidly with dilution of the acid and with increasing molecular weight of the disulphide. The oxidising action is slightly greater than with sulphides. Free sulphur is not formed by the action of sulphuric acid on either sulphides or disulphides.

186. Sulphides.—It has been found[51] that although alkyl sulphides of low molecular weight and also secondary sulphides are readily

removed from light distillates by a purely solvent action of sulphuric acid, the higher sulphides, e.g., diphenyl and dibenzyl sulphides, are much less readily extracted. Fuming sulphuric acid exerts a greater solvent action. Unsaturated alkyl sulphides are very easily dissolved by sulphuric acid.

187. Sulphoxides and Sulphones.—These are removed unchanged by the solvent action of sulphuric acid and may be recovered therefrom by diluting the acid ; a convenient method of isolation adopted, for example, by Thierry.[52]

The action of sulphuric acid on the various sulphur compounds present in light distillates is summarised in Table 5.

TABLE 5. THE ACTION OF SULPHURIC ACID ON VARIOUS SULPHUR COMPOUNDS (BIRCH AND NORRIS)

Compound	Product in Oil Layer	Product in Acid Layer
Hydrogen sulphide, H_2S	Elemental sulphur.	———
Mercaptan, RSH	Disulphide, R_2S_2.	$R_2S_2O_3$.
	(Trisulphide, R_2S_3).	(RSO_3H?).
Sulphide, R_2S	———	Sulphide, R_2S.
Disulphide, R_2S_2	———	Disulphide, R_2S_2.
Elemental sulphur, S ..	Elemental sulphur, S.	———
Sulphoxide, R_2SO ..	———	Sulphoxide, R_2SO.
Sulphone, R_2SO_2	———	Sulphone, R_2SO_2.
Alkyl sulphate, R_2SO_4 ..	———	Alkyl sulphate, R_2SO_4.

188. Sulphuric Acid Refining Practice.—Sulphuric acid refining of light distillates is popularly considered to be a wasteful, uneconomic and troublesome process, but, because it is wasteful when applied to one particular distillate, it does not necessarily follow that it is wasteful on another distillate. It may be said at once that concentrated sulphuric acid is not generally suitable for the treatment of light distillates containing large amounts of unsaturated hydrocarbons, nor yet is it to be desired in the treatment of benzoles where the finished spirits are to be used for blending with other stocks for the production of motor fuels. However, contrary to general belief, sulphuric acid may be satisfactorily applied to the refining of liquid-phase cracked spirits, but the refining operation must be scientifically and accurately controlled. In one or two cases, sulphuric acid is satisfactorily employed for the refining of vapour-phase cracked spirits.

Successful refining of light distillates by means of sulphuric acid is only possible when due regard is paid to the following variables :—

(*a*) Amount of acid used,

(*b*) Strength of acid used,

(*c*) Degree of agitation,
(*d*) Time of contact,
(*e*) Settling time,
(*f*) Temperature,
(*g*) Treatment after acid washing,

and a number of other factors. Each of these variables will now be considered separately.

189. (a) Amount of Acid Used.—Straight-run spirits may be effectively refined with very small amounts of sulphuric acid, but, generally, cracked spirits require treatment with larger quantities. Cracked spirits often contain larger amounts of sulphur compounds than straight-run spirits and frequently trouble is met in bringing the sulphur content down to the maximum permissible limit, which in the United States is 0·1 per cent. Large amounts of sulphuric acid are necessary to achieve this and heavy refining losses are, therefore, often experienced. This is the reason why sulphuric acid refining lost much of its popularity when cracked spirits were first produced.

TABLE 6. EQUIVALENT QUANTITIES OF SULPHURIC ACID REQUIRED FOR TREATING
(Refers to sulphuric acid of 93·2% strength, $d = 1{\cdot}835$, 66°Bé.)

% by Volume	Ml. per Imp. gallon	Ml. per U.S. gallon	Pounds per barrel of 42 U.S. gallons = 35 Imp. gallons
0·1	4·5	3·79	0·644
0·2	9·0	7·58	1·288
0·3	13·5	11·37	1·932
0·4	18·0	15·16	2·576
0·5	22·5	18·95	3·220
0·6	27·0	22·74	3·864
0·7	31·5	26·53	4·408
0·8	36·0	30·32	5·152
0·9	40·5	34·11	5·796
1·0	45·0	37·9	6·44
1·5	67·5	46·8	9·66
2·0	90·0	75·8	12·88
2·5	112·5	94·8	16·10
3·0	135·0	113·7	19·32
3·5	157·5	132·7	22·54

Straight-run spirits are treated with quite small amounts of sulphuric acid, e.g., from 0·1 to 2·0 per cent. by volume of concentrated (97 per cent.) acid (C.O.V.). In the case of these products, refining is relatively simple, as there are not more than traces of unsaturated hydrocarbons present. Some straight-run gasolines, however, require heavier treatment because of their high sulphur content. Thus, straight-run gasolines from Winkler county (Texas) crude, which contain 0·16 per cent.

sulphur (in the form of organic sulphur compounds) and which are very corrosive, are treated with two separate portions of sulphuric acid; firstly with 0·3 per cent. of concentrated acid and then, after separation of the acid sludge, with 0·5 per cent. of fresh acid. Faragher and Morrell[53] have described the refining of Muskegon crude oil, in which the spirit fraction, although containing only 0·02% sulphur, could not be sweetened with either hypochlorite, blowing with air in the presence of plumbite and lead sulphide sludge, or normal acid treatment. Eventually it was found that by blending this spirit with a cracked pressure distillate, and by refining the blend with plumbite followed by sulphuric acid (0·5 per cent. by volume of acid) a satisfactory refined product could be obtained.

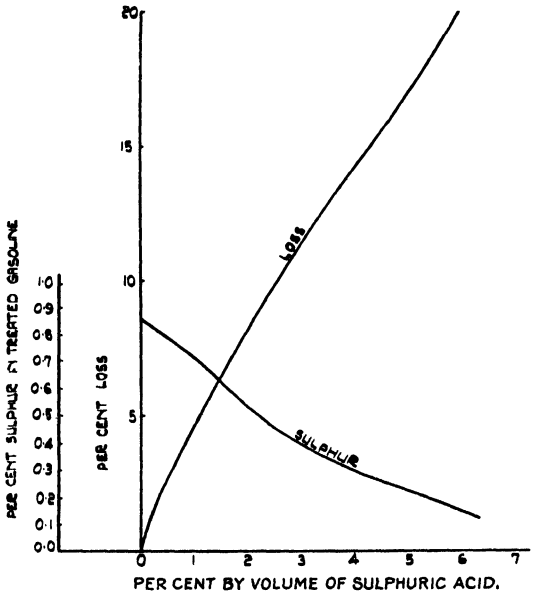


Fig. 5.—Diagram showing the Amount of Sulphuric Acid required to Refine Cracked Distillates

190. Care must be exercised in the treatment of cracked distillates to avoid losses. As already mentioned, polymerisation accounts for a large part of these losses. Fig. 5 shows the average volume losses incurred when a typical liquid-phase cracked spirit is refined by sulphuric acid treatment and the amount of sulphuric acid usually required to reduce the sulphur content to the permissible maximum, when the acid is used in the conventional manner.

The refining effect of sulphuric acid increases with the amount of sulphuric acid used, but is not proportional to it, increasing much more slowly, as shown in the following figures of Trusty,[54] referring to gum stability.

TABLE 7. EFFECT OF QUANTITY OF SULPHURIC ACID USED ON THE PROPERTIES OF THE FINISHED SPIRIT

Acid. Lbs./bbl. oil	Colour of finished Spirit (Saybolt)	Potential Gum Content of finished Spirit. Mgs./100 mls.
0	8	274
1	16	268
2	17	243
3	21	196
5	25	143
6	27	92
9	22	46
10	21	22
15	20	12
20	20	3
40	20	0

On the other hand, there appears to be evidence that the use of either insufficient or excess acid results in a poor colour of the finished product, particularly in the case of vapour-phase cracked spirits.

TABLE 8. THE EFFECT OF THE QUANTITY OF SULPHURIC ACID USED IN THE REFINING OF DUBBS CRACKED SPIRIT ON THE PROPERTIES OF THE FINISHED SPIRIT (POTTHOFF)

Pounds of Acid per barrel	Sludge Loss %	Polymer Loss %	Total Loss %	c.c. Tetra-ethyl Lead per U.S. gallon	Benzole Equivalent	Octane Number
0	0	0	0	0·1	47	73
2	1·0	0·6	1·6	0·2	46	72
5	1·8	1·0	2·8	0·4	45	70
10	3·5	1·8	5·3	0·5	44	69
20	8·0	3·3	11·3	1·3	33	64
50	15·3	6·3	21·6	2·5	27	51

A.S.T.M. DISTILLATIONS

Pounds of acid per bbl.	0	2	5	10	20	50
Specific gravity	0·749	0·749	0·749	0·75	0·753	0·754
Gravity °A.P.I.	57·3	57·3	57·3	57·0	56·6	56·1
I.B.P. °F.	98	100	101	106	105	104
10% Distillate at °F.	148	148	152	158	163	166
20%	180	182	185	187	195	198
30%	209	210	212	214	223	230
40%	235	236	239	239	250	250
50%	259	260	263	264	273	281
60%	282	284	286	284	294	301
70%	300	306	309	307	312	327
80%	334	336	335	338	340	346
90%	367	362	361	361	368	372
End Point	399	397	405	410	405	404
Colour (Saybolt)	16	20	25	25+	25	24
Copper dish gum content (mgs/100 mls)	370	219	140	24	63	59

191. Details regarding the effect of various amounts of sulphuric acid in the refining of a 405°F. (207°C.) end point spirit, obtained by cracking in a Dubbs plant, have been published by Potthoff,[55] whose results are summarised in Table 8. An inspection of the data indicates that the refining loss reaches a considerable magnitude as the amount of acid used exceeds 5 pounds per barrel. The ratio between the sludge (or solution) loss and the so-called polymerisation loss decreases as the amount of acid used is increased. The loss in anti-knock value becomes excessive when more than 10 pounds of acid per barrel is used. Using this amount of acid, the direct loss in anti-knock value may be assumed to be the cost of the tetra-ethyl lead required to raise the anti-knock value back to its original figure. At 0·35 cents per ml. per U.S. gallon, this is equivalent to $(0{\cdot}5 - 0{\cdot}1) \times 0{\cdot}35 \times 42 = 5{\cdot}88$ cents per barrel. The effect of the acid in raising the boiling range of the treated spirit (due to polymerisation reactions) is apparent from the distillation data.

192. Fractional Addition of Acid.—A better refining action is often obtained if the acid is divided into several portions, settling being allowed and the acid sludge separated after each addition, than if all the acid is added at once. This point is of particular importance when oleum is used as the refining agent. A further advantage is that an economy in acid consumption is obtained. It seems probable that the action of sulphuric acid on asphaltic substances and unsaturated compounds of high molecular weight may take place in several phases, and that at the commencement of this action reaction products are separated from the oil and that these react further with any excess of acid present. It has been observed, in the refining of some hydrocarbon fractions, that, by the addition of a very small amount of sulphuric acid, a very feebly acid sludge is separated, by far the greater part of which is soluble in benzene, but when this sludge is treated further with acid it reacts with the latter and entirely loses its solubility in benzene. The same sludge, insoluble in benzene, is also formed when a light distillate is at once treated with a large amount of acid. The circumstances that the acid sludge formed at the commencement dilutes the further supplies of acid and thus influences their action must also be taken into account.

In the case of light distillates containing water (and most distillates do contain a certain amount of water after being treated with aqueous reagents, such as plumbite, etc.), the fractional addition of acid is often practised. Acid sludge is generally employed for the first treatment and merely acts as a dehydrating agent. This obviously effects an economy in acid consumption.

193. (b) Strength of Sulphuric Acid Used.—The stronger the acid employed in the refining of a hydrocarbon oil, the greater the degree of refining obtained and also the greater the refining loss experienced.

The production of entirely colourless and saturated water-white oils, without taste or smell (e.g., paraffinum liquidum, white oils, etc.), is well known to be almost impossible with ordinary concentrated sulphuric acid and oleum is often used. 100 per cent. sulphuric acid is far more drastic in its action than 90 per cent. acid.

The usual strengths of sulphuric acid employed are as follows :—

(1) 20% oleum.
(2) 98% acid. Sp. gr. 1·84. Degrees Bé = 78·8
(3) 93·2% acid. Sp. gr. 1·835. Degrees Bé = 66·0
(4) 77·7% acid. Sp. gr. 1·706. Degrees Bé = 60·0

the stronger acids being generally used in treating straight-run products and the weaker acids in treating cracked spirits. As a rule, acid as dilute as 77% (sp. gr. 1·7) is too weak for ordinary refinery use ; acids between 98% and 77% (1·84–1·7) have freezing points so high that they are not suitable for cold climates, and 98% acid (1·84 sp. gr.) is the weakest grade customarily used. Acid stronger than 98 per cent. will not reduce the sulphur content of the finished spirit below a point attainable with larger quantities of 98 per cent. acid and extracts an unduly large proportion of desirable constituents, as well as having a tendency to give a spirit unstable to light and of high gum content. There is no doubt that 98 per cent. acid is a more effective treating agent than 93 per cent. acid, but the stronger grade leaves in the treated distillate, even after a caustic wash, compounds (probably di-alkyl sulphates) which evolve free acid on rerunning and thereby cause corrosion of rerun stills, condensers and coolers, rundown lines, etc.

194. Sometimes it is a distinct advantage, in the case of spirits which react very vigorously with sulphuric acid, to give a preliminary wash with 1·7 sp. gr. sulphuric acid, in order to remove the more reactive hydrocarbons before contacting the spirit with concentrated acid. This also facilitates the handling of the acid sludge which, in this case, is more fluid and is not so liable to get held up in agitators, mixing vessels, pipes, etc. Such a method has been described for the refining of vapour-phase cracked spirits by Retailliau,[56] who first of all removes the most unstable unsaturated hydrocarbons by means of 30 per cent. acid. This does not cause any appreciable evolution of heat and does not remove useful components. Furthermore, it makes the subsequent treatment with a stronger acid (in this particular case, 75 per cent. acid) less violent and thus diminishes local overheating, thereby reducing polymerisation of the useful components. The amounts of acid used by Retailliau are 1·4 lbs. per barrel of the weaker acid and 3–12 lbs. per barrel of the stronger acid.

Besides this removal of the most unstable unsaturateds, a dilute

sulphuric acid solution has also the advantage of removing organic nitrogen bases which may be present and which are objectionable in the finished product, because they are of bad odour and cause poor colour stability. When no dilute acid is used, the nitrogen bases may not be entirely removed by the acid because, as Retailliau has remarked, the latter causes almost instantly the formation of polymerised material, which forms a protective film around the small acid globules which decreases their refining action. Large amounts of concentrated acid remove these bases entirely, but it is obviously advantageous for economical reasons to use the smallest amount possible.

195. (c) Degree of Agitation.—Arrangements must be made for the efficient contacting of acid and spirit, for if the agitation or mixing is poor, larger amounts of acid will be required to obtain the required refining action and, moreover, side reactions will be facilitated by local overheating. The advantages of orifice mixers, dispersion contactors and centrifugal pumps over the older agitators are obvious in this connection. These are described later.

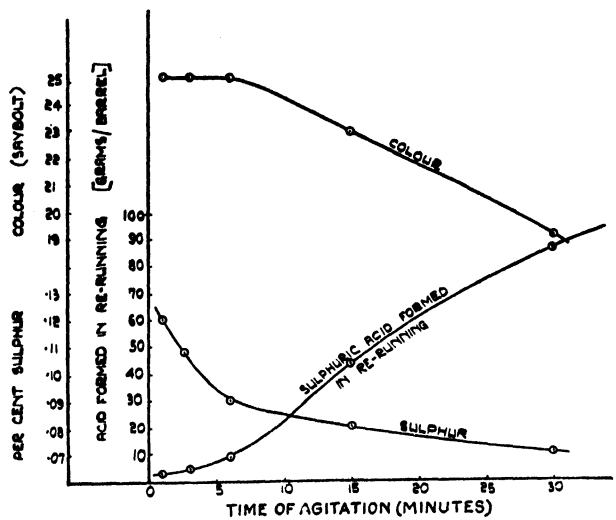


FIG. 6.—CURVES SHOWING THE EFFECT OF TIME OF CONTACT IN THE ACID REFINING OF CRACKED DISTILLATES (TRUSTY AND PIERCE)

196. (d) Time of Contact between the Acid and the Oil.—Careful regulation of the time of sulphuric acid treatment is important for several reasons. The ability of the sulphuric acid to react with and destroy desirable hydrocarbon constituents continues after the sulphur removing power of the acid has been exhausted, consequently, to avoid excessive treating losses, the distillate should be exposed to the action of the acid no longer than is necessary to reduce the sulphur content to the desired point. Furthermore, increased time of contact leads to the formation

of alkyl sulphates which increase the sulphur content of the treated spirit and which decompose with the formation of free acids on subsequent distillation. Excessive time of contact between the acid and the oil being treated often causes a poor colour in the finished product. On the other hand, increase in time of contact causes a progressive increase in the amount of sulphur removed. Generally, however, this is poor compensation for the larger refining losses experienced. The effect of time of contact upon the properties of the refined spirits produced is shown in Fig. 6, which is reproduced from the published work of Trusty[57] and of Pierce.[58]

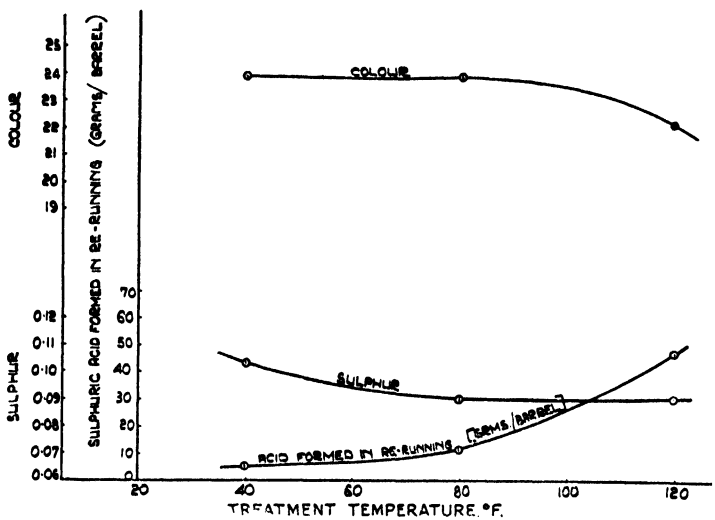


FIG. 7.—CURVES SHOWING THE EFFECT OF TEMPERATURE IN THE ACID REFINING OF CRACKED DISTILLATES (TRUSTY & PIERCE)

197. (e) **Settling Time.**—In view of the cost of neutralising acid-treated distillate, it is very natural to assume that the longer the settling time allowed for the acid to disengage itself from the oil the lower would be the neutralisation costs and the better the results on subsequent distillation. This, however, is not the case, for an increase in settling time produces the same undesirable effects as an increase in time of treating, i.e., loss of colour, higher production of dialkyl sulphates and increased amount of corrosive acids formed in subsequent distillation. The last of these undesirable effects causes an increase in the cost of neutralising agents necessary to destroy the acids formed.

198. (f) **The Effect of Temperature.**—The effect of temperature on the reactions which take place between a light distillate and sulphuric acid is very marked, the reactions increasing in speed and in extent to a remarkable degree with a slight rise in temperature. This is generally

a disadvantage. During cold weather periods, it is often noticed that there is a general improvement in the colour of rerun spirit and a general tendency towards a reduction in the cost of neutralising the rerun spirit. Pierce (*loc. cit.*) has quoted the results obtained on treating a cracked spirit with sulphuric acid at temperatures of 40°, 80° and 120°F. (4·5°, 26·5° and 49°C.), other conditions being constant throughout. His results are reproduced in Fig. 7, and show that, in the case of the particular spirit examined, good finished colour was obtained at temperatures up to 80°F., but that, at higher temperatures, the finished colours were not so satisfactory and the amount of corrosive acid formed in rerunning was increased. On the other hand, the amount of sulphur removed increased as the treatment temperature was raised. No figures for the treating losses sustained were given.

The use of low temperatures for sulphuric acid refining has been advocated by many workers, particularly by Halloran[59] and by Klemgard,[60] who claim that very low refining losses are obtained, while sulphur contents are satisfactorily reduced. The following comparison of the results obtained at ordinary temperatures and at a temperature of 0°F. (−18°C.), in the treatment of a cracked spirit, has been given by Klemgard.

	Low Temperature	Ordinary Temperature
Refining Loss (% by volume)	4·0	16·7
Doctor Test	Neg. (usually).	Positive.
Copper Dish Corrosion Test	Fair.	Poor.
Copper Dish Gum Test	Little Gum.	84 mgs./100 mls.
Colour (Saybolt) ..	25+	25+
Sulphur %	0·09	0·14
Unsaturateds % ..	20·0	17·0

The principle involved in the use of sulphuric acid at subnormal temperatures is that, under these conditions, the ease with which the acid reacts with unsaturated hydrocarbons is reduced to a greater extent than the ease with which it attacks sulphur compounds. In this way polymerisation losses are reduced. A further point of interest is that at low temperatures it is claimed that sulphuric acid exerts a purely solvent action on sulphur compounds and does not react with them in a chemical sense.

199. Much information regarding the effect of temperature in the acid refining of cracked spirits is given in *E. P.*, 301,450 of the Standard Oil Company of California, dated September 5, 1929,* and reference

* See also *U. S. P.*, 1,869,885, August 2, 1932.

should be made to this patent for further information. Of particular interest, however, is the graph reproduced from this patent, shown in Fig. 8. This refers to the treatment of a cracked distillate with sulphuric acid of specific gravity 1·84 (60° Beaumé), in order to reduce the sulphur content to 0·15 per cent. It will be noted that as the maximum treating temperature is decreased from 140°F. (60°C.) to 28°F. (−2·2°C.), the amount of acid required also decreases, but, at lower temperatures, larger amounts of acid are required. This increase in acid requirements at the very low temperatures may probably be due to the increased viscosity of the acid when its freezing point is approached. The figure also shows that the yield of spirit increases from about 63·5 per cent., at a maximum treating temperature of 140°F. (60°C.) to about 75·5% at a temperature of 5° to 20°F. (−15°C. to −6·5°C.).

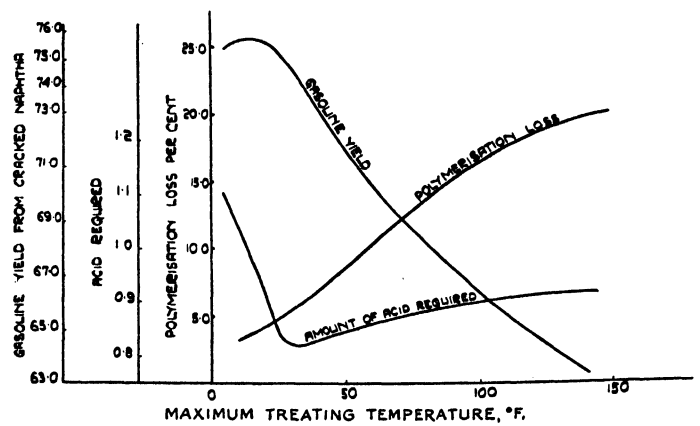


FIG. 8.—CURVES SHOWING THE EFFECT OF TREATING TEMPERATURE IN PRODUCING A SPIRIT OF 0·15% SULPHUR CONTENT FROM A CRACKED DISTILLATE

(Courtesy of Controller, H.M. Stationery Office)

The polymerisation loss is markedly reduced by operation at lower temperatures and falls from about 19 per cent. at 140°F. (60°C.) to about 3 per cent. at 5°F. (−15°C.). These curves show that the optimum treating temperature for maximum gasoline yield for the particular naphtha employed, using 1·84 sp. gr. sulphuric acid, is about 15° to 20°F. (−9·5° to −6·5°C.). For minimum acid requirements, the optimum temperature is between 25° and 30°F. (−4° and −1·5°C.). The true optimum temperature is determined by the balance between the cost of the acid, the cost of refrigeration (which progressively increases as the temperature is reduced) and the increased yields of spirit.

A diagrammatic representation of the plant used in acid treating at low temperatures is shown in Fig. 9.

The low-temperature sulphuric acid treatment process has recently

been combined with the Stratford process which involves a continuous treatment by quickly contacting the acid with the oil and separating the acid sludge by centrifuging. The Stratford process is dealt with later—see paragraph 219.

200. (g) Treatment after Acid Washing.—The success or failure achieved in acid refining, particularly when applied to cracked distillates, is largely determined by the treatment given to the spirit after acid washing. It has already been shown that acid treatment often leads to the presence of mono-alkyl and di-alkyl sulphates in the treated oil. Furthermore, unstable polymerised unsaturated hydrocarbons are formed and, even after prolonged settling, the oil contains a certain amount of suspended acid particles. These various impurities must be removed if a colourless and stable product is required.

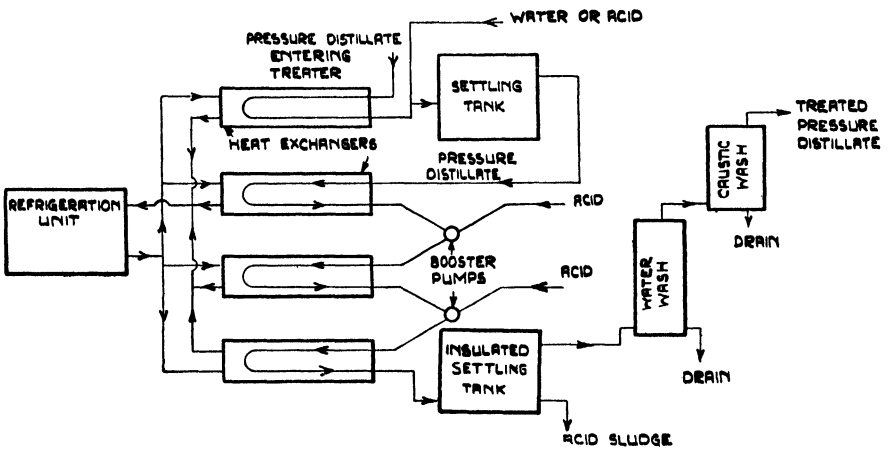


FIG. 9.—DIAGRAMMATIC FLOW SHEET OF LOW TEMPERATURE SULPHURIC ACID TREATMENT PROCESS

After removing suspended acid particles (so-called " pepper "), it is customary to wash acid-treated distillates with water to remove water-soluble acid products as far as possible, and then to wash thoroughly with caustic soda to remove mono-alkyl sulphates and acidic bodies not completely removed by water. The spirits are then distilled at as low a temperature as possible, or in the presence of large quantities of steam (in order to avoid decomposition) to remove high boiling polymerised material. The treatment is then concluded by an alkali wash to remove acidic bodies, such as sulphur dioxide and sulphuric acid, formed by decomposition in the distillation.

With regard to the water wash after acid treatment, this should preferably be done thoroughly as it leads to an economy in the subsequent soda treatment. The strength of caustic soda used in the neutralising treatment before rerunning should, preferably, be about 3–

4 per cent. by weight (6° Beaumé). There is usually no advantage in using stronger solutions, but it has been shown that, in some cases, an advantage is obtained by using caustic soda of 23·6–28·5% strength (30—35° Beaumé), which is said to remove dialkyl sulphuric esters.[61]

With regard to the effect of the storage time that elapses between neutralisation and rerunning, it has sometimes been observed[58] that the longer the spirit is allowed to stand between these two operations, the better the colour of the finished material and the smaller the amount of acid formed during rerunning. Little information on this point is available, but the effect may be due to the fact that the small quantities of caustic soda remaining associated with the spirit after washing with this reagent exert a stabilising effect upon it and have a slow action on dissolved alkyl sulphates.

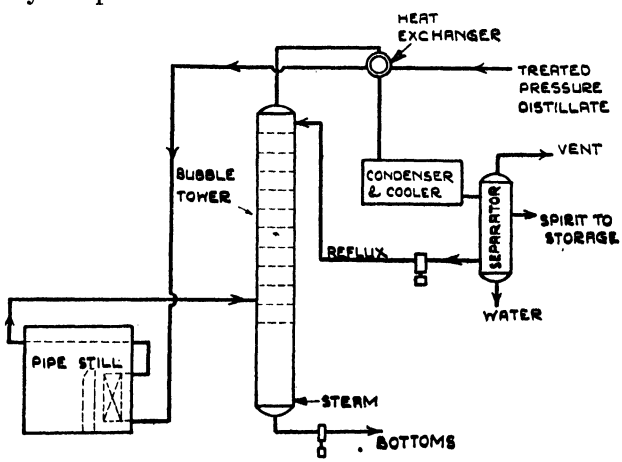


FIG. 10.—FLOW DIAGRAM OF ATMOSPHERIC SINGLE-FLASH PIPE STILL RERUN UNIT

201. In the rerunning operation, it is desirable to operate at as low a temperature as possible because the decomposition of alkyl sulphates is accelerated by high temperatures. Pronounced decomposition may take place at temperatures as low as 175°–200°F. (79·5°–93·5°C.), as shown by the following figures.

TABLE 9. DECOMPOSITION OF TREATED PRESSURE DISTILLATE DURING RERUNNING [58]

Liquid Temperature					
°F. ..	150	200	225	250	300
°C. ..	65·6	93·3	107·2	121·1	148·9
Colour following test	Yellow	Red	Dark	Dark red	Black
Sulphur dioxide liberated (grams per litre of oil)	None	0·0395	0·0398	0·079	0·316
Coke or tarry material	None	None	Trace very slight	Trace slight	Trace slight

Low operating temperatures are obtained by the use of liberal amounts of steam, or, if economy in steam is required, by the use of vacuum.

In the rerunning of acid-treated cracked distillates or so-called treated pressure distillates, three general types of plant are employed, depending upon special requirements. These are

(1) Atmospheric single-flash units,
(2) Atmospheric recycle units,
(3) Combined atmospheric vacuum units.

202. Atmospheric Single-Flash Units.—These are used when it is permissible to heat the treated distillates to temperatures up to 375°F.

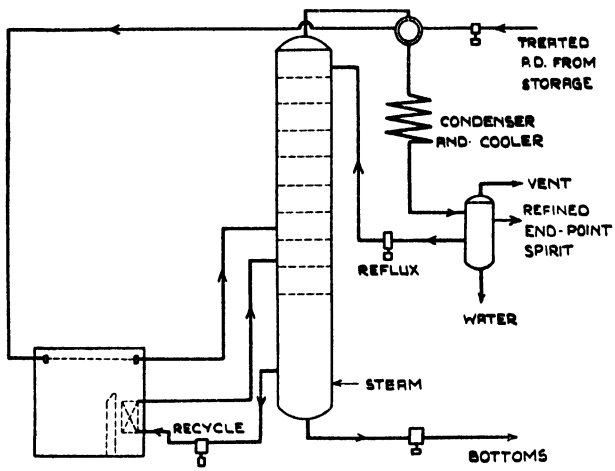


FIG. 11.—FLOW DIAGRAM OF ATMOSPHERIC RECYCLE PIPE STILL RERUN UNIT

(190·6°C.), the temperature necessary to flash off the required amount of material. The heating element of the pipe still is designed with the heating surface so proportioned that excessive film temperatures are avoided in the radiant heat section as much as possible, but this type of unit is not capable of giving such a high degree of colour stability as either of the two other types of equipment. On the other hand, this type of unit has the lowest initial cost compared with the other units, is the most simple to operate and the least expensive to maintain, but its flexibility is somewhat limited. The arrangement is shown in Fig 10.

203. Atmospheric Recycle Units.—These have the advantage of operating at lower flash temperatures than the previous type. The bottoms from the first flashed charge are recycled through the heater and heated to the same temperature as the original charge. Stripping of the bottoms is accomplished by the introduction of steam. A diagrammatic flow sheet of this type of unit is shown in Fig. 11.

204. Atmospheric Vacuum Units.—This type of installation avoids extreme temperatures in the process at all times and makes use of either direct or indirect heating, the latter being used on pressure distillates particularly prone to decomposition. Distillation curves on the products obtained from a typical installation of this type are shown in Fig. 13, while a diagrammatic flow sheet showing the operation of the process is reproduced in Fig. 12.

TABLE 10. TECHNICAL DATA FOR OPERATING RERUN UNITS WHEN PRODUCING 392°F. (200°C.) END POINT GASOLINE*

Type of Unit	Single Flash	Recycle	Atmospheric Vacuum
Temperatures °F.			
Charge to vapour exchanger	70	70	70
Charge to pipe still (to steam heater on vacuum unit)	225	225	200
Charge from pipe still (from steam heater on vacuum unit)	375	325	275
Atmospheric flash temperatures	365	325	275
Recycle to pipe still	—	300	—
Recycle from pipe still	—	325	—
Bottoms from atmospheric tower	300	300	275
Top of atmospheric tower	275	255	240
Exhaust steam to atmospheric tower	365	325	275
Vacuum charge to heater	—	—	275
Vacuum charge from heater	—	—	275
Top of vacuum tower	—	—	190
Bottoms from vacuum tower	—	—	275
Exhaust steam to vacuum tower	—	—	275
Pressures.			
Top of vacuum columns	—	—	80 mm.
Utility Requirements.			
Vaporiser section of vacuum column	—	—	85 mm.
Steam to atmospheric tower (lbs./bbl. charge)	5·8	30·2	21·2
Steam to vacuum tower (lbs./bbl. charge)	—	—	2·5
Total exhaust steam.	5·8	30·2	23·7
Steam to fuel oil burners (lbs./bbl. charge)	3·08	2·32	—
Steam to pumps (lbs./bbl. charge)	16·20	22·80	18·1
Steam to ejectors do.	—	—	5·2
Total live steam.	19·28	25·12	23·3†
Cooling water (gallons/bbl. charge)	130	198	209
Heat developed by pipe still (B.T.U./bbl. charge)	5,780	4,340	3,520

† Steam for heating not included.

* *National Petroleum News*, 1931, **23**, (49), 33

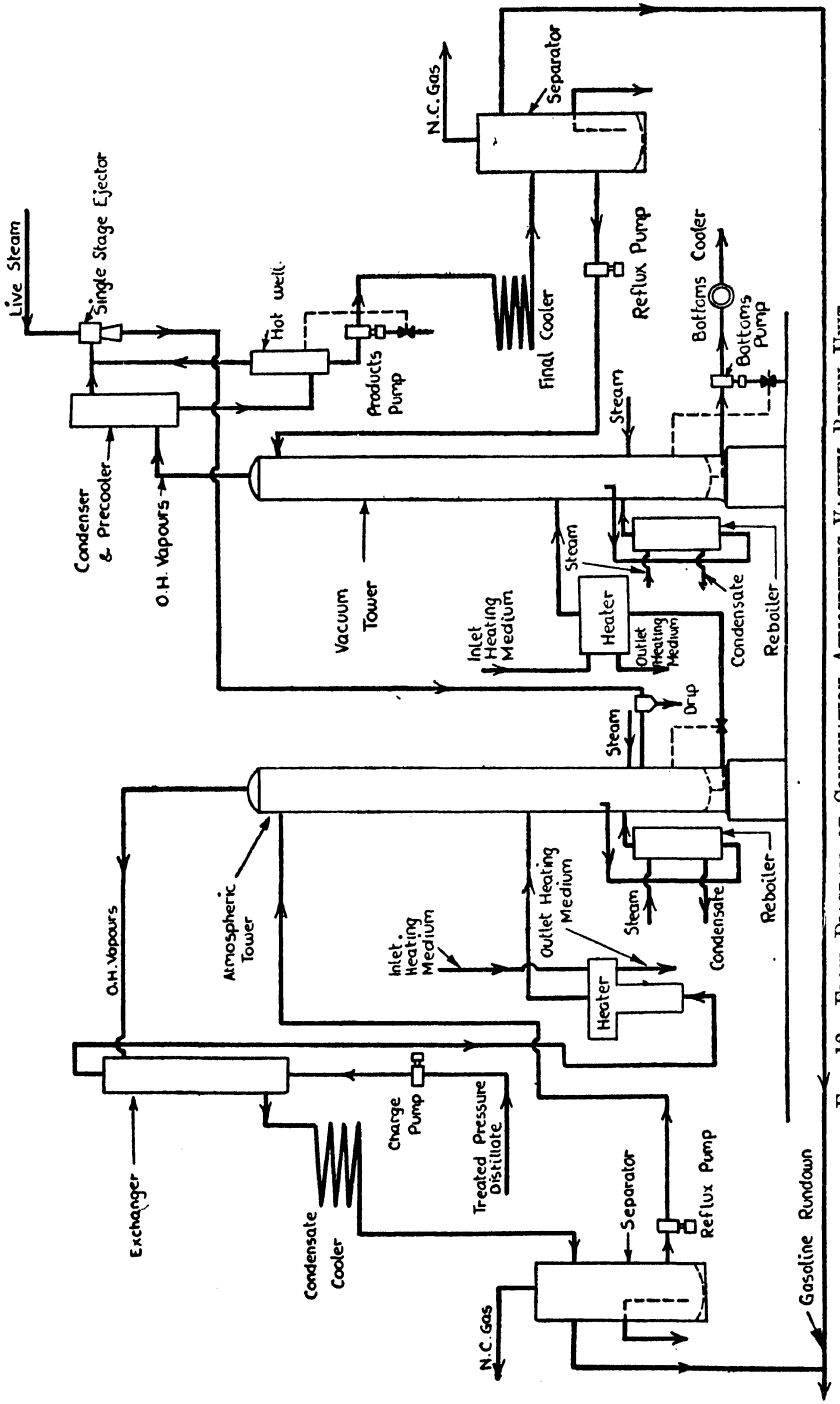


FIG. 12.—FLOW DIAGRAM OF COMBINATION ATMOSPHERIC VACUUM REBURN UNIT

205. Neutralisation after Acid Treatment by Means of Earths and Clays.—A modification of the normal acid and soda process for the refining of cracked spirits which appears to offer possibilities, is the use of adsorbent earths and clays instead of caustic soda to effect neutralisation after acid treatment. This modification often obviates the need for rerunning, but is not widely practised.

Such a process was first described by Egloff and Morrell[62] in 1923. Cracked spirit was treated with 93·2% (66°Bé) sulphuric acid in the usual way, the acid sludge allowed to settle and then drawn off. The acid-treated spirit was then filtered through a bed of roasted Fuller's earth (about 30 mesh) in order to neutralise any suspended acid particles and in order to adsorb any coloured matter present, after which it was steam distilled. The product obtained was stated to be " marketable gasoline passing specifications."

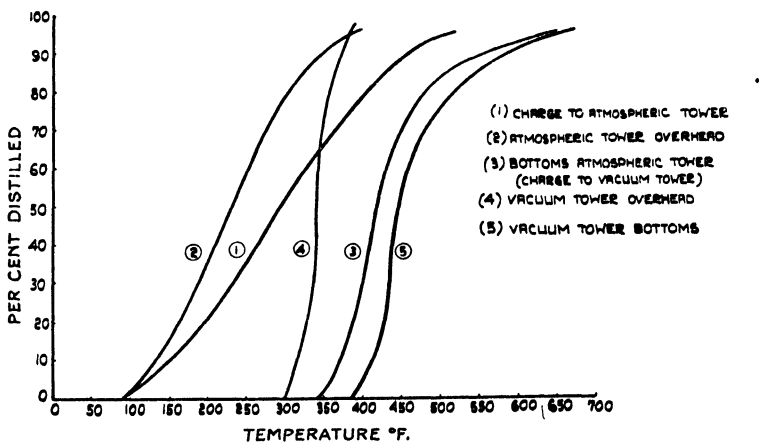


FIG. 13.—DISTILLATION CURVES—ATMOSPHERIC VACUUM RERUN UNIT (McKEE & Co.)

In such a process, it is evident that the more efficiently the acid particles are removed from the treated oil, the lower is the amount of adsorbent earth required to effect neutralisation. For this reason, plants using such a means of neutralisation generally make use of centrifuges for removing acid sludge and " pepper " because of the completeness of separation achieved.

With regard to the amounts of sulphuric acid and adsorbent earth used in such a process, the following remarks may be quoted.[63]

" On commercial plant operation a Jenkins 410°F. (210°C.) end point pressure distillate of 16 Saybolt colour, is being treated with 1 lb. of 66°Bé (93·2%) sulphuric acid and 2 lbs. of raw Fuller's earth per barrel with a resulting colour of +25. The material is not rerun and has satisfactory stability and gum content." Other cases are on record where similar cracked spirits are satisfactorily treated with 0·8 pounds of sulphuric acid and 0·8 pounds of earth per barrel.

The flow chart of a typical acid and clay refining process operating in this way is shown in Fig. 14. In this case contacting of the spirit with the acid is accomplished in a centrifugal pump while very complete separation of acid sludge is obtained by the use of a centrifuge. This arrangement gives a very short time of contact between the acid and the spirit being treated. This plant is operated by the Simms Oil Co., of Texas.[64]

206. A somewhat similar process has been used for the treatment of light oils obtained by coal carbonisation, at Rochester, N.Y., involving the use of silica gel.[65] In this case, a slight treatment is given with 0·05 pounds per barrel of 93·2% (66°Bé) sulphuric acid : this is followed by percolation of the oil through silica gel at a temperature of 135°C.

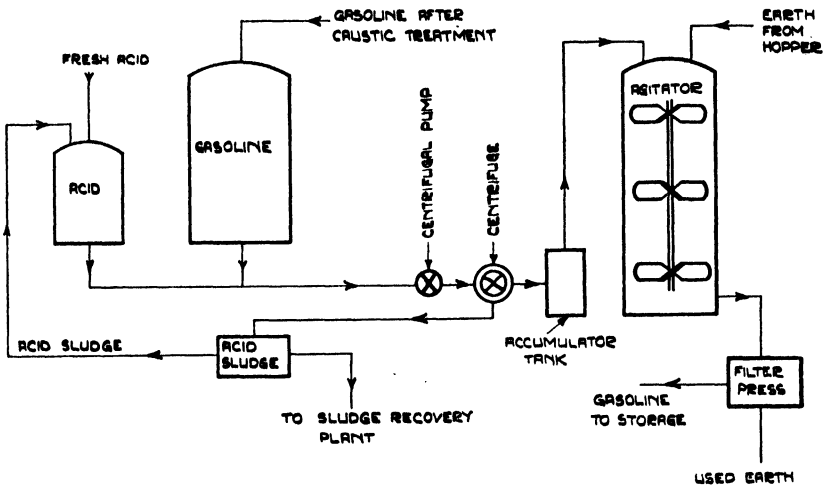


FIG. 14.—FLOW CHART OF SIMMS ACID AND CLAY TREATING PROCESS (WILLSON)

(275°F.), and the treatment is finished off with the common soda and rerunning operation. Here the silica gel functions primarily as a polymerising and colour removing agent. (See also E.P., 373,174. May 18, 1932. Silica Gel Corporation.)

207. The following are miscellaneous Patents, mainly recent, dealing with Acid Refining of Light Distillates.

U.S.P., 1,886,260. Miller, November 1, 1932.
U.S.P., 1,886,261. Miller and Connolly, November 1, 1932.
U.S.P., 1,886,612. Wagner and McIntire, November 8, 1932.
U.S.P., 1,827,537. Morrell (assignor to Universal Oil Products, Co.), June 28, 1926.
U.S.P., 1,859,262. Shaw, May 17, 1932.
U.S.P., 1,858,394. S. H. Diggs, May 17, 1932.

U.S.P., 1,817,969. R. Cross, August 18, 1931.
U.S.P., 1,873,728. C. R. Wagner, August 23, 1932.
U.S.P., 1,869,885. W. N. Davis and W. H. Hampton, August 2, 1932.
E.P., 371,752. Gewerkschaft Mathias Stinnes, April 28, 1932.
U.S.P., 1,853,921. J. C. Morrell, April 12, 1932.
U.S.P., 1,854,417. J. C. Morrell, April 19, 1932.
E.P., 345,596. Naamlooze Vennootschap de Baat. Petr. Maat, March 26, 1931.

Plant Used in the Treatment of Light Distillates with Liquid Refining Agents

208. In the early days of the petroleum industry, there was only need for the single acid treatment of light oil distillates, followed by a water wash or a neutralisation wash with caustic soda solution. Consequently the equipment needed for the operations involved was of the simplest possible type. The development of the cracking process has, however, necessitated the use of elaborate treating equipment and batch treatment methods have been largely replaced by continuous methods.

Chemical treatment of oil distillates involves two fundamental principles, (1) efficient contact between the oil and the reagent and (2) withdrawal of the reaction products from the refined oil. Efficiency of contact implies both efficient mixing and adequate reaction time.

209. Batch Methods of Treatment.—In batch treatment methods a quantity of distillate is fed into a tank or agitator and there mixed with a measured quantity of refining agent. Mixing is effected either by stirrers or by air blowing, and after the allotted reaction time the spent reagent and the treated oil are separately withdrawn.

The agitators commonly used vary in size from 300 to 1,500 barrels in capacity and range from 30 to 35 feet in height and from 10 to 25 feet in diameter, though smaller ones are often used. They are, usually, of cylindrical shape with cone-shaped bottoms and steel roofs, the latter fitted with explosion hatches. In some cases, the extension of the shell serves as the support, together with gussets or trusses under the cone proper, and in other cases the agitators are supported by lugs on steel or concrete columns. The pitch of the cone for light straight-run spirits need not exceed 4 inches per foot from the horizontal, but in agitators built for use with cracked spirits, this can conveniently be increased to 6 inches, owing to the greater viscosities of the acid sludges produced in treating these oils.

Experience has shown that the once-favoured hemispherical globe roof (i.e., the so-called " Gas-bag " roof) is a source of danger, since the accumulation of gas under the roof, together with any air used for agita-

tion, presents ideal conditions for an explosion. A low globe roof or a flat roof is preferable and plenty of explosion hatches are advisable. Cases are on record when even a 10 per cent. relief area has not prevented the roof of a light oil agitator from being blown off by an explosion.

In most cases agitators for acid treatment are lead lined. They are equipped with charging lines for oil and reagents, spray pipes for water washing, an air line for agitation and branched draw-off lines for the removal of oil and spent reagents. Air agitation, however, is the cause

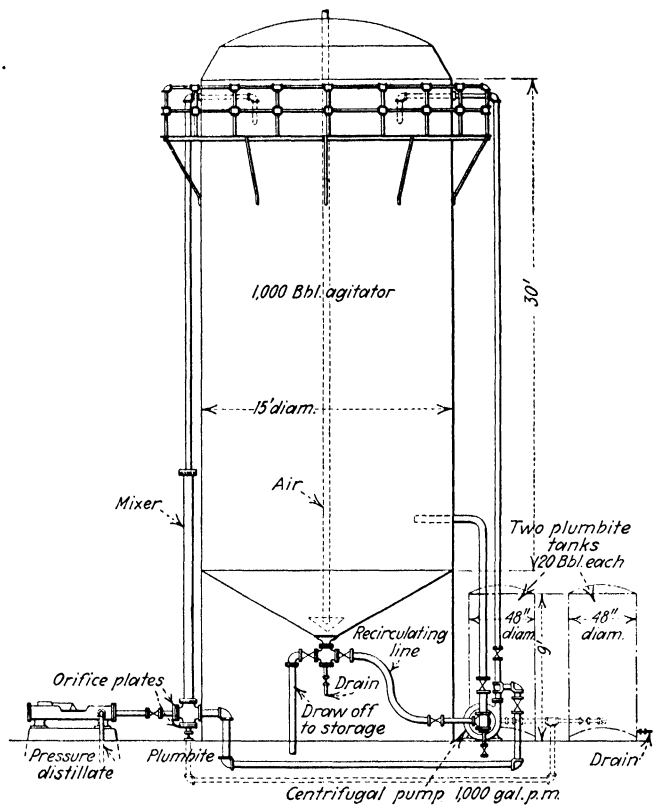


FIG. 15.—ARRANGEMENT OF 1,000 BARREL AGITATOR (MORRELL AND BERGMAN)

of much loss by evaporation and is now more or less replaced by mechanical mixing.

Perhaps one of the best methods of obtaining efficient mixing of the contents of an agitator is to employ a circulating pump which pumps the agitator contents from the bottom through an outside line up into the top, where the mixed fluids are discharged underneath the level of the liquid in the agitator. The circulating pump is preferably of the centrifugal type as the impellers of the pump serve to mix the

reagent and the oil as they pass through the pump. For a 1,000 barrel agitator the centrifugal pump should have a capacity of at least 1,000 gallons per minute, so that the contents of the agitator may be circulated and mixed within a reasonable time. The pump may be made entirely of cast iron fitted with acid-resistant bronze to eliminate corrosion of working parts. The pump may also be used for charging the agitator. Two or more batch agitators may be used as a semi-continuous treating plant in the manner shown in Fig. 16.

210. Continuous Treating Systems.—These consist of a combination of mixing, settling and washing equipment, the particular order depending upon the method of treatment. Each individual treatment with a refining agent requires a mixing and settling element.

Many types of mixers are used, but of these the orifice column and baffle plate columns are the most popular. In the former, the arrange-

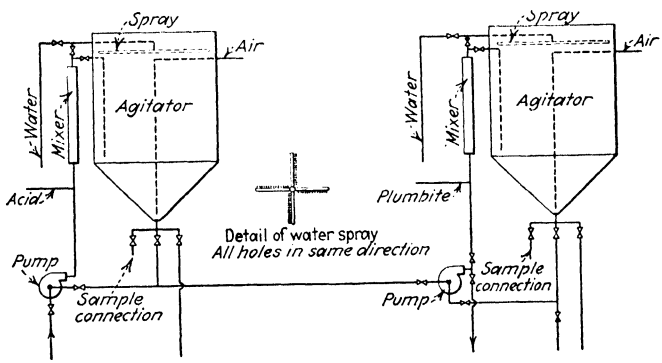


FIG. 16.—ARRANGEMENT OF SEMI-CONTINUOUS TREATING PLANT USING TWO BATCH AGITATORS (MORRELL & BERGMAN)

ment of which is shown in Fig. 17, the oil and the treating reagent are pumped in the desired proportions through a vertical chamber fitted with a number of plates containing a number of small orifices. Turbulent flow through these orifices causes intimate mixing of the two components. In the latter type, columns fitted with baffle plates are used. In another type of mixer, the stream of oil carrying the treating agent is forced through a nozzle or jet which mixes the two intimately. After efficient mixing in one of these devices, the mixture of oil and refining agent is passed to a settling chamber, from which the spent agent can be continuously withdrawn and the treated oil passed to the next stage in the process. The design of continuous treating plants has been dealt with extensively by Morrell and Bergman[66] and by Morrell,[67] and the following remarks are, for the most part, based upon their observations.

211. In the case of orifice columns, the superficial velocity of the liquid through the column should be quite low, but a fairly high pressure drop should be allowed for across each plate, in order to get adequate mixing. The orifice area should be divided into several small holes, rather than one large hole. In the design of an orifice column, the usual orifice formula is used, namely,

$$Q = CA\sqrt{2GH}$$

where Q = flow in cubic feet per second,
C = discharge coefficient = 0·65 for light distillates,
A = area of orifice in square feet,
G = 32·2 ft. per sec. per sec.,
H = head of liquid in feet.

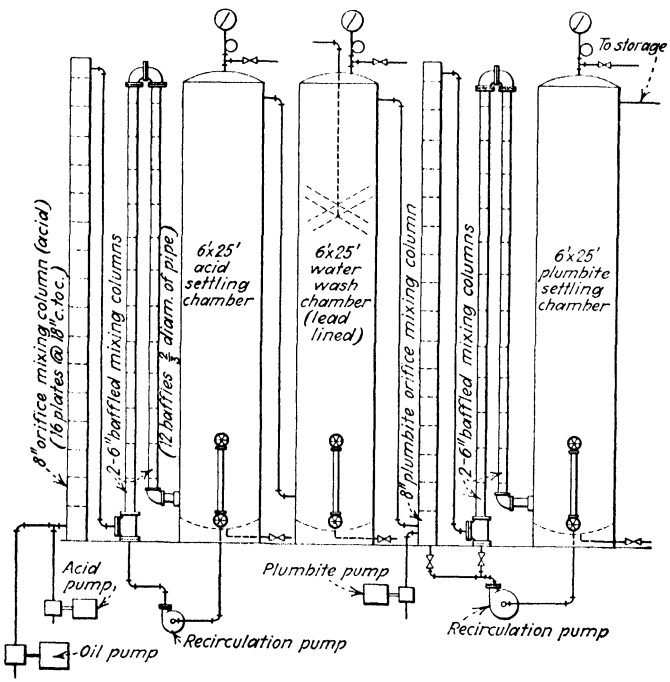


FIG. 17.—ARRANGEMENT OF CONTINUOUS TREATING PLANT

from which the required size of orifice, for a given throughput and pressure drop, may be calculated. Usually, a 30 to 40 pound back pressure (pressure drop), exclusive of the liquid head on the column, will give very good contact in mixing, using approximately 15 to 20 orifice plates per column.

In order to simplify the use of the above formula, Morrell and Bergman have constructed an alignment chart, showing the relationship between the area and diameter of the orifice, the head of liquid and the

rate of flow. This is reproduced in Fig. 18, and an example shows that, for a capacity of 300 barrels per hour with a chosen friction head per plate of 10 feet of liquid, the orifice area required is 4·1 square inches. This may conveniently be divided into two openings, each of $1\frac{5}{8}$" diameter, or into four openings of $1\frac{1}{8}$" diameter. The head of liquid in feet can be reduced to pounds per square inch if the specific gravity of the liquid is known.

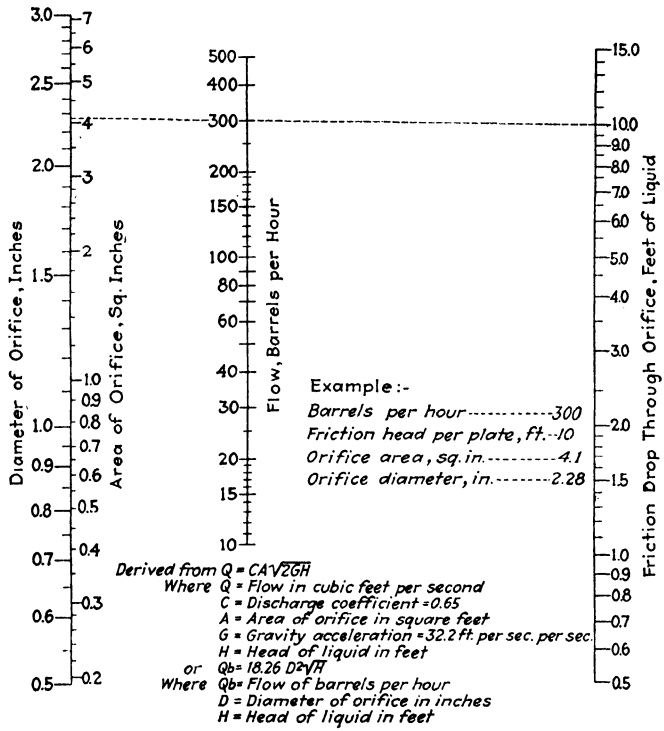


FIG. 18.—ALIGNMENT CHART SHOWING RELATION BETWEEN DIAMETER OF ORIFICE, HEAD OF LIQUID AND RATE OF FLOW (MORRELL AND BERGMAN)

212. The construction of an orifice column may be made as follows. Either the pipe may be slotted on alternate sides and the orifice plates recessed by the thickness of the pipe on one side, the plate being dropped in the slot with the recessed side next to the slot and the slot closed by a heavy weld: or flanges may be used with an orifice plate between each pair of flanges. Both of these methods of construction are shown in Fig. 19. Alternatively, the plates may be drilled through the centre and threaded on a rod passing down the centre of the pipe. The plates may be secured in position by using locknuts or else by welding. The whole assembly is then dropped into the pipe, allowing about 1/16 inch clearance between the circumference of the plates and the inside

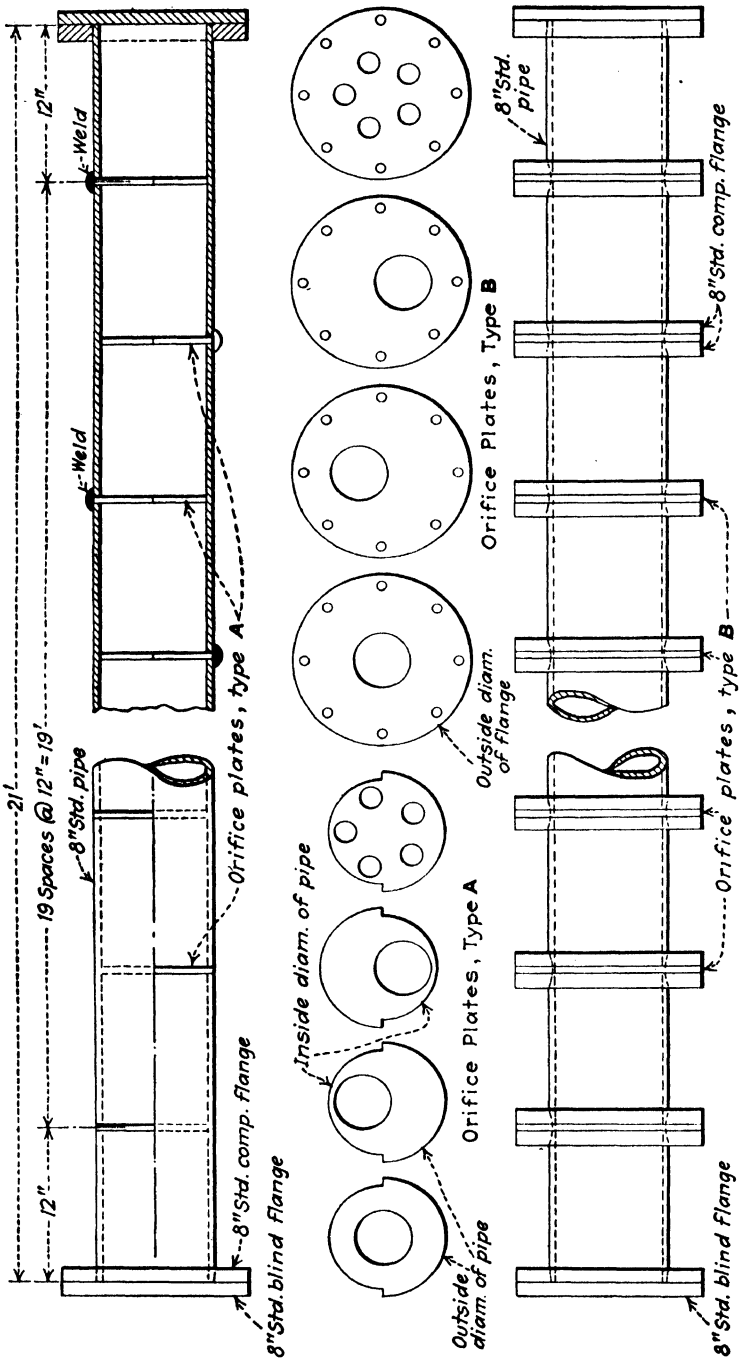


FIG. 19.—CONSTRUCTION DETAILS FOR TWO TYPES OF ORIFICE MIXERS
(MORRELL AND BERGMAN)

diameter of the pipe. This clearance must be deducted from the total orifice area.

213. Baffle plate columns are not efficient mixers when used alone, but when used in conjunction with an orifice column they serve the purpose of maintaining over an extended time the thorough mixture made by an orifice column, and also permit recirculation of sludges and partially spent reagents through a separate mixing chamber. Baffle plate column mixers have the advantage of low working pressure drops.

214. Packed Mixing Columns.—These are generally made by filling a length of pipe with Raschig rings, metal packing or screened gravel. The metal packing usually takes the form of short iron or steel nipples or rings. These mixers are relatively cheap to instal and give, in some cases, moderately good results with small pressure drop. Figures for the pressure drop found in such columns have been given by Morrell and Bergman (*loc. cit.*).

215. Jet Mixers.—Two fluids, such as a light distillate and a refining agent, are sometimes brought into intimate contact by passing them at high velocity through a vertical tube or a number of smaller tubes in parallel, in such a way that the high velocity jet of oil flowing through the throat of the nozzle induces suction which is used to draw in the refining agent. This type of mixing device is most efficient when approximately equal quantities of oil and treating agent are to be mixed, but does not give general satisfaction when the amount of treating agent is very small compared with that of the oil, as for example, in acid washing. A feature of the jet mixer is the very short time of contact that it effects between the two liquids. Depending upon circumstances, this may be either an advantage or a disadvantage. The jet type of mixer is employed to much greater advantage when the treating agent is pumped through a nozzle into a stream of distillate passing from another pump and the resulting mixture fed through further nozzles before passing to a separator. In this way the above-mentioned disadvantages no longer appear, time of contact can be made long or short as desired and small amounts of treating agents may be handled satisfactorily.

216. Blow Cases.—Blow cases are devices used for feeding measured quantities of refining agents into the treating plant. They consist of vessels capable of withstanding pressure, fitted with delivery and charging lines and also with relief valves, and they function by applying a known and predetermined pressure of air, when the reagent is forced at the desired rate into the treating plant. They are generally used in conjunction with batch equipment and must be fabricated in materials

capable of withstanding the corrosive action of the liquids with which they are to be used. A constant rate of flow from a blow case is obtained by maintaining a constant pressure differential across an orifice through which the reagent leaves the blow case. The relationship between the differential pressure and the quantity of reagent delivered is, in the case of sulphuric acid of 1·835 sp. gr. (66°Bé), shown in Fig. 20, from which it will be evident, for example, that a 3/32 inch diameter orifice will pass 300 pounds of acid per hour with a pressure differential of 8 pounds. For other treating agents, the equation

$$Q = CA\sqrt{2GH},$$

in which C = approximately 0·61, may be used.

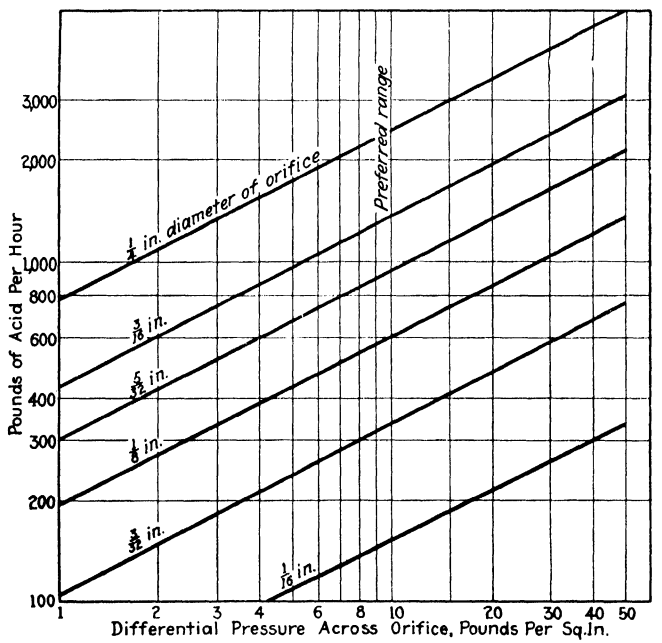


FIG. 20.—CURVES SHOWING FLOW OF 1·835 SPECIFIC GRAVITY SULPHURIC ACID THROUGH ORIFICES OF DIFFERENT DIAMETERS

Morrell and Bergman recommend that the differential pressure across the orifice be kept between the limits of 6 and 20 pounds for good results. Too low a pressure causes large variations in the quantity flowing, due to comparatively small pressure fluctuations, while too high a pressure necessitates a small orifice, which is easily plugged or corroded.

217. Settling Tanks.—Settling tanks used in a continuous treating plant should be large enough to give the required time element to settle out sludge or excess treating agent used. Generally, a settling time of one hour is ample. Normally, the inlet to the settling tank is made at

the point where the separation level is maintained and the inlet is made tangential to the tank so as to give a whirling motion to the feed. This assists settling.

218. Reagent Pumps.—In continuous treating processes, pumps are used for the handling of refining agents. These are either of the positive piston, duplex or rotary type. Acid-resistant bronze or cast iron and steel pumps with suitable liners are used for the handling of both acid and caustic soda solutions.

For use with sulphuric acid of all strengths the alloy Duriron has been found eminently suitable and is quickly finding favour. This alloy is a high silicon cast metal alloy and is not lined or coated. It contains approximately 14·5 per cent. silicon, with small amounts of carbon and manganese, the rest being iron. Duriron is procurable in the form of pumps, valves, pipes and all kinds of fittings.

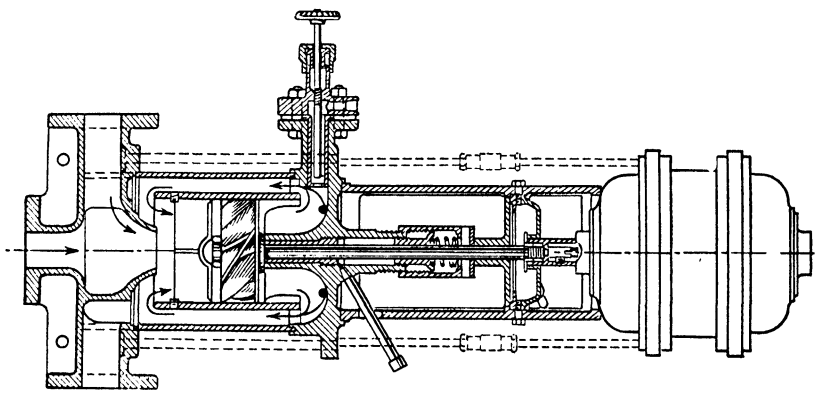


FIG. 21.—SECTION OF "STRATCO" DISPERSION CONTACTOR

Of particular interest is its use in centrifugal pumps and also in mixing nozzles manufactured by the Duriron Company, Inc., Dayton, Ohio. Such pumps are built in sizes from 2″ suction and 1½″ delivery to 10″ suction and 8″ delivery, and because of the extreme hardness of the metal employed can be used for handling abrasive clay-acid mixtures.

219. The Use of Dispersion Contactors and Centrifuges in the Acid Treatment of Light Distillates.—It has already been shown that in sulphuric acid refining it is desirable to reduce the time of contact between the oil and the acid as much as possible consistent with the degree of refining required, and also to effect complete separation of acid from the oil after treatment. To meet these requirements the Stratford Engineering Company of Kansas City have developed suitable machines for use in continuous treating systems.[68]

Separation of acid sludge from treated oil is effected by means

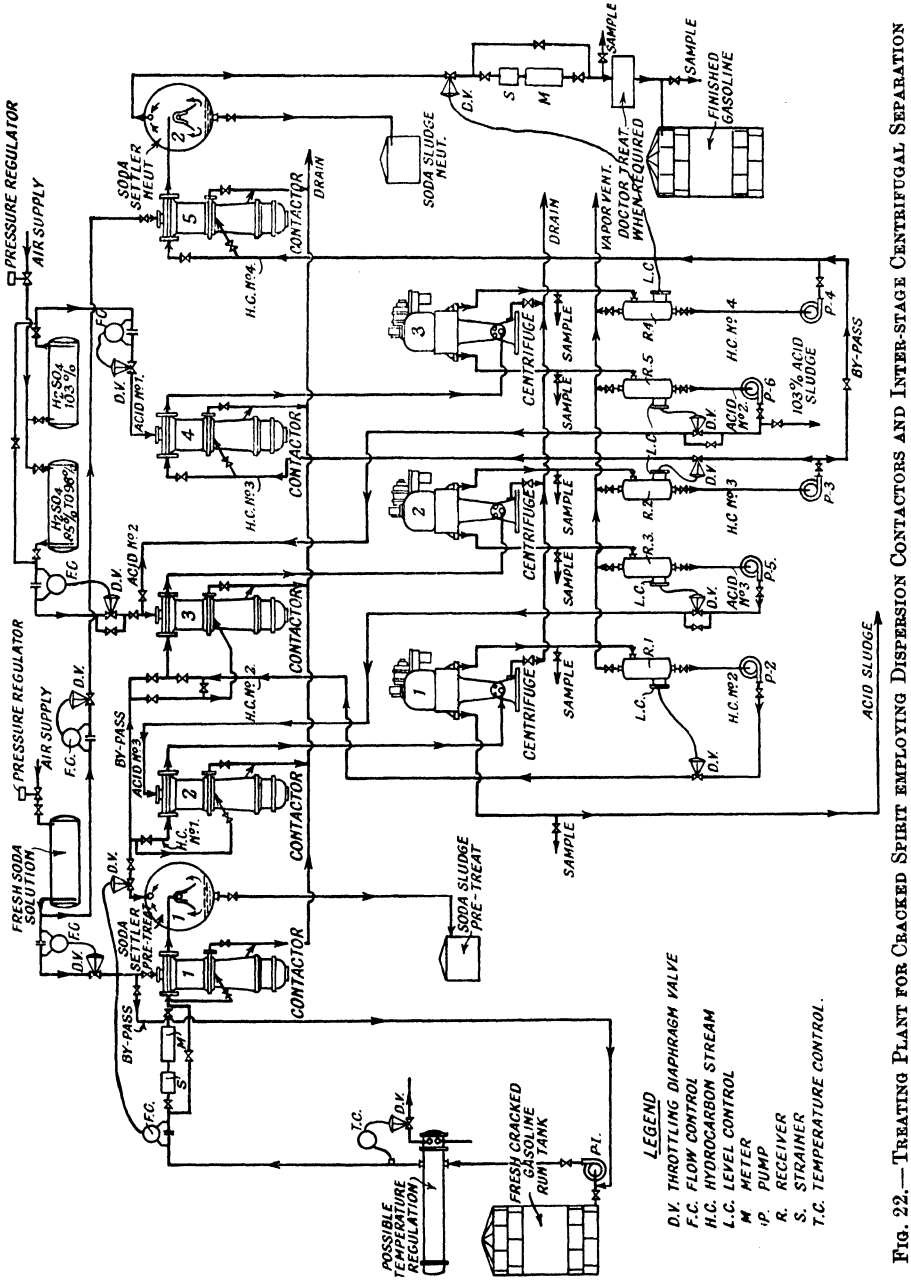


Fig. 22.—Treating Plant for Cracked Spirit employing Dispersion Contactors and Inter-stage Centrifugal Separation

of centrifuges, which are among the most efficient devices available for rapid, continuous and complete separation of distillates from

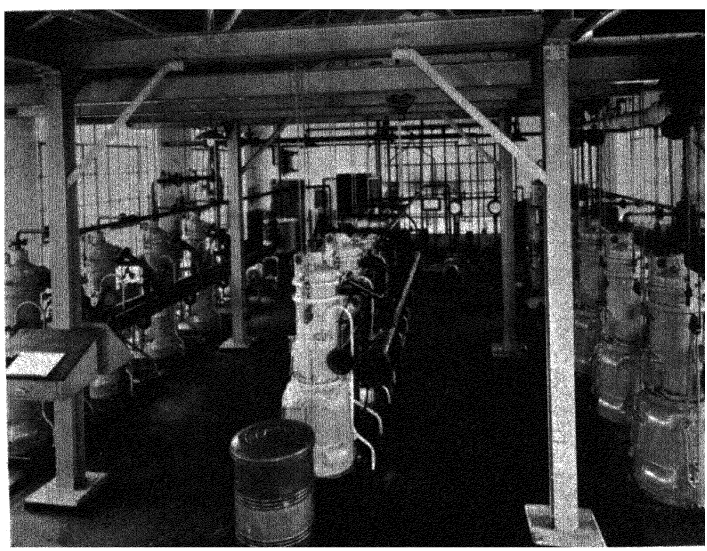


FIG. 23.—STRATFORD ACID TREATING INSTALLATION

(Courtesy of Alco Products Incorporated)

Facing p. 215]

treating agents (when they are properly designed for this purpose) and satisfactorily withstand corrosion. Mixing of the distillates with fresh reagents is effected by so-called dispersion contactors, which are machines equipped with a screw propeller (surrounded by a circulation tube) for impressing high velocity flow to the liquid. Dispersion and intimacy of contact are accomplished by frequent changes in the velocity of the stream and by frequent enforced changes in the direction of flow, all of which occurs within a zone of controlled, turbulent flow. These dispersion contactors are fitted with primary mixing heads wherein the entering stream of distillate is intimately mixed with the treating agents introduced. The discharge nozzle for the treating agent may consist of atomising nozzles of various types. The mixed liquids then pass at high velocity down along the axis of the circulation tube. There is a zone of high turbulence between the stationary shearing blades and the blades on the screw propeller on the inlet side. As the liquid passes through the propeller its flow is accelerated. When the liquid leaves the propeller on the discharge side, the stream contacts with diffuser vanes, by which it is straightened. The direction of flow is reversed at the bottom of the contactor and the stream continues its way in a closed circuit through an annular space. Since the liquids fed to the contactor enter a down-flowing stream at its centre, in a zone of reduced pressure, all possibility of cross-circuiting is said to be eliminated. The discharge from the contactor is withdrawn through a narrow annular slot which takes off the out-flowing mixed liquids around the entire periphery of the contactor shell.

A cross-sectional view of the "Stratco" dispersion contactor is reproduced in Fig. 21.

A great advantage attending the use of these machines for refining processes is the very small space required for the plant. Reactions can also be speeded up enormously and acid refining completed within a fraction of a second. In some cases, cracked spirits can be treated in this way without the need for rerunning.

Fig. 23 is a photograph of a typical Stratford acid treating installation.

220. Other Types of Continuous Treating Plants.—A counter-current continuous treating plant embodying somewhat novel features is that used for the treatment of gasolines and kerosenes with alkaline hypochlorite, sulphuric acid and alkalies.[69, 70] This is known as the Holley-Mott washery, and was originally used in the production of trinitrotoluene.

The plant is arranged as a series of pairs of vessels of which one is an agitator and the other a separator, as shown diagrammatically in Fig. 24. The oil and reagent are metered in at opposite ends of the series,

flowing continuously in counter-current, and emerging at the ends remote from those at which they are respectively entered, the oil being thus alternately agitated with and separated from the reagent, which becomes progressively stronger from pair to pair. This is effected without the aid of pumps, by taking advantage of the difference in density of the three liquids, oil, reagent and the emulsified or finely divided mixture of oil and reagent.

Into a pair of vessels, connected in the manner shown, the oil and reagent enter into the agitator vessel continuously and are stirred into a very intimate mixture. This mixture flows continuously into the separator by the connection at mid-level, and forms two layers of which the higher one, i.e., the oil, passes into the next agitator. In a similar manner, the treating agent flows in the reverse direction. The bottom

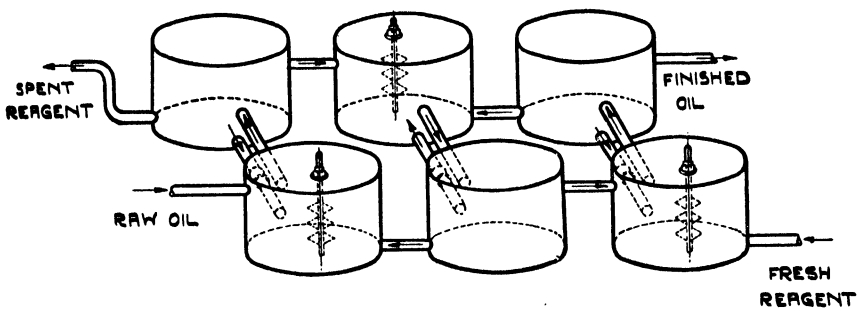


FIG. 24.—DIAGRAMMATIC REPRESENTATION OF ANGLO-IRANIAN OIL CO.'S CONTINUOUS COUNTER-CURRENT TREATING PLANT (DUNSTAN)

connections, which carry valves, are provided in order to allow any desired ratio of oil to reagent to be maintained in the agitator whatever the rates at which reagent and oil are fed into the plant. For example, while oil and sulphuric acid may be fed in at rates by volume of 800 and 1, respectively, the ratio of oil to acid may be maintained at 4 to 1, or any other desired ratio.

To obtain intimate contact, the agitator vessel is designed to give maximum turbulence for a given power consumption. The vertical paddle shaft, or stirrer, is mounted eccentrically in the agitator vessel and carries three diamond-shaped blades, set 120 degrees apart in plan.

This type of plant has proved very satisfactory.

THE DISPOSAL AND RECOVERY OF ACID SLUDGE

221. The acid sludges resulting from the sulphuric acid refining of light distillates are normally of red or brown colour, though in some cases they may be almost black. They are quite fluid and can be easily handled by means of suitable pumps, etc. Regarding their chemical

composition, comparatively little is known, but they contain, in addition to unused acid, neutral and acid esters, alcohols, sulphur and nitrogen compounds, together with polymerised material. Pilat and Starkel[71] found that acid sludge from the refining of Galician kerosene contained

(1) Up to 8 per cent. of sulphuric acid in the form of sulphonic acids and sulphuric acid esters,
(2) 52 per cent. to 63 per cent. of free sulphuric acid,
(3) 10 to 30 per cent. of organic tar.

The usual acid recovery processes involve two separate steps. First, the separation of acid from the tar-like components by dilution with water and settling and, secondly, the reconcentration of the separated dilute acid. The first operation is normally conducted in a series of lead lined tanks fitted with cone or slanting bottoms to facilitate the withdrawal of the stratified layers, and also fitted with open or closed lead coils connected to steam and air lines. The bottoms are often lined with acid-proof bricks. Manholes for cleaning and draw-off lines are also provided, together with vapour lines passing to an absorption tower, where the vapours are neutralised with weak alkali, thus eliminating the fume nuisance.

The operation of these separating plants presents many problems, as it is rarely found that a method effective for the treatment of one sludge is equally successful on another, even of the same type, without some modification. The general method for the treatment of light oil acid sludges is to mix the latter with a quantity of water such that the operation gives a dilute sulphuric acid of about 34·6% strength (sp. gr. = 1·26, °Bé = 30) after separation. This mixture is agitated with live steam, or heated, until the evolution of sulphur dioxide has subsided, and then allowed to settle. The time of heating is generally about two hours and the settling time four to six hours. During this time the mixture separates into three layers: weak acid at the bottom, " acid tar " in the middle and " acid oil " at the top. These liquids are drawn off to their respective storage tanks. In some cases, the " acid tar " and " acid oil " are given a second wash after the weak acid is drawn off. A small quantity of water is added and the mixture heated and settled as in the previous operation. The acid extracted in this operation is very weak (8·5–16·4%, sp. gr., 1·06–1·12, °Bé, 8–15°), and is used as the extracting agent in the place of water in the separation of a subsequent batch of sludge.

222. Acid Concentration.—The weak acid recovered in the above operation is substantially free from pungent odours; it is straw to dark brown in colour, free from suspended tars and oils and, if well separated, can be used straight away for reconcentration, but it always contains sulphonated products as impurities, with the result that concentrated

acid made by direct concentration is nearly always very dark in colour and contains varying amounts of free carbon in a fine granular form. Some acids, especially those obtained from sludges resulting from the treatment of highly cracked distillates, can only be concentrated to a certain point, after which decomposition begins and the acidity remains practically constant.

Dark-coloured recovered acids containing the requisite percentage of free acid fully serve their purpose for refining, in so far as their treating efficiency is concerned. Carbon in the combined form has no detrimental effect upon the treated oil and experimentation has shown that it does not build up by repetition through the cycle. It is removed from the acid by the separating and concentrating process, and the recovered acid, after passing through six or seven cycles and being strengthened by fuming sulphuric acid to meet refinery requirements, reaches a point when the percentage of carbon remains substantially constant.[72]

223. The Chemical Construction Corporation Acid Sludge Conversion Process.—The Hechbleikner process has been developed by the Chemical Construction Corporation, U.S.A., for the recovery of sulphuric acid from acid sludges.[112] In this process the acid sludge is pumped or conveyed according to its consistency, to a rotary kiln, which is heated by the hot gases of combustion of oil or gas fired in a separate furnace. The kiln may be of iron or steel, lined or unlined ; it is ribbed and contains loose rods to assist in the prevention of caking of the sludge during decomposition. The sludge is heated by direct contact with the combustion gases, and is decomposed into coke and sulphur dioxide mixed with water vapour and hydrocarbon gases. The coke, which is a dry granular material, is discharged at the hot end of the kiln, and is removed by means of a screw conveyor. The gases formed from the acid sludge leave the kiln at 250–350°F., and may contain up to 15% SO_2. They are cooled by passage through washers, which condense and remove the bulk of the water and related oils. The latter may represent up to 12·5% of the sludge. After passing through the washers, the gas is comparatively clean and only requires drying before passing to the converters. A washer containing 85–93% sulphuric acid completes the drying, and absorbs the light hydrocarbon gases still present in the gas. The dry gas is then mixed with air to bring its composition to about 8% SO_2, 11% O_2, 4% CO_2 and 77% N_2, and is passed to the standard type of "Chemico" acid plant, which uses a vanadium catalyst, and converted to sulphuric acid of the required strength. A recovery of about 90% of the acid content of the sludge may be expected from this process.[111]

224. Patents on Acid Recovery.

E.P., 365,945. Du Pont Ammonia Corporation, January 28, 1932. The acid sludge is treated with an aqueous sulphuric acid solution of ammonium sulphate in such an amount that the ammonia content of the resultant mixture is, at least, 0·8 mols per mol of H_2SO_4. Tar, oil, resinous and carbonaceous matters are caused to coagulate, the operating temperature being such that substantially all the ammonium sulphate or bisulphate formed remains in solution. The latter is reacted with phosphate rock to form superphosphate, which can be used as a fertiliser.

225. The Use of Copper Salt Solutions as Refining Agents.—Various proposals[107] have been made to utilise copper salt solutions as refining agents, among the earliest being that of Frasch,[108] who desulphurised oils by distilling over copper oxide.

Cuprammonium sulphate has been used in aqueous solution by the Houston Oil Company of Texas for the treatment of cracked distillates.[74] This is prepared by adding caustic soda to copper sulphate solution until all the copper is precipitated as copper hydroxide. The precipitate is then redissolved by adding ammonia, the resulting "blue solution" then being ready for use. It is claimed that the solution is capable of removing disulphides and mercaptans from light distillates.

Hounsell[75] has described the use of this reagent in the treatment of a very sulphurous Dubbs pressure distillate from Smackover crude. The distillate was first treated with 7 pounds of sulphuric acid per barrel and then water-washed. It was then thoroughly mixed with "blue solution" in orifice columns, the amount of the solution being so controlled that the spent liquor, which carried a black precipitate (presumably copper sulphide), was still faintly blue, showing a slight excess of the reagent. After rerunning, a satisfactory refined product was obtained.

Cupric chloride solutions have also been used for desulphurising operations, the reactions involved being as follows:—

$$4RSH + 2CuCl_2 \rightarrow RS\text{-}SR + 2RSCu + 4HCl \quad . \quad . \quad . \quad (1)$$

$$2RSCu + 2CuCl_2 \rightarrow RS\text{-}SR + 4\,CuCl \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The cuprous chloride so produced, although practically insoluble in water, is quite soluble in solutions containing a high concentration of chloride salts. Cupric chloride is regenerated by air blowing, i.e.,

$$4CuCl + 4HCl + O_2 \rightarrow 4CuCl_2 + 2H_2O \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It has been found that rather low concentrations of cupric copper are adequate, so that in commercial operation the sweetening reagent

solution can be prepared from copper sulphate and common salt (sodium chloride). Since the amount of air required is small, regeneration can be effected by dissolving air in the gasoline prior to treatment. Hydrogen sulphide should be removed prior to treatment with copper salts.

The cupric chloride treatment may be applied in two ways—the wet treatment and the solid treatment. In the former, sour gasoline, free of H_2S, is contacted with treating solution in a continuous manner, and the solution either simultaneously or subsequently regenerated by air. In the solid treatment, the reagent is prepared by impregnation of adsorbents such as Fuller's earth with the copper solutions, and the gasolines treated by filtration. In some cases the reagents have been prepared by incorporating 25 parts by weight of ammonium chloride and 25 parts of crystalline copper sulphate with 50 parts of 16–30 mesh Fuller's earth, and drying at 120°C.[109] A detailed account of the use of cupric chloride as a refining agent has been given by Schulze and Buell.[110]

226. Zinc Chloride as a Refining Agent.—The Lachman Process.—The use as refining agents of metal salts, and more particularly zinc chloride, is well known, as shown in various patents dating from 1883.[101] In the Lachman process[76] gasolines are refined by bringing their vapours into contact with an aqueous solution of zinc chloride and then condensing.

In an installation described by Albright[102] the combined vapours of cracked spirit and reformed naphtha is passed to the first tower in a series of three, into which zinc chloride of 50% concentration and steam at a temperature of 410° F. is injected. The purpose of the steam is to maintain the strength of the zinc chloride solution at a constant figure. The treating tower is fitted with 44 bubble trays each containing 21 caps. The spent treating solution in the bottom of the tower is removed once every eight hours and passed to a recovery unit.

The treated vapours from the treating tower are passed to a second tower lined with acid-proof tile and filled with limestone, the purpose of which is to neutralise acids (particularly hydrochloric acid) formed in the process, and carried over with the treated vapours. The final bubble tower serves to fractionate out any polymers formed, ammonia being injected into the vapour outlet line to effect a further removal of acids not neutralised by the limestone. The pressure on the system varies from about 50 lbs. per sq. in. on the inlet to the treating tower to about 20 lbs. per sq. in. on the final bubble tower. The spent zinc chloride solution withdrawn from the base of the treating tower contains sludge, and the active agent is recovered by

dilution with water and settling. The sludge bottoms are finally filtered and the coke dumped.

According to another method of operation of the Lachman Process[103] the zinc chloride solution is kept at about 50% concentration in special circulating tanks, but under the temperature conditions employed in the treating tower water is driven off and the effective strength of the solution is about 80–85%. The used zinc chloride solution passes to a settling tank and to a make-up tank where it is diluted down to 50% concentration and recirculated. Doctor treatment is applied to the treated spirit before pumping to storage.

A typical flow diagram of the Lachman process is given in Fig. 25.

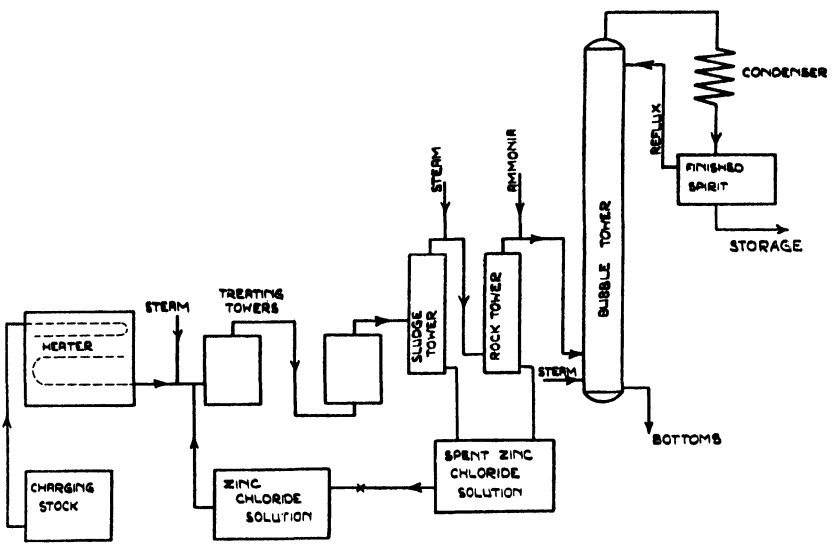


FIG. 25.—FLOW DIAGRAM OF THE LACHMAN REFINING PROCESS

It is claimed that this treatment gives products of satisfactory colour and gum stability, with no decrease in anti-knock value, and very small treatment losses. The chemical action of the zinc chloride appears to be mainly catalytic and little polymerisation occurs. Treatment losses average 1% and polymerisation losses 1–3%. Hydrogen sulphide should be removed prior to the Lachman process—otherwise a high consumption of zinc chloride, due to the formation of zinc sulphide, occurs.

The reduction in sulphur content obtainable varies with the nature of the sulphur compounds present, but the average reduction is stated to be between 20 and 40%. Mercaptans are reacted upon and partly removed, depending on the time of contact, but it is usually cheaper only to remove part of the mercaptan content by this process and to give a finishing treatment with plumbite. The consumption of

zinc chloride is said to be very small and amounts in practice to from 0·3–1·0 lbs. per barrel of oil treated. Treated spirits are said to be free from chlorine or contain traces only.

Lachman (*loc. cit.*) has quoted figures showing the relative costs of the zinc chloride process and normal acid refining, in which a saving in favour of the former is claimed. These are reproduced in Table 11, but do not take cognisance of sludge formation and polymerisation. Moreover, the cost of sweetening by means of "Doctor" solution is not included. This amounted to \$0·001–\$0·003 per barrel of oil treated.

TABLE 11. COMPARATIVE COSTS OF SULPHURIC ACID AND ZINC CHLORIDE REFINING PROCESSES PER BARREL OF OIL TREATED (LACHMAN)

Item	Zinc Chloride	Sulphuric Acid
Labour	\$0·0096	\$0·0212
Fuel	0·0100	0·0168
Water	0·0048	0·0050
Steam	0·0120	0·0122
Electricity	0·0002	0·0054
Zinc chloride	0·0158	—
Sulphuric acid	—	0·0442
Caustic soda	—	0·0323
Ammonia (for neutralisation)	0·0018	—
Repairs	0·0040	0·0108
Cost per barrel treated	\$0·0582	\$0·1479

Ferric chloride solutions have been suggested as refining agents[77] and also anhydrous aluminium chloride.[78, 79]

THE EDELEANU LIQUID SULPHUR DIOXIDE REFINING PROCESS

227. This refining process was first proposed by L. Edeleanu and worked out by him and his co-workers for commercial operation, the need for a new refining process being the necessity of obtaining from Rumanian distillates products comparable in quality with Pennsylvanian kerosene. The historical development of the process has recently been described by Edeleanu, in a paper to which a very comprehensive bibliography is appended.[80] Originally intended for the treatment of kerosenes and later developed as a refining process for lubricating oils, the process has only comparatively recently been adapted to the treatment of gasolines.

The action of liquid sulphur dioxide on a crude gasoline is as follows:—First, sulphur dioxide dissolves in the oil up to a saturation limit determined by the existing conditions of temperature, pressure and solubility. Beyond this saturation limit, a separation occurs in the

solution and the liquid sulphur dioxide exerts a selective solvent action on the spirit and dissolves out those constituents richer in carbon (i.e., more unsaturated) than the remainder. Paraffin hydrocarbons are practically insoluble in sulphur dioxide. Naphthenic hydrocarbons are but slightly soluble at −10°C., but their solubility increases appreciably with rise in temperature. On the other hand, aromatics and unsaturated hydrocarbons are generally soluble in liquid sulphur dioxide at all temperatures above the freezing point. Sulphur compounds are also soluble. The selective solvent action of sulphur dioxide is markedly improved by a reduction in the operating temperature.

By treatment with such a solvent, therefore, oils may be separated into two fractions, one soluble in the solvent and the other not. Of these, the first contains a greater proportion of aromatic and unsaturated hydrocarbons than the second and, consequently, from the anti-knock point of view, is the better fraction. Generally cracked or straight-run spirits are treated by this process in the following manner. The spirits are fractionated and the fraction distilling, say, between 165° and 220°C., is extracted with liquid sulphur dioxide, and the soluble portion blended with the lighter fraction. The insoluble portion is discarded or used (if from a straight-run product) as a kerosene constituent.

This process is a means of improving spirit quality by the removal of high boiling material of poor anti-knock value, but it does not obviate the need for sulphuric acid refining. Typical results, showing the increase in knock rating obtainable with different spirits, are shown in Table 12.

TABLE 12. RESULTS IN IMPROVING THE KNOCK RATINGS OF GASOLINES BY SO_2 TREATMENT (EDELEANU)

Armstrong Variable Compression Engine. Speed 750 r.p.m.
Cooling Water Temperature and Air Inlet Temperature 50°C.

Gasoline	1		2		3	
	Benzole Equivalent	Octane Number	Benzole Equivalent	Octane Number	Benzole Equivalent	Octane Number
Treated with acid and SO_2, but without elimination of high boiling hydrocarbons insoluble in SO_2 ..	28·8	67·0	24·0	64·5	20·4	62·7
Treated with SO_2 and H_2SO_4. The high boiling hydrocarbons insoluble in SO_2 eliminated	43·7	75·9	44·8	76·6	44·3	76·3

The arrangement of the plant used is evident from the accompanying diagrammatic flow sheet (Fig. 26).

228. Other Selective Solvents used in Refining Operations.—Various other selective solvents have been proposed as refining agents for gasolines, but none of these has been applied to such an extent as sulphur dioxide. Examples are ethyl alcohol,[81] solutions of phenol in methyl alcohol[82] and phenol itself.[83] Solvent refining processes are widely employed in the treatment of lubricating oils and kerosenes.

Earth Refining Methods

229. Treatment with adsorbent earths and clays has been practised for many years in the refining of vegetable and mineral oils, but only during the past twenty years or so has it been applied to petroleum distillates. At the present time, the treatment is growing in favour in the refining of cracked spirits.

Theoretical Principles underlying Earth Refining Operations

230. The Theory of Gibbs-Freundlich.—Diatomaceous earths, Fuller's earth, activated charcoal and other such refining substances owe their action to the phenomenon known as "Adsorption." As explained in Chapter III the phenomenon rests on the tendency for a solute to change its concentration in the surface film of a solution whenever a change in the surface tension is effected. When the surface tension is lowered with increasing quantity of solute, the solute is observed to concentrate in the surface layer; and when the surface tension is lowered with decreasing quantity of solute, the latter is observed to concentrate in the body of the solution. Since the effect may be shown at liquid-solid interfaces, as well as at liquid-gas interfaces, the introduction into the solution of a solid possessing a very large surface, such as either of the above-mentioned substances, gives an opportunity for extensive surface concentration changes. If, in a specific case, the surface tension at a Fuller's earth solution interface is lowered by surface concentration of solute, the introduction of Fuller's earth may cause a noticeable removal of solute from the solution. Depending upon the nature of the solvent and of the porous solid, the concentrated surface layer of solution adheres more or less lightly to the surface of the solid, and practicable separation of solute from solution may be effected. It is necessary for a successful adsorbent to possess a large surface.

Freundlich has elaborated a formula based on the above theory to indicate quantitatively the relation of adsorption to concentration of solution and the quantity of adsorbent, as follows,

$$\frac{x}{m} = Kc^{\frac{1}{p}},$$

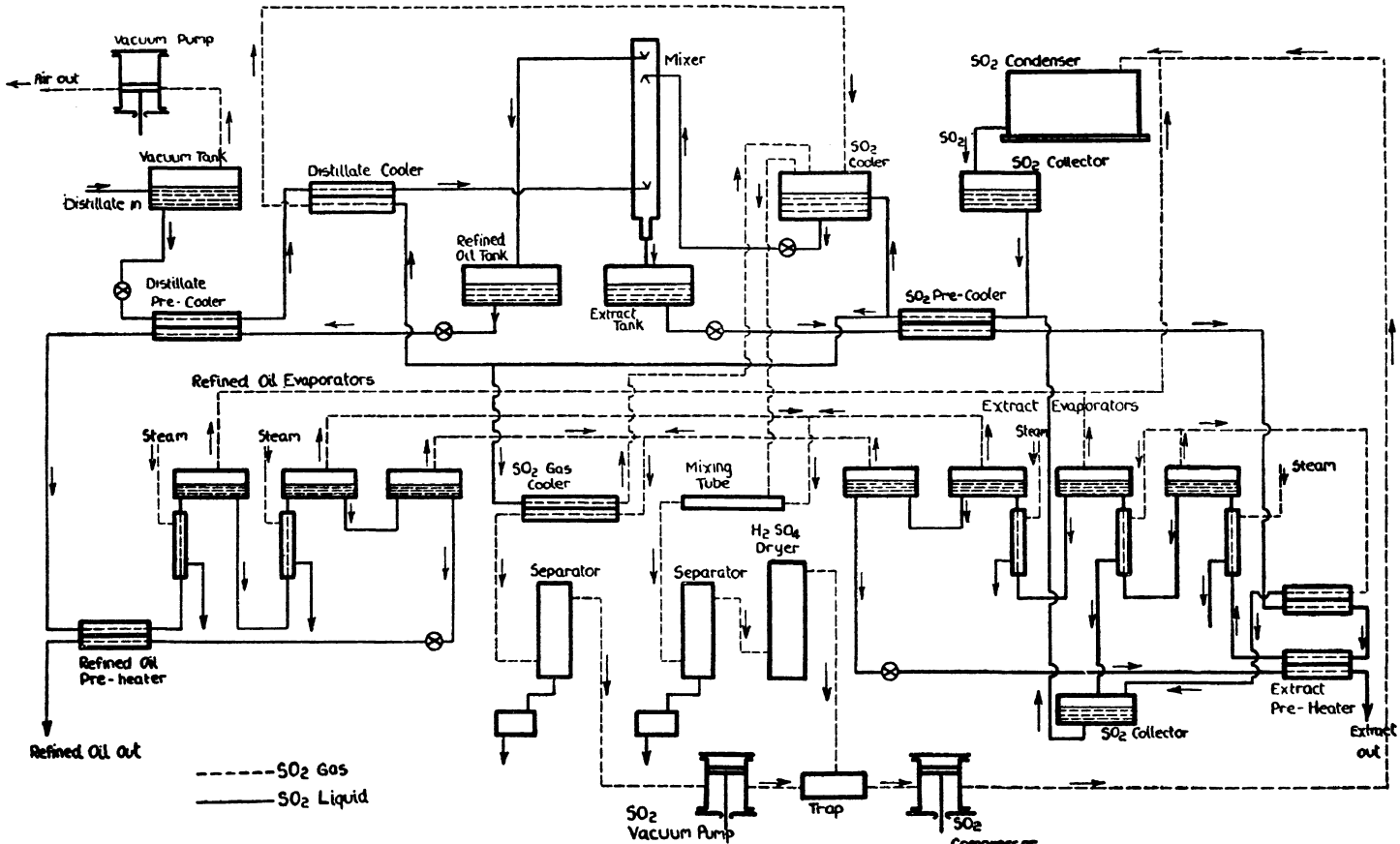


FIG. 26.—FLOW DIAGRAM OF THE EDELEANU REFINING PROCESS FOR LIGHT OILS

of sodium silicate by sulphuric acid. Physically, it is a hard, semi-transparent, glassy substance, and is used in the powdered or granular form, according to the nature of the process in which it is used. It is activated before use by heating to about 150°C., in a current of air, its moisture content thus being reduced to about 7 per cent. After use for adsorption of sulphur and colour compounds, it may be regenerated by heating in a current of steam.

Waterman and Tussenbrock[86] have shown that, although silica gel has no appreciable adsorptive action on either hydrogen sulphide or elemental sulphur, thiophene or carbon disulphide, it is a useful adsorbent to employ for the removal of mercaptans and sulphides from light distillate solutions.

Wood, Sheely and Trusty[49] have also found that silica gel is without action on elemental sulphur, H_2S, thiophene and carbon disulphide.

Silica gel may also be employed for neutralising acid-treated oils. The Silica Gel Corporation own the world-wide patent rights covering the use of this material.

235. Alumina Gel.—Chowdbury and Bagchi[87] have investigated the desulphurising activity of alumina gel, which they prepared by the slow addition of ammonia under vigorous stirring to a solution of an aluminium salt at a temperature not exceeding 25°C. They found that it was very similar in activity to silica gel, but observed the interesting fact that mixtures of silica gel and alumina gel are more active than either of the separate constituents, as shown in the following figures :—

% Silica Gel in Mixture of Silica & Alumina Gels	Grams Adsorbent in 25 mls. Solution	Initial Concentration of Sulphur %	Final Concentration of Sulphur %	Removal of Sulphur %
0·0	2·11	0·117	0·088	24·8
2·4	1·98	0·117	0·083	29·1
23·7	2·05	0·117	0·047	60·0
63·7	2·12	0·117	0·070	40·2
100	1·95	0·117	0·094	20·0

Alumina gel can be reactivated after use to its original efficiency.

236. Bauxite.—In general, bauxite is considered to be a mixture of gibbsite (Al_2O_3 $3H_2O$) and diaspore (Al_2O_3 H_2O) and frequently is classed as an aluminous laterite. It occurs in many parts of the world, of which the following are of interest.

Great Britain and Ireland. Bauxite occurs in Antrim, Ireland, in several localities, but, although it is mined to a considerable extent, it is too impure for oil refining purposes. In Scotland, an aluminous clay occurs in Ayrshire, but this is not a true bauxite.

France. France has recently resumed its place as the world's largest producer of bauxite. The most important occurrences are in Var, where the ore is obtained at Thoronit and elsewhere. It is of dark red colour, but high in alumina content and suitable for aluminium manufacture. In Herault, a white bauxite is mined. Neither of these varieties is suitable for oil refining.

India. Large deposits of bauxite exist in India, particularly in Bombay, near Belgaum, and in Kolhapur at Radhanaqui, Dhangarvadi and Patagaon. Indian bauxite is used by the Anglo-Iranian Oil Company for oil refining in Iran and at other centres of their activity.

237. Little is known relative to the type of bauxite most suitable for oil refining. It is known, in a general way, that the more highly hydrated varieties are more effective than those containing little combined water and that heating to 500°C. is necessary for high activity. At this temperature there occurs little, if any, dehydration of the monohydrate, while gibbsite is reduced to the monohydrated condition or almost to the anhydrous state. It would seem likely that it is the colloidal hydrated alumina when partially hydrated that is the most effective as a refining agent, and, if this is so, a bauxite of high combined water content that has the smoothest heating curve (with the least marked "arrest points") would have the greatest activity. Experimental evidence on this point is lacking, however.

It is fairly safe to say that a high combined water content is desirable and not too high a percentage of iron oxide, and, from the fact that Indian ores are used successfully, it would seem that titanium oxide is not detrimental.

The chemical analyses of some typical bauxites are as follows :—

	Antrim, Ireland	France		India, Jubalpur	Africa, Gold Coast
		Red	White		
Alumina	50·7	66·2	54·4	60·5	60·6
Iron oxide ..	7·1	19·3	0·3	2·7	9·8
Silica	10·4	0·9	26·7	2·0	1·4
Titania	5·4	0·9	2·9	8·5	2·2
Water	25·6	12·4	15·7	25·0	25·6

At the present time, no correlation has been found to exist between refining efficiency and chemical analysis.

238. Activation and Regeneration of Indian Bauxite.—The optimum conditions for the activation and regeneration of Indian bauxite have been determined by Dunstan, Thole and Remfry.[88] Fresh bauxite should be activated for use by roasting at a temperature of 400–600°C. Collapse of the pores with subsequent loss of activity

occurs at 700–800°C. The following table shows the effect of roasting temperature on the colour and sulphur content of a treated Iranian kerosene and indicates that bauxite is most active as a desulphurising agent when its moisture content is about 0·7%.

Temperature of Roasting. °C.	% Moisture Remaining	Colour of Filtrate (Saybolt)	% Sulphur Removed
none	—	—	—
200	26·0	3	—
300	9·7	20·5	24·0
400	4·0	23·5	48·5
500	1·0	22·5	58·6
600	0·68	21·5	65·6
700	0·34	21·5	61·2
800	0·22	20·5	—
900	0·0	20·0	40·3

Used bauxite is best regenerated as follows :—

The earth is allowed to drain for about an hour and then steamed out. Shortly after steam begins to issue from the bottom of the filter, the extraction is stopped and the bauxite then treated with superheated steam (150°C.) until it comes out dry to the touch, though still containing 7–12 per cent. of moisture and oil. Further steaming removes but little oil in proportion to the amount of steam used. The bauxite is next roasted to remove moisture and burn out adsorbed impurities that are not removed by steam. This necessitates a temperature of about 550°C., in the presence of an ample supply of air, which must be maintained for a sufficiently long period of time. The cooling period must be reduced as much as possible, as the hot bauxite rapidly adsorbs moisture from the air and in so doing loses its adsorptive properties.

239. Desulphurising and Decolorising Action of Indian Bauxite. —Dunstan, Thole and Remfry (*loc. cit.*) have found that bauxite obeys Freundlich's rule when adsorbing sulphur and colour compounds. This rule may be summarised as follows :—

$$\left(\frac{x}{m}\right)^n = Kc$$

Where (in this case) x = per cent. of colour or sulphur compounds, m = weight of bauxite per 100 parts of oil treated, c = per cent. of colour or sulphur in the oil before treatment and n is a constant.

In the case of colour compounds the value of n was found to be unity and a plot of $\frac{x}{m}$ against initial colour concentrations was consequently

a straight line. In the case of sulphur compounds, however, the value of n was found to be 1·3.

The deviation is, no doubt, due to the disturbing influence of coloured compounds which are preferentially adsorbed. Fig. 27, which is a reproduction of that given by Dunstan, Thole and Remfry, shows that colour compounds are adsorbed much more readily than, and in preference to, the sulphur compounds. Thus, until 85% of the colour has been removed, only a small fraction of the sulphur is taken up, but once the colour is adsorbed then the removal of sulphur follows the normal course.

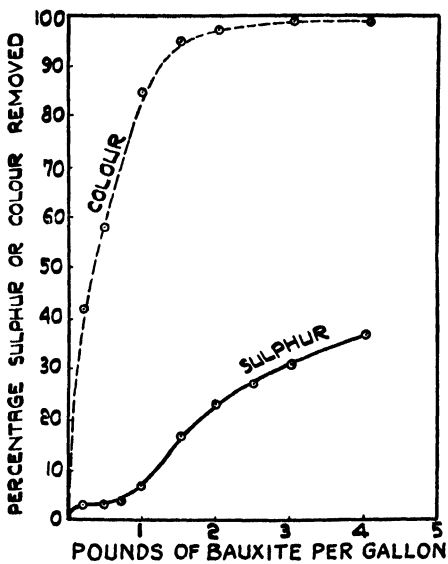


FIG. 27.—CURVES SHOWING THE ADSORPTION OF COLOUR AND SULPHUR COMPOUNDS BY INDIAN BAUXITE FROM IRANIAN KEROSENE (DUNSTAN, THOLE & REMFRY)

There is definite evidence to support the idea that chemical action proceeds at the same time as the adsorption of sulphur compounds by bauxite. Bauxite cooled in a vacuum has but little desulphurising action, and is only active in this respect when cooled in contact with air. It is believed that oxidation of sulphur compounds occurs through the agency of air present in the pores of the bauxite.

240. Florida Fuller's Earth or Floridin.—Extensive deposits of Fuller's earth are found in Florida, U.S.A., and this earth is being used to an ever increasing extent in petroleum refining in all parts of the world. This earth is also known as Floridin or Florida Fuller's earth.

Large mesh Floridin, e.g., 16/30, 30/60 or 20/90 mesh, is particularly suited for the vapour-phase earth refining of gasolines, as this earth has a very high refining efficiency; it is hard in nature, it does not dis-

integrate during roasting or handling and may easily be regenerated many times, without appreciable loss in efficiency.

Floridin, when of fine mesh, is suitable for the treatment of acid-washed spirits, but is not suitable for the treatment of neutral oils in the liquid phase, where removal of sulphur compounds and unstable unsaturated hydrocarbons is required rather than the removal of colour. For decolorising paraffin wax a coarse mesh Floridin is very suitable.

Roasting and regeneration. Floridin does not need to be roasted for the contact filtration of acid-treated oils.

For percolation and vapour-phase treatment fresh Floridin is roasted at 260–310°C. and used Floridin is regenerated at 600°C.

241. Methods of Earth Refining of Petroleum Oils.—There are three main methods of earth refining at present practised in the oil industry.

1. Percolation treatment.
2. Contact filtration treatment.
3. Vapour-phase treatment.

Percolation Treatment.—The percolation treatment is but rarely used in the refining of gasolines, other methods being more efficient. Percolation is used for the treatment of kerosenes, lubricating oils and waxes. In this process, the earth is packed in vertical cylindrical containers. The earth used for this purpose is, of course, granulated, and the temperature of the oil being percolated is adjusted according to its nature and viscosity, the pressure employed and the time of contact required. The oil may pass either downwards or upwards in the vessel, and its passage may be effected either by gravity, pressure or the application of a partial vacuum. In this process, the product first to emerge from the percolating vessel is of light colour and very highly refined, and the quality slowly deteriorates as the quantity of oil which is passed through the earth is increased, i.e., as the adsorbent material gradually becomes spent. If desired, the finished product can be collected in two or more fractions, these being graded according to colour, or it may be run into one tank. The degree of exhaustion of the refining material is determined by the colour of the last samples coming through the filter. Frequently the filters are employed in series, so that the adsorbent earth is virtually travelling in a counter-current direction, that is to say, the percolator containing the freshest earth is used for treating the finishing product, whilst the raw oils first come in contact with material which is nearly spent. When the earth in the percolator is nearly exhausted, it may be steamed to effect the removal of oil and then burned by the application of superheated steam and hot air *in situ*, or it may be removed to a roasting furnace, where a certain amount of low grade oil can be recovered and the adsorbent revivified. The material generally depreciates in quality according to the number of times it has

been employed and losses are encountered in revivification, as it is necessary to screen out fine material after roasting. The process has been employed very largely in the past for the treatment of lubricating oils in American refineries.

Kerosene bauxite filters installed by Scottish Oils, Ltd., at Grangemouth, Scotland, have been described.[89] The filters are loaded with bauxite to within a foot or so of the top by means of overhead trucks and are then filled with kerosene, which gradually trickles through the bauxite to the bottom whence it is drawn off. The top layers of bauxite in the percolator are occupied in mechanically removing suspended matter, the next layers eliminate the sulphur compounds. In this way, three active zones move downwards until the coloured compounds are being extracted at the very bottom of the filter, but as no sulphur is taken out until almost all colour has gone, it will be seen that, at this stage, no sulphur is being eliminated at all. In other words, the bauxite is exhausted for desulphurising purposes ; it is still capable, however, of removing colour. For this reason, " series filtration " gives the most efficient and economical results. The principle underlying series filtration is that of putting the various layers of a large filter into a number of smaller ones, so that each layer is capable of rejection as soon as it is exhausted, while no layer is rejected until completely exhausted both for decolorising and desulphurising.

242. In working the series filtration operation, much light is thrown on the elimination of colour and sulphur compounds, for it is found that only when the filtrate comes into contact with fresh bauxite in the last filter does any appreciable desulphurisation takes place. Colour is progressively removed in passing through the series of filters, but sulphur compounds are only removed in the last filters, as is shown in the following table :—

Filter	Colour of Filtrate Saybolt	% S in Filtrate	% of Total S Removed by Filter
1	16	0·286	0
2	17	0·286	0
3	18	0·286	0
4	19	0·252	12
5	22	0·129	52

In percolation processes, it must be remembered that

(1) The longer the column of earth, the better the bleach.
(2) The coarser the earth, the more rapid the flow and the poorer the bleach.
(3) The finer the earth, the larger the surface of contact and the better the bleach.

(4) The higher the temperature, the faster the flow and the poorer the bleach.

(5) The higher the temperature, the less viscous the oil, the more intimate the contact and the better the bleach.

In points (4) and (5), the higher temperature has opposite effects on the bleaching of an oil. As a corollary of the above five facts, filtration should take place at the lowest temperature and with the finest earth commensurate with speed of filtration. The above remarks only apply to oils of appreciable viscosity, e.g., lubricating oils.

243. The Edington Witz Refining Company use, at their Long Beach Refinery, the percolation earth treating method for finishing acid-treated gasoline. Two filters are used which operate in series. The first filter contains a mixture of " Hy-flo Supercell "—a filter aid—and Floridin, in the ratio of 1 to 3 by weight, while the second filter contains Floridin alone. The object of the filter aid in the first filter is to help the coagulation of dispersed acid particles so that they may more readily be adsorbed by the earth. In this plant, 1 part by weight of earth is sufficient for the neutralisation and clarification of 500 parts by weight of acid-treated gasoline.[90]

After use on acid oils, earths cannot be regenerated and are disposed of after being used only once. In the case of lubricating oils of low viscosity, 1 part by weight of Fuller's earth or Floridin is required in the percolation treatment of 1 part of oil, whereas, in the case of lubricating oils of medium viscosity, 1½ parts of earth may be required. In the case of paraffin wax which contains less colouring matter, 1 part of Floridin will effectively treat from 2 to 6 parts.

244. The Contact Filtration Method of Earth Refining.—In the contact filtration method of earth refining the oil to be treated is agitated or in some other way intimately mixed with the earth, which is ground to a very fine mesh, and after the required action is completed, the mixture is filtered and the earth removed. Contact filtration is quicker in operation than the percolation treatment when viscous products are being processed and possesses the added advantage that smaller amounts of decolourising earths are required to produce a given effect. Finer earths can be used in contact filtration than in percolation.

The contact filtration method is generally employed on oils which have been previously treated with sulphuric acid. There is no doubt that the effect produced by a given quantity of earth is enormously increased by a very slight preliminary acid treatment. The action of sulphuric acid on gasolines and other mineral oil products is to cause a coagulation of colloidal matter and polymerisation of undesirable gum-forming constituents. This coagulation and polymerisation makes

these materials more readily affected by the earth and, consequently, less earth is required.

When used on acid-treated oils, earths also remove suspended acid and acid sludge and provide a very convenient means of neutralisation. When acid-treated oils are washed with water, the acid particles dispersed in the body of the oil become diluted, with the result that the polymerised material, etc., dissolved in the acid is liberated and passes into solution in the oil, thereby causing a considerable " throw-back " in colour. When caustic soda is introduced, a certain amount of soda is absorbed by sulphuric acids present and some of the sodium salts remain in the oil, whilst others enter into the soda solution and, being of a soapy nature, are very liable to generate emulsions. Earth treatment after acid washing removes all danger of throw-back and prevents the formation of any emulsion. In this case, the treatment is named the " Dry Contact " process.

245. The Instill Refining Process.—A method which has just been adopted for coke oven benzole refining in this country is the so-called " Instill " process. In this, the benzole, after removal of bases, is treated with a mixture of adsorbent earth and iron persulphate, which has marked polymerising action upon unsaturated hydrocarbons, but which is much less vigorous in its action than concentrated sulphuric acid. (For further details see Chapter VI.)

Vapour-Phase Earth Refining Process

246. The Gray Process.—The first basic patents concerning this operation were issued in 1914, but the first commercial unit was not installed until 1924 when a plant was put into operation at the Barnsdale refinery of the Barnsdale Refinery Company having an earth capacity of 8 tons.[91, 92, 93, 94] The process is now widely used, particularly in America. The operation is shown diagrammatically in Fig. 28. Gasoline vapours, under the pressure and temperature conditions at which they are available from a cracking plant fractionator or rerun unit, are passed through a bed of Fuller's earth or other similar adsorbent contained in a lagged but unheated tower. Selective polymerisation of the highly reactive gum-forming unsaturated hydrocarbon takes place with the formation of higher boiling compounds and after leaving the earth the vapours are passed to a fractionating tower where treated gasoline of the required end point and vapour pressure is produced. High boiling polymers are separated from the treated gasoline in this tower and the heavier fractions are withdrawn from the bottom of the clay towers—these being of sufficiently high boiling point to be in the liquid state at this point. To

assist the drainage of the heaviest polymer from the clay, a certain amount of vapour condensation is allowed to take place in the tower or alternatively provision is made to flush the clay with condensate from treated vapours. Unless this is done the clay becomes clogged with polymers and quickly loses its activity.

Usually two or more towers are used in series and a liquid separator or knock-out drum is arranged between each pair of towers. In most plants the major part of the refining reaction takes place in the first tower and the succeeding towers are used to bring the treated gasoline

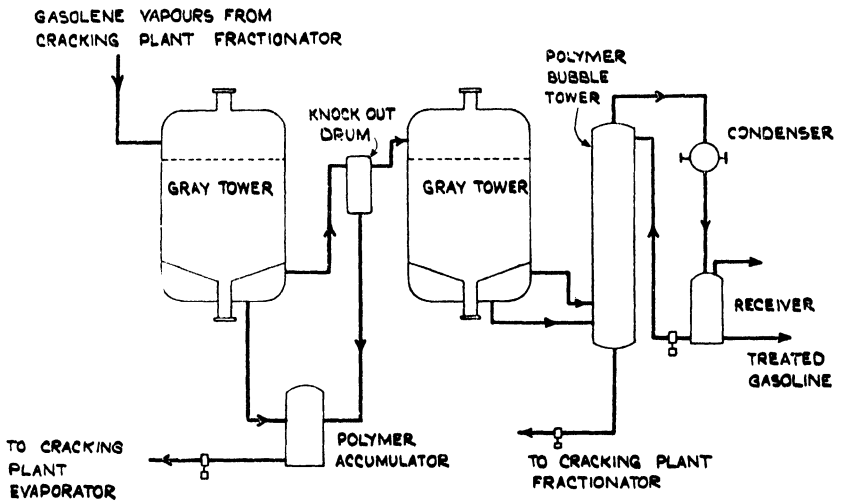


FIG. 28.—FLOW DIAGRAM OF THE GRAY REFINING PROCESS

to specification quality. The connections between the towers are so arranged that the order of flow can be reversed, so that the clay need be changed in only one tower at a time and the tower containing fresh clay can always be the last one of the series.

247. With regard to suitable types of clays, Riverside (Texas) earth, weighing about 55 lbs. per cubic foot, is satisfactory and Attapulgas, Floridin and Olmstead (Illinois) earths, weighing about 35 lbs. per cubic foot, have also been employed successfully. All these earths have about the same efficiency on a volume basis.

In the Argentine a Patagonian clay called "Tosca" has given good results and in Rumania acid-treated absorbents such as "Granosil" have been employed. The suitability of a treating material depends not only on its activity, but also on its mechanical strength, which must be high enough to allow its being milled to particles of the proper size without undue loss in fines and its recovery, when desired, without

too much disintegration. The particle size does not influence the activity of the adsorbent or the extent of the polymerisation reaction to any marked degree, but excessive pressure drop in the clay towers must be prevented. Usually adsorbents of 60/90, or 30/60 mesh, are employed, the latter being more satisfactory. Fuller's earth can be used in the process without the preliminary dehydration required of earths used in the percolation treatment of lubricating oils, since the temperatures employed in the clay towers are such as to produce the necessary amount of dehydration *in situ*.

248. Treating temperatures range from 280 to 500°F. (138–260°C.), depending upon the gasoline being treated. However, the temperature is only variable within a limited range. The lower limit is the dew point of the vapours, below which a true vapour-phase operation is not possible, and the upper limit is the temperature at which the complete separation of treated spirit and polymers is not possible. In normal operation the temperature is maintained as near the dew point as possible so that condensing vapour may act as a solvent for the polymers, thus facilitating their drainage from the earth. The polymerisation is exothermic, and, using fresh clay, temperature rises of up to 30°F. are frequent. This temperature differential gradually decreases during the first week of operation until it finally settles down at about 5–10°F., in which range it usually remains for the duration of the clay cycle.

With regard to operating pressure this is nearly always fixed by the pressure of the fractionating tower to which the unit is attached; but is normally 50–200 lbs., although some plants operate at pressures as high as 400 lbs. The higher pressures allow higher throughout rates per ton of adsorbent but usually give rise to higher polymer losses. The yields of finished gasoline per ton of clay are roughly proportional to the absolute pressure over the range 25–150 lbs.

The time of contact varies with the distillate to be refined and the specification desired in the finished product. In most plants the throughput ranges from 1–4 barrels of feed per ton of Fuller's earth per hour and the highest rate is about 6 barrels per ton per hour. The higher rates are only used when allowable gum contents of the finished gasolines are high and where the addition of inhibitors to the final product is allowable.

The earth capacity of clay towers in commercial use ranges from 4 to 100 tons. The yields of finished gasoline range from 1,000 to 20,000 barrels per ton of clay depending upon a variety of factors. Usually the earth is not regenerated after use, but is either dumped or used as fuel.

In the case of Dubbs, Holmes-Morley, Tube and Tank and similar

cracking processes, in which the cracked gas produced is small in amount and low in olefine content it is permissible to treat the gasoline in the presence of the cracked gas. In the case of vapour-phase cracking processes, however, this is not permissible because the gas produced contains high proportions of reactive constituents which cause rapid deterioration of the earth.

249. Mandelbaum[73] has given the operating costs of a typical clay tower installation as follows :—

Average throughput ..	2,000 barrels per day		
Amount treated per ton of clay	2,000 barrels		
Capital and installation cost	$33,100		
Fixed charges (20% p.a. on capital and installation cost)	$6,620 p.a.	= 0·92 cents	/bbl.
Adsorbent at $18 per ton ..		= 0·90 ,,	,,
Handling adsorbent at $1 per ton		= 0·05 ,,	,,
Steam and services ..		= 0·25 ,,	,,
Repairs and maintenance ..		= 0·15 ,,	,,
	Total	2·27 ,,	,,

In this case the clay was not recovered and was only used once. In the United States a royalty charge of six cents per barrel of finished gasoline is in force. Similar rates are charged in other countries.

For details regarding the properties of gasolines refined by this process, original papers should be consulted.[73]

250. The Osterstrom Refining Processes.—A process was developed by Osterstrom and the Pure Oil Company,[99] especially for the treatment of Gyro cracked gasoline, in which, as shown in Fig. 29, the crude distillate is mixed with a measured amount of clay and pumped through a pipe still. Here, under a pressure of 200–500 lbs. per sq. in., the distillate clay mixture is raised to a temperature of 600–650°F. (316–343°C.), and the time of treatment (as well as the precise temperature and pressure conditions) is determined by the characteristics of the distillate undergoing treatment, the amount and kind of clay used and the quality of the finished product desired. Leaving the pipe still, the mixture passes through a pressure-reducing device into a vaporising drum, where the polymers and clay separate from this treated spirit. The latter passes to a fractionator and the mixture of polymers is cooled and filtered. This process, described by Holland,[100] and protected by various patents,[99] reached the stage

of commercial development some time ago, but is not in widespread use and has now been replaced by a liquid-phase process, also known as the Osterstrom process, a description of which is as follows :—

As shown in the flow diagram (Fig. 30), crude cracked gasoline is

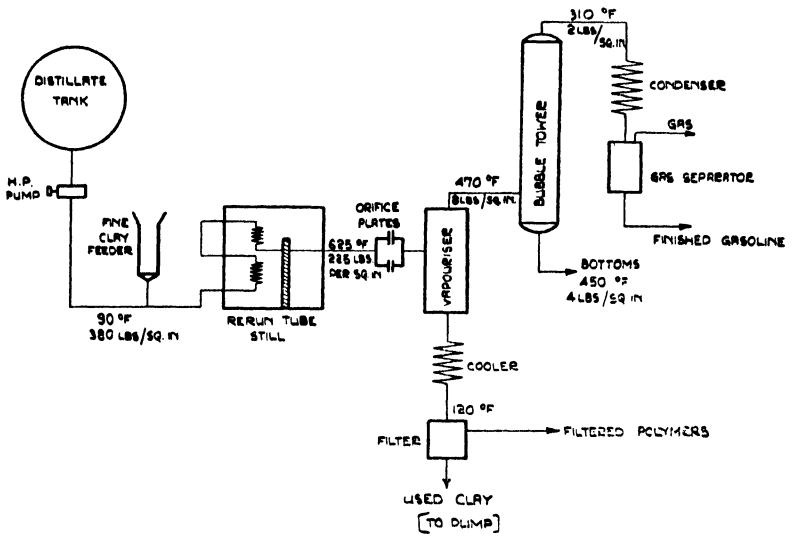


FIG. 29.—FLOW DIAGRAM OF THE OSTERSTROM VAPOUR-PHASE REFINING PROCESS (HOLLAND)

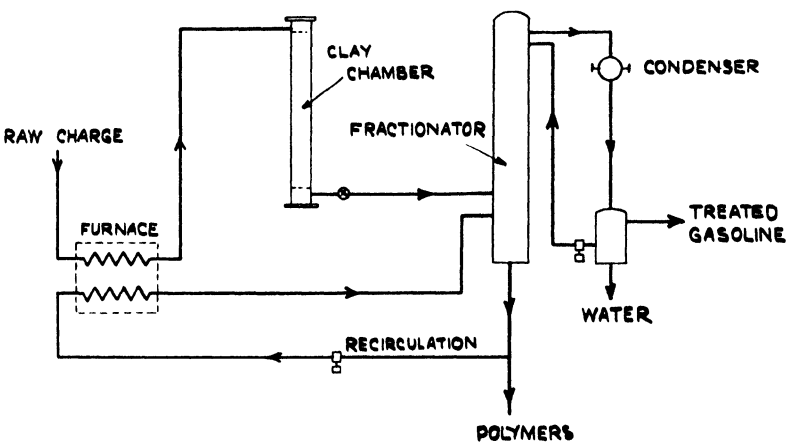


FIG. 30.—LIQUID-PHASE OSTERSTROM REFINING PROCESS

heated in a pipe still to 500–600°F. (260–315·6°C.) at about 1,000 lbs. pressure and then passed through clay contained in a vertical vessel of about 2–4 tons capacity. The clay used is usually 30–60 mesh and this quantity is usually sufficient for treating as much as 100 barrels per hour of gasoline. The products leaving the clay chamber

are flashed at a lower pressure into a fractionator where polymers, which leave the clay in solution in treated gasoline, are separated.

High yields of gasoline per ton of clay are obtained by this process —reaching 72,000 barrels per ton when handling Gyro gasoline and producing a refined product of 4 hours' induction period as determined by the oxygen bomb test.

251. The Stratford Liquid-Phase Earth Refining Process.— In this process, described in U.S.P. 1,768,342, cracked spirit vapours from the fractionating tower of a rerun unit are introduced at the base of a bubble-plate column where it passes counter-current to a descending slurry of fine clay in treated gasoline, which is introduced just below the top plate. The clay slurry is prepared in a mixing tank and kept in agitation by stirrers. Treated vapours leaving the top of the treating tower are passed through heat exchangers and condensers in the conventional manner. The slurry passing out of the bottom is collected in a settling tank, where a preliminary separation of part of the oil is effected and the oil so separated is pumped to the middle of the fractionating column. The remaining oil is removed from the spent clay *in vacuo* by heat exchange.

A typical plant having a treating capacity of 2,400 barrels per day comprises a $7\frac{1}{2}$ ft. diameter treating tower, approximately 30 feet high and containing 12 bubble trays. These trays are equipped with $5\frac{1}{2}$ in. weirs so that the depth of clay slurry on each tray is at least this height. About 200–250 gallons of slurry containing approximately 250 lbs. of fine clay (200 mesh) is charged to the treating tower per hour, the concentration of clay depending upon the type of gasoline being treated and the results desired.

Comparatively small amounts of cracked gasoline are treated per ton of clay used, optimum results in most cases being obtained at ratios in the range of 800–1,000 barrels of gasoline per ton of clay. On the other hand the refined gasolines produced are of very good quality.

Regeneration of Used Earths

252. Earth Regeneration Furnaces, etc.—As already mentioned, earths may in some cases be regenerated after use and part, or all, of their original activity may be restored. Whether or not an earth can be regenerated after use is determined by the nature of the earth itself, the nature of the oil treated and the type of refining process in which the earth is used.

Generalising, it may be said that earths used for neutralising acid-treated oils and earths used in contact filtration processes cannot be

regenerated after use, but earths used in percolation and vapour-phase processes may be regenerated many times. Earths used in vapour-phase refining may be regenerated as many as 40 times with very little loss in efficiency.

Three kinds of earth roasting furnaces are in general use :—

(1) Rotating furnaces.
(2) Vertical shaft furnaces.
(3) Multiple hearth furnaces.

253. Rotating Furnaces.—The furnaces consist of long cylindrical, horizontal, slightly inclined shells which are rotated. Baffle plates are bolted to the inside. The earth is fed in at one end by means of a hopper and is moved down the rotating furnace by means of the baffles. The temperature of the furnace is maintained by gaseous fuel which is burnt within the shell. The earth may travel co-current or counter-current to the burning gas.

254. Vertical Shaft Furnaces.—Various models of vertical shaft furnaces have been used in U.S.A. with considerable success in roasting Fuller's earth and Floridin. These are fitted with several separate and individual roasting shafts, each provided at the bottom with a gas or oil burner and an outlet for the dried earth. At the top of the furnace the shaft leads to a dust collector which retains and returns to the hopper all dust and earth carried up the stack. The bottom of the hopper is provided with six sliding sleeve valves, one for each shaft. The feed controls are opened or closed by means of levers placed in convenient command of the operator. Each shaft is provided with a series of projecting baffles, with downward inclined upper surfaces and extending midway across the shaft, alternating from opposite sides for the purpose of giving the earth a zig-zag course down the shaft from its entrance to the discharge.

The shafts are built of interlocking refractory blocks capable of withstanding a temperature of 1350°C., the baffles are parts of the blocks themselves.

A great advantage of this type of regenerating furnace is the small floor space required.

255. Multiple Hearth Furnaces.—Multiple hearth furnaces are at present becoming popular in the United States and are displacing rotary furnaces. In these furnaces, the earth to be roasted is fed consecutively on to a series of hearths, on each of which it is kept in motion by rabble arms. In the operation of a multiple hearth furnace the control of four variable factors is required :

(1) Temperature of the several hearths.
(2) Time of earth on each hearth.
(3) Rate of feed.
(4) Contact of earth and air.

These factors are not all independently variable. For instance, if the time element must be increased and the feed rate held constant, the rabble arms must be slowed down and the temperatures of either the upper or lower hearths must be changed.

Fresh earth can be roasted fairly easily and temperature control is easy to obtain. The first three or four hearths are maintained at a temperature of 350°C., and the lower hearths are used to cool as much as possible. The outlet temperature is maintained at 90–100°C. The speed of the central shaft is slow (about 2 r.p.m.) so as to keep the time of contact as long as possible in order to evaporate all moisture.

Earth that has been used is not so easy to roast, as it often contains oily matter that will burn, with the result that the earth smoulders and smokes. An attempt is made to roast used earth under the following conditions :—

Temperature	Hearth No. 2	430°C.
	Hearth No. 3	540°C.
	Hearth No. 4	540°C.
	Hearth No. 5	470°C.
	Hearth No. 6	380°C.
	Hearth No. 7	205°C.
	Hearth No. 8	135°C.

The best method of roasting earth in large scale practice is to roast at 540°C., until the efficiency drops to 85%, and then to roast once at 620°C., in order to restore the activity of the earth to its original value. If this cycle is continued, the longest life and greatest yields will be secured.[95]

256. The Use of Catalytic Agents in Regenerating Used Earths. —Lang, Anderson and Von Fuchs[96] conducted experiments in an attempt to find a catalyst that would permit earth to be regenerated by roasting at lower temperatures than those normally employed. It is well known that the use of too high temperatures for burning carbonaceous matter from used earths seriously impairs the quality of the roasted product. Also, if too low temperatures are employed, the carbonaceous matter is incompletely removed. It was felt that the addition of a catalyst to accelerate the combustion of the carbonaceous material might permit the desired combustion at a much lower temperature and thus obtain the good, without the bad, effects of high temperatures.

Many substances were tried as catalysts, including nickel, cobalt, manganese, iron, copper, cadmium, aluminium and zinc. The addition of metal to the earth was detrimental in each case, except in the case of aluminium and cadmium, which were without any apparent action. Copper was very detrimental and caused the earth to lose much of its activity. No successful catalyst was found.

257. Methods of Testing Earths for Adsorptive Capacity.—In large scale operation it is often necessary to have a routine test by which it can be determined whether a consignment of earth is of the required efficiency, and by which the operation of a roasting furnace may be controlled. Many such tests have been devised, but none of these is quite successful. These tests are as follows :—

258. The Ergometric Method of Test.—Dunstan, Thole and Remfry[88] have described an apparatus which they name the Ergometer, in which is measured, in an arbitrary way, the amount of heat evolved when a given quantity of bauxite or similar adsorbent is moistened with a given quantity of oil or water. The Ergometer consists of a metal cylinder $1\frac{1}{2}''$ diameter by $1\frac{1}{2}''$ high, and holds about 50 g. of 20 '90 mesh earth. When in use, 20 ml. of light kerosene is poured into the cup-shaped lid and allowed to flow through four small holes on to the bauxite, this quantity just being sufficient to wet the earth. A thermometer placed in a central pocket records the temperature rise due to the moistening of the bauxite. The maximum temperature is taken as the Ergometer number, which is regarded as a measure of the adsorptive capacity of the bauxite. Dunstan, Thole and Remfry state that a new bauxite of good quality which has been properly roasted will give a temperature rise of about 16°C. Regenerated bauxite gives a 12–14°C. rise. If the temperature rise is less than 10°C., faulty roasting is at once suspected.

This apparatus and method of test is quite suitable when used to compare different samples of the same earth, but when used to estimate the relative efficiencies of different kinds of earth it is unreliable.

Water may be used in the place of kerosene, but, in this case, the temperature rises are greater and more erratic.

259. Turpentine Temperature Reaction.—Venables[97] has described a similar method in which results are taken arbitrarily as the temperature rise obtained by adding 7 ml. of fresh turpentine to 5 g. of earth contained in an insulated test tube, the bulb of the thermometer just being covered by the earth.

This method of test is but little used.

Methylene Blue Tests.—In this method of test, suggested by Hill, Nicholls and Cowles,[98] a certain weight of adsorptive earth is

shaken for a predetermined time with a certain volume of an aqueous solution of methylene blue dye. The earth adsorbs a certain quantity of colouring matter and results are expressed in terms of the colour of the resulting solution.

Results obtained by this method are far from satisfactory, and earths containing a small amount of residual alkalinity decolorise very large amounts of dye irrespective of their adsorptive capacity.

The best method for testing earths for adsorptive capacity is as follows :—

Small scale experiments are carried out in the laboratory to determine the efficiency of the earth compared with that of a standard sample in terms of the quality of refined oils produced. Thus, it is previously determined what gum content and colour is desirable in refined spirit, and each sample of earth tested on the crude spirit to be refined, colour and gum determinations being determined on the refined spirits.

The Use of Earths Impregnated, or Mixed, with other Refining Agents

260. Various proposals have been made to refine cracked spirits by vapour-phase treatment with earths mixed with other refining agents, and claims have been made that such mixtures permit a greater degree of desulphurisation than is obtainable with earths alone. Furthermore, various combinations of earth refining processes with other treatments have been proposed. The following patents cover a variety of such processes.

U.S.P., 1,825,861. Gray Processes Corporation.
U.S.P., 1,840,158. Cross.
U.S.P., 1,749,240. Black.
U.S.P., 1,886,260. Miller (assignor to Silica Gel Corporation), November 1, 1932.

261. The Day Refining Process.—The Day process, owned by Universal Oil Products Co., comprises treating gasolines with added aqueous hydrogen chloride in the presence of a free metal. Brass has given satisfactory results. A series of U.S. patents[104] has been issued covering the process and it is now in successful commercial operation after a very thorough development. As an indication of the results obtained by this process, the results of treating gasoline produced by the cracking of Pondera gas oil are of interest.[105] A treating chamber is lined with acid-proof cement and one course of brick and is filled with brass. Stabilised distillate is passed through a heater and discharged to the bottom of the treater at the required temperature where it is met by a stream of fresh hydrochloric acid.

The heated distillate and acid are contacted by upward flow through the brass and then discharged through a pressure control valve to a fractionating column wherein the treated gasoline and polymers are fractionated. The acid in the treated distillate is neutralised by ammonia solution injected before the vapour condenser. The hydrochloric acid pump is constructed of Hastalloy and the acid lines of Everdur.

This process has been employed in a large variety of cracked distillates and has given promising results. It has considerable application in the desulphurisation of high sulphur distillates when followed by the use of a small amount of sulphuric acid. Polymerisation losses are claimed to be low.

Treated temperatures range from 440 to 470°F. and the operating pressure is usually 100 to 150 lbs. per sq. in. The consumption of brass varies from 5·3 to 15·7 lb. per barrel and the gasoline throughput from 0·03 to 0·04 barrels per day per lb. of brass.

262. Future Developments in Refining Practice.—The refining of light distillates preparatory to their use as motor fuels is made necessary because they contain a deficiency of hydrogen. Thus we may regard sulphur compounds, oxygenated bodies and nitrogen derivatives as major impurities only because the addition of hydrogen could convert them into hydrocarbons and sulphuretted hydrogen, water and ammonia respectively, of which the three latter substances could be removed without any difficulty. Furthermore gum-forming diolefines and other unstable unsaturateds could be effectively converted into useful hydrocarbons by the addition of hydrogen. Hydrogenation is a logical refining method because it can be controlled to do exactly what is required and nothing more.

It remains to be seen whether or not the high pressure hydrogenation process will be used to any great extent in the refining of petroleum oils, but at present its very high cost prevents its wide adoption.

The subject of "Hydro-fining," i.e., refining by means of hydrogenation, is dealt with in Chapter VII.

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Chapter V

STORAGE, DISTRIBUTION AND INSURANCE

Storage and Distribution

275. Introduction.—Because of the highly inflammable and volatile nature of motor spirit, its storage and distribution are among the major problems confronting Oil Companies, and special precautions are essential.

At one time the product for which the largest demand existed was kerosene, and although losses from evaporation and danger from fire were present, the necessity for storage in congested areas did not exist and the extreme danger to lives and property was, therefore, absent.

Since the demand for motor spirit is now practically universal, the need for storage in confined and thickly populated areas is necessary and special regulations under the Petroleum Acts have had to be drafted.

The losses due to evaporation may assume enormous proportions and to keep these within reasonable limits greater attention has had to be paid to the design of the tanks and necessary fitments, because in addition to the monetary loss caused by the escape of the lighter fractions in the form of vapours, there is the possibility of the formation of explosive mixtures. For this reason various forms of fire extinguishers have appeared on the market.

The transportation of petroleum products is now amply covered by Railway Regulations and by the Petroleum Acts. Local Regulations, based upon these Acts, are drawn up by Municipal Authorities and these differ from each other in certain details depending upon the particular circumstances existing.

The cost of distributing motor spirit is a variable to which it is difficult to allot a definite value, although some idea of the distributing costs can be obtained from our knowledge of the price of motor spirit ex pumps and certain costs such as Excise tax, freightage and retail profit.

Storage

276. Tanks.—The type of tank which is now in general use consists of a steel cylinder, the plates of which are welded or riveted, fitted with a steel roof securely fixed to the shell at the periphery.

In districts where the variations in temperature are not great the losses due to evaporation are normal and the additional expense incurred in fitting one of the many roofs designed to eliminate evaporation is often not justified. In this country the difference between day and night temperature is not excessive and as a result only a small variation in the volume of the vapour space occurs, small quantities of air are drawn in during the night and only small quantities of gasoline vapours are expelled during the day. This, of course, does not apply in districts where the variations of temperature are greater.

Over 80 per cent. of the tanks in use to-day have the conventional cone type roof. These cone roofs are made up of plates of about 10 gauge steel and are either welded or riveted. Where the welding or riveting is correctly performed the leakage past the joints is very small and should an explosion occur, the roof is weak enough to be blown off without danger of the shell collapsing.

A description of an ordinary cylindrical tank is unnecessary but a detailed description will be given later of the various roofs designed to eliminate losses due to rapid variations in temperature.

During the Great War difficulty was experienced in obtaining steel sheets and experiments were carried out in the construction of reinforced concrete containers for the storage of oil. Where the storage farm is to be a permanency, these containers undoubtedly show many advantages over steel tanks. They are not subject to corrosion and therefore require no protection against corrosive agents. Concrete is not subject to electrolysis. In addition to the fact that the shape of the tank is not important when reinforced concrete is used, these tanks can be designed to better advantage in resisting external stresses due to earth pressure or to the hydrostatic head in soils developed by ground waters. The size of the tank is immaterial and the low conductivity of the concrete insulates the oil against extreme temperature changes. The roof of the tank can be made practically gas proof and, as a result, the fire risks on oil stored in concrete tanks are materially reduced.

The great disadvantage of concrete tanks is that once they are built they can never be moved and, as a result, their salvage value is practically nil. The steel tank, on the other hand, has a very high salvage value and this factor, irrespective of the other disadvantages, weighs in favour of steel construction.

277. The three fundamental factors which control evaporation have been listed by Fleming[1] as follows :

(*a*) The area of the oil surface exposed,
(*b*) The amount of air passing over that surface,
(*c*) The degree to which the air becomes saturated with gasoline before leaving the tank.

Since to accommodate a given quantity of gasoline two variables exist, the determination of the oil surface exposed is a problem not easy of solution. The two variables are firstly the height of the tank and secondly the diameter. If the diameter is reduced to cut down the area of the exposed surface, the height must be increased to store the same quantity. Thus a tank which is 100 feet diameter and 10 feet high would have to be 10 feet diameter and 1,000 feet high to reduce the area of surface exposed to one hundredth of what it was previously. Obviously, a reduction of surface area by this means is unworkable and other means must be developed.

Ludwig Schmidt,[2] of the U.S. Bureau of Mines, conducted a series of tests to estimate the evaporation losses of gasoline and put forward the following points to be observed if evaporation losses are to be reduced to a minimum.

(1) Foundations to be firm to guard against distortion of the tank.
(2) Sample hatches, valves and other fittings should be located as near the edge of the tank as possible so that the gauger will not need to walk or stand on the roof of the tank.
(3) Vapour-tight tanks should be equipped with vacuum and pressure relief valves and vapour-tight sample and gauge hatches. Swing lines should enter the tank through a stuffing box.
(4) Vapour space inside the tank should be reduced to a minimum to eliminate as much air as possible above the surface of the oil.

The entry of air into the tank above the liquid is one of the chief causes of evaporation losses. The air mixes with the petrol vapours and with temperature variations contracts and expands. As the mixture contracts air is sucked into the tank and becomes saturated with vapour; as the temperature increases, the mixture expands and the petrol-laden air is expelled.

The amount of air passing over the surface depends upon two factors, windage and breathing, and Fleming has listed these factors as follows:

(*a*) From Windage.
  (1) Tightness of the roof and fittings.
  (2) Number and location of vents.
  (3) Breather valves on the vents.

(*b*) From Breathing.
  (1) Volume of vapour space.
  (2) Degree and frequency of temperature variations in the vapour space.
  (3) Pressure at which the valves are set.
  (4) Degree of unsaturation of air inhaled.

The following three factors determine the degree to which the air becomes saturated :—

(*a*) Vapour pressure of the oil, which is affected by
(*b*) Temperature of the oil at the surface. And
(*c*) Time which air is left in the tank in the case of a tank which is frequently worked.

From these factors seven conditions which it is desirable to maintain may be put forward.

(1) Minimum oil surface exposure.
(2) Gas-tight roof and roof fittings.
(3) Breather valves on vents.
(4) Minimum vapour space.
(5) Minimum temperature variations.
(6) Roof capable of holding maximum pressure.
(7) Minimum temperature of oil surface.

Under fixed conditions the amount of breathing in a tank is proportional, although not directly, to the vapour space allowed, and for this reason this space should be maintained as small as possible, leaving only sufficient room for expansion of the oil.

The quantity of petrol vapour contained in the air in the vapour space, and the amount of expansion and contraction which occurs, varies throughout the vapour space. Immediately above the oil the air contains the greatest quantity of vapour, but the mixture at the top of the tank is hotter than elsewhere on account of the heat of the tank roof being transmitted to the vapour at that point. If the mixture is permitted to remain in the tank for an appreciable period with little or no breathing the air-vapour mixture becomes uniform in temperature and in petrol content. Breathing is not, therefore, proportional to the vapour space until the air-vapour mixture becomes uniform throughout in temperature and petrol content.

The type of oil stored, the temperature changes, and the character of the tank determine the amount of air-vapour mixture discharged. Providing the tanks and tank roofs are made gas-tight, windage losses are reduced to a minimum and only breathing losses are incurred.

In order to reduce the vapour space, tank roofs are being built with much lower pitch than formerly, allowing only the minimum slope on the roof for weather drainage.

The provision of more than one vent is a fruitful source of loss, since wind is permitted to blow through one and out of the others, carrying with it gasoline vapours.

Vacuum and pressure relief valves are installed on most modern tanks and are set to operate at a safe working pressure for the particular

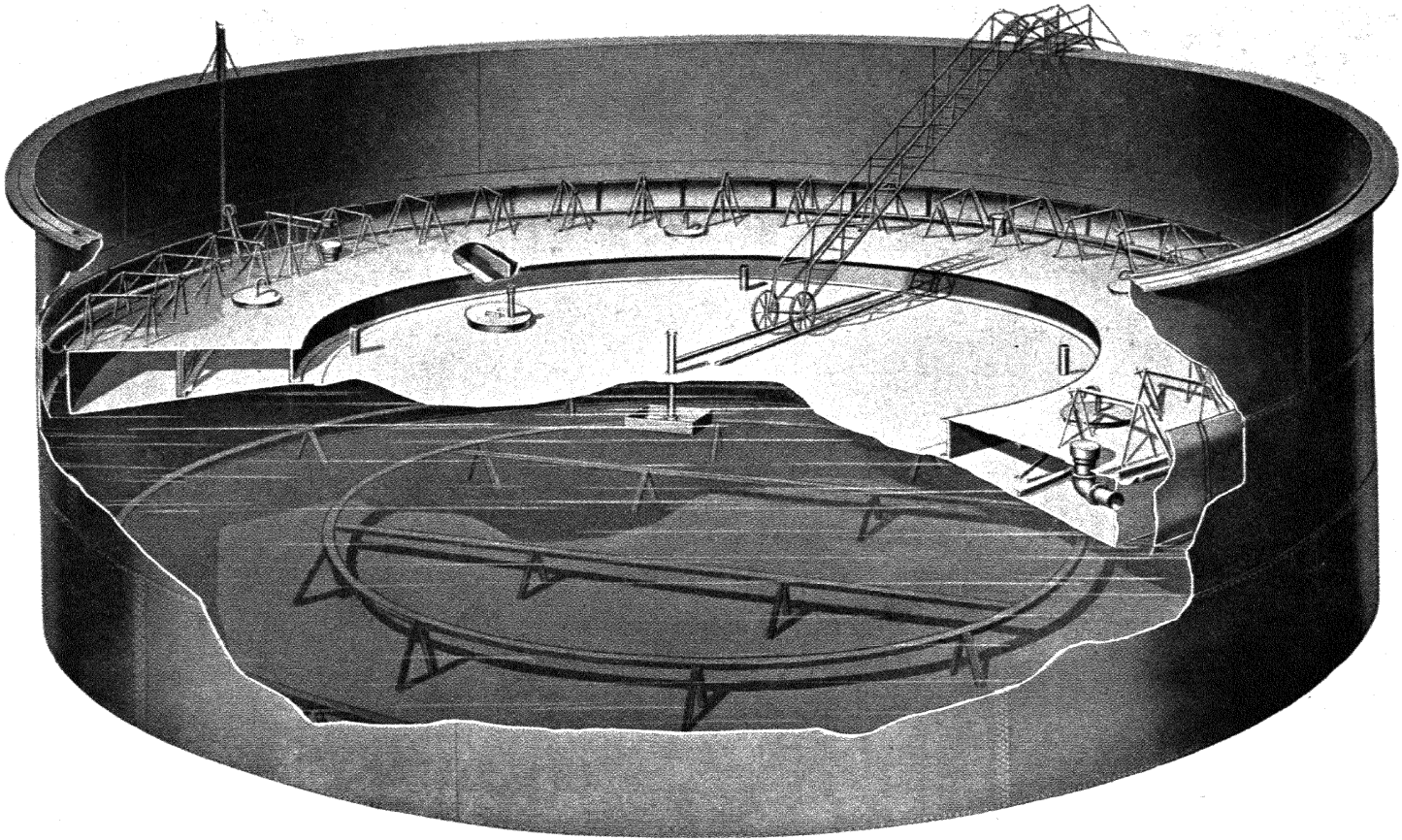


FIG. 1.—CUT-AWAY VIEW OF WIGGINS FLOATING ROOF
(*Courtesy of Chicago Bridge and Iron Works*)

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roof employed. No danger is experienced with these valves provided they operate at the pressure at which they are set, but should they fail to operate a burst roof often results. These valves therefore need careful selection.

278. The Wiggins Floating Roof.—In order to obtain a tank which would comply with as many of the foregoing conditions as possible, J. H. Wiggins developed a floating roof. This floating roof, by virtue of its particular construction, eliminates filling and emptying losses, as well as breathing losses.

The roof is a circular steel deck, which rides directly on the oil, and a seal. This roof, which is slightly smaller in diameter than the tank shell, has a steel rim erected around its outer edge. The space between the deck rim and the tank shell is closed by means of a seal which consists of a series of shoes and a continuous band of flexible material connecting the top of the shoes to the top of the deck rim. The shoes are fixed end to end in a continuous band with the same flexible material and are held in contact with the tank shell at all times by spring hangers which support them.

With the exception of the space bounded by the deck rim and the tank shell, the surface of the oil is completely covered. Air cannot reach the oil under the deck and as a result the condition which might allow the contents of the tank to fire is removed.

The space between the deck rim and the tank shell is gas-tight and the maintenance of a space in a gas-tight condition is an effective means of reducing evaporation where the volume is small. There is no change of vapour volume as the roof rises and falls and loss of vapours by this action is eliminated. Since breathing is approximately proportional to vapour volume, thermal breathing is small.

A secondary seal is often placed above the main seal to make certain that no air currents can possibly enter the tank as the roof rises and falls. This seal is merely a metal flap connected to the top of the shoes and extending completely round the tank. The seal makes contact with the tank shell at all times even when rivets and joints are encountered.

A vent is placed on the seal to prevent unsafe pressures developing beneath the seal.

One objection to the floating roof is that the oil immediately below the deck can boil if the roof becomes hot enough. This results in evaporation of the lighter fractions. This objection has recently been overcome to a great extent by the development of a double roof of pontoon type. The outer edge of the deck is built in the form of a continuous annular pontoon which is divided at regular intervals by bulkheads to form watertight compartments. Insulation is, therefore, provided at the seal, where it is of most value.

279. The Fleming Vapourless Tank.—Following on the development of the floating deck, Fleming produced a vapourless tank. In this tank no vapour space is permitted and an inverted water seal protects the surface of the oil and allows expansion and contraction of the oil. In order that this tank may function correctly it must be full of oil at all times, otherwise a vapour space is formed and any contraction or expansion will blow the seal.

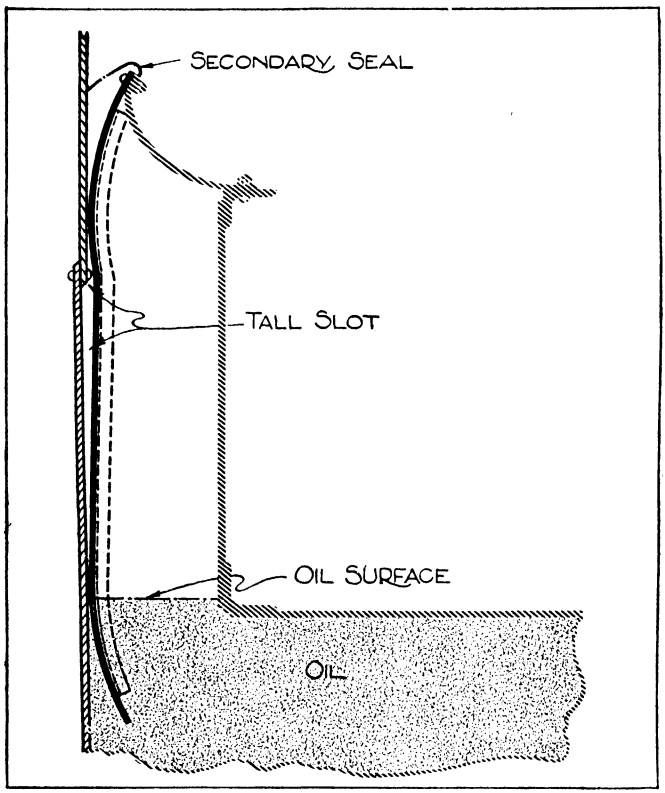


FIG. 2.—SECTION OF SEAL OF WIGGINS FLOATING ROOF
(Courtesy of Chicago Bridge and Iron Works)

Although this tank is ideal for standing storage when completely full, it cannot function correctly if the tank is to remain only partly full. To overcome this difficulty a breather roof was developed by J. H. Wiggins.

280. The Wiggins Breather Roof.—This tank is a gas-tight structure which permits a variable volume for the air-vapour mixture accumulating above the oil. The roof, when in its normal position, rests on a steel framework erected inside the tank. This framework

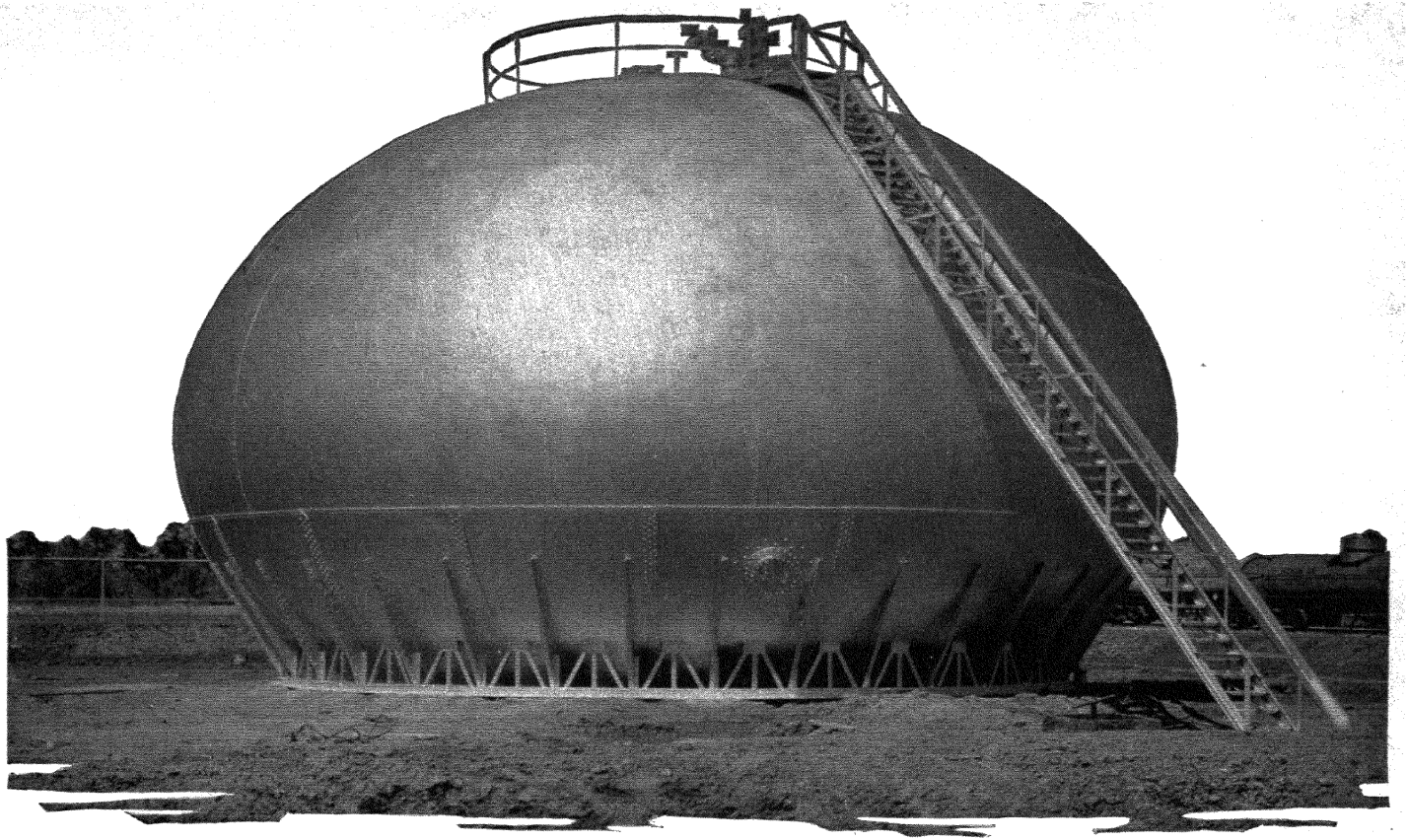


FIG. 3.—HORTONSPHEROID
(*Courtesy of Chicago Bridge and Iron Works*)

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permits the roof to slope downwards from the tank rim forming an inverted frustrum of a cone.

The roof is composed of plates, welded together to form a huge diaphragm, and is welded securely to the angle at the top of the tank shell. This diaphragm is not connected in any way to the framework inside the tank but merely rests upon it when in the downward position.

A volume relief valve is placed in the roof so that the air inside the tank may be vented whilst the tank is being filled. After the tank has been filled, any variation in the volume of the air-vapour space is taken care of by the breather roof.

During the coolest part of the day the roof rests upon the framework, but with an increase of temperature the air-vapour mixture expands and instead of a portion of it being forced out of the vent the roof rises sufficiently to provide the increase in volume space required. Providing the volume relief valve is set to operate at some temperature greater than that likely to be normally experienced the roof rises to allow for any expansion that may take place inside the tank and no losses are incurred. A breather roof, therefore, eliminates almost completely standing losses, but does not eliminate filling losses.

In the case of working tanks filling losses are the greatest source of loss and in an effort to reduce these to a minimum a pressure container, spheroidal in shape, and known as the Hortonspheroid, has been developed.

281. The Hortonspheroid.—The principle of the Hortonspheroid is as follows :—

When petrol is stored in a sealed tank it exerts a pressure in proportion to its vapour pressure at the temperature concerned. Any air which is present increases this pressure, the partial pressures of the petrol vapour and the air being in the proportions of their mol fractions, and the total pressure is the sum of the partial pressures of the petrol vapour and air present.

The Hortonspheroid is designed to withstand a certain maximum pressure and the relief valve with which it is fitted may be adjusted to operate at any desired working pressure determined by the vapour pressure of the petrol to be stored.

Assume the pressure relief valve is set to operate at a pressure of two atmospheres and the vacuum valve is adjusted to open at a pressure slightly below one atmosphere. As the petrol enters the tank, vapour mixes with the air : when the total pressure of the two components exceeds two atmospheres, the pressure relief valve opens, causing an escape of the petrol vapour-air mixture.

When the tank is emptied, assuming no change of temperature and vapour pressure, no air can be admitted by the vacuum valve, pro-

vided the vapour pressure of the petrol does not fall below one atmosphere, and the petrol evaporates and fills the space above the liquid as the level falls. Hence no air is present in the tank after the first filling since it was then all expelled and the vapour pressure within the spheroid maintains the vacuum valve closed.

Once the conditions for setting the pressure and vacuum relief valves have been established, the pressure inside the tank remains constant for each subsequent filling and emptying provided the temperature and vapour pressure of the petrol remain constant. This is an ideal case.

Assume now that the spheroid is filled with a petrol having a vapour pressure below one atmosphere, say 10 lbs. per square inch absolute, the pressure relief valve is set at 25 lbs. per square inch absolute and the vacuum relief valve is to operate at slightly below one atmosphere pressure.

At the commencement the tank is filled with air at a pressure of approximately 15 lbs. per square inch absolute, but as petrol is admitted and the air becomes saturated with petrol vapour, the total pressure gradually rises until it reaches 25 lbs. per square inch absolute, and as the liquid level rises this vapour is expelled. When the container is emptied, assuming no change in temperature or vapour pressure, more vapour is formed to fill the space above the falling liquid level, but since the vapour pressure is only 10 lbs. per square inch absolute, air is drawn in through the vacuum relief valve until the total pressure reaches that of the atmosphere.

On refilling the container with the same petrol, assuming the partial pressure of the air in the vapour-air mixture to be 5 lbs. per square inch at the commencement, the pressure of the air increases to 15 lbs. per square inch before the pressure relief valve opens.

By partially filling the spheroid in order that the combined vapour-air pressure does not exceed the figure at which the pressure relief valve is set to operate, filling losses may be eliminated.

In the case quoted, the tank could be filled approximately two-thirds full without vapour loss.

282. An estimate of the actual losses[3] incurred by evaporation will help in deciding the steps to take to reduce these losses.

The methods which have been used for measuring evaporation losses may be classified as follows :—

(1) Gauging the tank before and after the loss and correcting for temperature.
(2) Determination of the volume and petrol content of vapours which escape from the system.
(3) Determination of a particular property of the oil which changes

as evaporation takes place, for example, gravity, vapour pressure, etc.

Measuring the volume of oil before and after any loss has been incurred gives the amount of evaporation to a fair degree of accuracy. Ideal conditions must, of course, exist, for the accuracy to be high, and such conditions are present in the case of standing storage where no transfer of stock is necessary during the test. In order that the volume of the tank may be accurately measured and thus ensure a minimum of errors in the resultant calculations, warping of the tank bottom and movement of the gauge hatch during the test must be allowed for.

Since the measurement is by volume it is necessary to correct for temperature and this is probably the most uncertain feature of the gauging method. The coefficient of expansion of petrol is about 0·00045 for 1°F., so that corrections to a base temperature for comparisons require better than 1°F. accuracy in the determination of temperature for the study of small losses. The temperature throughout a full tank may vary over a range of 5°F. and the difficulties of securing a true average are thus apparent. The general practice is to take temperatures at varying depths in a vertical line, but this procedure is questionable.

Since the difficulties of accurately measuring the evaporation losses of a single tank are so great, it is apparent that, when a large number of tanks have to be gauged, accurate estimates of losses are impossible, particularly when stock is being transferred from one tank to another.

Because of these difficulties the gauge method is considered unsatisfactory in practice.

The second group of methods for measuring evaporation losses consists in determining directly the volume of vapours escaping and in analysing these vapours for petrol content. The volume can be obtained by general methods, such as a dry meter, an orifice, or a calibrated breather bag. Where filling with ordinary petrol is very rapid, the figures can be estimated by assuming the gas displaced to be equal to the volume of liquid introduced.

The most common of the analytical methods used for the analysis of the vapours are absorption in mineral seal oil, adsorption by charcoal and condensation by freezing mixtures. The results obtained by the different methods will naturally vary. Fractional analysis of the vapour undoubtedly gives the most accurate results but this method of analysis is often too slow to employ for a large number of samples.

The accuracy of loss measurements is chiefly dependent upon the significance of the vapour analysis and if this is known very good results are attainable.

The various methods which are founded on the change of some

property of the oil have a wide adaptability, because where evaporation can be determined by examination of a sample, elaborate field equipment and technique are unnecessary.

If gravities are carefully determined by means of the pyknometer, they are fairly sensitive to evaporation effects and thus the specific gravity of the stock may be taken as a measure of the loss. It is necessary, however, to determine by independent experiment the effect of loss on gravity for the particular stock under investigation.

The use of specific gravities of small cuts distilled by fractionation represents an improvement over the gravity method. The results are plotted as gravity against percentage distilled both for the original and final oil, the percentage distilled in the latter case being corrected to the basis of the original oil. The horizontal distance between the two curves is then taken as the evaporation loss incurred by the oil.

283. The vapour pressure of a petrol is a property which is very sensitive to evaporation loss, since the light components are most responsible for vapour pressure. Several methods of determining vapour pressure are in present use, such as the Reid bomb, described in Chapter XI (Volume II).

Any evaporation loss which a petrol incurs is reflected in a lowered vapour-pressure curve of the depleted spirit. If the vapour pressure curves for the original and final petrol are plotted on the same scale, the horizontal displacement between the two is a direct measure of the loss. This assumes, of course, that the actual petrol lost contains the various light hydrocarbons in the same proportions as exist in the saturated vapour.

Since the curves are usually not quite parallel, the loss is taken as the average of the horizontal displacement at several points. Initial vapour pressures are disregarded because of their erratic nature.

The chief utility of this method lies in the study of evaporation losses due to movement of stocks. For such purposes the petrol may be sampled at various stages in its movement and the vapour-pressure measurements give an indication of the percentage evaporated at any time. Leakage and spillage losses cannot, of course, be dealt with by this method.

According to tests carried out, the accuracy of this method is about 0·75 per cent. which justifies estimations of losses as low as 0·04 per cent. An overall accuracy of this order depends upon great care in taking and handling samples.

284. Cooling of Tanks.—In addition to the design of the tank, efforts have been made to reduce as far as possible the factor which causes evaporation, namely heat. Many methods have been tried, for

example, painting the roof and sides of the tank with some type of light coloured paint, by insulation, and in some instances by using water sprays.

Tanks are painted a light colour, white or grey, on the assumption that light colours reflect the heat and dark colours absorb it. It has been pointed out that most of the sun's rays reaching us are contained in the infra-red part of the spectrum and that a paint which reflects the visible light in a perfectly satisfactory manner may not reflect but absorb most of the heat rays. Ordinary paints consist of small reflecting particles embedded in a carrier. This carrier may be opaque to the heat rays although it allows light rays to pass through. It is essential, therefore, to ensure that the infra-red rays are excluded and only those paints which possess this property should be used.

Aluminium paint is effective under most conditions and has been used extensively. A more modern method of spraying the tanks with aluminium is to use aluminium rod and pass it through a gun which melts and atomises the metal. The effect is to coat the tank with a layer of pure aluminium, but the process is costly.

Reduction of evaporation losses has also been attained by covering tanks with a layer of porous material [4]; gypsum, constantly kept wet, is often used.

Experiments have recently been conducted in covering tanks with tin or aluminium foil. The foil is rolled on after the tank has been covered with an adhesive, but this method is expensive and when moisture finds its way under the foil the tank is relieved of its coating.

The spraying of the tank roofs with water reduces the evaporation losses both by the cooling effect of the water and also by the reduction in temperature produced by the evaporation of the water. However, few installations have sufficient water available for this method of cooling.

Mechanical difficulties and first cost have rendered the water top tank unpopular. An additional load is placed upon the tank shell when a water top tank is used and this may cause the collapse of the tank in the event of fire.

Insulation of the tank roof minimises excessive vapour-pressure changes not only by reducing the temperature in the vapour space during the day, but also by maintaining the temperature fairly constant during the night.

It is probable that a combination of internal pressure with light coloured paints would be effective and economical in reducing losses. The use of relief valves which close quickly and tightly as soon as the pressure inside the tank is reduced to the operating pressure of the valves is also found to be economical.

285. Fire Fighting Equipment.—Except in the case of extremely volatile liquids the danger of an explosion is not present and provided suitable means are available for extinction purposes an oil fire can be dealt with effectively.

Where a tank on fire contains an oil which is a mixture of many fractions with a wide boiling range, the heat tends to evaporate the fractions of low boiling point, leaving behind the heavier fractions which absorb sensible heat.

In the case of crude petroleum there is generally a layer of water below the oil and when the heated oil reaches this the water may be converted into steam. Oil and water are immiscible and both exert their own vapour pressure. The result is either a frothing action which causes some of the contents of the tank to flow over or an explosion.

The Standard Oil Company of California[5] conducted a series of tests on this frothing action, which is termed a " boilover," and arrived at the following conclusions :—

A boilover can only occur when

(1) Water is present in the tank below the oil,
(2) The oil is viscous and tends to froth when the steam attempts to pass through it,
(3) The tank contains oil which is a mixture of fractions having a wide range of boiling points which enables the hot layer to spread downwards to the water.

Fire is a form of combustion in which oxygen is one of the combining elements and in order that combustion may continue oxygen must be supplied continuously. Also, if combustion is to commence spontaneously the combustible material must be heated to its ignition temperature in the presence of oxygen.

It is obvious, therefore, that if a fire is to be prevented or extinguished, the temperature of the combustible material must be maintained or reduced below its ignition temperature and/or oxygen must be prevented from contact with it.

A consideration of these facts suggests methods for preventing or extinguishing a conflagration and these methods may be listed as follows :—

(1) To cool the burning liquid below its ignition point,
(2) To prevent admixture of oxygen with the vapours emanating from the volatile liquid.

The second method may be subdivided,

(*a*) Smothering, by the use of such ingredients as carbon dioxide, carbon tetrachloride, water, steam, etc.,

(*b*) Starving, by the use of a foam-producing material, which will blanket the surface of the oil and so prevent the production of vapour.

Water has been and will continue to be the most popular agent for fighting fires of all types, but unless it is efficiently applied to oil fires it may possibly increase the dangers already present.

Since in an oil fire it is the vapours which ignite it is obvious that there must be a vapour space immediately above the oil. In order that water in the liquid phase may be effective in cooling the burning liquid, the water must be applied directly through this vapour space and by its chilling action so reduce the temperature of the surface oil that the rate of evaporation is reduced below that necessary to maintain an explosive mixture. In other words, the percentage of vapour being given off must be reduced to below 1 per cent. if the fire is to be extinguished by this means.

286. Means of ignition of inflammable liquids in addition to the application of actual fire are lightning, spontaneous combustion due to chemical reaction and static electricity.

Lightning has been the cause of a large number of tanks firing and the necessary precautions should be taken to ensure that storage tanks are properly insulated from electrical discharges. During the last five years the number of oil storage tanks destroyed by lightning has been considerably reduced by suitable design of the tank.

Records show that the number of steel roofed tanks which have been struck by lightning in recent years is remarkably small. In fact, no matter what kind of oil is stored, providing the tank is earthed effectively in the strictly electrical sense, the danger to the all-steel storage tank or steel roofed tank appears to be negligible. The Chief Engineer of the Standard Oil Company of New Jersey, in a speech before the National Fire Protection Association, is reported as having said, " it is impossible to set fire to an all-steel gas-tight tank by lightning, and tanks have been seen to function as lightning conductors and no damage result."[6]

The greatest danger appears to exist with tanks having wooden roofs. These roofs are covered with thin gauge iron sheet to protect them from the weather and rest upon oil-soaked wooden columns. The roofs are thus effectively insulated from the steel or concrete shell which may be considered to be earthed. The roofs are seldom, if ever, gas-tight, and the probability exists that the gas issuing from the space may have a composition within the explosive range.

A lightning stroke may not be responsible for a fire but certain effects arise out of such a stroke without being directly caused by it. The passage of storm clouds over the earth's surface may result in enormous potential differences being set up and electric charges may be induced in

metal structures as a consequence. An electric condenser may in effect be reproduced. When the lightning stroke frees the bound charge, lateral discharges may take place, and the sudden release of the induced charge may cause sparking to pass across the small space between metallic members that are in close proximity but not actually connected.

Although this phenomenon is very common during lightning storms the amount of damage is remarkably small and as a result it is not fully appreciated.

The presence of inflammable vapours makes the problem much more serious. A steel tank fitted with a leaky wooden roof covered with thin steel plates is an example to consider. An electric charge may be " induced " in the roof and the gap between the shell and the roof being very small a lateral discharge may take place and this sparking may be sufficient to fire an explosive gas or vapour, providing the air-vapour mixture is of the correct proportion. Actually more fires are caused by lateral discharge than by the direct flash.

287. The erection of gas-tight tanks, or tanks in which mechanical and electrical continuity has been ensured between the roof and the shell, eliminates to a great extent the dangers from lateral discharge. If the roof and the shell are rigidly connected there is no possibility of sparking when the induced charge is released and the tank, as a whole, forms an excellent conductor to earth. It may not be possible for a tank to escape if it receives the immediate discharge but there is no reason why other tanks in the same farm should be fired by lateral discharge.

Several methods have been devised to ensure electrical continuity. One American system provides a brass cap fixed on the peak of the conical roof and from this cap a large number of copper cables are carried, spoke fashion, to the edge of the tank wall. The cable is electrically connected at this point. In addition, cables are run in concentric circles around the roof and where these cross the lateral spokes, electrical connections are made.

In addition, the cables are connected to roof plates at as many points as possible, and every plate is, therefore, connected electrically to the shell.

The necessity for a gas-tight structure is shown when a comparison is made between oil tanks and gas holders. Although gas holders are considerably higher than the normal oil tank and are therefore a better mark for lightning, the losses in oil tanks are considerably greater than in gas holders. The reason for this lies in the fact that gas holders are entirely of steel construction and are gas-tight and even if sparking did occur there would be no possibility of firing since no inflammable mixture of air and gas exists.

The erection of lightning conductors on oil tanks was considered a necessity a few years ago, but since the necessity of earthing a tank has been proved these have been dispensed with. Too much emphasis may be laid on earthing a tank whilst forgetting the far more important point of lateral discharge. A tank standing in water has been destroyed during a thunderstorm. This tank was well earthed and the cause of this fire was undoubtedly lateral discharge on the defective roof.

288. Gas-tight structures, mechanically and electrically continuous, prevent to a great extent fires caused by lightning storms without the necessity for the use of lightning conductors.

The danger from fire by spontaneous combustion is remote in any country where the atmosphere is humid, but in a dry atmosphere the risk is considerable under certain conditions.

Sulphur-containing crudes, and particularly raw distillates from these crudes, give off gases containing sulphuretted hydrogen and organic sulphur compounds. Iron sulphide is formed by the action of these gases on the steel roof or walls of the tank. Nascent iron sulphide absorbs oxygen at a great rate and becomes heated to incandescence. In a dry atmosphere this action may be dangerous and may cause fires. The corrosive effects may, of course, be serious in a humid atmosphere but the risk of fire is remote.

289. Static electricity[7] has undoubtedly been responsible for many fires, but in numerous cases it has been held responsible to cover carelessness on the part of someone engaged on the tank or tank wagon. It has, in fact, assumed such serious proportions in the minds of many engineers concerned with the storage and distribution of petroleum products that it has become a habit to blame it for any fire which occurs without any obvious reason.

Storage tanks, tank lorries and the mechanism for transferring the liquids are the parts most liable to be affected by static electricity. Uninterrupted metallic connection from the lorry to the tank should be maintained by using flexible tubing with metallic lining so that any charge may be passed to earth immediately it is formed. The tank and loading and discharging apparatus should be securely earthed by some means and the lorry itself must be earthed during loading and discharging. This is best done by a permanent clip which may be clipped on to the hose from the lorry itself.

When filling a vehicle from a pump care should be taken against a static charge set up in the vehicle itself during running. As a precaution it is best to bring the nozzle of the flexible tubing into contact

with any unpainted part of the vehicle before opening the tank of the vehicle. It is also advisable to see that the nozzle of the filling apparatus is in contact with the tank of the vehicle during pumping.

In a petrol installation it is doubtful whether any danger exists since the air-vapour mixture above the liquid in the tank is seldom, if ever, within the limits of inflammability.

Petrol has a very high vapour pressure and as a result the amount of air present in the vapour space of the tank is considerably reduced. Kerosene, on the other hand, has a relatively low vapour pressure and the relative proportion of air to vapour present in the space above the liquid is, therefore, greater and the air-vapour mixture may be within the limits of inflammability. The danger from static electricity when filling a tank with kerosene is, therefore, always present and must be guarded against.

290. The combustible limits of petroleum vapour lie between 1 per cent. and 6 per cent. When the percentage of vapour in the air-vapour mixture is less than 1 per cent., there is insufficient of the inflammable ingredient to support combustion. If the percentage of vapour is in excess of 6 per cent., there is insufficient oxygen in the confined space to permit combustion to continue. As the percentage of vapour in the air-vapour mixture approaches the mid-point between 1 per cent. and 6 per cent., the mixture is in a highly dangerous state and an explosion will undoubtedly occur.

In the course of an investigation into fire dangers in petroleum storage, carried out by A. Williams-Gardner,[8] an examination was made of the atmospheres existing in storage and process tanks containing inflammable volatile liquids. These tests were made in tanks which were being continuously emptied and filled with liquid and samples of their atmospheres were taken when filling, emptying and during the short periods when the contained liquids were in a state of quiescence. The investigation was carried out during the month of October when the tank atmosphere temperatures were in the neighbourhood of 17°C. in the majority of cases. Samples of the tank atmospheres were taken and analysed in a Bone and Wheeler Gas Analysis apparatus. No sample examined was found to be an explosive mixture of air and hydrocarbon vapour at atmospheric temperature and pressure. The determination of the total hydrocarbon content was made by mixing a known quantity of the sample with a known and adequate quantity of a 50 per cent. air/50 per cent. oxygen mixture free from carbon dioxide and completely exploding the mixture. The contraction in volume (C) on explosion and subsequent contraction (A) on removal of carbon dioxide, formed by the combustion of the hydrocarbons, by absorption in

aqueous caustic potash, were measured. The total volume of paraffin hydrocarbons present (V) was then given by the equation

$$V = \frac{1}{3}(2C - A)$$

from which the percentage hydrocarbon content (by volume) of the sample was calculated. The hydrocarbons present in the tank atmospheres were considered to be entirely composed of paraffins.

The ratio C/A, where C and A are the values previously obtained, was found to vary with different paraffins, decreasing in value as the number of carbon atoms in the molecule increased. Thus the lower members of the series have the following values :—

	Hydrocarbon	*C/A Ratio*
Methane ..	CH_4	2·00
Ethane ..	C_2H_6	1·25
Propane ..	C_3H_8	1·00
Butane ..	C_4H_{10}	0·875
Pentane ..	C_5H_{12}	0·80
Hexane ..	C_6H_{14}	0·75

The size of the paraffin molecules present is roughly indicated by the C/A ratio obtained. Only when not more than two members of the series are present can the exact proportion of the individual members be obtained by explosion analysis. For the purpose of an approximate result it may be safe to assume that not more than two members are present at a time and for the purpose of calculating the probable limits of inflammability of mixtures of air and inflammable vapours the above assumption was made.

291. The following relationships may be derived from a consideration of the chemical reactions taking place when a mixture of oxygen and any two consecutive paraffins combine under conditions of complete combustion.

For a mixture containing ethane and propane

$$\text{Ethane} = 2(C - A)$$

$$\text{Propane} = \frac{1}{3}(5A - 4C)$$

For propane and butane

$$\text{Propane} = \frac{1}{3}(8C - 7A)$$

$$\text{Butane} = 2(A - C)$$

For butane and pentane

$$\text{Butane} = \frac{1}{3}(10C - 8A)$$

$$\text{Pentane} = \frac{1}{3}(7A - 8C)$$

For pentane and hexane

$$\text{Pentane} = 4C - 3A$$

$$\text{Hexane} = \frac{2}{3}(4A - 5C),$$

where C and A have the same significance as before.

Providing the proportions of the individual combustible gases in the mixture and the values of the upper or lower limits for each combustible component are known, the limit of inflammability (L) may be calculated by the equation

$$L = \frac{100}{\frac{P_1}{N_1} + \frac{P_2}{N_2}}$$

where P_1 and P_2 are the proportions of the individual combustible gases in the mixture and N_1 and N_2 are the values of the upper or lower limit for each combustible gas, depending upon which mixture limit is required.

The explosive limits for pure paraffins mixed with air are as follows :—

Hydrocarbon	*Limit of Inflammability (% by Volume)*	
	Lower	*Upper*
Methane ..	5·6	14·8
Ethane ..	3·1	10·7
Propane ..	2·2	7·3
Butane ..	1·6	5·8
Pentane ..	1·4	4·5
Hexane ..	1·2	3·3

The results of typical tests on storage tanks are given in Table 1, which show that, with the exception of aviation spirit, only butane and pentane were present in the vapour space. In the case of aviation spirit the C/A ratio indicated a predominance of pentane and hexane.

The limits of inflammability for the above, obtained by calculation, compare favourably with some actual experimental determinations carried out on petrols by Burrell.[9]

TABLE 1

Contents of Tank	State	Total Hydro-carbons (at 45°C.)	Volume Per Cent. in Total Atmospheres			Calculated Limits	
			Butane	Pentane	C/A Ratio	Lower	Upper
Treated No. 1 Spirit	F.	10·8	6·7	4·1	0·86	1·5	5·0
Treated No. 1 Spirit	Q.	5·05	2·25	2·80	0·829	1·5	5·0
Treated No. 1 Spirit	E.	5·81					
Untreated No. 1 Spirit	E.	7·06					
Untreated No. 3 Spirit	F.	11·9					
Untreated No. 3 Spirit	Q.	10·6	8·3	2·3	0·849	1·6	4·8
Untreated No. 3 Spirit	E.	9·7					
Untreated O.R.D. Spirit	F.	9·2					
Treated O.R.D. Spirit	Q.	8·4	6·5	1·9	0·856	1·6	4·8
Treated O.R.D. Spirit	E.	8·75					
Crude Oil	F.	6·35	5·6	0·75	0·864	1·6	5·6
„ „	E.	6·73					
			Pentane	*Hexane*			
Aviation Spirit	Q.	5·05	3·44	1·61	0·782	1·3	4·1

F = Filling. Q = Quiescent. E = Emptying.

Assuming that the vapours issuing from the vent in the roof of a tank have ignited, combustion will often continue even when the percentage of vapour in the air-vapour mixture exceeds 6 per cent., because the issuing stream can collect oxygen from the atmosphere. In such a case as this there is the danger of the flame flashing back into the tank and causing a serious explosion.

The volatility of the material and the explosive range over which combustible air-vapour mixtures can be obtained are most important criteria of the fire risk. With high volatility a mixture may be above the maximum whilst with low volatility the mixture may be below the minimum explosive limit.

The following table shows the temperatures at which the lower and upper limits of inflammability of pure liquids are reached, calculated from the vapour pressure-temperature curves.

TABLE 2

	Lower Limit	Corresponding Temperature. °C.	Upper Limit	Corresponding Temperature. °C.
Pentane	1·35	Below 0	4·50	Below 0
Petrol	1·5	—	5·3	—
Petroleum Benzine	1·1	—	3·8	—
Benzene	1·4	—5	4·7	5
Toluene	1·4	7	4·7	30
Ethyl Alcohol ..	4·0	15	13·6	35
Ethyl Ether ..	1·8	Below —30	5·2	—28
Acetone	2·35	Below —20	8·5	Below —20
Carbon Disulphide..	4·1	,, ,,	—	—

It has been determined experimentally that flame advances through an explosive mixture at a rate of somewhat less than 15 feet per second, so that providing the vapours are issuing from the tank at a rate faster than this, and are maintained at this rate, the flame does not travel back. This does not apply in a case where, due to leakage, air is permitted to mix with the vapour to bring the air-vapour mixture to a point between 1 per cent. and 6 per cent. vapour content. Detonation may occur under such conditions and the speed of the flame is considerably greater in this case.

292. The use of water in the form of a jet is not effective when the oil on fire is non-viscous and it is necessary in this case to cool the whole contents of the tank definitely to preclude the formation of sufficient vapour to continue the conflagration.

With viscous oils, on the other hand, streams of water injected into the tank to produce violent agitation may mix the hot surface layer with the cool oil underneath. This mixing may so reduce the temperature of the surface layer that evaporation falls below that necessary to continue the fire.

A jet of water injected, without care, into a tank cools just the area it strikes, and is ineffective elsewhere. Therefore, unless sufficient water is injected to cover the surface completely, extinction of the fire becomes an impossibility. With the larger tanks complete covering by sprays is a difficult matter and it is obvious that little reliance can be placed on this method. Water, in the form of jets, may be valuable as an auxiliary to other methods of fighting fires, in such ways as cooling the tank shells, in protecting structures in the vicinity from the heat and in many other ways.

Water, in the form of a fog, is, however, being used with success in fighting tank fires.[10] The water is finely atomised to form the fog, which spreads over the surface of the oil, and the minute particles of water cool the fire by absorption of heat. The heat absorbed con-

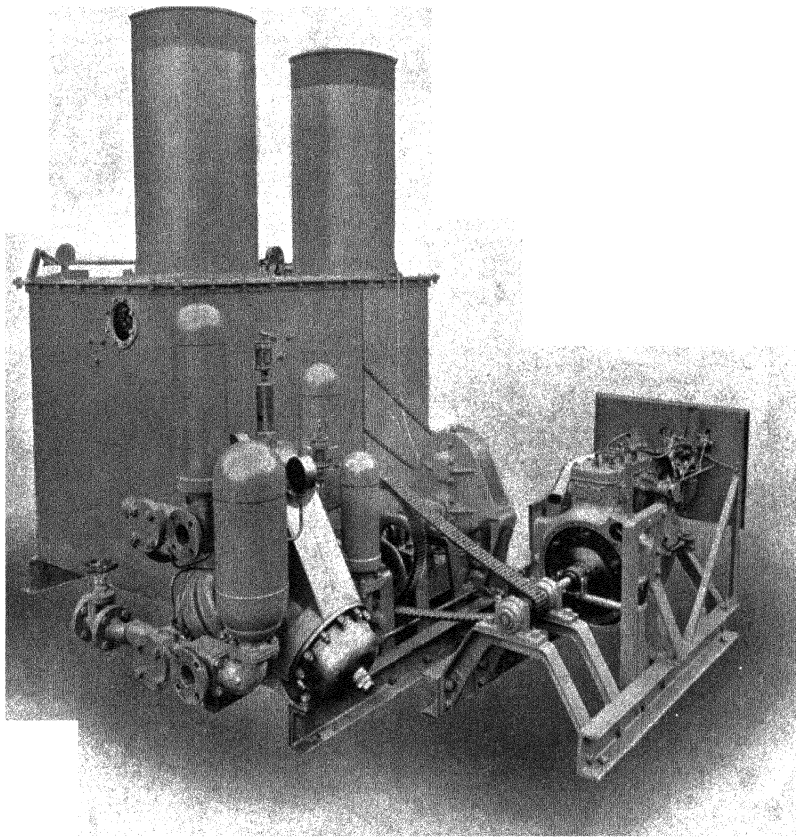


FIG. 4.—FIXED TYPE FIRE-FOAM PRODUCING MACHINE

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verts the small particles of water into steam and in addition to the cooling action the fire is smothered by the exclusion of oxygen.

The amount of heat transfer depends upon the temperature gradient and the surface area. Thus, the more finely the water is divided, the greater is the surface area and the greater is the efficiency of the water as a heat absorbing agent. In addition, the water dilutes the vapours to a point where they will not burn.

The apparatus used for converting the water into steam is a type of sprinkler valve. This valve will convert ½ gallon of water per second into a fog covering 180 square feet, in an unconfined space. Where the space is confined, the efficiency rate is much greater. By the use of a fog the damage that may be caused by the application of water is eliminated since the minute particles are quickly converted into steam.

In effect, the use of water in the form of fog may be considered as a cooling, smothering and starving action and the reduced cost of this method should make it a popular fire-fighting agent.

In an oil fire of any considerable size it is practically impossible to cut off the air so completely that the fire will be smothered. A small tank fire may be dealt with by the use of such agents as carbon dioxide, carbon tetrachloride, etc., but the application of such vapours to a large tank fire is not only a costly, but also a difficult procedure. These vapours dilute the air-vapour mixture to a point below which combustion can no longer be continued: they have practically no cooling effect, but due to the fact that they are non-conductors of electricity, they are particularly useful in and around high voltage equipment.

293. A blanket of foam is the most common and usually the most effective means of fighting fires. In effect, foam is a combination of the two previous methods, water and a vapour. Evaporation is retarded in two ways, (1) the production of vapour is prevented by blanketing the surface of the oil and (2) by cooling due to the water with which the foam-making material is mixed.

In addition to these effects the foam bubbles exclude oxygen for a sufficient period to enable the burning material to cool of its own accord.

Unless foam is properly and effectively applied the foam system will not necessarily be successful in extinguishing a fire and three fundamental principles must be seriously considered.

(1) In order that foam may be effective in extinguishing an oil fire it is essential that the condition which permits evaporation to continue should be eliminated. Thus, although the blanket of foam segregates the oil from the burning vapours above, if the outside of the tank is being heated vapours will rise and

pass through the foam blanket to enable combustion to be continued. This results in the foam being destroyed.

Any fire which is heating the tank on the outside should, therefore, be extinguished before the application of the foam. Where several tanks are on fire the windward one should be extinguished first to prevent the heat from this one vaporising the oil in the next tank.

(2) Fire breaks down the foam blanket and the rate of breakdown depends upon the method of application, the amount of foam surface exposed, the character of the oil to which it is applied and the quality of the foam. It is obvious, therefore, that foam must be applied to a fire at a rate greater than it is likely to be destroyed in order to maintain an efficient blanket. The method of application depends upon the size of the tank and other available facilities.

(3) The rate at which foam is applied to a fire is a vital factor. If the foam is allowed to fall from a great height or be forced violently on to the surface of the oil, part of the foam may be projected beneath the surface. This action may break down the foam and reduce its effectiveness. Also any particles of foam which are forced below the surface pick up oil and, due to the increased buoyancy, rise to the surface where the oil burns and the foam is destroyed.

Any turbulence caused by the foam stream being projected forcibly, or from too great a height, on to the surface of the oil, tends to prevent the formation of a continuous foam blanket and in the case of volatile liquids, such as petrol, its efficiency is so reduced as to render it incapable of extinguishing the fire.

Where fixed mixers are installed, it may happen that the drop from the mixer to the oil surface is too great to prevent the foam from being forcibly projected beneath the surface. In order to overcome this condition a chute may be installed for the transfer of the foam from the mixer to the oil surface. This chute is built in spiral form from the top of the tank to the bottom and when the foam commences to flow it is transported down the spiral chute until it reaches the oil, and then flows across the surface.

294. All refineries, garages, local depots and any other building in which petroleum products are in any way dealt with should be equipped with extinguishing devices which are best suited to dealing with the first stages of the fire. These devices may be sand buckets, small portable extinguishers or hand pumps. The numbers of these various devices which must be installed are clearly defined by regulations and all devices

should be maintained in first class order to be ready to fight any conflagration that may start.

These small devices are obviously of little use if the fire gets out of hand and to cover this emergency chemical extinguishers are necessary. The latter may be of the Soda-Acid or Dry Powder types.

The fire extinguisher which has been adopted after most exhaustive tests by the Air Ministry for the protection of its aerodromes in all parts of the world is the " Bromylene " extinguisher manufactured by the General Fire Appliance Co., of London.

The charge of this extinguisher is froth impregnated with chemicals and the ingredients of the froth are sulphate of alumina, sodium bicarbonate, pure extract of quillaia, pure extract of liquorice and a small amount of some glutinous substance. The chemicals consist of methyl bromide mixed with certain patent preparations.

Methyl bromide is a colourless mobile liquid with a smell resembling that of chloroform and boils at 4·5°C. It has a vapour density relative to air of 3·3 compared with a vapour density of 1·5 for carbon dioxide and a vapour density of 5·4 for carbon tetrachloride, measured at 0°C. The mixture of methyl bromide and carbon dioxide generated by the combination of sulphate of alumina and sodium bicarbonate therefore has a vapour density between 3·3 and 1·5, depending upon the proportions of each vapour present.

In practice it is found that an excessive quantity of methyl bromide breaks down the adhesive qualities of the froth. The ideal to be aimed at is to preserve the adhesive and blanketing qualities of the froth and the quenching qualities of the methyl bromide. The correct proportion has, therefore, been calculated to attain this ideal.[11]

295. A typical fixed installation of the foam type may be as follows.

A generator is connected to a water line having sufficient water pressure to produce the required foam output. The compound is fed into the hopper, drawn into the water stream and fed into the nozzle at the top of the tank. Here a chemical reaction takes place between the ingredients and the foam is formed.

Another type of foam installation utilises two solutions, usually aluminium sulphate and sodium bicarbonate, resulting in the production of aluminium hydroxide and carbon dioxide. To render the foam produced more stable an organic colloid such as glue or liquorice is usually added. Two equal-sized solution tanks are connected to some type of pump capable of dealing with them. The solutions are pumped separately to a mixing chamber at the top of the tank to allow the mixture to be formed as near as possible to the seat of the fire.

An air compressor may be supplied for stirring the solutions and a heater for maintaining the solutions at an efficient temperature during

cold weather. All control valves should be situated at a safe distance from the tanks.

Portable generators have been successfully used and have the added advantage that they can be run up to the tank on fire with the knowledge that no damage has been done to the equipment by the initial explosion. With a fixed installation the initial explosion may quite easily shatter the mixing chambers and prevent the correct application of the foam.

296. At present no regulations exist specifically stating the distance apart of tanks in a tank farm, but the various companies have agreements between themselves. It is possible, however, that these agreements will be embodied in Government Regulations in the near future.

All tanks for the storage of low flash-point oils, that is, oils of flash-point below 150°F., are guarded by fire walls having a capacity equivalent to 105 per cent. of the total tank capacity, and provided this capacity is maintained the number of tanks inside the wall is immaterial. For oils of flash-point above 150°F., the capacity is 25 per cent. of the total tank capacity.

In addition to the fire walls the tanks are often equipped with a drencher system. Water lines are run around the periphery of the tank and over the roof, and the valve controlling the flow of water is placed outside the compound. The water after flowing over and around the tank is caught by an interceptor and only the last interceptor contains water. The clearing of the intermediate interceptors prevents burning oil flowing on the water and being carried outside the compound. This drencher system may be used during the hot season to maintain the temperature of the tanks as low as possible and should a fire occur at one tank the water may be used to prevent the fire spreading to the adjacent tanks. It is thus possible to confine the fire to one area and so enable it to be attacked by all the available fire-fighting devices instead of having to spread them among a number of tanks.

297. As a safeguard against explosion or fire in tankers transporting inflammable petroleum products, the method adopted by the Standard Oil Company of California is of considerable interest.

The method consists of eliminating, to as large an extent as possible, the presence of oxygen in all the cargo compartments. In ordinary practice, as the oil is pumped out of the tanks air flows in to take its place. The mixture of the remaining vapours and the incoming air is liable to form an explosive mixture, which only needs a spark to cause an explosion. The explosion hazard can be completely eliminated provided an inert gas which contains little or no oxygen is pumped into the tank as the liquid is pumped out.

On a steamship such an inert gas is available, without the necessity for installing special apparatus, in the form of flue gas. This waste gas when properly cooled makes an ideal inert gas for introduction into the vapour space of the tanks.

The flue gases are passed from the stack to a washer through a series of " bubble caps " and rise through a layer of water in the bottom of the washer. As the gases pass up through the main chamber of the washer they are continually washed by sprays of water and are cooled from a temperature of perhaps 400° or 500° Fahrenheit to the temperature of the sea water circulating through the washer. To make quite certain that only cooled gases are passed to the tanks an automatic valve is installed which is linked to the line by a fusible unit. If, for any reason, the gases coming from the washer should be too warm, the fusible link is melted and the valve automatically closes. A further safeguard is installed which closes the automatic valve should the pressure in the water line supplying the nozzles of the cooler drop below a certain point.

When the oil is pumped out of the tank, the vacuum which tends to form in the cargo tank draws the flue gas out of the stack through the washer into the tank being emptied.

A further safety feature is brought into action when the tanks are being filled. Under ordinary circumstances, the vapours occupying the tank when empty must be expelled to make room for the oil being pumped and are simply forced out of the vents. As a result, extreme precautions must be exercised during the loading period. Although the cargo tanks of a ship utilising the flue-gas system are filled with an inert gas the vapours coming off the oil being pumped are still dangerous if they are allowed to pass through the vents on deck. A further safeguard is, therefore, installed in the form of a pipe connection from the vents to the bottom of the hollow mast. Instead of opening the vents the main distributing line valve is opened and the vapours are forced through this line and out at the top of the mast. A check valve prevents any vapours finding their way back to the washer and the stack.

Danger exists, for example, when the tanks are being repaired or cleaned and it is under such circumstances as these that the flue-gas system is a successful measure of protection.

By the installation of a blower to take the flue gas out of the stack through the washer and force it through the distributing pipe lines, flue gas can be circulated through the empty tanks of the vessel until all oil vapours have been displaced by fresh air and the work carried on in safety.

Where an inert gas of this type is available there appears to be no reason why a similar system should not be used with ordinary storage tanks.

298. Regulations of the Fire Officers' Committee for Approved Foam Installations and Foam Hydrant Services.

Solutions and Solution Tanks.

1. At least four Imperial gallons of each solution must be provided and maintained in respect of each square foot of oil surface of the largest tank to be protected.

Where the foam system, in addition to protecting oil tanks, is extended to supply hydrants for the protection of buildings, the minimum quantity of each solution shall in no case be less than 4,000 Imperial gallons and sufficient ingredients shall be kept on the premises to enable the solution tanks to be fully recharged unless it be certified that the conditions are such that the necessary full supply of chemicals can always be obtained (*a*) within twelve hours, in which event spare chemicals need not be provided, or (*b*) within more than twelve but not more than forty-eight hours, in which event one-fourth only of the full supply need be kept on the premises.

2. Solution storage tanks must be constructed of steel or iron (lead lined in the case of the aluminium sulphate solution tank) or of wood (preferably redwood) bound with wrought iron hoops of round cross section fitted with adjustable malleable iron tightening lugs and the hoops and lugs painted with two coats of bituminous paint, one before and the other after fixing in position.

3. Solution storage tanks must be fitted with covers to protect the contents against heat. The covers should be raised a little above the tanks so as to allow free ventilation.

4. A monthly test must be made of the bicarbonate solution and a record of the tests must be forwarded to the leading office quarterly. Whenever the monthly test indicates that the specific gravity has fallen below 1·0625 the solution must be made up to not less than that strength.

5. Solution mixing tanks must be provided.

6. Provision must be made by means of hot water circulating coils (placed inside at the bottom of the tanks) to prevent the temperature of the solution falling below 50° Fahrenheit. The temperature of the solutions must not be raised by means of artificial heat above 90° Fahrenheit.

7. A perforated air pipe or pipes must be placed inside at the bottom of each tank (with the perforations pointed downward) and an air pump must be provided to enable the solutions to be kept uniform by periodical agitation.

Pumps.

8. Pumps, if of the plunger type, must be triple or quadruple acting and so designed as to ensure that each plunger shall make a full stroke. Whether plunger type or centrifugal pumps be employed they must be so

arranged as to make it impossible to deliver other than the proper proportions of each solution.

9. The capacity must be determined by the maximum quantity of solution required to deal effectively with the largest tank, consideration being given to the frictional loss in the installation piping.

10. Pumps must be constructed of non-corrodible metal in parts liable to be affected by the solutions.

11. A relief valve and pressure gauge must be fitted on each discharge pipe.

12. Suction pipes must be of non-corrodible metal and be fitted with non-corrodible metal strainers.

13. Arrangements must be made so that the pumps can be periodically tested, also for the cleansing of the pipe lines after the solutions have been passed through them.

14. A warranty must be given (*a*) that power sufficient to work the pumps at efficient pressure is to hand, and (*b*) that not less than eight men shall be available at all times throughout the year, of whom at least three shall be fully conversant with the working of the system.

Where the premises protected are not extensive and the conditions generally are favourable, a warranty as to a lesser number than eight men (but in no case less than three) will be considered.

15. Arrangements must be made so that all piping can be properly drained.

Hydrant Service.

16. The hose used in connection with hydrants must be rubber lined and of not less than $1\frac{1}{2}$ inches internal diameter.

Where oil or spirit tanks are protected it is required that the pipe lines shall be carried up the exterior thereof and drop the foam at each delivery point down an approved form of shoot or tube so designed and constructed as to ensure the foam being conveyed to the surface of the oil or spirit without being unduly broken up by an excessive fall or dried up by the heat of a fire during its passage downwards.

Plans and particulars of projected Installations must be submitted to the Fire Insurance Companies for approval.

Dry Powder Continuous Foam Generators

Conditions.

1. At least three men fully conversant with the operation of the installation shall be available to work the plant at all times of the day and night.

Where any of the tanks protected exceeds 50 feet in diameter the number of men required to be available shall be as specified in No. 14 of the Rules relating to solution tank systems.

2. An adequate supply of water must be always available from hydrant connections (*a*) with a main, the pressure of which, with the generators in use, never falls below say, 35 lbs. per square inch at the generator or (*b*) with a fire pump of not less than 250 gallons per minute capacity, which can be brought into operation at a few minutes' notice at any time of the day or night.

3. One generator and one mixing chamber may be accepted for the protection of an oil tank not exceeding 25 feet in diameter; two generators and two mixing chambers for an oil tank exceeding 25 feet but not exceeding 40 feet in diameter; and three generators and three mixing chambers for an oil tank exceeding 40 feet but not exceeding 50 feet in diameter. Special consideration will be given to installations for the protection of oil tanks exceeding 50 feet in diameter provided particulars of the number and capacities of the generators, the number of mixing chambers or distributing points and the diameters of the oil tanks be given in each particular case. Generally speaking, the arrangements should be such as to permit the delivery of not less than 10 cubic feet of foam per minute for each 100 square feet of the surface area of the tank (requiring approximately 8 Imperial gallons of water per 10 cubic feet of foam).

4. At least 8 lbs. of dry powder shall be provided and maintained in respect of each square foot of oil surface in the largest tank protected. The quantity of powder required where buildings are to be protected shall never be less than 1,200 lbs.

5. Permanent metal piping must be provided from the generators to all oil or spirit storage tanks protected thereby. It must be carried up the exterior of the tanks and drop the foam at each delivery point down an approved form of shoot or tube so designed and constructed as to ensure the foam being conveyed to the surface of the oil or spirit without being unduly broken up by an excessive fall or dried up by the heat of a fire during its passage downwards.

6. Where oil tanks are equipped with a Wiggins or similar type of floating roof the quantity of dry powder to be provided may be calculated on the basis of 4 lbs. per square foot instead of 8 lbs. as specified in Rule 4, and a delivery rate of 5 cubic feet of foam per minute for each 100 square feet of surface area of the tanks will suffice.

Particulars Required.

(*a*) A plan of the premises to a scale not less than 40 feet to the inch, together with a descriptive report upon the buildings and/or oil tanks shown thereon.

(*b*) The name of the installing engineers and type of generator.

(*c*) The number of generators to be provided and their positions, with details of the diameter, length and run of any permanent piping

to be connected therewith, also distance from the generator to the furthest tank to be protected.

(*d*) Details of the water supply to be used (e.g., if a town's main, the diameter thereof, the minimum standing and running pressures available therefrom ; and if a pump, the capacity thereof, the power supply and the source from which it draws).

(*e*) The minimum number of men fully conversant with the system who will be available at all times throughout the year to bring it into operation at a few minutes' notice.

(*f*) The quantity and diameter of hose provided, the diameter of the jets, the number of tins of dry powder kept on the premises, the weight of each, and the position of the building or buildings in which they are stored.

299. Fire Insurance.[12]—A fire insurance contract is a contract of indemnity. It relieves the insured of the direct loss he will suffer in the event of the property being damaged or destroyed by fire and the amount the insured is entitled to recover under the contract is determined by the extent he has suffered pecuniarily by the fire and nothing more. Thus, no insured person can recover more than the actual loss he has sustained, no matter how many contracts he may have taken out on the property.

In the case of refineries, it is necessary to take out insurances on buildings, machinery and storage tanks. The premium rates on the buildings are dependent upon the fire risk, the fire protection appliances with which the buildings are equipped and the situation of the refinery. Obviously, the conflagration risk is higher if the refinery is situated in an area where there is nothing but oil, and the Companies must, of course, provide for that risk. The value of the building for insurance purposes is the expenditure that would be incurred to erect the building at the building costs existing at the time. It is of little use to insure buildings for their selling price and reconstruction costs only must be considered.

With regard to machinery the amount recoverable on an insurance policy is the actual monetary value of the machinery at the time of the fire. Since machinery deteriorates with usage, it is necessary to consider the length of time it has been in use and a certain amount must be written off the new price according to the accepted annual rate of depreciation of the particular machinery concerned.

As regards storage tanks, reduced premiums are allowed wherever Foamite extinguishers or one of the drencher systems are installed. The reductions may be as high as 65 or 70 per cent. of the normal rates.

The premium rates depend largely on the same factors as do those of the refineries. Obviously, if the tanks are situated in an area

in which factory chimneys are constantly emitting sparks, the fire risk is greater and the greater the risk the greater the premium. If the fire protection equipment is adequate so that any conflagration can be dealt with expeditiously and efficiently, the fire risk is considerably reduced and the premium is less in consequence. The erection of dams sufficiently large enough to hold the oil contained in the tanks reduces the fire risk and again enables reduced premiums to be demanded.

The tanks at local depots are a small fire risk and the rates are only nominal. The same applies to the pumps and underground tanks at garages. Here again the fire risk is small, provided the necessary precautions against smoking or the carrying of naked lights in the vicinity of tanks or sheds is observed.

300. Distribution.—With the exception of short pipe lines around refineries or from landing stages at seaboard stations, the distribution of fuels in this country is carried out by barge, rail wagon or lorry. The distances which the fuel has to be transported does not warrant the erection of long pipe lines such as have been erected in the U.S.A. No district is so far from any one of the main distribution centres that unnecessary delay in delivery results.

The crude petroleum, or in most cases, the refined product, is brought from the country of origin to this country by tanker. When crude oil is transported it is passed to the refineries and the distribution of the refined products follows precisely the same procedure as when the refined products are brought from abroad.

The tanker calls at the ocean installation. This station must have sufficient storage accommodation to be able to receive cargoes from, or deliver cargoes to, ocean-going tankers, and to maintain sufficient stocks at all times to feed the markets in its area. Tankage must, therefore, be available to receive cargoes even when stocks have not been completely used up. In other words, storage accommodation must be so adjusted that a reserve is always available.

Marine conveyance is by far the cheapest method of transport and it is, therefore, necessary to locate the ocean installations in such positions that they are as near as possible to the centre of consumption. The number and position of these ocean installations are governed chiefly by the proximity of these ports to thickly populated centres. The bulk of the population of Great Britain is located around London and the industrial areas of Lancashire, Yorkshire, Midlands, South Wales, Newcastle and Glasgow, and in Ireland around Dublin, Belfast, Cork and Limerick, and ocean installations at or near these areas actually serve three-quarters of the whole population of Great Britain and Ireland. The ports selected depend to a large extent upon the

facilities given by the local authorities, to the facilities available for berthing the tanker and discharging the cargo, and to the ease with which the outlying districts may be fed from these main installations.

301. No two ports have precisely the same regulations, some are lenient, others are very strict, but in order to assist the various ports a Model Code of Harbour Bye-Laws has been drawn up to comply with the conditions specified under the Petroleum (Consolidation) Act, 1928.

Briefly, this Model Code provides a basis upon which the various ports can work, modifying the sections to comply with the local regulations in force.

Any ship carrying petroleum, on nearing the Harbour and during the time that such ship remains in the Harbour, must display by day a red flag with a white circular centre of definite dimensions, and by night a red light in such a position that it is plainly visible, and any other navigation lights which may be required by other regulations, rules or bye-laws. A self-propelled petroleum barge which cannot comply completely with this bye-law must display by day, in a conspicuous position, above the deck, a metal flag painted red with a white circular centre and by night an all-round red light.

The Harbour Master must be informed immediately of the quantity of petroleum spirit on board and the manner in which such spirit is stowed. The ship must be moored at the place appointed by the Harbour Master and must not be removed without written authority except to leave the Harbour.

The time and place of loading or landing of petroleum spirit must be notified and no loading or landing is permitted at any quay other than that directed by the Harbour authorities. Inflammable vapours must be removed from any hold containing casks, barrels or other vessels of petroleum spirit prior to unloading and after removal.

No petroleum spirit is permitted to be landed or loaded except between sunrise and sunset unless such loading or landing is commenced not less than one hour before sunset. In this event, the landing or loading may proceed, provided no repairs are necessary to the plant or pipes or nothing occurs to interrupt landing or loading. Should a breakdown occur the pumping must cease and not be continued until sunrise.

No artificial light or fire is permitted on board the ship or at or near the place where the spirit is being pumped during the process of landing or loading.

Smoking and carrying fuses, matches or any other appliance capable of producing ignition is forbidden at or near the place of landing or loading.

Pipes and casks, barrels or other vessels, must be reasonably free from leaks. Should pumping cease for some reason other than the completion of the landing or loading, the tanks and hold of the ship must immediately be closed.

Unless, in the opinion of the Harbour Master, it is impracticable to maintain a distance of 100 feet between two petroleum ships no two ships shall approach nearer than this distance except for the purpose of transhipment.

Certain other rules have been compiled and in addition most ports supplement the Model Code with rules and bye-laws of their own.

302. Geographical limitations may place certain important areas out of economic range for direct delivery from the ocean installation and yet may be sufficiently important to warrant coastal cargoes to supply them. In this case, coastal tankers receive cargoes from the ocean installation and deliver them to the sub-installations around the coast. The primary purpose of the ocean installation is to maintain a supply of the necessary products so that there shall be no intermission of deliveries to the sub-installations and depots, but, in addition, these installations serve as bonded warehouses and clearing stations for the Customs. By the Finance Act, 1928, all liquid petroleum products imported into Great Britain and Northern Ireland are subject to a Customs Duty. This duty is, however, rebated in certain circumstances.

The heavy hydrocarbon oils, which are described as petroleum oils, coal tar and oils produced from coal, shale, peat or any other bituminous substance and all liquid hydrocarbons but not those which are solid or semi-solid at a temperature of 60°F., in accordance with the tests prescribed by the Commissioners of Customs and Excise, no longer receive a rebate from the Customs duty, as in previous years, except in certain cases.

These oils are termed " Heavy Oils " other than those fuels which are used for a mechanically propelled vehicle constructed or adapted for use on roads. The term " Heavy Oils (Road Fuel) " is applied to the latter oils for purposes of the Custom and Excise Tariff, and oils falling within this latter category and delivered for use on or after August 8th, 1935, are liable for duty at the rate of eightpence per gallon. All other heavy oils receive a rebate at the rate of sevenpence per gallon when delivered for home consumption. The duty payable on these oils is, therefore, one penny per gallon. Registered Fishing Boats are exempted duty in respect of any hydrocarbon oils and Coasting Vessels are exempted in respect of hydrocarbon oils, other than light oils, used as fuel for their machinery while engaged on a voyage in home waters.

All light hydrocarbon oils of which not less than 50% by volume distils at a temperature not exceeding 185°C., or of which not less than 95% by volume distils at a temperature not exceeding 240°C. and which gives off an inflammable vapour at a temperature of less than 22·8°C., when tested in the manner prescribed by the Acts relating to Petroleum, must pay this tax of eightpence per gallon. Light oils and heavy oils used as road fuel thus pay the full tax, and other heavy oils pay one penny per gallon.

In addition, under the provisions of Section 4 of the Finance (No. 2) Act of 1931, it is illegal to mix hydrocarbon oils in respect of which a rebate of duty has been allowed under the Finance Act of 1928 with any light hydrocarbon oil unless a licence has been granted by the Commissioners of Customs and Excise and the amount of duty, which would have been paid on the oil if the rebate had not been allowed, has been paid. It is, therefore, illegal to mix kerosene or kerosene distillate or any other heavy hydrocarbon oil on which a rebate has been allowed with petrol or other light hydrocarbon oil unless the necessary licence has been obtained or the duty paid on the heavy oil. By the Act of 1928, however, every product must be bonded until released and it is, therefore, convenient to use ocean installations as bonded warehouses. To avoid paying the duty on the small quantity usually lost by leakage on every transfer, it is customary to transfer the taxable products from the ocean installation to the sub-installation in bond.

The ocean installation serves a third purpose. From the fields to the ocean installation the products are dealt with by the ton, since weight is not affected by change of temperature. In the British markets, however, the products are sold by the gallon and it is at the ocean installation that the change over from tons to gallons is made.

303. The ocean installation receives products by sea-going tanker and so acts as the centre for distribution to local depots. In addition to this, these bulk installations may also act as depots supplying the products to the dealers in exactly the same manner as the local depots. Filling sheds and a fleet of bulk and can lorries are, therefore, provided.

From the ocean installation the products may be shipped by coastal steamer to sub-installations, to local depots by rail car, barge or lorry, or to the dealer by lorry.

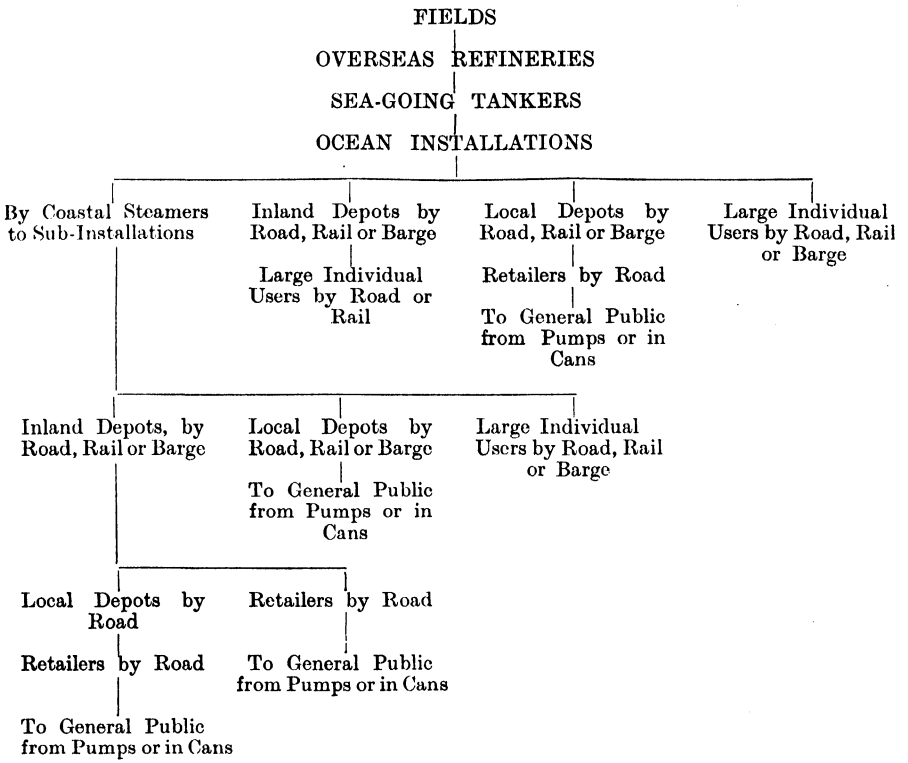
In a similar manner the sub-installation may supply the dealer direct or may feed the local depots in bulk either by barge, rail car or lorry.

Again, the inland depots are fed from the ocean installations

and these inland depots supply the local depots, or the dealer direct, usually by lorry.

The country is divided into areas, each area being served by the ocean installation, sub-installation, inland depot or local depot most conveniently placed for the purpose.

This network is shown in the following chart.



304. The possibility of a sudden cessation of transport facilities such as occurred during the General Strike of 1926 must not be overlooked and such strategic points as will prevent such a cessation should be chosen in all cases. There must be flexibility in the programme of feeding the depots, and the careful selection of convenient sites assist greatly in obtaining this.

Road transport is at a disadvantage with the railways when long distances have to be covered and from a cost point of view any distance greater than 50 miles should never be attempted by lorry. The rail car can carry at least twice as much as the road lorry and at a distance of something under 50 miles comes into successful competition both in regard to time, cost and convenience. With the reduced rail rates this competition is much more severe and bye-laws, in force and pending,

have so handicapped road haulage that except for journeys of a few miles the lorry is no longer economic.

Motor spirit, kerosene and black oils have different freight rates and these rates are sub-divided according to the method of packing for transport. The products may be transported in rail tank cars, in barrels or in cans and conditions of minimum charges are fixed. Thus, any quantity of spirit less than 8 tons shipped in a rail tank car is charged for as 8 tons. Larger consignments receive better rates but, unfortunately, no greater tonnage than 14 tons is encouraged by further reducing the rate. Where a consignor can offer a really large consignment over a period special rates are available and twice the distance does not necessarily mean twice the cost.

The familiar rail tank car is known to all and no description is necessary. These cars are divided into two categories, " ordinary " and " starred," and are classified according to whether they are to carry black oils or white oils. The two types of car are those with overhead discharge and those with bottom outlet.

All rail tank cars commence in the " ordinary " category and must be well run in on the slow local goods. When they have passed the Railway Clearing House tests they are " starred " and are then permitted to be attached to the fast goods trains.

The type of car most generally used for motor spirit is the overhead discharge car in which the liquid is pumped out by a 2-inch pipe reaching to the bottom.

305. Transportation by barge has the advantage over the other two methods in that much larger quantities can be carried. Cargoes of 500–1,000 tons may be moved from ocean installations to sub-installations by small draught tankers or by power-driven barges suitable for shallow waterways. Special barges, carrying as much as 60 tons per trip, have been designed for working the canals and rivers of the Midlands.

A Model Code of Bye-laws has been drawn up for canals in precisely the same way as for harbours to comply with the conditions set forth in the Petroleum (Consolidation) Act, 1928.

A red flag with a white circular centre must be displayed by day and a red light, which is visible from every side at a distance of 100 yards, by night. Petroleum spirit may be conveyed only by a petroleum vessel and no other cargo is permitted except in holds provided for the purpose and isolated from the petroleum spirit.

A petroleum vessel, with the word " inflammable " clearly painted on both sides, may not be navigated on the canal except in tow of a horse, or of an efficient tug propelled by mechanical power or of a self-propelled petroleum vessel. During a fog the master of a petroleum

vessel is only permitted to navigate his vessel for such a period as is necessary to enable the vessel to reach a safe mooring and except in these circumstances no mooring is permitted other than in an authorised place. When moored there must be a distance of at least 100 feet between the petroleum vessel and the next one.

The navigation of a vessel through a tunnel is prohibited when another vessel is within or about to enter the tunnel and only those vessels approved by the Canal Authority are permitted to pass through the tunnel either self-propelled or towed.

The landing of petroleum spirit and the precautions to be taken are governed by precisely the same rules as for the sea-going tankers.

306. When a consignment is to be made, whether by tanker, barge, rail car or lorry, each tanker is examined to ensure that no water is present and is then filled by pipe line. The quantity delivered is then measured by volume in the case of all tanks except rail cars, which are weighed.

The quantity delivered from a tanker to a shore installation is obtained by dipping the installation tanks and checking up with the ship's measurements. The quantity delivered by barge may be checked either in the installation tanks or by barge measurements where the barge is calibrated. Road tank wagons are always calibrated and measured by dipping.

The fuel is thus transported by one of the three methods to the sub-installations, inland depots or depots for despatch to the retailer whose business it is to supply the general public. Whichever of these depots deals with the retailer the same procedure is adopted.

The transportation of petroleum spirit is governed by the Petroleum Act of 1928, and by the Petroleum Spirit (Conveyance) Regulations, (1926, No. 1340 ; 1927, No. 511 and 1932, No. 1052). Statutory Rules and Orders are issued from time to time by the Secretary of State for the Home Department amplifying or modifying the various sections of the Act.

Local deliveries of petroleum spirit may be made in tanks of capacities up to 2,500 gallons in all districts, provided the general design of the vehicle has been approved by order of the Secretary of State as suitable for the conveyance of such quantities. For a mechanically-driven road tank wagon a fire-resisting screen must be placed between the tank and the driver's cabin, this screen being carried up above the top of the tank and down to within twelve inches of the ground. The exhaust from the engine must be placed wholly in front of this screen.

If the tank has a capacity greater than 600 gallons, it must be divided

into self-contained compartments no one of which may contain more than 600 gallons.

Except in the case of syphon emptying tanks, the draw-off pipes must be fitted with internal valves in addition to strong and secure taps and screwed caps.

The filling of the tank must be done through pipes carried nearly to the bottom of the tank and these pipes must be terminated in such a manner that a liquid seal at the bottom is provided at all times, or alternatively, the covers over the filling openings, except during the filling operation, must be kept locked.

The dipping pipes must be carried down to the bottom of the tank and any openings in them, other than the upper orifice, and all ventilating openings, must be covered with fine wire gauze of not less than 28 meshes to the linear inch and the ventilating openings must be protected by covers when not in use.

The dangers of static electricity have become apparent during the last few years and this subject has been referred to earlier in this Chapter.

307. The general method of distributing petroleum spirit to the general public is by roadside pump. The 2-gallon can has gone almost completely out of favour owing to the convenience offered by the pump and this change-over has certainly resulted in a reduction of distributing costs.

The supply of spirit for feeding the pumps is sent from the depot by lorries that make deliveries in bulk, and is deposited in underground tanks which may contain upwards of 300 gallons. These tanks must be licensed as petroleum storage and their installation is governed entirely by local regulations. The tanks are usually horizontal cylinders constructed of $\frac{1}{4}$-inch mild steel plates, welded inside and out. The suction pipe, which reaches to within $1\frac{1}{2}$ inches from the bottom of the tank, is closed with a foot valve. The space between the tank bottom and the foot valve is allowed to prevent water being lifted. The filling pipe is a 2-inch pipe reaching to within 3 inches of the bottom of the tank and this pipe may also serve as a gauge tube for measuring the contents of the tank by a dip-rod. Water is prevented from entering the tank by the provision of a screw cover. A vent tube is taken from the tank to some convenient place well away from the tank.

The tank may be embedded directly into the ground or placed in a concrete pit filled with sand, but whichever is used the filling point should always be below the ground level, access being gained through a manhole cover. Local regulations, of course, dictate the exact type of installation.

Pumps are of the visible, piston or electrically operated types and,

in most cases, some indicating device, a graduated measure or a meter, is installed for checking the quantity delivered. All pumps are inspected regularly by Government Inspectors to ensure correct measures being supplied to the public.

A small demand still exists for spirit in cans and, as a result, the motor fleet must fall into two categories, i.e., lorries for bulk deliveries and lorries for can deliveries. The fleet therefore consists of lorries ranging in capacity from one ton trucks up to lorries capable of transporting 2,500 gallon loads. Lorries of capacities below 600 gallons have tanks of the portable type and in many cases are capable of conveying spirit both in bulk and in cans.

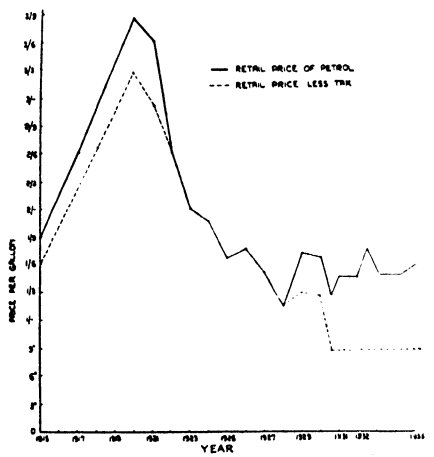


FIG. 5.—VARIATION IN PRICE OF PETROL, 1914–1935 (U.K.)

The storing of petroleum spirit, otherwise than for sale, is controlled by Statutory Rules and Orders, 1929, No. 952, and no person may keep spirit in any storage place which does not comply with these regulations.

In brief, the regulations for private storage provide that the building must be adequately ventilated unless it is in the open air, and that fire extinguishing apparatus, capable of dealing with petroleum fires, or a supply of sand, must be kept in or near the storage place. The storage place must not form a part of, or be attached to, any dwelling place unless it is separated by a substantial floor or partition constructed of a material not readily inflammable. Not more than sixty gallons of petroleum spirit is permitted to be stored in any one storage place. No vessel other than a fuel tank of greater capacity than two gallons is permitted to be stored, unless the storage place is situated more than twenty feet from any building, highway or public footpath and a retaining wall or excavation has been made to prevent the spirit flowing in case of fire.

Two 2-gallon cans is the maximum permitted, where the storage place is nearer than twenty feet to any building or other inflammable structure, without permission from the local authority.

308. Cost of Distribution.—The cost of distributing petrol varies from place to place, but so careful has been the selection of the locations for the various types of depots that this variation is slight.

Fig. 5 gives an indication of the variations in the price of petrol from 1915 to 1932.

In March, 1929, His Majesty's Government requested the three largest purveyors of petrol to explain the reason for increases in the price of petrol and kerosene, and the statement then made gives a good idea of the distributing costs at that time.

The price of motor spirit in Great Britain is governed by the price ruling in the Gulf of Mexico, since 70 per cent. of the motor spirit requirements of this country are, or were, drawn from this source.

Since No. 1 Spirit is a blend of various spirits, no direct comparison with " U.S. Gulf " prices is possible and in the example used to give some idea of the distribution costs commercial spirit was taken.

The following table is taken complete from the statement furnished to His Majesty's Government on March 18th, 1929.[13]

TABLE 3. COST OF COMMERCIAL SPIRIT (GREAT BRITAIN)

	Price in Pence per Imperial Gallon	
Cost Prior to Arrival in U.K.		
" U.S. Gulf Export," Price (March, 1929) 9½ cents per American gallon or	5¾	
Cost of ocean transport, marine insurance and leakage	¾	
	—	6½
Charges in U.K.		
(1) Duty imposed by Parliament	4	
(2) Dues, coastwise and rail freights	1	
	—	5
		11½
Distribution Costs.		
Companies' inland distribution costs for " bulk " delivery, including cost of collecting duty		2½
Total Costs—Delivered Wholesale ..		1 2

Deliveries in packages, cans or barrels, constitute approximately only 20 per cent. of the total United Kingdom deliveries. The foregoing costs are those for " bulk " delivery.

The retail price of commercial quality spirit paid by the private motorist in March, 1929 was 1/5 per gallon in the London zone and 1/5½ per gallon in the provinces. The dealers' margin in both cases was 3d.

per gallon so that the prices realised by the Companies was 1/2 and 1/2½, respectively.

Large commercial users who take their supplies direct from the "Wholesaler" are granted a rebate which results in the price received by the Companies, in the aggregate, falling below the retail or ex-pump price by approximately 3½d. per gallon. The average price realised by the Companies was, therefore, not 1/2 and 1/2½ but 1/5 and 1/5½ less 3½d. in each case, i.e., 1/1½ in the London zone and 1/2 in the Provinces, respectively. The total cost delivered wholesale was 1/2 per gallon, so that for commercial spirit a loss was made in the London zone for every gallon sold on rebate agreement.

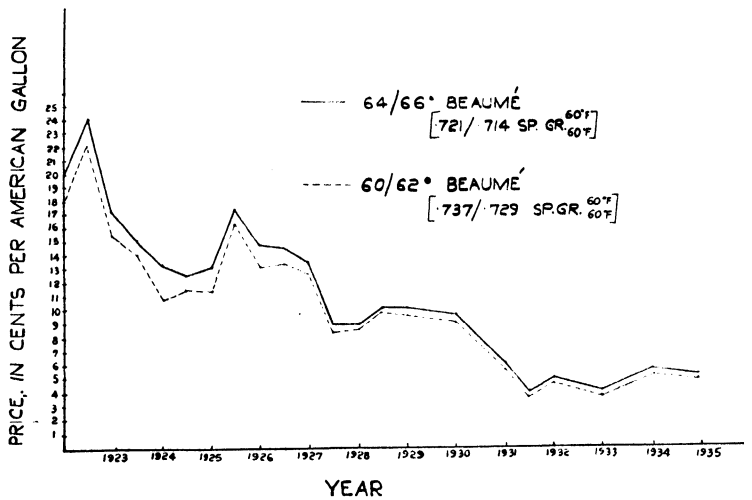


FIG. 6.—U.S. GULF EXPORT PRICES OF PETROL, 1922-1935

Many private car owners use First-quality ("No. 1") motor spirit and a complete service in almost every village, however remote, must therefore be maintained. This requires a special system of detailed distribution and, as a result, the cost of distribution of the First-quality spirit is appreciably higher than that of the "Commercial Spirit." Owing to the distinctive qualities of these First-grade brands, a higher price is realised than for the commercial grades.

In order to secure and ensure sufficient supplies of first-quality products, the Companies draw supplies from different sources and do not confine themselves to any single source of supply. The first-quality spirit is thus a commodity produced to meet a special requirement and no direct comparison can, therefore, be made with U.S. Gulf prices.

The accompanying graph shows clearly how the price of Motor Spirit has fluctuated in the United States Gulf area during the period 1922–1935.

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Chapter VI

BENZOLE, ITS PRODUCTION AND USE AS A MOTOR FUEL

311. Introduction.—Although benzene, or "benzole" as it is known in the impure state, was known to be a product of the carbonisation of coal at a much earlier date, it was not recovered from carbonisation gases until late in the nineteenth century, and Irwin, of Hardman and Co., Manchester, was probably the first to effect this on a large scale. This was done by creosote oil scrubbing in 1882. Benzene itself was first recognised as a chemical entity by Faraday in 1825.[1] By 1907, the production of rectified benzole from carbonisation processes in England had reached 2 million gallons per year, and by 1924 the figure was 15 million gallons. At the present time, the production is about 30 million gallons.

During times of national stress, an adequate supply of benzole is a necessity because of its great value in explosives manufacture, but in normal times, the supply of benzole for this purpose more than meets the demand and the disposal of this material as a motor fuel, or as a constituent of motor fuels, is conducted on a large scale. In many countries the proportion of benzole disposed of as a motor fuel considerably exceeds that used for all other purposes.

The use of benzole as motor fuel was first begun as an industrial undertaking in this country by the firm of William Butler and Co., of Bristol, in 1903, who marketed a grade known as "90's benzole" in two-gallon tins at about 1/- per gallon. The undertaking was not very successful. In 1907, the idea was again drawn attention to, but not until 1913, when the Petrol Substitutes Joint Committee was formed, was any extensive propaganda launched. During the Great War (1916), as a result of the realisation of the importance of benzole as a home-produced motor fuel, proposals were made for dealing with the production and distribution of benzole for this purpose after the War. These proposals finally culminated in the formation in 1919 of the National Benzole Association. The National Benzole Company was subsequently formed and has been largely responsible for building up a satisfactory marketing organisation for the disposal of benzole in this country. This company is owned by the chief benzole producers and net profits realised return to the industry on a profit-sharing basis. It is the only important benzole marketing organisation in this country

and disposes of benzole in the form of a mixture with petroleum spirit. This mixture is known as " National Benzole Mixture."

The use of benzole as a motor fuel in Germany was recommended at about the same time as in Great Britain, and in 1910, Germany was utilising about half her benzole production for this purpose. An association known as the " Benzol-Verband " now owns a large distributing organisation for motor benzole in Germany. In France a similar association to the National Benzole Association, known as " l'Union Française des Producteurs de Benzols " (Unibenzols), was formed in 1927, and now includes nearly all the benzole producers in France. A Belgian association was formed early in 1930, under the name of " l'Association Belge des Producteurs de Benzols " (Bengo-Benzols).

The Production of Benzole in High Temperature Coal Carbonisation Processes

312. The tars and gases produced by the carbonisation of coal at gas works or at coke ovens are the chief sources of benzole. At gas works, the coal is carbonised with the object of producing gas, which, after suitable purification, is distributed for town supply for heating and lighting. At coke ovens, the chief object in carbonising coal is to produce a coke for metallurgical purposes and much of the gas produced as a by-product is used in an unpurified condition for heating the carbonising retorts and ovens.

Coke Oven Practice.—In modern by-product coke oven plants, the coal is first crushed into the form of a slack and is then washed with water to remove impurities and charged to the ovens whilst still containing 4 to 8 per cent. of moisture. The coal is either charged into the ovens, which are built up side by side to form a battery, through openings in the roof of each oven, or compressed by means of a combined coal compressing and charging machine and pushed into the oven through a charging door at one end. Typical dimensions of a by-product coke oven are 35 feet long and 9 feet high, with an average width of 18 to 20 inches, the carbonising capacity being 8 to 10 tons of coal per oven per 24 hours. Recently there has been a tendency to build larger ovens with a capacity of 15 to 20 tons. The charge of coal is heated from both sides by burning gas in suitably arranged flues between the ovens. The flue gases are usually at a temperature of 900 to 1,200°C. As soon as the oven is charged and sealed, connection with the gas main is made. A pressure is developed during carbonisation and this forces the gas into the main. After passage through the by-product recovery plant, part of the gas is returned to the ovens for heating purposes. When carbonisation is complete, doors are opened at both ends of the oven, the resulting coke is discharged and the ovens refilled with a fresh charge of coal.

Various methods of heating are employed. In the so-called " waste heat " type of plant, the hot gaseous products of combustion are led from the heating flues to boilers where they are utilised for steam raising. In regeneration types of plants, the heat of the gaseous combustion products is used to preheat the ingoing air to the oven flues. This is effected in various ways. Usually about 50 per cent. of the total gas produced in regenerative ovens is available for industrial or town supply purposes.

Although, in coke oven plants, the manufacture of coke is the primary object, the recovery of by-products, such as tar, ammonia and benzole, is important from the financial standpoint. The tar present in the gases in vapour form is first recovered by passing the gas through a series of coolers, the last traces, which are difficult to condense, often being removed by various forms of tar extractors. A small amount of benzole is often condensed with the tar, but most of this remains in the gas at this stage. At the same time as the tar is condensed, water is also precipitated, carrying with it certain quantities of water-soluble compounds such as ammonia, hydrogen sulphide and hydrocyanic acid. The resulting solution is known as " ammoniacal liquor." Ammonia left in the gas is recovered by washing the cooled gas with water. The ammonia, which is present in solution in two forms, " free " and " fixed " (i.e., chemically combined), is driven off from the aqueous solution thus obtained in two stages. Uncombined ammonia and ammonia present in the form of easily decomposed salts, such as the carbonate and sulphide, can be driven off by simple distillation, but salts such as ammonium chloride must be decomposed by boiling with lime or some other similar method. Ammonia thus set free is used for the manufacture of ammonium sulphate by interaction with sulphuric acid. At the present prices of ammonium sulphate, the recovery of ammonia is often not economic.

After the removal of tar and ammoniacal liquor, coke oven gas contains benzole vapours and higher boiling hydrocarbons, hydrogen sulphide, organic sulphur compounds such as carbon bisulphide and thiophene, and various other impurities. When the gas is intended for industrial purposes it is further purified after benzole recovery.

In coke oven operation in this country the average yield of crude benzole obtained is 3 gallons per ton of coal carbonised. Approximately 97% of the coke oven capacity is accompanied by benzole recovery plant.

313. Gas Works Practice.—In gas works operation, with the primary object of producing gas for town's supply, coal is carbonised in retorts which are usually tubular and smaller than coke ovens. The usual arrangement of these retorts is one in which the latter are

placed horizontally and in which the retorts have a charging capacity of about half a ton of coal. The retorts are heated either by coke or by producer gas, obtained by the incomplete combustion of coke. Retorting temperatures of 1,000–1,200°C. are employed. Coal gas produced in horizontal retorts at gas works is often mixed with blue water gas, an impure mixture of oxides of carbon and hydrogen which has a lower calorific value than coal gas and which is produced by passing steam through burning coke maintained incandescent by an air blast, thus :—

$$C + 2H_2O \rightarrow CO_2 + 2H_2$$
$$C + H_2O \rightarrow CO + H_2$$
$$CO_2 + C \rightarrow 2CO$$

During recent years various forms of vertical retorts, which permit the carbonisation of coal in large quantities in one retort, have been introduced. These may be operated continuously, the coal being fed in at the top, carbonised during its slow passage down the retort, and the resulting coke discharged at the bottom. Steaming is generally employed, with the production of a certain amount of water gas *in situ*. Water gas is used chiefly as a means of coping with fluctuations in the demand for gas. When the diluent effect of the water gas is too severe, a "carburetted" water gas of higher calorific value than ordinary water gas is manufactured by spraying on to a hot chequer work in the gas stream an oil such as petroleum gas oil, which is cracked at the temperatures employed. The cracked products are mainly gaseous and remain in the gas phase. Average properties of the above various gases are detailed in Table 1.

TABLE 1. AVERAGE PROPERTIES OF TYPICAL INDUSTRIAL GASES[2]

	Horizontal Retorts	Continuous Vertical Retorts. No Steaming	Continuous Vertical Retorts. Steaming	Debenzolised Coke Oven Gas	Producer Gas	Blue Water Gas	Carburetted Water Gas
Oxygen	0·4	0·4	0·4	0·4		—	0·4
Carbon dioxide ..	2·0	3·0	4·0	2·0	4·0–7·0	4·7	5·6
Carbon monoxide ..	8·0	9·0	18·0	7·4	26·0–29·0	41·0	30·5
Hydrogen	52·0	53·0	49·4	54·0	11·0–12·0	49·0	37·0
Nitrogen	4·0	6·0	6·2	5·6	52·0–54·5	4·5	5·5
Methane	30·0	25·0	20·0	28·0	0·5–2·6	0·8	14·0
Hydrocarbons ..	3·6	3·0	2·0	2·6	0–0·4	—	7·0
Assumed composition of hydrocarbons	$C_{2\cdot5}H_5$	C_4H_8	C_4H_8	$C_{2\cdot5}H_5$	C_2H_4	—	$C_{2\cdot5}H_5$
Specific gravity (Air = 1)	0·4	0·43	0·48	0·38	0·87–0·9	0·55	0·63
Calorific value (gross) B.T.U./cu. ft. ..	560	540	475	525	126–163	295	500

After the gases have been removed from the retorts, they are cooled and water present is separated as ammoniacal liquor and tar is removed by some form of extractor. Purifiers containing layers of moist ferric oxide are employed to remove hydrogen sulphide and a large proportion of the hydrocyanic acid present. After purification, coal gas is free of hydrogen sulphide and ammonia, but contains some benzole, in addition to very small amounts of organic sulphur compounds, hydrocyanic acid, carbon dioxide and naphthalene.

The average yield of benzole obtained in this country from gas works operation is 2·0 gallons per ton of coal carbonised, but only 37·5% of the plants in use are accompanied by benzole recovery installations.

Benzole Recovery from Coke Oven Gas and Coal Gas

314. The amount of benzole condensed with the tar in the initial cooling of carbonisation gases is dependent upon the amount of cooling employed, but is usually only about 5 per cent. of the amount of benzole left in the gas. That condensed with the tar is recovered from the latter by simple distillation processes. Benzole recovery from the gas is usually carried out after the gas has passed through its various purifications in order to avoid the recovery of very impure benzole and in order to minimise corrosion of recovery equipment.

Two general methods of benzole recovery are employed, (1) absorption processes and (2) adsorption processes, the theories of which have already been described in Chapter III.

The Absorption Process.—The absorption process is usually referred to in the benzole industry as the oil washing process and consists of scrubbing the gas with a high boiling oil in a manner similar to that adopted for recovering gasoline from natural gases. The plant used is very simple. The rich gas containing the benzole is passed through a series of scrubbers where it is washed with sufficient oil to remove the benzole. This oil then passes via heat exchangers, etc., to a still where it is stripped of its benzole content by a combination of direct and steam heating. The process, is, of course, continuous. Numerous oils are used in this recovery process as wash oils, but creosote is very popular for this purpose, both in England and on the Continent. Creosote is obtained by the fractional distillation of high temperature coal tar and boils roughly between 200° and 320°C. When used for benzole recovery, it often has the following properties :—

Specific gravity at 60°F., 1·010–1·035.
Tar acids, 8–9 per cent.
Naphthalene, not more than 7 per cent. deposited at 45°F.
Initial boiling point, 200–220°C.

50 per cent. distillate at 250°C.
80 per cent. distillate at 300°C.
Water, traces.

Blast furnace creosote, obtained from tar produced in the manufacture of pig iron in a blast furnace, is also used as a wash oil. This contains very little or no naphthalene and is more paraffinic than ordinary creosote. Normally, it contains about 20 to 25 per cent. of tar acids, but these are generally extracted for use in disinfectants because of their high germicidal properties. Petroleum gas oils and straw oils are also used, but only to a small extent in this country.

For information concerning the relative efficiencies of various wash oils, reference should be made to the Reports of the Benzole Research Committee.

Most coke oven plants using the wash oil process operate at 75 to 85 per cent. efficiency of recovery of benzole from the gas. The efficiency is limited to this figure by incomplete stripping of the benzolised wash oil, by the use of insufficient wash oil, and by inefficient scrubbing. The cost of recovery increases very rapidly as the efficiency approaches 100 per cent. In gas works, the removal of benzole from the gas causes a reduction in calorific value generally to the extent of about 5 per cent., and this necessitates the manufacture of a proportionately larger amount of gas for the delivery of a given heating value. Furthermore, benzole in the gaseous form in purified town's gas is much more valuable than in coke oven gas, because the former commands a higher price. For these and for other reasons, it is not usually practicable to remove more than about 60–70 per cent. of the benzole content of purified town's gas.

Often thickening of the wash oils is observed. This thickening may be caused by oxidation, reaction with hydrogen sulphide when crude gas is being washed, presence of tar fog and ammonia in the gas, polymerisation of the oil constituents, or by the admixture with high boiling constituents extracted from the gas. Usually, coal tar oils are superior to petroleum gas oils in regard to this thickening phenomena, since the former dissolve the resinous substances produced, whereas, with the latter, separation of sludge occurs.[7]

315. The Adsorption Process.—The adsorption process for the recovery of benzole from coal carbonisation gases is similar to that adopted for the recovery of gasoline from natural gases and which has already been described in Chapter III. The adsorption process offers many advantages over the much more widely used oil washing process. Of these, one of the most important is that a higher recovery efficiency is obtained at a lower steam consumption. Efficiencies of 90–95 per cent. have been obtained and the benzoles recovered contain a higher propor-

tion of benzene. On the other hand, the adsorption process is essentially intermittent in operation. This causes an increase in labour and supervision charges except on large installations. Moreover, the success of the adsorption process depends to a large extent on the removal of naphthalene from the gas. Since this can be accomplished economically only by means of an oil washer, the advantages of an adsorption plant are largely discounted owing to the ease with which benzole recovery can be combined with the removal of naphthalene in a single washer.

Of the adsorbents employed, active carbon and silica gel are the most important.

The Active Carbon process for benzole recovery was developed by the Baeyer Company and is now used by the Gas Light and Coke Company, the suppliers of a large part of London's gas requirements, at their Beckton works, where a unit is in operation dealing with 75 million cubic feet of coal gas and giving a daily output of about 16,000 gallons of benzole.[3] The coal gas contains on an average 2·0–2·5 gallons of extractable hydrocarbons per 10,000 cubic feet, an amount of benzole equivalent to 3·25 gallons per ton of coal carbonised. The crude recovered benzole is nearly water-white in colour and contains 90–95% of benzene and toluene. Its specific gravity averages 0·8745.

The Silica Gel Corporation, Baltimore, have developed the use of silica gel for benzole recovery processes and various plants using this adsorbent are now in operation in America.[2, 4]

The Composition of Crude Benzoles

316. When either gas works or coke oven coal tars are distilled, the first fraction, known as crude naphtha or light oil, contains the benzole present and constitutes about 4 to 5 per cent. of the tar. Redistillation of this crude naphtha gives the commercial products known as 50/90's benzole and 90's benzole. The first of these, when tested in a standard distillation apparatus, yields 50 per cent. by volume at 100°C., and 90 per cent. at 120°C., and the latter benzole, which is sometimes known as 90 per cent. benzole, yields 90 per cent. by volume between 80°C. and 100°C. The quantities of these products obtainable from different crude naphthas vary to a great extent according to the source of the latter and it is, therefore, not possible to give truly representative figures.

The composition of crude benzoles depends upon the coal carbonised and upon the carbonisation conditions. Vertical retorts, which operate at a lower temperature than horizontal retorts, give benzoles containing appreciably higher proportions of paraffin and unsaturated hydrocarbons than those produced in horizontal retorts, while inclined retorts produce benzoles of intermediate composition. With low carbonisation temperatures, the proportion of solvent naphtha to benzole is

increased, i.e., high temperatures favour the formation of low boiling material. The same generalisations also apply to the liquid products of coke oven carbonisation. Short carbonising times with correspondingly high temperatures give benzoles containing small amounts of paraffins and unsaturated hydrocarbons.[5]

The effect of carbonisation systems upon the composition of a large number of benzoles is shown in the figures of Whitehead,[6] reproduced in Table 2.

TABLE 2. EFFECT OF RETORTING SYSTEM UPON THE COMPOSITION OF CRUDE BENZOLES

Retort System	Specific Gravity	Composition (Per Cent. by Volume)					
		Paraffins	Benzene	Toluene	Xylenes	Unsats.	Wash Oil Residue
Horizontal	0·896	1·3	50·3	16·4	8·0	5·6	17·7
Inclined	0·875	5·3	32·5	18·0	13·7	12·7	17·7
Vertical	0·860	12·6	26·7	11·5	20·1	11·0	17·7

Typical crude coke oven benzole compositions are reproduced in Table 3. A crude 65's benzole may be assumed to contain approximately 65 per cent. of motor benzole having a final boiling point of 125°C., and approximately 70 per cent. of motor benzole having a 95 per cent. distillate temperature of 145°C.[2]

Generally speaking, benzoles recovered from coal gas or coke oven gas by adsorbents such as silica gel or active charcoal contain less impurities than those recovered in wash oil processes, since they can only contain impurities derived from the gas.

TABLE 3. TYPICAL COMPOSITIONS OF CRUDE BENZOLES[2]

	1	2	3	4	5	6	7	8
Distillation Test % Vol. Distillate at 120°C.	60	65	69	69·5	71	74	80	87
Composition, % Volume								
Motor Benzole ..	60·5	64·5	69·5	70·5	68·8	73·0	74·0	82·9
Solvent Naphtha ..	7·0	6·0	5·0	1·8	7·5	5·5	8·2	4·0
Heavy Naphtha ..	2·5	1·0	1·0	1·0	1·0	1·0	0·8	0·6
Creosote	19·0	18·0	14·5	16·5	12·7	11·0	9·0	5·0
Loss on Washing ..	11·00	10·5	10·0	10·2	10·0	9·5	8·0	7·5
Tests on Refined Motor Benzole								
Specific Gravity ..	0·879	·884	·883	·879	·878	·877	·876	·881
Distillation ..								
I.B.P.,°C. ..	82·0	81·6	81·5	78·0	82·1	82·7	82·7	82·1
% at 100°C. ..	88·5	90	90	92	89·5	87·5	86·0	86·5
% at 120°C ..	96·0	96·5	96·5	—	96·5	96·5	96·5	96·5
F.B.P.,°C. ..	120	123	124	117	124	125	123	122

In addition to aromatic hydrocarbons, crude benzoles contain small amounts of paraffin and naphthene hydrocarbons. Benzole forerunnings, i.e., the fractions boiling below 80°C., contain appreciable quantities of unsaturateds, such as cyclopentadiene ; while the xylene fraction often contains a small quantity of styrene and the fraction of b.p. 176–187°C. often contains indene. The total unsaturated hydrocarbon content of crude benzoles is generally 5–10 per cent., while the " forerunnings " fraction may contain as much as 60 per cent. unsaturateds.

Certain non-hydrocarbon constituents are also present in crude benzoles, such as phenols, pyridine, aniline, coumarone and traces of hydrocyanic acid and cyanides. The chief sulphur compounds present are carbon disulphide and thiophene, the former being present in concentrations up to 2·2 per cent. of the crude benzole and the latter in concentrations up to 1·5 per cent. In addition, other sulphur compounds, such as thiotolenes, thioxenes, mercaptans, sulphides and elemental sulphur are often present to a slight extent.

The Refining of Benzoles

317. Normal Practice.—The problems involved in the refining of benzoles for use as motor fuels are very similar to those encountered in the refining of petroleum cracked spirits, but essential differences in the composition of these two types of materials necessitate certain modifications in treatment. In benzoles, as in cracked spirits, the reactive unsaturated hydrocarbon constituents are those that are removed in normal refining processes, because of the ease with which they form gums and resins. In cracked spirits, however, the other constituents are mainly paraffins and naphthenes, whereas in benzoles, aromatic hydrocarbons predominate. For the most part, nevertheless, sulphuric acid is the refining agent employed for the treatment of these materials.

In the case of benzoles recovered by wash oil processes, these are generally fractionated prior to chemical refining to remove a small quantity of low boiling wash oil fractions with which they are contaminated. The benzole fraction is then refined, and fractionated into forerunnings, refined benzole, refined light solvent naphtha and refined heavy solvent naphtha. The first step in the refining process is a light treatment with caustic soda solution (6–12 per cent.) to remove phenols, followed by treatment with sulphuric acid of about 40 per cent. strength to remove pyridine bases.

In England, the treatment of benzoles with concentrated sulphuric acid is almost without exception a batch process, carried out in so-called " benzole washers," i.e., agitators. The quantity of concentrated acid used in the refining processes naturally varies between fairly wide limits, but is often about two per cent. by volume of 87–95 per cent. acid.

This quantity may be as much as 4 per cent., but rarely exceeds this figure. After acid treatment, the benzole is washed with about 1 per cent. of 7–10 per cent. caustic soda solution to effect neutralisation and is then distilled.

The losses incurred in this treatment vary from 3 to 10 per cent. by volume and are usually about 7 per cent. Of this loss, about 1·5 per cent. is incurred in redistillation and is partly accounted for by polymerisation.

The chemistry of the sulphuric acid refining of gasolines and benzoles is described in Chapter IV.

318. The Ufer Benzole Refining Process.[8]—In this process, water or ammonium sulphate liquor is added to the mixture of benzole and acid tar remaining after contact between benzole and sulphuric acid. This causes the separation of resins from the acid tar, to form a separate layer or redissolving in the benzole. The acid liquor formed is removed and used in the manufacture of ammonium sulphate, and the resinous material, obtained either by simple settling or by distilling the washed benzole, is disposed of. The following advantages of the Ufer Process have been enumerated:—[2]

(1) Benzole losses are reduced, the benzole in the acid tar being thrown back into the benzole by the water, whilst the benzole in the resinous layer is recovered in a subsequent distillation.

(2) No expensive plant is required to treat the acid tar, and sulphuric acid, suitable for use in the ammonium sulphate plant, is recovered directly.

(3) The consumption of alkali is reduced. Nearly the whole of the unconsumed acid is removed from the washed products, so that only a small quantity of reagent is required for neutralisation.

(4) Accumulation of acid tar is prevented, since the resinous fraction left on distilling the washed benzole can be added to the coal tar, or the resinous layer separating between the washed product and the sulphuric acid can be drawn off before neutralising and added to this tar, the ammonia always present in the tar neutralising the traces of free acid. The Gas Light and Coke Company have used the process satisfactorily. The products are practically free from unsaturateds and compare favourably in stability with benzoles refined by the usual acid-washing process.

318a. The Removal of Carbon Disulphide from Benzoles.—The Methanol-Soda Process.—A process recently developed by the National Benzole Company for the removal of carbon disulphide from benzoles is based on the well-known reaction of this substance with caustic soda to form alkali xanthates[12] in alcohol solution.

Methanol is the alcohol used and the refining agent is a solution of caustic soda in this solvent. This is vigorously agitated with the crude benzole, about 2–5% of the solution being employed. After the methanol and caustic soda have been contacted with the benzole for the required time, the contents of the washer are allowed to settle, and the recovery process may be adjusted to give either carbon disulphide or sodium methyl xanthate as required, in addition to methanol. Carbon disulphide is obtained by the addition of dilute mineral acid to the diluted methanol-soda residues, or alternatively by distillation either with or without previous neutralisation with dilute acid. In the distillation process methanol is also recovered. Sodium methyl xanthate may be recovered by the distillation of the methanol-soda residues under reduced pressure.

Removal of carbon disulphide from crude benzoles may also be effected by fractionation, by treatment with aqueous sodium sulphide,[13] or by treatment with ammonium polysulphides.[14]

A benzole refining process involving the use of naphthalene sulphuric acid in methanol solution as the refining agent has been recently developed in France by the Société Eréal.[15]

319. The Instill Benzole Refining Process.—Among other methods proposed for the refining of benzoles, is the Instill process, in which the refining agent is a mixture of finely divided ferric sulphate and an adsorbent earth. Treatment is carried out at a temperature of about 55°C. and requires 1–1½ hours for completion. The cost of this process is stated to be about the same as that of the usual acid-washing process, but it is claimed that increased yields of refined benzole are obtained, often to the extent of 10 per cent. The process may be applied either as a percolation or agitation method of treatment, the former being claimed the more economical in refining agent requirements. Pyridine must be removed prior to Instill treatment because this forms double compounds with ferric sulphate.[13, 18]

320. Recent Developments in Benzole Refining in the United Kingdom.—Up till quite recently, the severity of the refining treatments given to benzoles intended for use as motor fuels was controlled by the specifications of the National Benzole Association which demanded compliance with an "acid wash" test. This consisted of treating the benzole with a certain quantity of sulphuric acid and measuring the colour developed in the acid layer. Such a clause did not allow benzoles refined by mild treatments to pass the specification and necessitated the use of sulphuric acid refining.

The National Benzole Association were among the first to investigate the phenomenon of gum formation in this country (see Chapter XIII, Volume II), and it was ultimately realised that the acid wash test was

unnecessarily stringent. The acid wash test was then eliminated and a gum test substituted. This has done much to encourage the development of less drastic and more economical refining methods and has led to the utilisation of benzoles stabilised against gum formation by the addition of inhibitors. More than 60 per cent. of the benzole produced and marketed in this country for use in motor fuels is now stabilised by the addition of inhibitor[9, 16] and a detailed account of this development has been given by Hoffert and Claxton.[17]

The refining of benzole in this country is carried out at numerous comparatively small refineries situated at coke oven works and cannot be centralised because of excessive freight charges. Refining costs are, therefore, likely to remain at a high figure compared with those realised in the refining of petroleum products. A further outcome of this situation is that entirely new methods of refining, especially those incurring high capital cost (such as hydrogenation), are not likely to be introduced in the near future.

Specifications for Benzoles and Allied Products

321. There are in existence at present in this country two specifications governing the quality of motor benzole, i.e., that grade of benzole intended for use as a motor fuel or as a constituent of motor fuel. These are British Engineering Standards Specification No. 135, 1921, and National Benzole Association Specification No. III, 1929. Of these, the former is being revised as it is very much out of date. The latter is the more important; practically the whole of the motor benzole manufacture in this country is made to comply with this specification, which was amended in October, 1932, as shown in Table 5.

TABLE 4. BRITISH ENGINEERING STANDARDS SPECIFICATION NO. 135, 1921. BENZOLE FOR MOTOR FUEL

1. *Definition.*
   The term "benzole" shall denote a liquid consisting essentially of a mixture of benzene and not more than 30 per cent. by volume of toluene and xylenes.
2. *Description.*
   The material shall be a clear water-white liquid free from undissolved water and other visible impurities.
3. *Distillation Test.*
   Not less than 60 per cent. at or below 90°C.
   „ „ „ 75 „ „ „ „ „ 100°C.
   „ „ „ 90 „ „ „ „ „ 120°C.
   End point not higher than 125°C.
4. *Residue.*
   The amount of non-volatile residue remaining when 20 mls of the material are evaporated and subsequently heated for two hours on a water bath at 100°C. shall not exceed 0·01 per cent. by weight.

5. *Coloration with Sulphuric Acid.*
   The coloration imparted to pure 90 per cent. sulphuric acid when 90 mls. of the material are shaken with 10 mls. of the acid for 5 minutes at ordinary temperature shall not be more than a light brown.
6. *Sulphur Content.*
   Total sulphur content not above 0·4 per cent. by weight.
7. The material shall give no reaction for free acid or free alkali.
8. The benzole shall give no reaction for H_2S.
9. The freezing point shall not be higher than −14°C.

TABLE 5. NATIONAL BENZOLE ASSOCIATION SPECIFICATIONS FOR MOTOR BENZOLE[11]

		No. III, 1929	No. III, 1932
1	*Colour.*	Not darker than 0·5 mls. of N/10 iodine solution in 1,000 mls. of distilled water.	As for 1929.
2	*Specific Gravity.*	At 15·5/15·5°C. shall not be lower than 0·8700 nor higher than 0·8850.	As for 1929.
3	*Impurities.*	The benzole shall be free from water and other visible impurities.	As for 1929.
4	*Distillation.*	At 100°C., not less than 60 per cent. At 120°C., not less than 85 per cent. At 145°C., at least 95 per cent. Residue above 145°C. shall remain liquid when cooled to 0°C. for 30 minutes.	As for 1929.
5	*Rectification Test.*	5 millilitres of benzole plus 5 mls. of 95 per cent. H_2SO_4 shaken for two minutes. The colour of the acid layer after standing for 10 minutes shall be not darker than a solution of 5·0 g. of potassium dichromate in 1000 mls. of a mixture of equal volumes of pure H_2SO_4 and water.	The benzole shall pass either the acid wash test as specified in 1929 or give not more than 8 mg. gum per 100 mls. in a standard oxidation test.
6	*Total Sulphur.*	0·4 per cent. maximum.	As for 1929.
7	*Free Sulphur.*	Nil.	No corrosion in a copper strip test at 50°C.
8	*Freedom from Acids, etc.*	The benzole shall not give a positive reaction for acids, alkalies or H_2S.	As for 1929
9	*Crystallising Point.*	Not above −5°C.	As for 1929

American, French and German benzole specifications are summarised in Table 6, while the National Benzole Association specification for other grades of benzole and solvent naphthas, all of which are sometimes used in motor fuels, are detailed in Table 7.

TABLE 6. AMERICAN, FRENCH AND GERMAN BENZOLE SPECIFICATIONS

		American Barrett Company Specification for Standard Motor Benzole[10]	French Benzole Specification (Unibenzols)[2]	German Benzole Specifications[2] (Benzol-Verband)		
				B.V. Benzole	B.V. Benzole N.	B.V. Benzole A
1	Specific Gravity at 15°C.	—	0·865–0·885	0·875–0·879	0·875–0·879	0·875–0·884
2	Colour.	Not darker than a solution of 0·0030 g. of potassium dichromate in 1 litre of water.	Water-white or slightly coloured.	Water-white to slightly yellowish.		
3	Odour.	Characteristic odour of aromatic hydrocarbons. No pronounced foreign odour.	—	—	—	—
4	*Distillation.*					
	Initial Boiling Point °C.	76°C.–82°C.	Above 65°C.	80–87°C.	80–87°C.	80–87°C.
	At 100°C. %	60% (min.)	60% (min.)	65% min. 75% max.	70% min. 80% max.	—
	At 120°C. %	90% (min.)	—	—	90% max.	—
	At 140°C. %	—	85% (min.)	90% minimum at 135°C.		
	At 170°C. %	—	95% (min.)	95% minimum at 145°C.		
	End Point.	Not above 170°C.	—	—	—	—
5	Sulphuretted Hydrogen.	—	Nil.	Nil.	Nil.	Nil.
6	Naphthalene.	—	—	0·1% maximum.		
7	Elemental Sulphur.	—	Trace only.	2 mgs./100 mls. maximum.		
8	Total Sulphur	0·5% (max.)	0·5% (max.)	—	—	—
9	Corrosion Test.	Copper strip not to show grey or black deposit when heated with benzole.	—	—	—	—
10	Acidity.	May be slightly alkaline but not acid.	Neutral.	—	—	—
11	Evaporation Test.	—	5·0 mgs. per 100 mls. max.	—	—	—
12	Acid Wash Test.	Specified.	Not specified.		Specified.	
13	Visible Water at 15°C.	—	—	Separation point below 10°C.	Nil.	Nil.
14	Index Number.	—	—	>96 <104	—	—
15	Residue on distillation.	—	Only slight black deposit.	—	—	—

TABLE 7. NATIONAL BENZOLE ASSOCIATION SPECIFICATIONS FOR PURE BENZOLE, 90's BENZOLE AND SOLVENT NAPHTHAS[11]

		Pure Benzole	90's Benzole	Coal Tar Solvent Naphtha	Heavy Coal Tar Naphtha	Heavy Coal Tar Naphtha (Unrectified)
1	Colour, mls. N/10 Iodine solution in 1,000 mls. of water.	0·2 (max.)	0·2 (max.)	0·25 (max.)	1·0 (max.)	Colourless to dark brown
2	Specific Gravity 15·5/15·5 °C.	0·8815 to 0·8855	0·8775 to 0·8835	Not below 0·8545	0·8600 to 0·9100	0·8550 to 0·9450
3	Distillation.	5 mls. to 95 mls. within 0·5°C. This temp. to be approx. 80°C.	Not less than 90 – 93% at 100°C. 97% at 120°C.	Not more than 5% at 125°C. At least 96% (A quality) or 91% (B quality) at 160°C.	Not more than 5% at 160°C. At least 90 % at 190°C.	Not more than 10% at 160°C. At least 90% at 190°C. (A quality) or 200° C.(B quality).
4	Acid Wash Test	Specified.	Specified.	Specified.	Not specified.	
5	Total Sulphur.	0·2% (max.)	0·4% (max.)	—	—	—
6	Free Sulphur.	Absent.	Absent.	—	—	—
7	Acids, Alkalies and H_2S.	Negative.	Negative.	Negative.	—	—
8	Residue on Evaporation.	0·01% (max.)	—	0·02% (max.)	—	—
9	Flash Point °F. (Abel).	—	—	—	Above 73°F.	Above 73°F.
10	Tar Acids.	—	—	—	Less than 0·25% by volume.	—
11	Tar Bases.	—	—	—	Less than 0·25% by volume.	—
12	Naphthalene.	—	—	—	Less than 2% by weight.	—

THE MAGNITUDE OF THE BENZOLE INDUSTRY

322. The quantity of benzole obtained in Great Britain as a by-product during the carbonisation of coal at gas works or coke ovens is

small compared with the total requirements of motor spirit, but is important because benzole has been until recently the only home-produced motor fuel other than that produced from Scottish shale.

The quantities of motor benzole consumed as motor fuel in the U.K. since 1928 are as follows :—

	Imperial Gallons	Per Cent. of Total Motor Fuel Consumption
1928	27,500,000	—
1929	35,240,000	3·7
1930	35,000,000	3·4
1931	29,000,000	2·7
1932	27,500,000	2·5
1933	31,000,000	

The production of benzole decreased somewhat during 1931–1933, owing to the depression in the basic industries, coal, steel and iron. This reduction would have been still greater but for the sale of coke oven gas to gas works and the use of oven coke for domestic purposes, since these outlets have helped to keep some coke ovens at work longer than would otherwise have been possible.

Most of the benzole produced in Great Britain has been obtained at coke ovens, as, until recently, few gas works were recovering benzole. The quantity of benzole produced as a by-product at coke ovens, however, is limited, since the quantity of coal carbonised at coke ovens depends on the demands for metallurgical coke and for gas. Recently, renewed interest has been taken in the production of benzole at gas works and many gas undertakings are now realising the advantages of recovering the benzole from the gas and are erecting modern recovery and refining plants.

The maximum possible production of benzole in Great Britain, calculated approximately from the quantities of coal carbonised annually at coke ovens and at gas works, and assuming an average yield of two gallons of refined motor benzole per ton of coal carbonised, is given in Table 8.

TABLE 8. MAXIMUM POSSIBLE MOTOR BENZOLE PRODUCTION IN GREAT BRITAIN

Year	Coke Ovens		Gas Works		Total	
	Gallons	Tons	Gallons	Tons	Gallons	Tons
1928	34,000,000	136,000	40,000,000	160,000	74,000,000	296,000
1929	40,000,000	160,000	38,000,000	152,000	78,000,000	312,000
1930	34,500,000	138,000	36,700,000	147,000	71,200,000	285,000
1931	25,300,000	101,000	36,300,000	145,000	61,600,000	246,000
1932	25,500,000	102,000	33,300,000	133,000	60,800,000	235,000
1933	26,200,000	105,000	34,700,000	139,000	60,900,000	244,000
1934	33,800,000	135,000	35,800,000	143,000	69,600,000	278,000

It will be seen that in 1929, the year in which the largest amount of coal was carbonised, the maximum possible production of motor benzole was rather more than 10 per cent. of the total motor spirit requirements, whilst in 1932 it had fallen to about 6 per cent.

The imports and exports of benzole into and from the United Kingdom have been as follows :—

Year	Imports		Exports	
	Gallons	Tons	Gallons	Tons
1930	4,656,470	18,300	420,369	1,650
1931	3,238,757	12,700	396,812	1,550
1932	115,477	450	638,638	2,500
1933	756,183	2,970	375,340	1,479
1934	277,920	1,090	68,809	270

During 1932, the imports were reduced to nil because of the high price of benzole, due to world shortage and the high import duty on motor spirit in this country. A contributing factor has been the development of tetra-ethyl-lead as an anti-knock agent.

In this country, motor benzole is sold at a price approximately 5·5 pence per gallon greater than No. 1 grade petrol and National Benzole Mixture.

323. Benzole Production in Other Countries.—The productions of benzole in various other countries are given in Table 9; statistics relating particularly to Germany are reproduced in Table 10.

TABLE 9. PRODUCTION OF BENZOLE, TONS

	1933	1932	1931	1930
Germany	253,000	207,500	260,000	250,000
U.S.A.	206,000	270,000	420,000	510,000
Great Britain	119,000	118,500	100,000	120,000
France	74,200	68,200	78,000	81,400
Belgium	37,000	34,000	35,000	35,000
Saar	30,000	28,000	31,000	40,000
Netherlands	23,000	21,500	22,000	22,000
Poland	18,000	17,000	19,000	22,000
Czecho-Slovakia ..	14,000	14,000	26,000	28,000
Spain	3,200	3,300	3,700	5,000
Italy	5,500	5,000	5,000	6,000
Total	782,900	787,000	999,700	1,119,400

TABLE 10. BENZOLE PRODUCTION AND CONSUMPTION IN GERMANY[2]
(MILLION GALLONS)

Year	Total Benzole Production	From Coke Oven Gases	From Gas Works and Coke Oven Tars	Imports	Exports	Benzole Used as Motor Fuel
1890	1·0	—	—	—	—	—
1896	1·75	1·0	0·75	—	—	—
1901	7·0	—	—	—	—	—
1904	10·0	8·5	1·5	—	—	—
1908	22·5	20·0	2·5	—	—	—
1911	32·5	—	—	—	—	—
1924	42·5	—	—	7·4	0·53	31·7
1925	56·5	—	—	10·9	3·45	50·0
1926	61·35	—	—	16·0	5·5	56·5
1927	74·1	—	—	33·7	4·2	85·0
1928	80·8	—	—	40·7	1·9	109·0
1929	92·5	—	—	14·25	1·65	112·5

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Chapter VII

THE PRODUCTION OF MOTOR FUELS BY THE HYDROGENATION PROCESS AS APPLIED TO MINERAL OILS AND COALS

325. Introduction.—The hydrogenation process has recently received considerable attention as a means of producing motor fuels from coal and other solid carbonaceous materials and as a means whereby motor fuels can be produced from petroleum residues, etc. It has also been recently adapted to the production of high-grade lubricants and burning oils and to the general refining of all classes of petroleum oils.

The process consists, essentially, in the treatment of coals and oils, etc., at elevated temperatures with hydrogen at high pressures, e.g., about 200 atmospheres. Catalysts are usually employed to increase the rate of reaction and direct the course of the reaction. As a result of this treatment, extensive decomposition occurs, but the products differ from those obtained in ordinary cracking processes in that they are much less unsaturated in chemical nature. Moreover, much higher yields are obtained and coke formation is entirely prevented.

After much experimentation and the expenditure of large sums of money by a few interested companies, the hydrogenation process has now shown itself to be technically fully proved, and it is extremely likely that it will play a large part in the production of motor fuels from coal in the near future, in those countries prepared to bear the heavy cost involved. The utilisation of hydrogenation in the petroleum industry has so far been mainly limited to the field of speciality products.

Historical Development

326. The hydrogenation process was applied by its originators in the first place to coal, and was not applied to the treatment of petroleum oils until a later date.

The first attempt to hydrogenate coal was made by Berthelot[1] in 1869, who treated finely powdered coal with saturated hydriodic acid at 270°C., for many hours. By this means, a yield of liquid hydrocarbons amounting to 60 per cent. was obtained. Berthelot found that wood and lightly carbonised charcoal were susceptible to the

same treatment, whereas fully carbonised charcoal did not react. In 1917, the method of Berthelot was modified by Tropsch,[2] who added red phosphorus to the reacting substances and found that, generally, the younger the coal the greater the susceptibility to hydrogenation. This result has since been confirmed by workers using other methods of hydrogenation.

327. Immediately after the Great War, much attention was given to the hydrogenation of coal in Germany, and a full account of the work done there in this field is given in Fischer's " Die Umwandlung der Kohle in Ole " and its English translation " The Conversion of Coal into Oils," New York, 1925 (Van Nostrand Company); London, 1925 (Ernest Benn, Ltd.).

The celebrated work of Bergius, who invented the high-pressure hydrogenation process, was begun before the War, and this process is often referred to as " Berginisation " in his honour. Bergius found that by subjecting heavy hydrocarbon oils to a temperature of 450°C., under a hydrogen pressure of over 20 atmospheres, saturated oils could be obtained. The application of the process to coal resulted from an observation of Bergius [3] that a " synthetic coal " produced by the treatment of cellulose for eight hours at 340°C., under a pressure of 100 atmospheres, could be hydrogenated at 400°C., to give a 70 per cent. yield of oils.

Probably the first patent disclosing the application of the Bergius process to coal is the English patent, No. 18,231, of August 1st, 1914. Described as " a process of treating coal and similar substances to obtain oils, ammonia and other products," it covered the action of hydrogen on coal at pressures above 10 atmospheres and at temperatures between 300°C. and 500°C. The patent claimed that, instead of hydrogen, gases containing hydrogen, such as water gas, may be employed, or substances which yield hydrogen, such as calcium hydride. A further patent in the names of Bergius and Billwiller[4] disclosed the advantageous use of an oil mixed with the finely ground coal, a procedure which acquired importance when the process was adapted for continuous rather than batch operation, in that the added oil enabled the coal to be pumped or injected into the reaction vessel. The original Bergius process did not contemplate the use of catalysts, but, apparently, iron oxide was added to the reaction mixture in the earliest experiments, presumably as a desulphuriser.

The importance of catalysts in this hydrogenation reaction was pointed out in 1925 by Bowen, Shatwell and Nash[5] in describing experiments on cellulose and in the following year by Bowen and Nash[6] in the description of experiments on cellulose, lignin and coal. In the case of cellulose, as small an amount of nickel oxide as 0·5 per

cent. was found to increase appreciably the yield of liquid reaction products. Still more useful catalysts were discovered later, such as molybdenum compounds which were more immune from sulphur poisoning. Such substances are described in a series of patents[7] that appeared about 1927. Since this date much has been published on hydrogenation research.[8,9]

328. A few years after the Great War, an agreement was entered into between Bergius and the I. G. Farbenindustrie Aktiengesellschaft whereby the latter acquired certain development rights and began extensive work on the perfection of the process. As a result of this, the process was much improved, and to the I. G. Farbenindustrie, more than any other company, is due the credit for the amazing manner in which they developed suitable and highly efficient catalysts whereby the process was made a practical proposition. Their progress was so rapid that late in 1927, in an authoritative publication on the position and policies of the I. G. by the German banking house of Schwarz, Goldschmidt and Co., it was stated that the cost of production per ton of refined oils by this process was calculated to be about 90 marks. Schemes were then advanced for the production of oils by the hydrogenation of German coals and as an encouragement the I. G. were licensed to transport the synthetic oils at a specially reduced rate on the German railways. The large scale hydrogenation of brown coal to petrol was stated to be proceeding in a highly satisfactory manner at the Leuna works of the I. G. in 1928.[10]

In 1926, developments in the field of hydrogenation had progressed sufficiently to attract the attention of the Standard Oil Company of New Jersey and in the fall of the following year an agreement was signed between that company and the I. G. Farbenindustrie Aktiengesellschaft for the mutual development of the process. Details of this agreement were not published at the time and were not revealed until two years later.

A 100 barrel per day experimental plant was erected at Baton Rouge, Louisiana, and during the next two years, work was done on the problem of applying the process to the treatment of petroleum oils. In 1929, construction of the first hydrogenation plant especially built for the treatment of oil was started at Bayway, New Jersey. This plant consisted of two units, each having a daily charging capacity of 2,500–5,000 barrels and was later followed by a similar, but improved, plant at Baton Rouge, which was placed in service on May 23rd, 1931. At the present time both of these plants are in commercial operation producing speciality products for the American markets.

In 1930, the Standard I. G. Company, the company formed a year previously to hold the patent rights of the Standard Oil Company

(New Jersey) and the I. G., relating to hydrogenation, transferred these patents for the United States to Hydro Patents Company, a newly recognised Delaware corporation. Various American refining companies were then allocated share holdings in this new Company, in proportion to their crude running capacity, but with a minimum holding of 500 shares. These companies were as follows :

Atlantic Refining Co.
Barnsdall Corporation.
Cities Service Co.
Continental Oil Co.
Mid-Continent Petroleum Co.
Pure Oil Co.
Shell Union Oil Corporation.
Sinclair Refining Co.
Skelly Oil Co.
Standard Oil Co. (New York).
Standard Oil Co. (California).
Standard Oil Co. (New Jersey).
Standard Oil Co. (Indiana).
Standard Oil Co. (Ohio).
Texas Oil Co.
Union Oil Co. of California.
Vacuum Oil Co.

329. In 1927, Imperial Chemical Industries also became interested in the hydrogenation process when they were attracted to the subject on account of the large difference between the cost of coal and that of oil, per thermal unit. In this year they acquired the British Bergius Syndicate and started independent research on the process, their experience in high pressure technique and hydrogen production with relation to the synthetic methanol and ammonia processes being especially valuable. Confining their attention to the hydrogenation of coal for the production of motor spirits, the investigations made by Imperial Chemical Industries proceeded so satisfactorily that full details regarding them were disclosed to the Fuel Research Board in 1930, and the Company announced that they could produce a 60 per cent. weight yield of petrol from coal and they gave estimated costs showing that commercial development was possible, but only with government assistance. Much discussion then took place, both in the popular press and in the technical press, concerning the advisability of such help. By some it was argued that the development of indigenous resources was desirable as a means of alleviating unemployment and as a measure of national defence, while others took the opposite view that since motor fuels of petroleum origin could be imported into the country at exceptionally low costs, coal hydrogenation could not be a complete and lasting success, unless the consumer was forced to pay a high price by the continuance of high taxes on imported materials.

The direct government support suggested for the I.C.I. coal hydrogenation project was not provided, but on July 17th, 1933, it was announced that the government had decided to encourage the production of motor fuels from all kinds of domestic sources by giving

a guarantee that for a period of nine years, beginning in 1935, a preference of fourpence per gallon would be allowed on all such home produced motor spirit. The stipulation was made, however, that, should the present import duty of eightpence per gallon remain on imported petrol, the guarantee period would be reduced to 4½ years. With other import duties the guarantee period would be shortened or lengthened in proportion. Immediately the British Hydrocarbon Oils Production Bill was announced in July, 1933, I.C.I. stated that they had sanctioned the building of a hydrogenation plant at their Billingham works capable of producing 100,000 tons per year of petrol. Owing to the fact that special spare plant facilities existed at Billingham at this time the capital cost of the plant was estimated at £2,500,000, the value of the existing plant utilised being an additional £2,500,000. During the course of construction of this plant it was decided to increase the capacity by tar hydrogenation and the flowsheet output was augmented to 150,000 tons per year. Contracts were made with the distillers for the supply of creosote oil and with low temperature carbonisation interests for the supply of low temperature tar. Of the total flowsheet output, approximately 10,000 tons is derived from low temperature tar, 40,000 tons from creosote oil and 100,000 tons from coal. The Billingham plant was erected and put into operation early in 1935 and the first shipment of finished petrol was despatched on April 9th.

The method by which the British Government encouraged the scheme has met with general approval and has the advantage that it involves no direct subsidy. If the venture is an economic failure, the Government will be involved in no financial loss except that brought about by the loss of import duty, amounting to about £1,500,000 per year.

In order to obviate wasteful competition in patent litigations, etc., and in order to ensure the most successful development of the hydrogenation process, an agreement was reached between the Standard Oil Company, the I. G. Farbenindustrie, Imperial Chemical Industries and the Royal Dutch Shell Oil Company, whereby mutual exchange of information and patents relating to the process was effected, and a further Company, International Hydro Patents, was formed. This agreement has had a far-reaching effect, and is undoubtedly proving of great value to all the companies concerned. The I.G. Farbenindustrie retains all rights in the process for operation in Germany, the Standard Oil Company for operation in the United States and Imperial Chemical Industries for operation within the British Empire.

The Chemical Reactions Involved in Hydrogenation Processes

330. The hydrogenation process, as applied to the production of

motor fuels from coal and other carbonaceous materials, must not be confused with the much more simple hydrogenation process employed in the " hardening " of fats and the saturation of vegetable oils. In the first case, substances of high molecular weight are broken down into bodies of much lower molecular weight, the process being described more accurately as " *destructive hydrogenation,*" whereas the hardening of fats, etc., is a process in which the unsaturated substances treated absorb hydrogen and do not break down. In this case, the process may be described as one of simple *reduction.*

As already shown in Chapter II, the cracking, or thermal decomposition, of petroleum oils results not only in the production of lighter oils, but also in the production of some material of higher molecular weight than the original starting material. This heavier material is formed by the polymerisation of some of the more reactive unsaturated hydrocarbons formed by thermal decomposition, thus, for example :

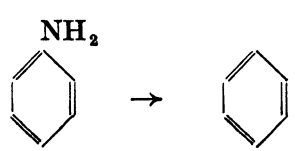
$$C_{20}H_{42} \xrightarrow[\text{cracking}]{} C_{10}H_{22} + C_{10}H_{20}$$

$$x\ C_{10}H_{20} \xrightarrow[\text{polymerisation}]{} (C_{10}H_{20})_x$$

The coke produced in cracking processes is a good example of the wasteful effect of such polymerisation. In the hydrogenation process this does not occur, except to a very small extent, because the polymerisation reaction is prevented. The products of simple thermal decomposition absorb hydrogen and become saturated and hence do not polymerise and form high-boiling oils or coke. As a result, the products of the hydrogenation process consist, when desired, almost entirely of low boiling point oils, and the conversion to motor fuel can be practically complete.

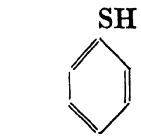
A further important fact concerning hydrogenation processes is that the products contain only very small amounts of nitrogen, sulphur and oxygen compounds. When such compounds are present in the feed stocks they are almost quantitatively converted into ammonia, sulphuretted hydrogen and water, respectively, as shown in the following simple examples.

(*a*)



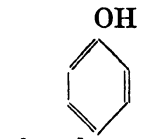
aniline → benzene + ammonia

(*b*)



phenyl mercaptan → benzene + sulphuretted hydrogen

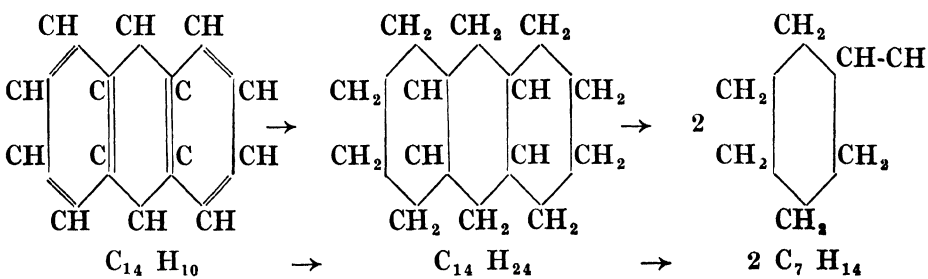
(*c*)



phenol → benzene + water

This latter reaction probably proceeds through the intermediate formation of cyclohexanol.

As a result, in contrast to the products of cracking processes, the oils produced by the hydrogenation process are comparatively free from these objectionable compounds. The hydrogenation process is of particular value in the production of motor fuels from those higher boiling oils of low hydrogen content which are not suitable for simple cracking, e.g., those oils containing large amounts of aromatic hydrocarbons. In such cases, the hydrogenation process is of value because in it these refractory aromatic hydrocarbons are first of all reduced by the hydrogen into bodies which readily undergo decomposition, e.g., anthracene is a very stable body under the action of heat alone, but is converted into saturated bodies in the presence of hydrogen which then break down easily, thus :



$C_{14}H_{10} \rightarrow C_{14}H_{24} \rightarrow 2\,C_7H_{14}$

In the simple cracking of aromatic oils, large quantities of gas and coke are produced, but hydrogenation gives a yield of motor spirit of from 80–90 per cent.

331. The difference between simple cracking and hydrogenation may also be shown by a consideration of the ultimate chemical analyses of the starting materials and of the products. Of the various petroleum products ranging from motor spirit to fuel oil, the former contain the

most hydrogen and fuel oil the least, as shown by the following representative figures[11]:

	% *Carbon*	*C/H Atomic Ratio*
Crude Oil	85–86	1·4–1·7
Fuel Oil	86	1·0–1·5
Gas Oil	86	1·75–1·85
Kerosene	86·5	1·9
Motor Spirit	85·5	1·9–2·1
Benzole	91·5	1·1

and the reactions occurring in a typical cracking process may be represented by the equation:

$$5CH_{1\cdot8} + 5CH_{1\cdot5} \rightarrow 0\cdot5CH_{3\cdot2} + 3CH_2 + 5CH_{1\cdot5} + CH_{1\cdot3} + 0\cdot5CH_{0\cdot2}$$

Fresh feed	Recycle stock	Gas	Petrol	Recycle stock	Fuel oil	Coke.

When the same material is treated in the hydrogenation process for the production of motor fuel, about 95 per cent. by weight of petrol is obtained and 10 per cent. gas with a hydrogen absorption of approximately 5 per cent. by weight.

As already shown, saturation of unsaturated molecules takes place as a preliminary to cracking, and subsequent to cracking, in all cases. This saturation reaction (absorption of hydrogen) is exothermic, as shown in the examples:

(*a*) $C_6H_{12} + H_2 \rightarrow C_6H_{14} + 30{,}000$ cals.
Hexene — Hexane

(*b*) $C_6H_6 + 3H_2 \rightarrow C_6H_{12} + 50{,}000$ cals.
Benzene — Cyclohexane

and the heat evolved is often utilised in bringing the reactants up to reaction temperature (see later). These saturation reactions are, however, reversible, high temperatures favouring the opposite reaction, i.e., dehydrogenation. The lower the molecular weight of the material undergoing treatment, the higher the temperature necessary to secure dehydrogenation and it therefore happens that at a temperature at which a light oil is completely hydrogenated, a heavier oil may be dehydrogenated. Consequently, different oils require different conditions of temperature for their satisfactory treatment.

The two separate reactions which occur in the hydrogenation process, namely, saturation and cracking, must be suitably controlled so that they may proceed at the correct relative rates. If the cracking reaction proceeds to a greater extent than hydrogenation, the presence of excessive amounts of unsaturated and aromatic hydrocarbons

results in the products, and coke is formed; whereas, if the hydrogenation reaction proceeds too far, an insufficient quantity of light oil is formed, the gasoline produced has a poor anti-knock value and a greater amount of hydrogen is consumed. The successful balance between these two reactions is achieved by the use of suitable catalysts and by the employment of suitable temperatures and suitable hydrogen pressures.

It will be seen, therefore, that by the proper choice of operating conditions, the properties of the products of the hydrogenation process may be varied within wide limits, and, in particular, gasolines of either low or high knock-rating, good or poor volatility, can be produced at will. This flexibility was not evident in the original Bergius process and has mainly resulted from the successful development of suitable catalysts by the I. G. Farbenindustrie and from the discovery that oils of different types require different methods of treatment.

The interpretation of the results of the destructive hydrogenation of petroleum oils in the light of thermodynamic data has been commented on by Sweeney and Voorhies[75] who quote the following example of naphthalene, a condensed ring molecule :—

$$C_{10}H_8 \text{ (gaseous)} + 4H_2 \rightarrow C_6H_6 \text{ (gaseous)} + C_4H_{10}$$

at atmospheric pressure

$$\text{whence} \quad -\Delta^\circ F. = 51{,}300 - 79 \cdot T_K$$

$$\text{and} \quad \log \frac{pC_6H_6 \; pC_4H_{10}}{p\,C_{10}H_8} = \frac{11{,}200}{T_K} - 17{\cdot}4 = 4 \log pH_2.$$

At high hydrogen pressures considerable driving force is available for the production of benzene and butane from naphthalene, but at very low hydrogen pressures, such as exist in ordinary cracking processes, it is theoretically impossible to effect such a reaction. Naturally more important is the corollary truth that, in the presence of sufficient hydrogen pressure, the opposite reaction cannot proceed. This establishes the reason why, in the destructive hydrogenation of petroleum oils, polymerisation and condensation may be entirely prevented or controlled in a manner not possible in the ordinary cracking reaction.

332. Some Chemical Considerations on the Hydrogenation of Coals.—What is ordinarily called coal may be regarded as consisting of three distinct classes of substances :—

(1) The coal substance. This is the combustible organic matter of the coal, and is generally considered to consist of altered plant remains. It is composed of the elements carbon, hydrogen and oxygen, together with smaller amounts of nitrogen and sulphur.

(2) Moisture.

(3) Mineral impurities, which are responsible for the ash which remains after the coal has been burnt.

Although it is possible that a small proportion of the ash-forming constituents is chemically combined with a part of the coal substance, it is usual to regard items (2) and (3) as impurities mixed with the coal substance and since otherwise similar coals may be associated with different amounts of moisture or of mineral matter, it is necessary, when comparing coals for scientific purposes, to calculate results on an ash and moisture free (A.M.F.) basis.

Although coal is a very complex organic body, or mixture of organic bodies, considerable interest has been shown in its quantitative elementary composition, and the different kinds of coals from brown coals to anthracites show distinct differences in this respect. Thus, starting with fresh vegetable matter averaging about 50 per cent. of carbon, the natural processes of decay and transformation have led to peats, brown coals and lignites, and then to the familiar " bituminous " coals used in England for household purposes, containing about 75 per cent. of carbon. Coals still richer in carbon are " semi-bituminous " and " semi-anthracitic " coals and anthracites.

In banded bituminous coals, further differences in nature and composition are evident and four visible ingredients have been recognised. These are :—

1. *Fusain.* Soft fibrous coal, showing a woody structure and occurring in wedge-shaped patches on the bedding plane. This is a minor constituent of most coals and has a high carbon content, no matter what the composition of the coal with which it is associated.

2. *Durain.* Ordinary dull hard coal, opaque in thin sections and generally containing recognisable plant fragments.

3. *Clarain.* Ordinary bright streaky coal, transparent in thin sections and containing plant debris.

4. *Vitrain.* Less abundant than clarain, very bright and uniformly so, but does not contain plant debris.

It is not surprising to find that different coals, and the different constituents of the same coal, give different amounts of tar and gas when carbonised, and differ in the ease with which they undergo hydrogenation. Naturally, the younger coals containing a larger proportion of hydrogen than the older coals are more amenable to hydrogenation than the latter, while of the various coal constituents vitrain is hydrogenated with the greatest ease and fusain with the greatest difficulty. Anthracites have not yet been successfully hydrogenated to gasoline.

It is obvious that the best coals for hydrogenation are those containing but small amounts of ash and moisture, because other things

being equal a coal containing appreciable quantities of these materials is more expensive than one being comparatively free from these undesirable components. Generally speaking, a well washed slack coal is the best coal for hydrogenation purposes because it contains a high proportion of vitrain and has a low ash content.

Hydrogen Production

333. One of the main essentials for the economic utilisation of the hydrogenation process is a plentiful source of cheap hydrogen, consequently much attention has been given to this problem and numerous methods have been worked out and successfully applied to commercial scale operation.

In the hydrogenation of petroleum oils on sites within reasonable distances of producing oil-fields, as, for example, in the United States, natural gas is the cheapest and most convenient source of the large quantities of hydrogen that are required, while refinery and cracked gases constitute in many cases an alternative, if not so plentiful, supply. For the hydrogenation of coal, however, carried out naturally quite close to large industrial areas, coke oven gas and water gas constitute the most important sources of hydrogen, while the hydrocarbon gases produced in the hydrogenation process itself may be reformed into hydrogen by the use of those methods applied to natural gas. Considerable experience in the production of hydrogen from coke oven gas and water gas has been gained in the production of synthetic ammonia and synthetic methanol, and those firms who have developed these processes, e.g., the I.G. Farbenindustrie and Imperial Chemical Industries Limited, have benefited considerably from such experience. It is highly probable that these two great chemical companies produce hydrogen by such processes more cheaply than any one else in the world.

The Production of Hydrogen from Hydrocarbon Gases.—The "Reforming" Process.—Several methods have been successfully applied for the production of hydrogen from natural gases and other similar gaseous hydrocarbons. Of these, the following are the most important :—

1. *Interaction with steam* at elevated temperatures to produce a mixture of hydrogen and carbon monoxide. This mixture is then treated with more steam to convert the carbon monoxide into carbon dioxide which is then removed by scrubbing with solvents.

2. *Partial combustion with oxygen.*

This process is sometimes carried out at the same time and in the same apparatus as No. 1 above.

3. *Thermal decomposition.*

The first method is the one commonly employed, and is used at the

Bayway and Baton Rouge plants of the Standard Oil Companies. Its application in coal hydrogenation processes has been mentioned by Gordon.[11]

334. Production of Hydrogen by the Interaction of Gaseous Hydrocarbons with Steam.—This process, sometimes called the " methane-steam " process, has received much attention during the past few years.

The main reaction involved is :—

$$CH_4 + H_2O = CO + 3H_2,$$

first successfully accomplished by Sabatier and Senderens.[12] Conversion does not occur to any appreciable extent at temperatures below 350°C., while a temperature of about 1,000°C. is necessary for its practical completion.[13] Complete decomposition is obtained by working at 1,300°C., but it is possible, by using an excess of steam, to force the reaction to the right and obtain a good conversion to hydrogen at lower temperatures. Excess of steam is also desirable to prevent the deposition of carbon which is often evident when only the theoretical quantity of steam is used. Aliphatic hydrocarbons of higher molecular weight are more easily and more rapidly decomposed by this reaction than methane, but their decomposition is complicated by the increasing ease with which they deposit carbon, a fact which causes difficulties when solid catalysts are employed. However, by suitably restricting the composition of the hydrocarbon gas used, by controlling the temperature of the catalyst and by using an excess of steam, this objectionable factor may be diminished to such an extent that the process can be used commercially.

The free energy and equilibrium constants for the above reaction have been calculated[14] from the free energy data of Eastman[15] and Storch,[16] with the following results :—

T °K	1073	1173	1273
$\triangle$ F	−10,700	−16,722	−22,735
K_p	150·5	$1{\cdot}296 \times 10^3$	$0{\cdot}794 \times 10^4$

while an approximate calculation of the concentration of the various constituents in the equilibrium mixture at 900°C. shows the methane content of the gas to be somewhere near 1 per cent., which corresponds to about 96 per cent. conversion.

The equilibrium of this reaction has also been determined as a

function of temperature by Newmann and Jacob,[17] who approached equilibrium in both directions, with the following result :—

$$\log K_4 = \frac{-10308}{T} + 4{\cdot}87 \log T + 0{\cdot}000066T - 0{\cdot}000000081T^2 - 3{\cdot}04$$

$$\text{where } K_4 = \frac{P_{CO} \times P^3_{H_2}}{P_{CH_4} \times P_{H_2O}}$$

335. To obtain good conversions at temperatures below 1,000°C., even when using an excess of steam, it is necessary to use a catalyst. Fischer and Tropsch[18] have investigated the effect of a large number of such catalysts and working at temperatures between 860°C. and 1,000°C., they have reported high conversions at high space velocities. Their best catalysts were composed of nickel or cobalt promoted with aluminium oxide and supported on a refractory material. Such catalysts were reported not to be seriously affected by sulphur although the presence of sulphur compounds did have a noticeable effect upon the conversion of methane obtained. The necessity of using a gas of low sulphur content for this reaction is indicated. Iron, copper, molybdenum and tungsten were found to be poor catalysts, while clay was found to be the best carrier. Marek and Hahn[19] state that " nickel catalysts, promoted with alumina or thoria and supported on fire clay, magnesium oxide, or brick, are very suitable for the process, giving essentially equilibrium conversion at low rates of gas flow through the converter. At increasing rates of flow the increase in unconverted methane is practically linear with the increase in space velocity." In recent work, Hawk, Golden, Storch and Fieldner[14] have found that nickel-corundite and nickel-alundum catalysts are highly active and retain their initial activity over a considerable period. They also found cobalt catalysts to be entirely satisfactory. The use of nickel catalysts for this reaction has been mentioned in several patents.[20]

336. If the above process is operated at a lower temperature with a larger proportion of steam, it is possible to obtain reaction according to the equation :—

$$CH_4 + 2H_2O = CO_2 + 4H_2$$

This is very beneficial, for more hydrogen is produced, 4 volumes instead of 3, and carbon dioxide is produced instead of carbon monoxide. This reaction may be due to the water gas catalytic reaction

$$CO + H_2O = CO_2 + H_2$$

and in order to effect it, it is necessary to conduct the operation at 500°–600°C. At these temperatures, however, the conversion is objectionably low and it is necessary to employ more active catalysts which are, how-

ever, more susceptible to poisoning. Because of these features, the stepwise process of first converting the paraffin gases (e.g., methane) to carbon monoxide and hydrogen at a high temperature and of then oxidising the carbon monoxide by the water gas catalytic reaction at a lower temperature is, in most cases, the more applicable to commercial use.

The first of these reactions has the disadvantage of requiring a high temperature and large quantities of heat, because it is endothermic to the extent of about 5,000 calories per gram mole. of methane reacting.

Some typical results obtained in the conversion of natural gas and steam to carbon monoxide and hydrogen are shown in Table 1,[14] together with details of the catalysts employed. According to these figures, an exit gas containing 69·7 per cent. hydrogen, 0·9 per cent. carbon dioxide, 25 per cent. carbon monoxide and only 1·3 per cent. methane, can be obtained at temperatures of 995–1115°C. Space velocities of 400–500 volumes of inlet gas per volume of catalyst per hour can be employed.

337. Large Scale Plants.—At the Baton Rouge refinery of the Standard Oil Company of Louisiana, the reaction between natural gas and steam is the first step employed in the production of hydrogen. The reaction is carried out in tubes packed with catalyst and heated by direct firing in a radiant type down-flow furnace at a temperature of about 870°C., and at approximately atmospheric pressure.[21]

338. The Conversion of Hydrogen-Carbon Monoxide Mixtures.—After natural gas, or other hydrocarbon gas, has been converted essentially into a mixture of carbon monoxide and hydrogen, it is necessary to submit the former constituent to further treatment and the reaction

$$CO + H_2O \rightarrow CO_2 + H_2$$

is carried out, after which the carbon dioxide is removed by scrubbing with water, etc. This reaction is also employed in the production of hydrogen from water gas, and has acquired great importance because of the immense quantity of hydrogen made by it for ammonia synthesis. As worked out for this purpose, it is known as the B.A.M.A.G., and in the Bosch modification is the main source of hydrogen now used by the I.G. for ammonia synthesis. This particular process uses as "raw material" a mixture of water gas and producer gas and furnishes a mixture of hydrogen and nitrogen in the proportions required for ammonia synthesis.

The hydrogen-carbon monoxide mixture is passed, with excess of steam, through converters at temperatures of 400°–600°C. over catalysts. Excess of steam is favourable for conversion and at 400°C., with 3 volumes of steam per unit volume of gas, the equilibrium mixture

TABLE 1. CONVERSION OF NATURAL GAS AND STEAM MIXTURES
(HAWK, GOLDEN, STORCH AND FIELDNER[14])

COMPARATIVE TESTS ON CATALYSTS

Catalyst	Converting Temperature °C.				Gas Volumes, Litres		Exit Gas Analysis				Inlet Gas Analysis			Space Velocity of Inlet Gas (a)	Natural Gas Decomposed	Steam Concentration in Inlet Gas %
	Initial		Final													
	Centre	Out	Centre	Out	Inlet	Exit	CO_2%	H_2%	CO %	CH_4%	CH_4%	C_2H_4%	N_2%			
1	1145	—	960	—	70·8*b*	202·0*b*	2·5	71·1	22·0	4·3	—	17·2	—	362	88·0%	—
2	1115	1115	995	1065	56·7*b*	225·3*b*	0·9	69·7	25·0	1·3	80·9	17·2	1·9	400	95·0	57
2	1055	1235	915	1035	56·7*b*	219·5*b*	0·8	71·2	23·7	1·5	80·9	17·2	1·9	488	94·0	54
3	1140	1100	1005	1045	868	3114	2·6	68·7	26·1	0·8	80·9	17·2	1·9	301	97·1	60
4	1080	1230	955	980	147·8	474	1·9	63·8	21·3	9·7	80·9	17·2	1·9	246	69·0	58
4	1190	1160	960	980	49·8	113·9	1·6	48·7	15·7	30·1	80·9	17·2	1·9	284	31·3	53
5	1060	1030	810	910	124·6	486	2·4	67·4	21·0	3·0	80·2	17·6	2·2	197	88·4	58
5	1070	1070	735	910	81·6	314	2·4	72·0	21·7	3·1	80·2	17·6	2·2	262	88·2	58
5	1075	1080	745	920	73·6	279·5	1·8	69·7	21·2	5·1	80·2	17·6	2·2	333	80·8	55
7	1100	1115	780	975	710	2888	1·4	70·9	23·9	1·4	85·7	13·0	1·3	425	94·3	57
8	1075	1035	740	830	398	1631	1·2	71·1	23·5	2·2	88·4	10·8	0·8	396	91·0	57

(*a*) Space velocity = ratio of volume of reactants passed through the converter per hour to volume occupied by the catalyst.
(*b*) Gas volumes uncorrected.

Catalysts.

1. 0·23 Kg. nickel nitrate ($Ni(NO_3)_2 6H_2O$) dissolved in a small amount of water and deposited on pieces of burned corundite (a commercial refractory high in Al_2O_3) by evaporation, followed by ignition and reduction.
2. 0·45 Kg. nickel nitrate on burned corundite.
3. 0·9 Kg. nickel nitrate on burned corundite.
4. 0·45 Kg. cobalt nitrate on burned corundite.
5. 0·45 Kg. nickel nitrate and 1·17 Kg. aluminium nitrate on unburnt corundite. Atomic ratio of nickel to aluminium was 1 : 2.
6. Nickel and aluminium nitrates on unburned corundite. Atomic ratio of nickel to aluminium was 1 : 1.
7. 0·45 Kg. nickel nitrate on unburned corundite.
8. 0·45 Kg. nickel nitrate on burned corundite.

contains 0·45 per cent. of carbon monoxide ; with 5 volumes of steam it contains 0·26 per cent. The converters are carefully lagged and with efficient heat exchange and conservation they run autothermically due to the exothermic nature of the reaction. In practice, a 90 per cent. conversion of the carbon monoxide is obtained.[24] A diagram of the Badische Co. converter for use in this process is reproduced in Fig. 1, and shows the heat exchanger by which the inlet gas is raised to reaction temperature by the reaction products.

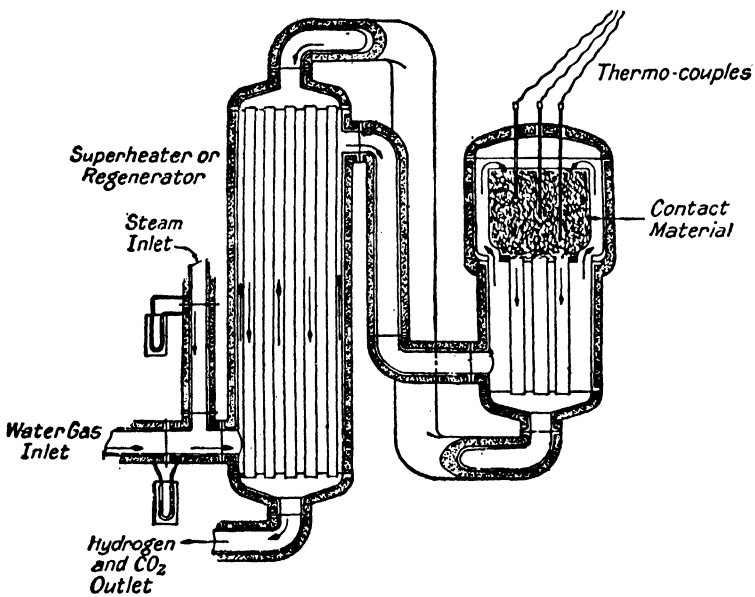


FIG. 1.—DIAGRAM OF THE BADISCHE CO.'S CONVERTER FOR THE WATER GAS CATALYTIC REACTION

Reproduced from "Hydrogenation of Organic Substances," by Carleton Ellis. Courtesy of D. Van Nostrand Co., Inc.

339. Catalysts.—The catalysts suitable for this reaction are of the most varied types, but it is believed that in practice an iron oxide catalyst, with a promotor such as chromate, is in almost exclusive use.[22] The Badische Company have also suggested spathic iron ore as a catalyst, which has not at any stage of the process been subjected to a temperature appreciably higher than 650°C. The catalyst may be employed in the form of grains, or may be shaped into pieces with the aid of binding agents, such as hydroxides or salts of iron, aluminium, etc. The presence of phosphorus, sulphur or silica is objectionable.

In a small scale laboratory apparatus, Evans and Newton[23] studied the effect of various catalysts and found that those containing cobalt oxide, pure or promoted and supported, give the best results, although they are short-lived in the presence of even small quantities of sulphur

compounds. On the whole, for ordinary working conditions, iron catalysts seemed the most satisfactory.

According to Byrne, Gohr and Haslam[21] the gas obtained by the treatment of natural gas with steam to produce carbon monoxide and hydrogen, followed by the above process, contains 78 per cent. hydrogen, 20 per cent. carbon dioxide and 2 per cent. unconverted hydrocarbon and other gases. At the Baton Rouge hydrogenation plant, the carbon monoxide conversion is carried out at a temperature of about 495°C., in the presence of a suitable catalyst.

Water gas, produced by the interaction of steam with coke at temperatures of about 1,000°C., and used as the principal source of the hydrogen required for ammonia synthesis, may be similarly treated for the conversion of its carbon monoxide content. Coke oven gas may also be treated in the same way after the removal of its methane content by interaction with steam. Typical analyses of water gas and coke oven gas are as follows :—

	Per cent. by volume	
	Water gas[24]	Coke oven gas[22]
Hydrogen ..	52·0	46·0
Carbon monoxide	39·6	7·0
Methane	0·4	20·0
Carbon dioxide ..	3·5	4·0
Nitrogen	4·0	15·0
Ethylene	—	2·0
Hydrogen sulphide	0·5	—

340. Removal of Carbon Dioxide.—The gas obtained, as a result of the above processes, consists almost entirely of hydrogen and carbon dioxide, with a very small content of unconverted hydrocarbon and carbon monoxide. It is generally sufficient for hydrogenation purposes to remove the carbon dioxide, but for ammonia manufacture the last traces of carbon monoxide are also removed, (1) as formate by scrubbing with hot concentrated caustic soda, or (2) by absorption into ammoniacal-cuprous formate.[22] These processes need not be considered here.

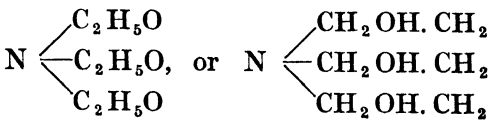
The carbon dioxide content of the gas may be removed by a variety of means of which scrubbing with water is the simplest. In order to reduce the volume of gas to be treated and in order to reduce the volume of scrubbing liquor required, this absorption is usually carried out under a pressure of a few atmospheres, before the gas is compressed right up to the required hydrogenation pressure.

The solubility of carbon dioxide in water as a function of pressure is given in Table 2.

TABLE 2. SOLUBILITY OF CARBON DIOXIDE IN WATER

Pressure in atmospheres	Volumes of CO_2 (at 0°C. and 760 mm.) per volume of water	
	15°C. (Siedel)	20°C. (Inter. Crit. Tables)
1	1·0	—
5	4·59	—
10	8·39	—
15	11·85	—
20	15·21	—
25	17·64	16·3
30	20·31	18·2
35	22·52	20·1
40	24·44	22·0
45	—	23·9
50	—	25·7

At the Baton Rouge plant, the absorption is carried out at a pressure of 250 lbs. per square inch, i.e., about 17 atmospheres, and the scrubbing liquor employed is triethanolamine. This substance, which has the formula



has basic properties and absorbs acidic gases such as carbon dioxide and sulphuretted hydrogen readily to form addition compounds which are decomposed on heating.

The gas scrubbing with triethanolamine is carried out at the pressure mentioned in a bubble plate column. The dissolved carbon dioxide is subsequently stripped from the scrubbing medium with steam at atmospheric pressure after which the stripped liquor is cooled and recycled to the absorption tower. The scrubbed gas thus obtained contains rather more than 97 per cent. hydrogen. It is then compressed to the pressure required for the hydrogenation process.

At the Oppau Plant of the I.G. Farbenindustrie, the carbon dioxide is removed, according to Ellis,[22] by scrubbing in towers 30 feet high, packed with rings, at a pressure of 25–30 atmospheres. Water is used as the scrubbing liquid, and the water leaving the towers, containing the carbon dioxide in solution, gives up its internal energy to operate Pelton wheels; about 60 per cent. of the energy used to inject the water is thus recovered.

A diagrammatic flow sheet of the process used for the production of hydrogen in coal hydrogenation processes is shown in Fig. 2 (after Gordon[11]), while a flow sheet of the process used at Baton Rouge for the hydrogenation of petroleum oils is shown in Fig. 3. In the former case, hydrogen is also produced from water gas in order to start up the

plant and to replace losses, the hydrocarbon gas made in the hydrogenation process not usually being sufficient to produce all the hydrogen required.

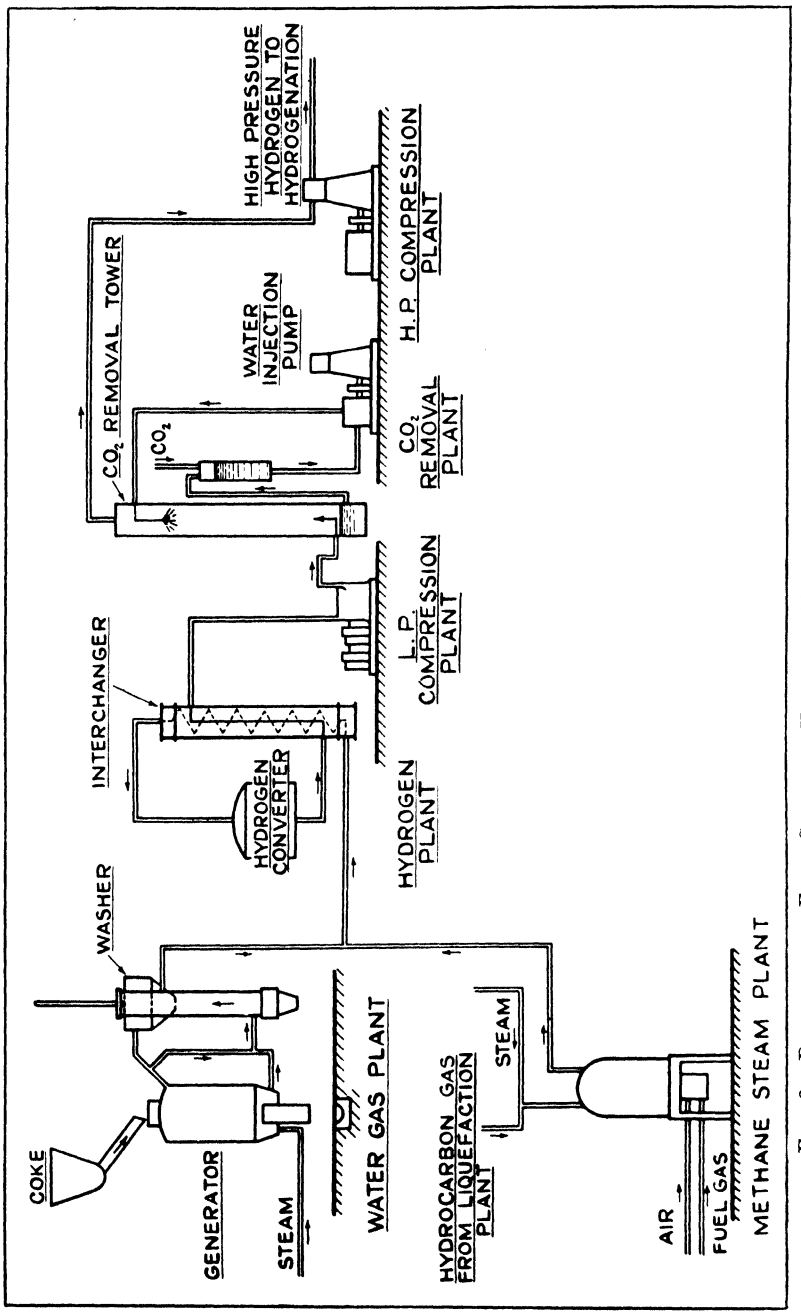


FIG. 2.—DIAGRAMMATIC FLOW SHEET OF HYDROGEN MANUFACTURE FROM WATER GAS (GORDON)
(Courtesy of the Institution of Mining Engineers)

341. Production of Hydrogen by Partial Combustion Processes.—If hydrocarbon gases are burnt in an insufficient supply of oxygen, hydrogen is produced according to the equation

$$2CH_4 + O_2 \rightarrow 2CO + 4H_2$$

This process is not used to any great extent for the production of hydrogen for hydrogenation purposes, but where the presence of nitrogen in the resulting gas is not a disadvantage, or where the presence of nitrogen is actually required, as in ammonia synthesis, it is used to a greater extent.

Partial combustion of hydrocarbon gas with oxygen instead of air may be carried out as a means of making hydrogen free from nitrogen, but this process is not popular as it involves the risk of severe explosions if adequate precautions are not taken.

342. The Production of Hydrogen by the Thermal Decomposition of Hydrocarbons.—At sufficiently high temperatures, methane and higher hydrocarbons decompose into their elements, thus :—

$$CH_4 \rightarrow C + 2H_2$$

and, theoretically, it should be possible to produce 2,000 cubic feet of hydrogen from every 1,000 cubic feet of methane so treated, in addition to 31·82 lbs. of carbon. This reaction has been studied by numerous investigators.[18, 25, 26, 27, 28, 29, 30]

Frank[31] has proposed a process for making hydrogen in which purified natural gas is passed through a furnace filled with incandescent coke or refractory material at a temperature of 1,200°C., while according to Rose[32] a gas containing as much as 98 per cent. hydrogen can be produced in a similar manner at a temperature of 1,650°C. According to Odell,[30] natural gas may be cracked to hydrogen in a water gas generator by making alternate air blasts and gas runs, and approximately 7 lbs. carbon black per 1,000 cubic feet of gas cracked can be recovered.

Of particular interest in this connection is the " Thermatomic process " of gas cracking, which has for its main object the production of carbon, marketed as " Thermax Brand." The process is operated by the Thermatomic Carbon Company, Pittsburg, Pa., and the gas produced is at present being burnt to waste. Typical analyses of the natural gas being used at the Sterlington, La., plant of this company and the resultant gas obtained therefrom are as follow :—[33]

	Natural Gas	*Resultant Gas*
Carbon dioxide ..	0·4	0·9
Illuminants ..	0·7	1·3
Hydrogen	—	85·4
Carbon monoxide ..	—	1·1
Methane	93·8	5·0
Nitrogen ..	5·1	6·3

The possible use of such a process for the production of hydrogen for hydrogenation purposes is, therefore, worth consideration. The furnaces being used at present are 14 feet in diameter and 25 feet high, and consist of riveted steel shells, insulated and lined with refractory brick and filled with chequer brick, similar to blast furnace stoves. The temperature range in the furnace is from 900° to 1,400°C. The process is intermittent, the chequer brick being first heated by a blast of natural gas and air introduced at the bottom, after which the stack is closed and natural gas is added from the top of the furnace for the decomposing part of the cycle. The resultant gases from the furnace are passed to a cooler chamber where water is sprayed counter-current to the gas stream to cool the gases sufficiently to allow them to be safely filtered through cloth bags to remove the carbon.

343. Other Methods of Hydrogen Manufacture.—The electrolytic method of hydrogen production is used to a certain extent in ammonia manufacture, and can compete with the water gas process when cheap electric power is available. This is shown in the following figures of Pollitt[34] referring to the cost of ammonia.

TABLE 3. WORKS COST OF MANUFACTURE OF 1 TONNE AMMONIA IN THE FORM OF 25 PER CENT. LIQUOR

Source of hydrogen	Cost of ammonia, £ per tonne
Coke oven gas	9·0
Water gas	7·2
Electrolysis	
H.T.A.C. current at 0·05 pence per K.W.H...	7·0
0·10 „ ..	9·3
0·15 „ ..	11·7

Water gas is produced by the action of steam on coke at temperatures of about 1,000° C. This process is usually carried out by blowing alternate blasts of air and steam through a bed of coke; during the air blast a high temperature is reached due to combustion of the coke and then, when the steam is turned on, the reaction

$$H_2O + C = CO + H_2 - 29{,}100 \text{ cals.}$$

proceeds.

The following figures show the effect of temperature on (*a*) the extent of the reaction and (*b*) the composition of the gaseous product obtained.

Temperature °C.	Per cent. steam decomposed	Composition of gas produced % by volume		
		Hydrogen	Carbon monoxide	Carbon dioxide
674	8·8	65·2	4·9	29·8
758	25·3	65·2	7·8	27·0
838	41·0	61·9	15·1	22·9
954	70·2	53·3	39·3	6·8
1010	94·0	48·8	49·7	1·5
1125	99·4	50·9	48·5	0·6

These indicate that at 1,000°C., about equal volumes of hydrogen and carbon monoxide are produced, indicating that the equation given above is realised. At 674°C., the reaction appears to approximate that given by the equation

$$C + 2H_2O = CO_2 + 2H_2$$

The following description of the operation of a water gas generator has been given by Ellis.

"A modern water gas generator is a cylindrical structure with a hearth below and a charging orifice above. The latter is provided with a lid and there is an upper and a lower steam inlet and an upper and a lower gas outlet. These are used in pairs, alternatively, the upper steam inlet with the lower gas outlet and vice versa, thus ensuring an even distribution of heat through the fuel. Fire having been made on the hearth, the generator is charged from the top, the lid of which is left open during the air-blowing. Steam inlets and gas outlets being closed, air is blown in at about 15 inches of water pressure, while the gases (ideally, 20% carbon dioxide, 70% nitrogen, etc.), escape through the open lid. When a temperature of about 1,000°C. has been maintained, air is shut off, the lid is closed, one steam inlet and the corresponding gas outlet are opened and steam is admitted at 120 lbs. per sq. in. When the temperature falls to the economical limit, the operation is recommenced, except for the fuel charging which occurs only after the third steaming which completes the cycle. After this a fresh fuel charge is added and the cycle re-begun."

With a generator having a hearth 5′ 6″ diameter, such a cycle would be as follows:

Air blast	2 minutes.
Steam upwards	6 minutes.
Air blast	1 minute.
Steam downwards	6 minutes.
Air blast	1 minute.
Steam upwards	6 minutes.

A typical analysis of water gas produced from coke of 83% carbon content, 6·0% moisture and 9·0% ash, is given in Paragraph 339.

THE PURIFICATION OF HYDROGENATION PLANT RECYCLE HYDROGEN

344. After passage through the hydrogenation reaction chambers (sometimes called "ovens" or "converters"), the hydrogen gas is contaminated with appreciable quantities of gaseous hydrocarbons such as methane, ethane, etc., and also with sulphuretted hydrogen. If the inlet gas contains a small amount of nitrogen, the exit gas will contain a proportionately larger amount of this constituent because of the amount of hydrogen consumed in the reaction chamber, and, consequently, means must be adopted to prevent its steady accumulation. The lower the purity of the hydrogen gas entering the reaction chambers, the lower the partial pressure of the hydrogen and the greater the loss of energy in compression. It is therefore essential to maintain the hydrogen content of the reacting gas as high as possible.

In the various flow sheets of the hydrogenation process which follow, it will be seen that the excess hydrogen leaves the converter carrying with it the whole, or part, of the hydrogenated product. The gas-oil mixture then passes through a condenser to a high pressure separator where the gas is separated at full pressure, in a continuous or semi-continuous manner.

Now the hydrocarbons methane, ethane, etc., are much more soluble in the condensed oil present in this separator than is hydrogen, consequently, appreciable quantities of these gases will be dissolved in the oil, the exact amount depending upon their concentration in the gas, i.e., their partial pressures, and upon the temperature. As a result, a certain amount of hydrogen enrichment occurs in the high pressure separator and sulphuretted hydrogen is also absorbed.

If the production of hydrocarbon gas in the hydrogenation reaction is small, no additional gas purification is necessary, but in many cases, e.g., the hydrogenation of coal, it is essential. Such additional treatment is carried out by means of oil scrubbing at or about the same pressure at which the hydrogenation plant operates. The oil used in this operation is usually of the gas oil boiling range, although lighter oils have been proposed, e.g., petrol denuded of its light ends[35] and kerosene.[36] The scrubbing is carried out in long vessels, capable of withstanding high pressure, mounted vertically. Counter-current flow is, of course, adopted.

Data on the solubility of gases in various liquids at high pressure have been presented in a recent paper by Frolich and his co-workers.[37]

The use of active charcoal for the purification of hydrogenation plant gases has been proposed by Lewis and the Standard Oil Development Company.[38] The gases are passed over the charcoal at pressures of

about 20 atmospheres and at ordinary temperatures; the gaseous hydrocarbons are preferentially adsorbed and the resulting gases are consequently enriched in hydrogen.

CATALYSTS FOR HYDROGENATION REACTIONS

345. Catalysts such as active nickel, platinum and palladium, used for organic reductions, are valueless in the destructive hydrogenation of oils and coals because of the many catalytic poisons such as sulphur compounds, asphalts, etc., that are present. As already mentioned, the original Bergius process was supposed to be essentially non-catalytic, although ferric oxide was added, presumably as a desulphuriser, and it was not until the I.G. Farbenindustrie started work on the hydrogenation process that the large-scale catalytic process was developed. All credit is due to this great German chemical firm for such a notable achievement.

Catalysts may be used in the hydrogenation process in either of two ways, they may be injected into the reaction chambers in a finely divided state mixed with the oil or they may be supported on trays, etc., in massive form inside the reaction chamber. In the hydrogenation of coal, the first method is employed, but the hydrogenation of oils is usually carried out using the massive catalysts, often in the form of pellets. All such catalysts must be immune from poisoning by sulphur compounds and any other substances found in oils and coals; when they are used in massive form they must possess mechanical strength and not be pulverised by the eroding action of oil and hydrogen at high temperatures; moreover, they must have a long life. That catalysts have been developed which fulfil all these exacting conditions is well shown by the fact that the Standard Oil Company of New Jersey have had in continuous operation at their Bayway refinery a large scale hydrogenation unit for a period of one year without a single shut-down. This is ample testimony for the durability and lasting activity of the catalyst employed.

Precise information on the behaviour of specific catalysts is very limited and in this connection the patent literature is not very helpful. In the patents of the I.G., for example, claims have been made concerning the catalytic activity of nearly all the elements of the Periodic Table, although by far the greater number of these patents refer to the elements chromium, molybdenum, tungsten, manganese, cobalt, nickel, zinc, aluminium and magnesium.

346. In the hydrogenation of phenols at temperatures of 450°–500°C., and at maximum hydrogen pressures of 240–320 kg. per square centimetre, Kling and Florentin[39] have found that complete conversion to hydrocarbons can be obtained by the use of dehydrating

catalysts mixed with small amounts of molybdic oxide (MoO_3). The extreme catalytic activity of such catalysts has also been reported by many other investigators. The favourable action of nickel has been reported on,[40] while the successful use of a mixture of molybdenum trioxide and sulphur as a catalyst for the hydrogenation of low-temperature tar has been described by Morgan[41] and also by Morgan and Veryard.[42] A study of the catalytic hydrogenation of tar was also made by King and Matthews,[43] who found that some catalysts had a bad effect on the reaction and accelerated coke formation (e.g., calcium oxide and hydroxide); some converted tar acids into neutral oil (e.g., iodine, hydriodic acid, molybdic acid, molybdic acid and sulphur, tungstic acid and sulphur): and others converted pitch into neutral oil (e.g., molybdic acid, molybdic acid and sulphur, tungstic acid and sulphur, tin oxide-chlorine, bromine and iodine). Molybdic acid was found to be the best general catalyst for the treatment of tar, and many experiments were made to find the most active form of molybdenum. It was found that the addition of sulphur increased its hydrogenating power, the catalyst then being in the form of MoS_2, with hydrogen sulphide present in the gas phase. The highest conversion of tar to petrol was obtained using ammonium molybdate supported on active charcoal together with sulphur. The claim that molybdenum and molybdenum compounds are more active as hydrogenation catalysts when mounted on a carrier is also made by the N. V. de Bataafsche Petr. Mij.[44] Roberti[45] reports that in the hydrogenation of Ragusa oil (d_{15} 0·964, I.B.P., 215°C., sulphur 2·9 per cent.) molybdenum trisulphide deposited on charcoal was the most active catalyst found, while molybdenum disulphide deposited on pumice retained its activity longest.

347. The following catalysts have also been proposed, among many others :—

1. The oxide and carbonate of uranium.[46]
2. " Ansolvo acids," i.e., acid complexes obtained by mixing organic acids with certain types of inorganic salts, e.g., double compounds of oleic acid and zinc chloride, etc.[47]
3. Composite catalysts,[48] e.g.,
   (*a*) Trioxides of molybdenum and chromium,
   (*b*) Zinc and molybdenum compounds,
   (*c*) Molybdenum, manganese and chromium,
   (*d*) Molybdenum, chromium and aluminium,
   (*e*) Molybdic oxide, zinc oxide and magnesium oxide.
4. Magnetic iron ore together with small amounts of tin or metals of Groups 5 and 6.[49]
5. Sulphides of the heavy metals. Mixtures of cobalt and nickel

sulphides or zinc and aluminium sulphides and molybdenum, chromium, tungsten and uranium or their compounds.[50]

6. Oil-soluble compounds of organic acids or phenols with one or more metals from the 2nd, 6th or 8th Groups; especially zinc, molybdenum, chromium or cobalt.[51]
7. Metal compound of 1·3 diketones, e.g., chromium and vanadium acetyl-acetonates.[52]
8. Massive catalysts supported in the reaction chambers in the form of metallic plates, wire, ribbon or gauze.[53]
9. Finely powdered metallic oxides, especially 90 per cent. chromium oxide and 10 per cent. molybdic oxide.[54]
10. Catalysts composed of at least three substances, e.g.,
    (*a*) Tungsten, chromium and manganese oxides,
    (*b*) Molybdenum, chromium and manganese oxides,
    (*c*) Molybdenum, chromium and kaolin, etc.[55]
11. Molybdenum compounds in the presence of H_2S.[56]
12. Massive or powdered catalysts, e.g., nickel or cobalt alloyed with tin.[57]
13. An organic compound of tin which is not volatilised but is decomposed at or below reaction temperature, e.g., stannous oxalate, formate, acetate, etc.[58]
14. Mixed catalysts for the hydrogenation of coal, e.g., copper and silver in massive form, together with tin in the form of tin-plated iron. These catalysts are said to have the property of deoxygenating coal, thus inhibiting the formation of phenolic bodies.[59]

The Baton Rouge Hydrogenation Plant of the Standard Oil Company of Louisiana

348. The methods adopted at Baton Rouge for the production and purification of hydrogen have already been described, while a flow sheet of the hydrogen producing plant is given in Fig. 3. This diagram also shows the process adopted for the "once-through" or "straight through" (i.e., no recycle) hydrogenation process. The recycle operation is shown in Fig. 4.

The stock to be hydrogenated is raised to the operating pressure by steam-driven plunger pumps, the exhaust steam of which is employed in hydrogen manufacture. The hydrogen from the compressors is mixed with the oil and delivered to tubular heat exchangers where the mixture is preheated by the hot hydrogenated products coming from the reaction chamber. Following this, the hydrogen-oil mixture is heated to about 700–850°F. (371–455°C.), in a gas-fired pipe coil, from which it is introduced into the reaction chambers. These are about 40 feet long, mounted vertically and are connected in series; three or four being used

in each of the two units of the plant. The reaction space is about 3 feet diameter, and is lined with a non-corrosive alloy and filled with a sulphur-resistant catalyst. Since the hydrogenation reaction is exothermic, an in-

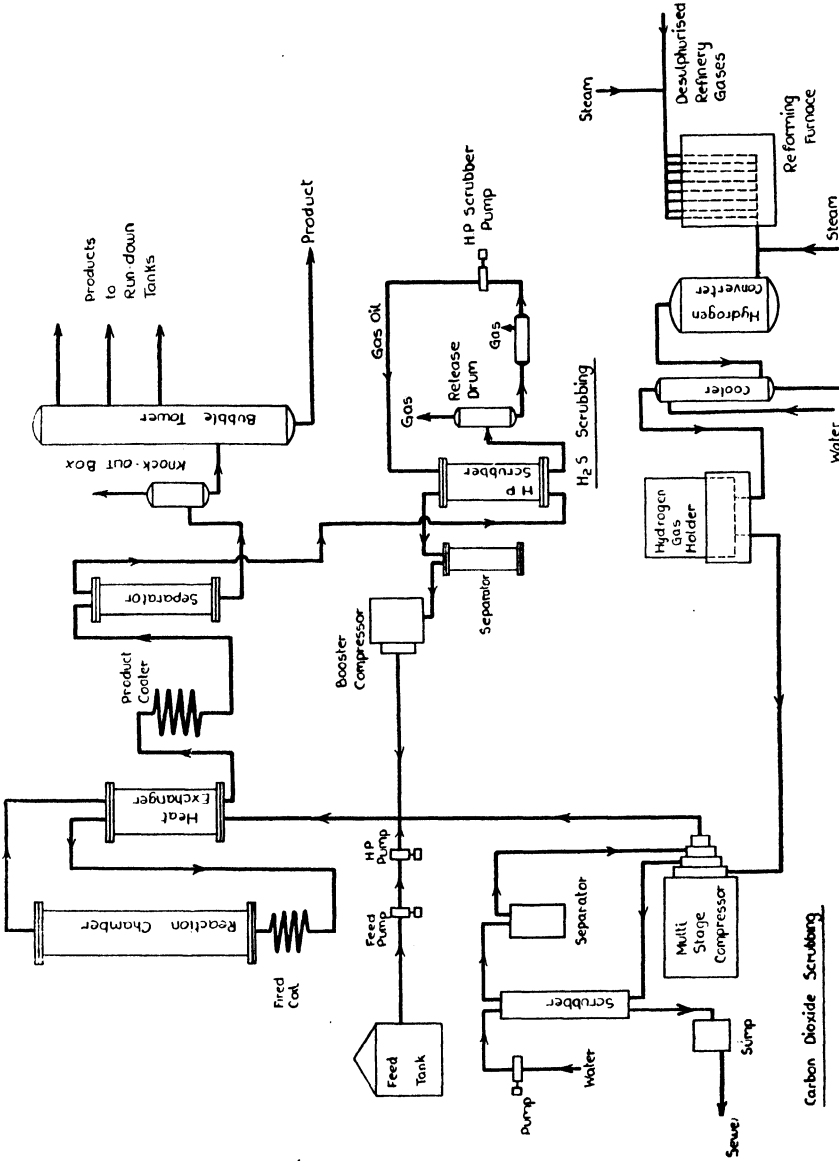


FIG. 3.—FLOW DIAGRAM OF HYDROGENATION PLANT AT BATON ROUGE, LOUISIANA (BYRNE, GOHR AND HASLAM)

crease in temperature takes place as the oil and hydrogen pass through the catalyst bed; this raises the temperature of the reactants to 750°F.–1,000°F. (399–538°C.) or more, depending upon the type of reaction

employed and, for this reason, the amount of heating carried out in the fired coil is relatively small. From the reaction chambers the mixture of hydrogenated products, gas and excess hydrogen, passes through the heat exchangers, a cooling coil and thence to a separator. Here the gaseous and liquid products are separated under full pressure, the liquid being withdrawn to a low pressure separator whence it passes to storage. The gas from the high pressure separator is conducted to booster compressors, where it is recompressed to 3,600 lbs. per square inch for mixing with fresh hydrogen. These booster compressors run with a 350–600 lbs. per square inch differential pressure. Gases which are formed in the process are, in many cases, removed to a sufficient extent from the

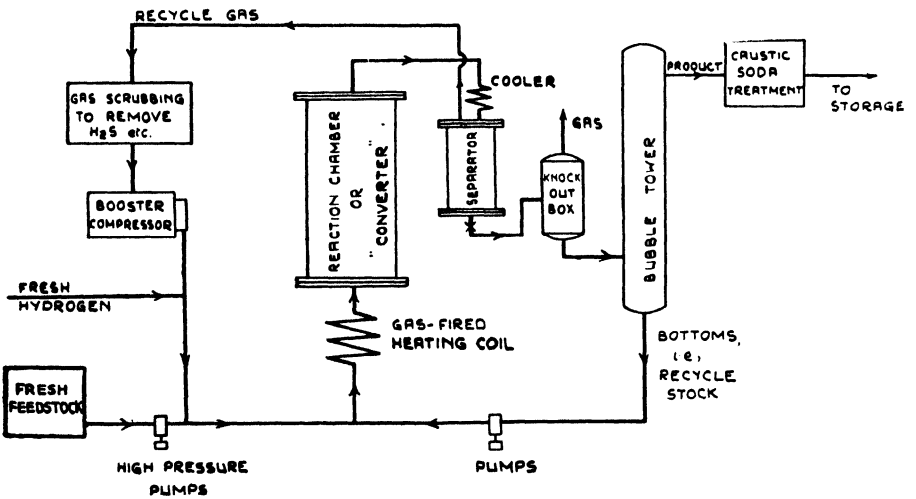


FIG. 4.—FLOW DIAGRAM OF RECYCLE HYDROGENATION UNIT

circulating hydrogen by their solubility in the liquid product; however, high pressure scrubbing equipment is provided for the removal of these gases if necessary, and, in this case, the gases coming from the high pressure separator are scrubbed with oil prior to recompression in the booster compressors.

The greater part of the work done by the Standard Oil Co., in the production of petrols by hydrogenation, has been concerned with the " recycle " system of operation in which that part of the hydrogenation product which does not boil within the petrol boiling range is returned to the process mixed with fresh feed. In this way, the ultimate yield of petrol obtained is materially increased and is, in some cases, as high as 105 per cent. by volume. When loss is sustained it is wholly accounted for by gas formation.

RESULTS OBTAINED BY THE STANDARD OIL COMPANY IN THE PRODUCTION OF MOTOR FUELS BY THE HYDROGENATION OF PETROLEUM OILS

349. As an outcome of the pioneer work carried out by the Standard Oil Company in this field, the hydrogenation process appears to possess six adaptations which are of immediate importance.[60]

1. Conversion of heavy, high-sulphur, asphaltic crude oils and refinery residues into gasoline and distillates low in sulphur and free from asphalt, without concurrent formation of coke.

2. The alteration of low grade lubricating distillates, to obtain high yields of lubricating oils of premium quality as to viscosity-temperature relationship and other properties.

3. The conversion of off-colour, inferior burning oil distillates or light gas oils, into low specific gravity, low-sulphur, water-white burning oils of superior burning characteristics.

4. The conversion of paraffinic or aromatic gas oils into low-sulphur, low-gum and colour-stable gasolines without production of coke or tar.

5. The desulphurisation and colour and gum stabilisation of high-sulphur, badly gumming cracked naphthas.

6. Manufacture of new and specialised products, such as high flash safety aviation fuels, and high-solvent-power naphthas for use as lacquer diluents, and the like.

Of these applications, Nos. 2 and 3 are outside the scope of this book and need not be considered here. Full details may, however, be found in the literature.[21, 22, 60, 61, 62, 63]

350. Conversion of Refinery Residues etc., into Gasoline and Gas Oil.—Residues from crude stills or cracking plants may be hydrogenated in the liquid phase to produce in excess of 100 per cent. by volume yield of a product consisting of gas oil and gasoline, the percentage of gasoline ranging from 10 per cent. to 40 per cent., depending upon conditions, the balance being distillate product. During hydrogenation, the asphalt is completely converted and 60–90 per cent. of the sulphur present in the feed stock is eliminated as hydrogen sulphide and as such is scrubbed out of the recycle gases. Even if the feed stock is highly asphaltic and of high sulphur content, the gasoline produced is said to be easily finished to give a low-sulphur, gum-stable product. The gas oil which is obtained may be hydrogenated in the vapour phase and converted completely to gasoline, or, if desired, be cracked to produce gasoline. If the tar produced in this cracking step were returned to the hydrogenation operation and none burned for fuel, the yield of gasoline would be approximately 100 per cent. The workability of the liquid-phase hydrogenation operation has been demonstrated on fuel oil residues from Crane Upton, Panuco, Venezuela, Panhandle, Mid-

Continent, Talang Akar, Long Beach, Smackover, and other crudes, as well as upon cracking plant tars.

The anti-knock value of the gasolines produced is dependent upon operating conditions, particularly the type of charging stock —crude residues from Smackover, Venezuela, Colombia and similar crudes giving lower anti-knock gasolines than residues from Mid-Continent crude. Typical results for this application of the hydrogenation process are given in Table 4.[62, 63]

TABLE 4. RESULTS OBTAINED IN THE HYDROGENATION OF HEAVY FEED STOCKS

Feed Stock	Topped Crane Upton Crude	Topped Crane Upton Crude	Topped Panuco Crude	Cracking Coil Tar
Sp. gr. of feed	0·915	0·915	0·905	0·984
Volumetric % of product ..	107·7	100·5	101·5	98·9
Sp. gr. of product	0·844	0·846	0·835	0·914
Weight % of product ..	99·3	92·9	93·7	91·9
Vol. % gasoline in product ..	22·0	30·0	25·0	14·0
Vol. % gasoline on the feed ..	23·7	30·15	25·4	13·9
Sp. gr. of gasoline	0·749	0·748	0·736	0·753
Weight % of gasoline (remainder is gas oil)	19·4	24·7	20·7	10·6
% Sulphur in feed	1·25	1·25	0·760	0·702
% Sulphur in total liquid products	0·198	0·530	0·108	0·246
% Sulphur in gasoline ..	0·034	0·056	0·049	0·019
Feed I.B.P. °C.	176·7°C.	176·7°C.	173·4°C.	171·1°C.
% at 100°C. (212°F.) ..	—	—	—	—
140°C. (284°F.) ..	—	—	—	—
190°C. (374°F.) ..	—	—	—	—
204·5°C. (400°F.) ..	—	—	1·0	0·5
237·8°C. (460°F.) ..	6·5	6·5	1·5	—
343·4°C. (650°F.) ..	40·5	40·5	34·0	34·5
371·1°C. (700°F.) ..	66·0	66·0	82·0	49·0
Product I.B.P. °C.	58·8	—	54·5	67·3
% at 100°C. (212°F.) ..	4·0	—	4·0	3·0
140°C. (284°F.) ..	8·5	—	10·0	6·5
190°C. (374°F.) ..	18·0	24·5	21·0	12·5
204·5°C. (400°F.) ..	22·0	30·0	25·0	14·0
237·8°C. (460°F.) ..	33·5	41·0	36·5	20·5
343·4°C. (650°F.) ..	77·5	79·0	76·0	67·0
371·1°C. (700°F.) ..	87·5	86·5	85·5	82·0

351. The relative economics of cracking and hydrogenation as means for producing gasoline from fuel oil, etc., has been dealt with recently by Kessler,[64] who has reached the conclusion that hydrogenation is relatively expensive, and cannot usually compete with straight cracking. Kessler has quoted the following figures.

Size of Plant, 16,000 barrels per day feed.

Capital cost per barrel = $1·37.

Operating Costs.	*Cents per Bbl. Feed.*
1. Steam	9·90
2. Water	2·08
3. Power	1·89
4. Wages and salaries	6·00
5. Repairs	8·22
6. Catalysts and chemicals	9·10
7. Overheads. 25% of items 4 and 5, 10% of item 6	4·46
8. Insurance, 1% of $1·37	1·37
9. Depreciation, 10% of $1·37	13·70
10. Royalty	7·67
11. Fractionating overhead product	5·46
12. Treating gasoline	1·62
13. Redistilling gasoline	0·85
14. Gasoline recovery	0·25
	72·57 cents.

= 1·73 cents per U.S. gallon of feed.

352. The Production of Gasolines from Gas Oils.—The plant used for this operation is practically the same as that used in the preceding case, but the reaction is carried out entirely in the vapour phase, as shown in Fig. 4. The yield of gasoline obtained is less than 100 per cent. by volume, when high anti-knock value is desired, but exceeds this figure if gasolines of low anti-knock value are produced. Using the recycle operation, the only products are motor spirit and gas; no tar or coke is formed.

The feed stocks which have been used in this adaptation of hydrogenation have included straight-run and cracked cycle gas oils from Mid-Continent, California, West Texas, Venezuela and Talang Akar, etc., etc., as well as such materials as Edeleanu extracts from kerosenes (see Chapter IV). It has been found that aromatic and naphthenic gas oils give higher knock-rating gasolines than paraffinic gas oils, and that the aniline point of the feed stock is a fairly reliable guide to the quality of spirit produced under given conditions of temperature and catalyst, etc.

This vapour-phase operation is limited to feed stocks having an F.B.P. of not more than 325°C., otherwise heavy ends and polymerisation products are deposited on the catalyst and cause gradual loss of activity.

Very effective catalysts have been developed and the gasolines produced are characterised by their low sulphur and gum contents. They are consistently easier to refine than cracked spirits from the same feed stocks, but high end-point gasolines produced under high temperature hydrogenation conditions, having high anti-knock values, are rather more difficult to refine, as is the case with cracked naphthas. The more active hydrogenation catalysts tend to produce spirits of lower anti-knock value, presumably because of the conversion of aromatics into naphthenes. This is shown in Table 5, in which results obtained on naphtha bottoms from mixed base crudes with three different catalysts are compared.[65] In this case, so-called high temperature conditions were employed, namely, 500° to 540°C.

TABLE 5. COMPARISON OF THREE CATALYSTS IN THE PRODUCTION OF GASOLINE FROM THE SAME GAS OIL AT PERIODS OF EQUAL CATALYST AGE

Feed Stock. Napthas bottoms from mixed base crudes.

A.P.I. gravity	32·3°	I.B.P.	402°F.
		10%	423°F.
Specific gravity	0·863	20%	430°F.
		50%	449°F.
Aniline point	108°F.	90%	512°F.
Sulphur	0·414%	F.B.P.	624°F.

Catalyst	A	B	C
Operating Conditions.			
Throughput, vols/vol. catalyst/hour	2·0	4·0	4·0
Volume % fresh feed	45	50	58
Vol. % yield distillate on fresh feed	86	89	90
Volumes gasoline/vol. catalyst/hour	0·78	1·78	2·09
Properties of Distillate (before finishing).			
A.P.I. gravity	45·0	42·7	45·7
Specific gravity	0·80	0·813	0·797
I.B.P. °F.	—	102	95
% at 158°F. (70°C.)	—	8·0	10·0
% at 212°F. (100°C.)	—	19·5	21·0
% at 284°F. (140°C.)	—	35·5	36·0
% at 374°F. (190°C.)	—	64·0	64·0
F.B.P. °F.	420	425	419
Recovery %	—	96	97
Colour, Saybolt	+10	+11	+4
Sulphur %	0·05	0·04	0·02
Glass dish gum, mgs./100 mls.	7·0	1·7	1·6
Doctor test after caustic washing	negative	negative	negative
Corrosion test after caustic washing	negative	negative	negative
Octane number, S.30 engine, 212°F., 600 r.p.m.	85	82	72

Low temperature operation (i.e., at 350–450° C.) may be obtained by the use of highly active catalysts developed by the I.G. These

catalysts also permit the employment of high reaction rates. Thus in gasoline production from gas oils by recycle operation, 122% volume yields of gasoline have been obtained from cracked charging stocks at a production rate of 1·5 volumes per volume of catalyst per hour. The combined feed to the unit comprises 60% fresh feed and 40% recycle. These high rates of gasoline production at low temperatures obviously mean that the efficient hydrogenating catalysts are also effective splitting catalysts. Moreover, at such low temperatures the hydrogen-deficient refractory molecules are hydrogenated to more saturated, and hence more "crackable" molecules. The highly active catalysts employed retain their efficiency only by virtue of being continually maintained clean (i.e., free of coke and polymers) owing to the hydrogenation reaction.

Some typical results obtained in low temperature operation are given in Table 6. The gasoline yields given above (122% volume)

TABLE 6. PRODUCTION OF GASOLINE FROM GAS OILS BY HYDROGENATION AT LOW TEMPERATURES

Feed Stock	Mixed Virgin and Cracked Gas Oil	Heavily Cracked Gas Oil
Sp. gravity 60°F.	0·9036	0·9248
5% point	448°F.	400°F.
50% point	536°F.	471°F.
Final b.p.	684°F.	565°F.
% Sulphur	0·864	0·500
% Fresh Feed in combined feed to hydro-plant	60	60
Gasoline production rate Vols./vol. catalyst/hour	1·5	1·5
Gasoline yield % volume	116	122
Properties of hydrogenated product.		
Sp. gr. 60°F.	0·7161	0·7432
Gravity ° A.P.I.	66·1	58·9
Distillate + loss at 122°F. (50°C.)	8·5	7·0
% at 140°F. (60°C.)	11·0	7·5
% at 212° F. 100°C.)	39·5	29·5
F.B.P.	374°F. (190°C.)	416°F. (213°C.)
Recovery %	95	97
Sulphur %	$<0·02$	$<0·02$
Colour (Saybolt)	+ 30	+ 30
Copper dish gum, mgs./100 mls.	nil	nil
Octane No., C.F.R. Motor Method	60·4	58·7
Ditto + 1 cc. lead/gallon	72·8	72·4

are superior to anything obtainable on cracking such aromatic, low hydrogen content feed stocks. Although the gasolines produced are of poorer octane number than those obtained in high temperature

operation, they have exceptionally good lead susceptibility, and are noteworthy for their exceptional cleanliness. These products average + 30 Saybolt colour and are of low sulphur content and possess good gum stability.

In publications by various members of the staffs of the Standard Oil Companies during 1929–1931, stress was laid on the production of motor fuels of particularly high anti-knock value by the hydrogenation of gas oils by the high temperature method of operation, and some of the results quoted are reproduced in Tables 7 and 8, the former referring to the effect of feed-stock aniline-point upon the knock-ratings obtained and the latter giving the properties of the spirits produced in greater detail. It is evident, however, from an examination of the most recent publications[65, 66, 75, 76] that the high temperature operations necessary for such high anti-knock production are not now regarded with so much favour and more attention has been devoted to the production of lower knock-rating material which is produced in greater yield.

TABLE 7. INFLUENCE OF FEED STOCK ON ANTI-KNOCK QUALITY

General Character of Feed Stock	Highly Paraffinic	Paraffinic	Inter-mediate	Aromatic	Edeleanu Extract
Aniline point of feed stock ..	161°F. (71·7°C.)	139°F. (59·4°C.)	102°F. (38·8°C.)	79°F. (26·2°C.)	10°F. (—12·3°C.)
Gasoline yield %	89·0	91·4	88·0	89·0	85·0
Octane number of gasoline at 212° F. (100°C.) ..	72·0	75·0	85·0	92·0	above 100

In some ways this is unfortunate, particularly with respect to the lower octane number of the gasoline produced, because the addition of tetra-ethyl lead is often not desirable or even allowable. There is a definite need in the petroleum industry for a plentiful supply of low volatility high octane number blending stock and this is not met by the methods of gas oil hydrogenation now in favour.

353. The relative merits of cracking and hydrogenation as methods of producing gasoline have recently been discussed, as applied to five different feed stocks. Table 9 summarises the operating conditions and products made from these materials, and shows that

(1) Both high temperature and low temperature hydrogenation offer increases in gasoline yields over cracking. Whereas cracking produces 90 to 95 volumes of liquid product per 100 volumes of feed, of which usually 50 to 70 volumes are gasoline and the rest tar, hydrogenation yields 90 to 120 volumes of gasoline on the same basis.

(2) Higher conversions, as indicated by the per cent. fresh feed, are realised with hydrogenation.

(3) Since only a caustic wash is required on the low temperature hydro-gasolines, negligible treating losses and losses in knock-rating are encountered on these products.

(4) The octane numbers (Series 30 engine, 212°F. or C.F.R. Motor Method) of the cracked gasolines are, in general, higher than those of the hydrogenated products. This apparent advantage, however, is counterbalanced in some measure by the superior lead susceptibility and "non-fading" properties of the hydrogenated fuels.

TABLE 8. PRODUCTION OF ANTI-KNOCK GASOLINES FROM GAS OILS

	Mid-Continent Gas Oil	California Cracked Gas Oil	West Texas Cycle Gas Oil	
Feed Stock.				
A.P.I. gravity ..	37·8	25·7	30·3	
Specific gravity	0·836	0·900	0·873	
I.B.P.	435°F. (224°C.)	342°F. (172·3°C.)	400°F. (204·5°C.).	
%at460°F.(237·9°C.)	3·5	31·0		
%at550°F.(287·8°C.)	90·0	91·0		
F.B.P.	629°F. (330°C.)	602°F. (315·9°C.)	620°F. (322·2°C.)	
Sulphur % ..	0·179	0·554	0·192%	
Aniline point ..	159°F. (70·6°C.)	790°F. (26·2°C.)	102°F. (38·9°C.)	
Hydrogenated Product (as received from hydro unit)			1	2
Yield % volume	86·5	89·0	94·5	88·0
A.P.I. gravity ..	56·4	43·7	39·6	42·3
Specific gravity ..	0·753	0·808	0·826	0·813
I.B.P.	86°F. (30·0°C.)	105°F. (40·6°C.)	110°F. (43·3°C.)	109°F. (42·8°C.)
% at 212°F.(100°C.)	36·0	19·0	13·5	12·0
% at 284°F.(140°C.)	61·0	47·5	25·0	32·5
% at 356°F.(180°C.)	83·0	85·5	—	—
% at 374°F.(190°C.)	87·5	90·0	50·5	70·5
F.B.P.	433°F. (223°C.)	417°F. (213°C.)	436°F. (224·5°C.)	412°F. (211·1°C.)
Octane number	75·1	94	82·2	85·0
Dissolved gum (mgs.)	3·6	2·8	9·0	—
Sulphur % ..	0·022	0·017	0·002	0·006

Haslam, Russell and Asbury[65] have recently compared the costs of producing motor fuels from gas oils by these two separate methods. Their conclusions may be summarised as follows :—

TABLE 9. COMPARISON OF HYDROGENATION * AND CRACKING † RESULTS

Feed Stock.	1	2	3	4	5
Type	Mixed Cracking Stock	Coastal Cycle Gas Oil	Heavy Naphtha Bottoms from Mixed Crudes	Mid-Continent Gas Oil (Light)	Mid-Continent Gas Oil
A.P.I.	28·4	26·0	30·8	40·7	33·4
Aniline Point°F.	90	125	110	146	156
50% at °F.	453	556	447	440	540
% at 400°F.	20	—	22·7	16·0	—
F.B.P., °F.	680	—	—	618	—

Operating Results	Cracking	High-Temp. Hydrogenation	Low-Temp. Hydrogenation	Cracking	High-Temp. Hydrogenation	Low-Temp. Hydrogenation	Cracking	High-Temp. Hydrogenation	Low-Temp. Hydrogenation	Cracking	High-Temp. Hydrogenation	Low-Temp. Hydrogenation	Cracking	High-Temp. Hydrogenation	Low-Temp. Hydrogenation
Total Throughput :															
Hydro, vol./vol./hr.	—	4·0	2·2	—	4·0	2·2	—	4·0	2·2	—	4·0	2·2	—	4·0	2·2
Cracking, bbls./day	15,000	—	—	15,000	—	—	15,000	—	—	15,000	—	—	15,000	—	—
Vol.-% fresh feed	31·5	46·0	72·0	38·0	42·0	67·0	32·0	59·0	76·0	43·5	76·0	91·0	35·0	55·0	70·0
Vol.-% 12° A.P.I. tar on fresh feed (cracking)	42·0	none	none	49·5	none	none	38·5	none	none	15·0	none	none	29·5	none	none
Gasoline (420°F. End Point) :															
Vol.-% raw gasoline on fresh feed	50·5	93·0	110·0	44·0	92·0	110·0	54·5	91·0	109·0	72·5	89·0	108·0	61·5	91·0	109·0
Vol.-% finished gasoline on fresh feed	47·0	89·5	109·5	41·0	88·5	109·5	50·5	87·5	108·5	67·5	85·5	107·5	57·0	87·5	108·5
Octane No. at 212°F. of finished gasoline ‡	78·5	74·0	64·0	72·2	67·0	58·0	75·5	69·0	60·0	68·2	64·0	57·0	69·6	63·0	54·0
Gasoline Production, bbls./day :															
(*a*) In a 5000 B/D total feed hydro plant	—	2060	3940	—	1860	3670	—	2580	4130	—	3250	4350	—	2400	3800
(*b*) In a 15,000 B/D total feed cracking coil	2220	—	—	2330	—	—	2420	—	—	4390	—	—	2980	—	—

* Recycle operation wherein the feed stock is totally converted to gasoline and a small amount of gas.
† Recycle operation to ultimate yield of gasoline and 12° A.P.I. tar.
‡ Octane numbers obtained on Series 30 engine at 212°F. and 600 R.P.M.

(1) The economic position of the hydrogenation process is markedly affected by gasoline price. At low gasoline prices, i.e., up to 6 cents per gallon, hydrogenation offers no, or only small, advantages over cracking. Higher gasoline prices are favourable to the hydrogenation process.

(2) The low-temperature hydrogenation process is more economic than the high-temperature process.

The hydrogenation process may find application in the future as an adjunct to the cracking process. In this way, refractory cycle stocks produced in cracking may be hydrogenated to give high motor fuel yields and a hydrogenated gas oil which could be cracked easily.

An economic examination of this method of operation has recently been made by Russel, Gohr and Voorhies.[76]

354. Figures have already been given for the properties of hydrogenated motor fuels; the following are of interest in showing the anti-knock fade properties of spirits produced under low temperature hydrogenation conditions from a Venezuelan gas oil.

Properties of Gasoline.

Sp. gr. 0·7136		
A.P.I. gravity 66·8		
% at 212°F. (100°C.) 47		
90% Point	334°F.	(167·8°C.)
F.B.P.	377°F.	(191·7°C.)
Colour (Saybolt)		30

S.30 *Engine*	*Octane Number*
(*a*) 212°F. jacket temperature, 600 r.p.m.	66·0
+ 1 ml. T.E.L. per U.S. gallon	76·6
+ 2 ml. T.E.L. per U.S. gallon	82·5
(*b*) 300°F. jacket temperature, 600 r.p.m.	62·5
+ 1 ml. T.E.L. per U.S. gallon	75·6
+ 2 ml. T.E.L. per U.S. gallon	79·7
(*c*) 375°F. jacket temperature, 900 r.p.m.	61·5
+ 1 ml. T.E.L. per U.S. gallon	75·1
(*d*) C.F.R. engine motor method	66·1
0·5 ml. T.E.L. per U.S. gallon	73·1
1·0 ml. T.E.L. per U.S. gallon	77·9
2·0 ml. T.E.L. per U.S. gallon	80·6

No information has been published regarding the anti-knock "fading" properties of hydrogenated gasolines of octane numbers 80 to 100, produced by high temperature operation. As these fuels are of an

aromatic nature, it might be expected that these would experience a fairly large octane number drop at high engine temperatures. Such spirits have been shown to possess greater anti-knock properties in the heavier fractions than in their light fractions, a state of affairs exactly the opposite to that existing in straight-run and cracked spirits. This is shown in Fig. 5.

High octane-number hydrogenated gasolines are valuable as blending agents for raising the anti-knock values of low grade fuels and in this respect are often as good as benzole in low concentrations, as shown in Fig. 6. The tetra-ethyl lead susceptibilities of low temperature hydrogenated gasolines are generally superior to those of cracked and most straight-run fuels.

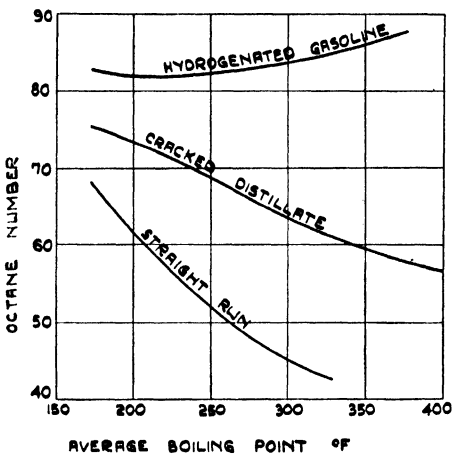


FIG. 5.—CURVES SHOWING THE ANTI-KNOCK PROPERTIES OF STRAIGHT-RUN DISTILLATES, CRACKED DISTILLATES AND HYDROGENATED GASOLINES PLOTTED AS A FUNCTION OF THEIR BOILING POINTS

355. The Chemical Stabilisation and Desulphurisation of Cracked Naphthas.—A further application of the hydrogenation process to meet existing market requirements is the stabilisation and refining, i.e., the so-called "Hydrofining," of cracked distillates and naphthas. In this process, hydrogenation is necessarily much less severe than in the production of motor fuels from gas oil, and the only chemical changes that occur are (1) removal of sulphur in the form of H_2S, (2) saturation of the more reactive unsaturated hydrocarbons which are responsible for colour and gum formation. When the process is so adjusted that no loss in anti-knock value is incurred, approximately half the sulphur in the feed stock is eliminated. On the other hand, the process can be so operated that all the sulphur is removed, the anti-knock value actually improved and the proportion of low-boiling fractions increased.[60] When no change in anti-knock

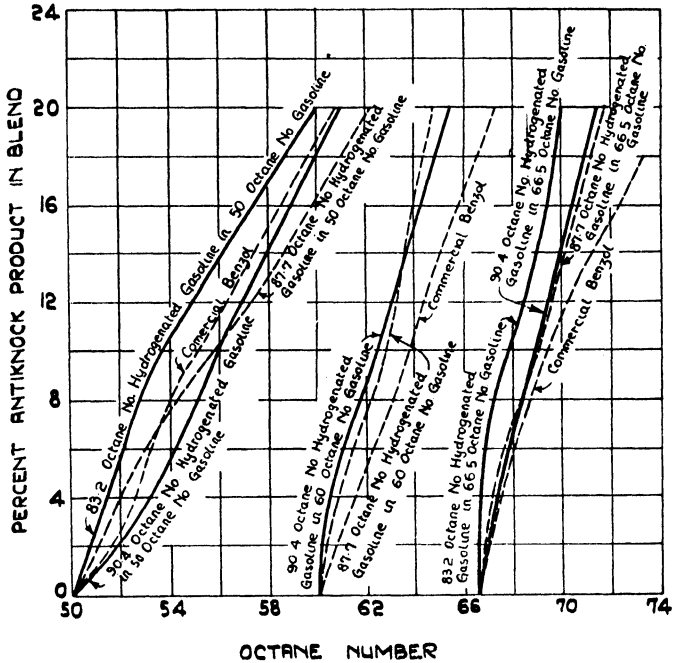


FIG. 6.—CURVES SHOWING THE ANTI-KNOCK BLENDING PROPERTIES OF HYDROGENATED GASOLINES AND BENZOLE

value is obtained, the yields of hydrofined product are over 90 per cent. by volume; when, however, the anti-knock value is increased, the yields are a little lower, due to gas formation. Typical results obtained in the hydrofining operation are given in Tables 10, 11, and 12.

TABLE 10. HYDROFINING CRACKED DISTILLATE

	Cracked Distillate	Hydrogenated Product (93% Yield)
Specific gravity	0·759	0·753
A.P.I. gravity	54·9	56·3
Sulphur %	0·097	0·055
Colour (Saybolt)	Yellow	+23
Octane number	81·6	82·2
Preformed gum (mgs.) ..	77·3	3·8
Copper dish gum (mgs.) ..	—	1·5
I.B.P.	88°F. (31·1°C.)	112°F. (44·4°C.)
% at 140°F. (60°C.)	—	5·0
% at 158°F. (70°C.)	—	12·0
% at 212°F. (100°C.)	35·0	38·5
% at 284°F. (140°C.)	—	69·0
% at 302°F. (150°C.)	60·0	—
% at 356°F. (180°C.)	—	92·0
% at 374°F. (190°C.)	82·0	95·5
F.B.P.	432°F. (222·2°C.)	390°F. (198·9°C.)

TABLE 11. FINISHING CRACKED SMACKOVER NAPHTHA BY HYDROGENATION[62, 63]

	Cracked Smackover Naphtha	Hydrogenated Product. 100% vol. Yield, 97% weight Yield
Total Product—		
Specific gravity	0·795	0·771
A.P.I. gravity	46·4	52
Sulphur %	0·395	0·019
Doctor test	Positive	Negative
Colour	Straw	+25 Saybolt
I.B.P.	51·1°C. (124°F.)	56·6°C. (133·9°F.)
% at 100°C. (212°F.)	14·5	12·0
% at 150°C. (302°F.)	40·5	45·0
% at 190°C. (378°F.)	64·0	73·5
% at 204·5°C. (400°F.)	71·5	82·0
F.B.P.	282·2°C. (540°F.)	261·1°C. (502°F.)
Gasoline Content of Product—		
Specific gravity	0·763	0·756
Sulphur %	0·188	0·006
Porcelain dish gum (mgs.)	12	1
Copper dish gum (mgs.)	21	4

TABLE 12. FINISHING CRACKED MID-CONTINENT NAPHTHA BY HYDROGENATION

	Feed. Cracked Naphtha	Acid Treated 7 lbs. 98% Acid/bbl.	Hydrogenated Product	
			No. 1	No. 2
% 205·5°C. (402°F.) end-point Petrol on feed	71·5	64·2	65·4	65·7
Specific gravity	0·764	0·766	0·754	0·804
A.P.I. gravity	53·5	53·0	56·0	44·5
Sulphur	0·39%	0·15%	0·13%	0·02%
Porcelain dish gum (mgs.)	12	8	3	3
Accelerated gum (mgs.)	51	37	3	4
Octane number (S.30 engine)	65·3	62·2	63·8	78·0

356. The Manufacture of High Flash-Point Anti-Knock Aviation Fuels by Petroleum Oil Hydrogenation.—The Standard Oil Company have announced that by the hydrogenation of low aniline-point stocks of aromatic character, it is possible to produce materials of Initial Boiling Point about 309°F. (154°C.) and Final Boiling Point about 411°F. (210·5°C.) and of very high anti-knock value, which may be used for aviation purposes with much less fire risk than is associated with the high volatility aviation fuels commonly employed. Attempts to use materials of similar boiling range cut from ordinary straight-run or cracked napthas have been unsuccessful because of the very low knock-rating that is obtained. So-called High-Flash Safety

Fuels obtained by hydrogenation have already been produced in the American market and Table 13 shows a comparison of the properties of commercial gasoline and kerosene with those of such safety fuels. As may be expected, this high flash-point material also serves as a good anti-knock blending agent to replace benzole or tetra-ethyl lead.

TABLE 13. COMPARISON OF PROPERTIES OF COMMERCIAL GASOLINE, KEROSENE AND HYDROGENATED SAFETY FUEL

	Average Commercial Gasoline (U.S.A.)	Kerosene U.S.A.	Hydrogenated Safety Fuel
Specific gravity ..	0·71–0·74	0·797	0·884
A.P.I. gravity ..	59·0–68·0	46·0	28·5
Initial Boiling Point ..	90°–105°F. (32·3°–40·6°C.)	380°F. (193·4°C.)	309°F. (154°C.)
Final Boiling Point ..	390°–435°F. (198·9°–224°C.)	550°F. (287·8°C.)	411°F. (210·6°C.)
Flash Point (Abel) ..	—40° to —55°F. (—40° to —48·5°C.)	110°F. (43·4°C.)	107°F. (41·6°C.)
Octane number (engine S.30) ..	65 to 75 at 100°C.	Below 50 at 100°C	93 at 300°F.* (149°C.)
Gum (copper dish) mgs./100 ccs. ..	5–7 mgs.	—	4·8 mgs.
Gum (porcelain dish) ..	2–4 mgs.	—	2·0 mgs.

* Hydrogenated safety fuel has a knock rating in excess of 100 octane number at an engine jacket temperature of 212°F. (100°C.)—S.30 engine.

TABLE 14. PRODUCTION OF HIGH-FLASH SAFETY FUEL

Feed Stock.

Specific gravity	0·90	I.B.P. 348°F. (175·5°C.)
A.P.I. gravity	25·5	F.B.P. 570°F. (298·9°C.)
Sulphur	0·89°C.	
Aniline point	10°F. (—10·2°C.)	

	Hydrogenated Product	
	Light Aviation Fuel	Safety Fuel
Yield on feed %	29·0	55·0
Gravity °A.P.I.	49·5	28·5
Specific gravity	0·783	0·885
Flash point (Abel)	—	107°F. (41·6°C.)
Colour (Saybolt)	30	28
Colour hold (Sunlight 1 hour) ..	no drop	no drop
Doctor test	passes	passes
Corrosion	passes	passes
Octane number at 300°F. (149°C.) (S.30 engine)	83	93
Initial Boiling Point	100°F. (37·8°C.)	309°F. (153·9°C.)
Final Boiling Point	335°F. (168·4°C.)	411°F. (210·6°C.)

In the production of high-flash fuels, the hydrogenated product is distilled into two portions. The bottoms fraction comprises the safety fuel and the overhead product a high quality light aviation fuel. An example of such a procedure has been given by Byrne, Gohr and Haslam[21] and is reproduced in Table 14.

The successful utilisation of such non-volatile fuels necessitates the use of special arrangement for engine starting, etc. Such matters are dealt with in Chapter XVIII (Volume II).

The Hydrogenation of Coal. Work conducted in England by Imperial Chemical Industries Limited

357. Details of the work done by Imperial Chemical Industries on the hydrogenation of bituminous coal have been given in the

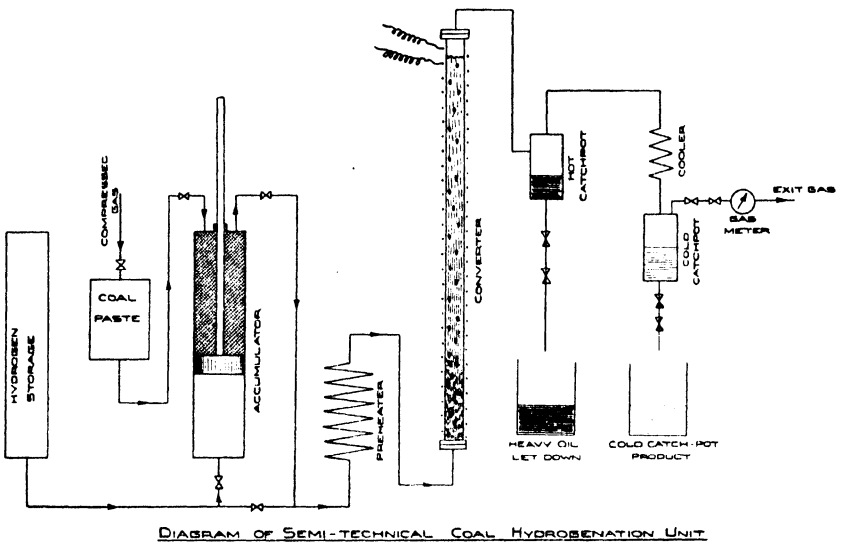


FIG. 7.—DIAGRAM OF SEMI-TECHNICAL COAL HYDROGENATION UNIT
(Reproduced by permission of Imperial Chemical Industries, Ltd.)

literature,[11, 67, 68, 69] and the following account is compiled from such published information. The first experimental equipment installed was of the type used by Bergius, i.e., a small pressure autoclave working on the batch principle and heated externally. In such apparatus the chemistry of the reaction was studied and numerous catalysts tested. The pilot plant built by Bergius used stirred, externally heated, horizontal converters, but the first small scale plants erected by I.C.I. employed no mechanical stirring, this being accomplished by hydrogen, the reactors were arranged vertically, and because of the exothermicity of the reaction the only external heating found necessary was that required to compensate for heat loss. In these small plants various sizes of reaction vessels have been employed, that

now being used being 20 feet high and 4 in. in diameter. A simplified flow diagram of such small plants is reproduced in Fig. 7.

In 1929, it was found that the most promising catalyst for the hydrogenation of bituminous coal was the element tin. This was first employed in the form of tinned iron plates arranged as a grid[70] but this arrangement, though practicable, was rapidly discarded in favour of a continuous injection of a very small amount of certain organic compounds of tin.[58]

Immediately after this discovery it was decided to erect a pilot plant at Billingham to hydrogenate 10 tons per day of bituminous coal. This plant was in operation at the end of 1929 and ran until 1931. The reaction vessel employed was of ingenious design, contrived to use the technique developed[72] for ammonia synthesis, and is shown in Fig. 8.

The coal paste and hydrogen were heated separately, an electric heater in the reactor being used for raising the hydrogen to its final temperature. The reaction vessel itself was arranged so that it did not have to withstand the mechanical stresses due to pressure and was separated from the pressure-resisting walls by a layer of heat-insulating material. The inner vessel thus withstood the temperature and not the pressure, and the outer wall the pressure and not the temperature. This made the use of expensive materials for the reactor forgings unnecessary.

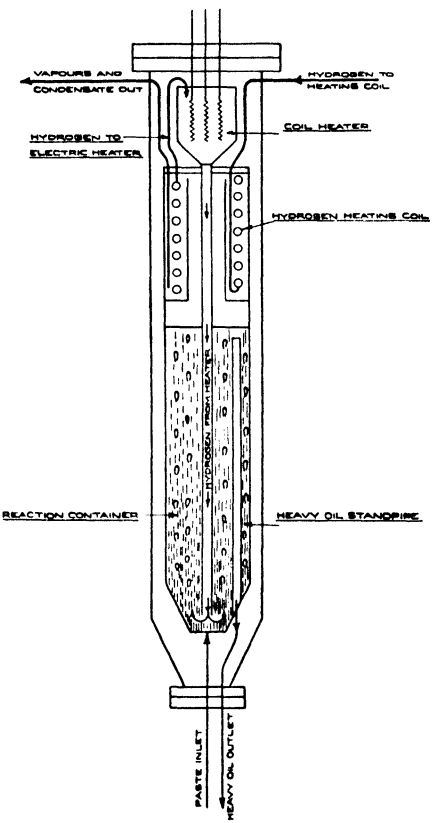


FIG. 8.—EXPERIMENTAL CONVERTER FOR COAL HYDROGENATOION

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The type of plant used by the I.G. for coal hydrogenation is shown in Fig. 9. The reactors (also called "converters") consist of cylindrical vessels with internal heat insulation. The heat exchangers are of the multi-tube type, contained in separate forgings and the appropriate number of converter and heat exchanger units are connected in series. The final heating is done by passing the hydrogen and oil simultaneously through tubes in a gas-fired furnace. This arrangement is similar to that adopted in the large scale I.C.I. plant.

During the period 1931–1933, intensive research conducted by I.C.I. showed that the range of coals which could be successfully hydrogenated was much increased by the use of coal cleaning, combined with the use of hydrogen chloride in the reaction vessel. Coal cleaning is beneficial not only for the obvious reason that it avoids expensive processing of coal ash, but also because the ash is usually alkaline and has a deleterious effect upon catalysis. Hydrogen chloride—added as such or as a compound which forms it under reaction conditions—neutralises the residual ash, and a further quantity has a beneficial effect on the hydrogenation reaction itself.[71] Full benefit of this discovery could not be made until a method was available for neutralising the hydrogen chloride in the vapours leaving the converter

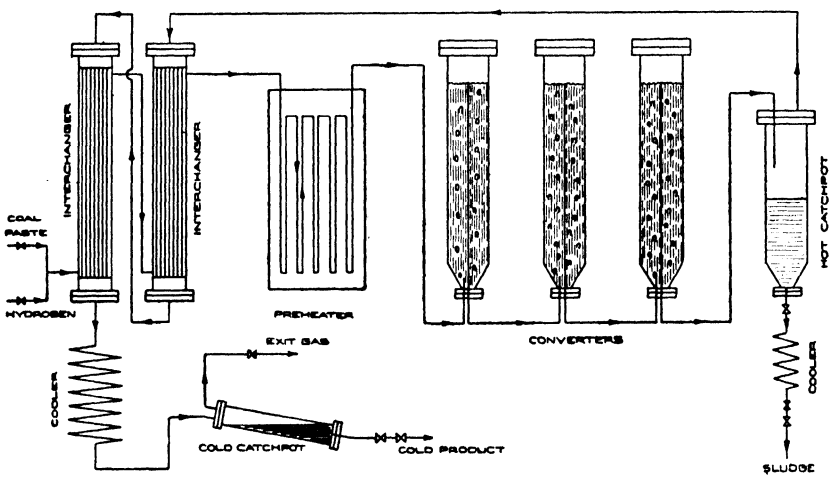


FIG. 9.—DIAGRAM OF FULL-SCALE HYDROGENATION PLANT
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before cooling. Even before hydrogen chloride was deliberately added, trouble was caused by corrosion in the coolers and heat exchangers after the converters, due to the condensation of hydrochloric acid. Further the tubes were liable to become choked through deposits of ammonium chloride and ammonium carbonate.

In 1933, a method was patented for making a stable suspension of alkali in oil, and for freeing the hot vapours at 450°C. from acidic constituents by scrubbing them with it.[72] This permitted the use of relatively high concentrations of hydrogen chloride in the reaction space, since the corrosion at reaction temperature is negligible. These two discoveries, the use of chlorine and tin compounds as catalysts, and the neutralisation of the vapours with alkaline paste, put the hydrogenation of coal on a sound practical basis.

A further change decided upon as a result of research was to divide

the hydrogenation process into three stages.[73] The primary hydrogenation of coal gives gas, petrol, middle oil and heavy oil. It is possible to control the reaction conditions so that there is neither a gain nor loss of heavy oil and the production is exactly enough to make coal into a paste for reintroduction into the converters.

This gives a simple plant arrangement but has the drawback that, in the first stage of the process, coal and heavy oil are being hydrogenated under identical conditions, which cannot be the optimum conditions for both. It was therefore decided to operate the first stage of the process so as to give a quantity of heavy oil in excess of that required for making fresh coal paste and to hydrogenate the excess heavy oil under its own optimum conditions. This results in increased yields.

358. The I.C.I. Commercial Scale Hydrogenation Plant.—The principal supply of hydrogen is obtained from water gas. The gas first made after the blow period in the water gas generators is relatively rich in nitrogen and this, together with a suitable proportion of producer gas, is used for ammonia production; the gas subsequently made on each cycle is directed by special automatic valves to the hydrogen gas system. The water gas plant, serving both the hydrogenation and ammonia plants, has an installed capacity of over 3·5 million cu. ft. of water gas per hour, the whole of which is treated for the removal of hydrogen sulphide by the well-known bog iron ore process. From the sulphur removal plant the water gas passes to the catalytic plant in which carbon monoxide is converted to carbon dioxide in the presence of steam, and thence to compressors having a delivery pressure of 825 lbs. per sq. in. prior to water scrubbing towers for carbon dioxide removal. Removal of last traces of carbon monoxide and carbon dioxide by scrubbing at full operating pressure (3,750 lbs. per sq. in.) with copper-ammonium solution then follows. The compressed hydrogen then enters the suction of the circulating machines on the hydrogenation plant recycle hydrogen system. The recycle hydrogen becomes impure partly through accumulation of nitrogen from the make-up gas, and partly through accumulation of light hydrocarbon gases formed in the process. Part of these gases is removed by solution in the products themselves and is recovered upon release of pressure. The purity of the recycle hydrogen is finally controlled by scrubbing with oil at full pressure. Fortunately, nitrogen is more soluble than hydrogen in oil, and thus is similarly removed from the system.

The clean coal required is produced by the Chance Flotation process, in which the flotation medium is a suspension of sand in water. The raw coal is screened and crushed and all fine particles and dust

removed by air elutriation. The subsequent sand and water flotation process is arranged to operate in two stages. First the coal is separated into refuse of low carbon content and a moderately clean coal of about 7 per cent. ash content. This partly clean coal then passes to the second stage where separation is made into clean coal with not more than 2·5 per cent. ash content and middlings of 15 per cent. ash content. The fines and middlings are used as boiler fuel.

The clean coal passes to the grinding mills via weighing machines which are contrived to deliver coal, pasting oil and catalyst in the required proportion. The coal "paste" contains 50 per cent. coal and is quite fluid and reasonably stable. The injectors for delivering the coal paste against the reaction pressure of 250 atmospheres (3,675 pounds) are hydraulically operated and are supplied with water at 60 pounds pressure. The coal paste then passes to the coal hydrogenation units which are similar in design to the other units used for heavy oil and vapour-phase hydrogenation. The coal paste and hydrogen are mixed together and are heated up to reaction temperature first in heat exchangers, and secondly in gas-fired preheaters. The coal, oil and hydrogen then pass together through the converters in series. On leaving the last converter, the gases and vapours are separated from the residual heavy oil which contains the ash and unconverted coal. The heavy residual oil is let down in pressure separately, part of it is used for making up the coal paste and part treated for recovery of oil and solid coke. The gases and vaporised oils go to the heat exchangers and coolers. The liquid oils are separated under pressure, and the gases go back to the circulators, after washing out any excess hydrocarbon gases in the gas-washing plant.

The converters, heat exchangers and preheaters of all the units are arranged in one line on heavily piled foundations. In each stall (i.e., unit) the converters, heat exchangers and interconnected piping, which are at elevated temperatures, are separated from the rest of the plant by a high brick wall which acts as a safety screen. The general arrangement of each stall is shown in the photograph reproduced in Fig. 10 and follows the line diagram given in Fig. 9.

The heavy oil let down from the hot separators is pumped partly back to the paste preparation plant and partly to the sludge recovery plant, where it is separated into coke, which is used as boiler fuel, and oil which is returned for making up coal paste. The light oil products from the cold separators are released in pressure in three stages. In this way the gas is separated into lean and rich fractions —the latter being treated for gasoline recovery. Butane recovery plant is also installed.

A simplified flow diagram of the whole process is reproduced in Fig. 11.

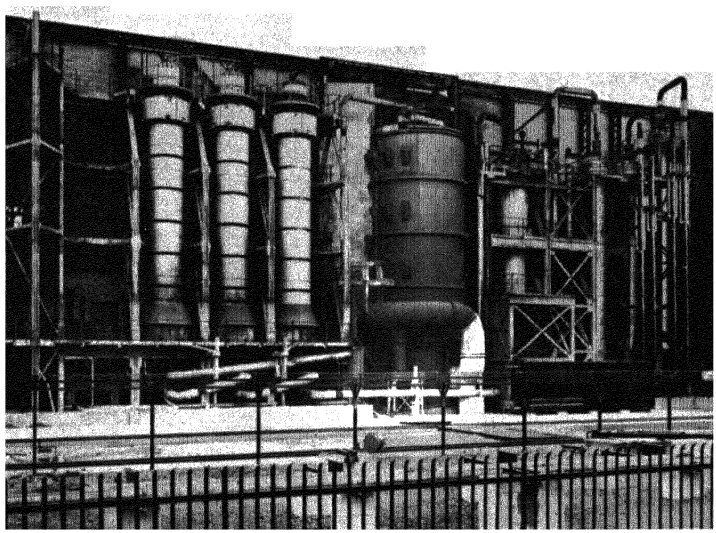


FIG. 10.—GENERAL ARRANGEMENT OF HYDROGENATION STALL—BILLINGHAM PLANT

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[*Facing p.* 358

Valuable information regarding the engineering details of the I.C.I. plant have recently been given by Smith.[74]

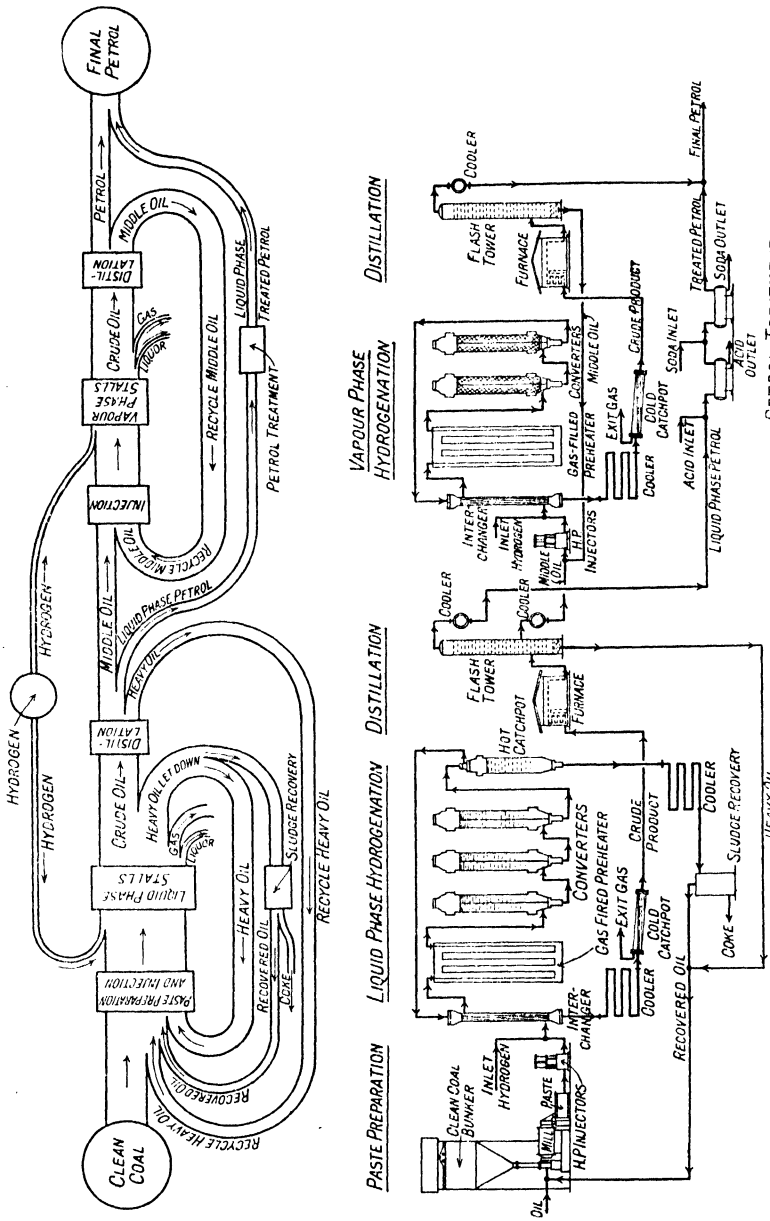


FIG. 11.—FLOW AND LINE DIAGRAMS ILLUSTRATING THE LIQUID PHASE AND VAPOUR PHASE SECTIONS OF THE BILLINGHAM COAL HYDROGENATION PLANT
(*Reproduced by the permission of Imperial Chemical Industries, Ltd.*)

359. Overall Yield of Petrol from Coal.—According to the latest available information,[68] the coal hydrogenation process can be operated in two different ways, either in the manner described in which the first

stage is adjusted to produce only that amount of heavy oil required for paste mixing purposes, or in a manner whereby a relatively larger proportion of heavy oil is produced in the first stage and this hydrogenated in a further stage to petrol. The yields obtained in the first stage of the process by these two methods of operation are given below as A and B, respectively.

	A	B
Petrol plus naphtha boiling up to 200° C.	31·3	14·0
Middle oil	37·3	32·2
Heavy oil	5·0	32·2
Gas	23·6	15·3
Organic insoluble matter ..	3·0	3·0
Aqueous liquor	9·6	9·8
Hydrogen absorbed ..	9·8	6·6

Middle oil produced in the first stage can be converted into petrol in the manner described, with the following yields :—

Petrol	80–93% by weight.
Water	5% by weight.
Gas	7–20% by weight.

The hydrogen absorbed is from 4·5 to 6·0 per cent. by weight, and the water produced is obtained from oxygenated bodies, e.g., phenols, present in the middle oil.

When the first stage of the hydrogenation process is adjusted to give the products (A) above, the overall conversion of coal to petrol is 61–66 per cent. by weight, on the basis of ash and moisture-free coal. Gas formation occurs to the extent of 31 to 26 per cent., the overall yield of liquor and organic insoluble matter amounts to about 14 per cent., and the overall hydrogen consumption is approximately 12 per cent. of the weight of the coal processed.

It has been estimated[69] that, in a new plant, in which the major part of the hydrogen requirements would be made by the methane-steam process, the overall consumption of raw coal would vary from 3·5 to 4 tons per ton of finished petrol, the exact figure depending upon both the ash and moisture content of the coal and its suitability for the process. The thermal efficiency under these conditions is about 40 per cent.

In the Billingham plant as at present operated, the coal consumption is 5 tons per ton of petrol because the hydrogen is made from water gas.

360. Properties of Coal Hydrogenation Products.—The properties of coal hydrogenation gasolines, as marketed in 1935, are reproduced in Table 15.

(1) refers to a gasoline obtained directly from coal which corresponds to current specifications for No. 1 Grade spirit.
(2) is a naphthenic type vapour-phase spirit made up to a typical Ethyl specification with lead.
(3) is a spirit to comply with Air Ministry D.T.D. 230 Specification for 87 octane number fuel and contains an unknown quantity of lead.

TABLE 15. PROPERTIES OF COAL HYDROGENATION PETROLS (I.C.I., LTD.)

	1	2	3
Specific gravity	0·740–0·745	0·734–0·738	0·730
I.B.P.	35°C.	35°C.	35°C.
90% vol. recovered at	158°C.	160°C.	150°C.
F.B.P.	170°C.	170°C.	165°C.
Residue	1·0%	1·0%	1·0%
Loss	1·0%	1·0%	1·0%
% Distillation + loss			
At 70° C.	20%	19%	21%
At 100° C.	40%	40%	50%
At 140° C.	75%	75%	87%
Reid vap. pressure at 100° F.	9 lb. per sq. in.	9 lb. per sq. in.	7 lb. per sq. in.
Octane No. C.F.R. motor method	71–73	80	—
Octane No. C.F.R. aviation method	—	—	87
Colour	+ 25 Saybolt	Red	Blue
Odour	Marketable	Marketable	Marketable
Sulphur, % by weight	0·05	0·01–0·02	0·01–0·02
Doctor test	Negative	Negative	Negative
A.S.T.M. copper strip corrosion test	,,	,,	,,
Gum, pyrex dish without air jet (mgm./100 ml.)	2·0	up to 3·0	up to 3·0

Very light refining treatments are applied to the crude spirits. The whole output receives a caustic soda wash to remove H_2S after which that produced in the vapour-phase units is ready for shipment. The liquid-phase gasolines are refined by conventional acid and soda treatment.

THE FUTURE PROSPECTS OF THE HYDROGENATION PROCESS

361. As applied to petroleum, the hydrogenation process has many definite points in its favour for the production of high grade materials selling at premium prices, such as lubricating oils, high quality burning oils, high-flash aviation fuels and solvents, etc., but as a means of producing gasoline, it would appear only to be of economic importance in the treatment of materials not amenable to cracking and in cases where high yields are required. In the production of high anti-knock material

it may be of importance in the future, but at the moment the protagonists of the process appear to favour low temperature operating conditions which give gasolines of only fair anti-knock properties.

As applied to coal, as a means of producing synthetic motor fuels, the process must necessarily remain for a very long time uneconomic as compared with the relatively simple methods now employed in producing petroleum fuels. Moreover, the process will need tariff protection for a very long period. It is a matter of considerable doubt if satisfactory hydrocarbon motor spirits will be produced in this country at a cost as low as that at which such petroleum spirits are imported from abroad. In 1931, it was stated[11] that for 1 ton of petrol produced, 1·6 tons of coal (ash-free dry basis) must be hydrogenated, and a further 1·55 tons is required for steam and gas production, a total of 3·15 tons, or allowing for ash and moisture, 3·65 actual tons. With coal at £0·625 per ton, this is equivalent to £2·28 per ton of petrol produced or nearly 2d. per gallon ; i.e., the cost of the coal alone required in the production of petrol from coal by hydrogenation is about 50 per cent. of the import price of petrol into this country.

Further disadvantages of the process are that high speed Diesel oils and lubricating oils of satisfactory quality have not yet been produced. The hydrogenation process will not be able to adapt itself well to a large increase in the demand for Diesel oils when Diesel-driven vehicles become more popular.

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CHAPTER VIII

PYROLYSIS AND POLYMERISATION PROCESSES FOR THE PRODUCTION OF GASOLINES FROM NATURAL AND REFINERY GASES

368. Introduction.

The outstanding development in motor fuel technology during the past two or three years is undoubtedly the perfection of pyrolysis and polymerisation processes whereby superior grade gasolines may be produced synthetically from both natural and cracked hydrocarbon gases.

The main processes in commercial operation at the time of writing are those owned and operated by the following groups :—

(*a*) Universal Oil Products Company.
(*b*) Pure Oil Co. and Alco Products Incorporated.
(*c*) Polymerisation Process Corporation and M. W. Kellogg Co.

Universal Oil Products Company operate a catalytic polymerisation process for the conversion of olefine hydrocarbons to gasoline, but have not as yet developed any such process for the treatment of paraffin gases. The Pure Oil Company have developed processes for both the thermal polymerisation of olefines and the non-catalytic pyrolysis of paraffins—the licensing agents for such processes being Alco Products Incorporated. Polymerisation Process Corporation was formed during 1935 to acquire the polymerisation patents held by Phillips Petroleum Co., Standard Oil Co. (Indiana), Standard Oil Co., of New Jersey, the Texas Co., and the M. W. Kellogg Co., and M. W. Kellogg Co. were appointed the licensing agents for the group. This combine has now developed a so-called " Unitary " process for the treatment of either paraffin or olefine gases, which comprises a combination of both thermal polymerisation and pyrolysis in one unit.

In addition to the above activities, various other processes are operated by independent concerns—such as the production of substantially pure benzene by high temperature pyrolysis, and the production of di-isobutylene by the polymerisation of isobutylene in the presence of sulphuric acid. Moreover, numerous kindred processes are in course of active development, and among these may be mentioned dehydrogenation of gaseous paraffins as a source of olefines,

alkylation of paraffins and aromatics, and isomerisation reactions of various kinds, all of which have, as the ultimate object, the production of high octane number gasolines.

369. Thermal Reactions of the Gaseous Hydrocarbons.—As a preliminary to the consideration of the various processes now in operation or in an advanced stage of development it is necessary to consider the chemistry of the reactions involved. Such a discussion however is outside the scope of this book and reference should be made to the following excellent publications :—

(1) *The Chemistry of Petroleum Derivatives.* C. Ellis. Chemical Catalogue Co.
(2) *Aliphatic Free Radicals.* F. O. Rice and K. K. Rice. J. Hopkins Press, Baltimore, Maryland, 1935.
(3) *Decomposition and Polymerisation of the Olefinic Hydrocarbons.* G. Egloff, R. E. Schaad and C. D. Lowry. J. Phys. Chem., 1931, **35**, 1825–1903.
(4) *The Decomposition of the Paraffin Hydrocarbons.* G. Egloff, R. E. Schaad and C. D. Lowry. J. Phys. Chem., 1930, **34**, 1617–1740.
(5) *Thermal Reactions of Cycloparaffins and Cycloolefines.* G. Egloff, B. L. Levinson and H. T. Bollman. J. Phys. Chem., 1931, **35**, 3489–52.
(6) *Polymerisation and Decomposition of Acetylene Hydrocarbons.* G. Egloff, C. D. Lowry and R. E. Schaad. J. Phys. Chem., 1932, **36**, 1457–1520.
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(8) *Catalytic Reactions at High Temperatures and Pressures.* V. N. Ipatieff. McMillan Co., 1936.

Briefly the reactions involved may be summarised as follows :—

(*a*) At very high temperatures, e.g., above 1,000°C. (1,832°F.) all the gaseous hydrocarbons decompose completely to carbon and hydrogen, if the heating period is sufficiently long. This is the so-called " methane-equilibrium,"

$$CH_4 \rightleftarrows C + 2H_2$$

and is the ultimate stage in the decomposition of all hydrocarbons and if products other than carbon and hydrogen are required, then the heating time and /or the temperature must be so adjusted that the primary or secondary products of decomposition are withdrawn from the reaction zone before the final decomposition reactions set in.

(*b*) Methane is the most stable of the gaseous hydrocarbons and the pyrolysis processes now in commercial operation do not employ reaction conditions severe enough to convert any appreciable quantity of methane into liquid products. Doubtless the experience now being gained will allow methane to be satisfactorily utilised at a later date.

(*c*) Methane is an important product of the thermal decomposition of the higher gaseous hydrocarbons, particularly under conditions of long contact time and /or high temperatures.

(*d*) Methane is the only thermodynamically stable hydrocarbon

at a temperature of 450°C. (842°F.) The stability in both the paraffin series and the olefine series falls, as a general rule, with increase in molecular weight. That is, butanes are more easily decomposed than ethane, while butylenes are more reactive than ethylene.

(*e*) In the thermal treatment of gaseous paraffin hydrocarbons at temperatures above 450–500°C. (842–932°F.) the first reaction products observed in the absence of catalysts are paraffins and olefines of lower molecular weight. In addition the products of simple dehydrogenation are also obtained in small yields. For instance, in the case of propane the following reactions occur

$$(1)\ CH_3 — CH_2 — CH_3 \rightarrow CH_3 — CH_2 = CH_2 + H_2$$
$$(2)\ CH_3 — CH_2 — CH_3 \rightarrow CH_2 = CH_2 + CH_4$$

while in the case of *n*-butane the reaction products are hydrogen, methane, ethane, propane, ethylene, propylene and butylene—formed by similar reactions.

(*f*) Under temperature and/or reaction time conditions more severe than those giving the optimum yield of gaseous olefines, the gaseous paraffins give valuable yields (up to 40% by weight—depending upon the precise conditions) of liquid products. These are formed from olefines resulting from primary and secondary reactions by further condensation processes, and are essentially aromatic in nature when the conditions are sufficiently severe. Under less severe conditions these liquid products are essentially olefinic in character.

(*g*) The gaseous olefines undergo polymerisation reactions at temperatures up to about 500°C. (932°F.)—these reactions being greatly facilitated by an increase in pressure.

$$\text{e.g.,}\quad C_4H_8 \rightarrow (C_4H_8)_2 \rightarrow (C_4H_8)_3,\ \text{etc.}$$

In the absence of suitable catalysts however, the polymerisation reaction is accompanied by others bringing about both rearrangement and decomposition, with the result that the liquid products obtained are not entirely olefinic in character—but also contain paraffins, naphthenes and aromatic hydrocarbons.

$$\text{e.g.,}\quad (C_2H_4) \rightarrow \underset{\text{Olefine}}{(C_2H_4)_x} \rightarrow \underset{\text{Napthene}}{(C_2H_4)_x} \rightarrow \underset{\text{Aromatic}}{(CH_2)_x} + \underset{\text{Hydrogen}}{{}_xH_2}$$

Paraffins may be formed by destructive alkylation reactions following the above.

(*h*) In the presence of suitable catalysts the gaseous olefines may be polymerised at temperatures sufficiently low that secondary isomerisation and other reactions do not occur to any marked extent, and the products then obtained are almost completely olefinic in character.

370. Preparation of Feed Stocks for Pyrolysis and Polymerisation Processes.—Feed stocks consisting of the lower, normally gaseous

hydrocarbons may be available in either the liquid or gaseous state. In general two types of liquid feed are common :

(*a*) Natural gas butanes and propanes resulting from the stabilisation of light gasolines,

(*b*) Heavy cracked gas fractions obtained in cracked gasoline stabilisation,

while gaseous feeds comprise both natural and cracked gases of various composition.

The feed to any pyrolysis process or combination process for the treatment of saturated materials is preferably concentrated in propane and butane before treatment. This concentration in the more reactive constituents may be accomplished in conventional stabilising equipment if the feed is available in the liquid state, but compression followed by condensation and /or oil absorption is necessary if a gaseous feed is handled.

A typical concentration scheme for a lean natural gas is given in Table 1.[1]

Cracked gas feeds to polymerisation plants should preferably be as rich as possible in C_3 and C_4 olefines, and as lean as possible in paraffins, hydrogen and ethylene.

371. The Separation of Gaseous Olefines from Mixtures with Paraffins and Hydrogen.—It is often desirable to segregate or concentrate olefines produced in pyrolysis processes, although usually the olefine-paraffin mixture is passed to polymerisation or other treatment without intermediate purification.

The methods of separation available are as follows :—

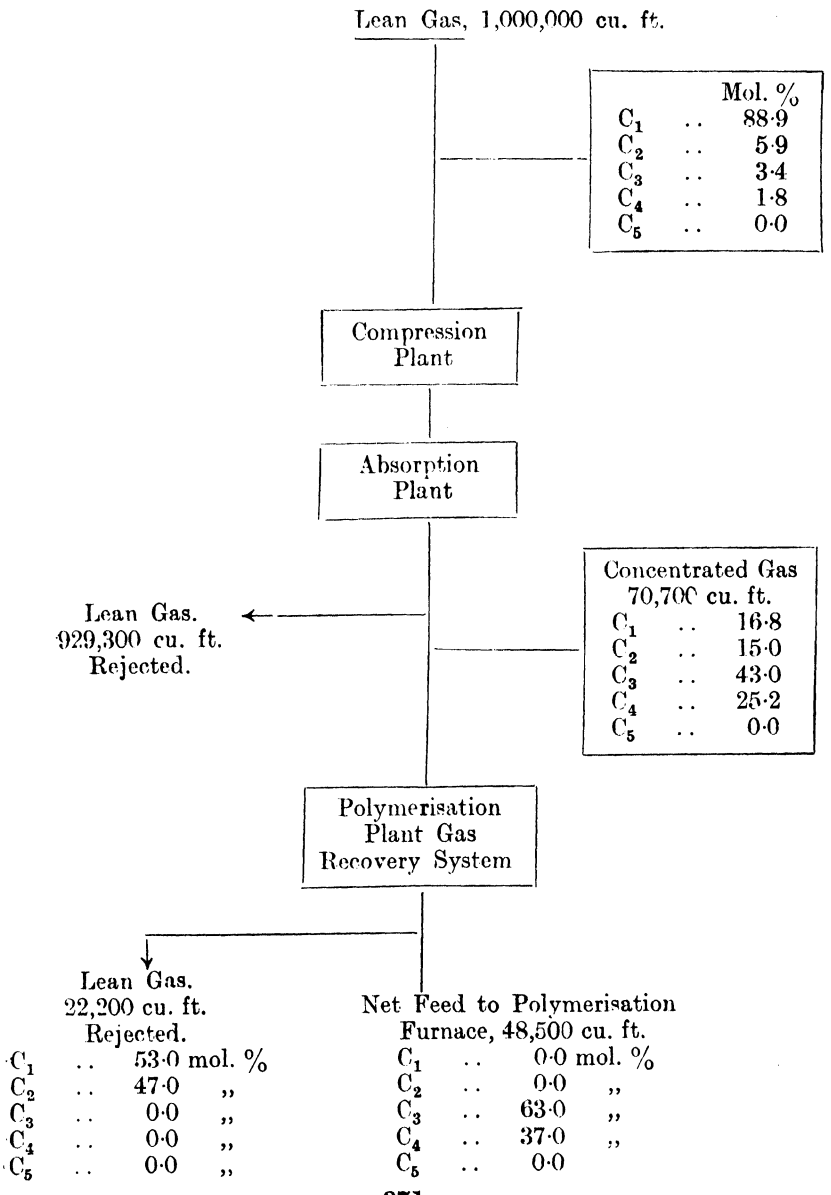
(*a*) Fractional distillation and partial liquefaction,
(*b*) Physical absorption with selective solvents,
(*c*) Chemical processes,
(*d*) Adsorption,

the applicability of which depends upon the gas mixture to be handled and the degree of separation required.

372. (a) Fractional Distillation, etc.—This can only be employed to separate constituents having boiling points not closely similar. Usually it can be relied upon to yield fairly good separation between fractions containing different numbers of carbon atoms per molecule, i.e., a mixture of propylene and propane can be separated from a mixture of butanes and butylenes, but it is not usually feasible to separate olefines from the corresponding paraffins by this method. Much can be done, however, to concentrate olefines by the refractiona-

tion of selected cuts. Thus Carney[2] has reported it possible, for example, to separate 90% butylene (a mixture of *n*- and iso-butylene) by fractionation of a C_4 fraction, or to vary the content of the more reactive butylene, iso-butylene, from 5% to more than 80% in a fraction containing only C_4 hydrocarbons.

TABLE 1. LEAN GAS CONCENTRATION SCHEME[1]



The process of Linde-Bronn, which has been applied in Germany and Belgium to the separation of the constituents of coke oven gas, is of interest as illustrating the potentialities of fractionation at low temperatures.[3] Coke oven gas is cooled under pressure to separate first the easily liquefiable impurities, and also an ethylene-methane condensate. In this liquefaction step the coke oven gas is cooled in a bath of liquid air or liquid nitrogen. Fractionation of the ethylene-methane condensate yields practically pure ethylene. Complete separation of methane and of carbon monoxide from the accompanying hydrogen can be accomplished by cooling the coke oven gas, after removal of the ethylene-methane mixture, to a temperature of about — 209°C. under 10 atmospheres pressure. This low temperature is secured with liquid nitrogen maintained under reduced pressure.

Although most fractionations are carried out at constant pressure and at varying temperatures—a process of "iso-thermal vaporisation"—i.e., fractionation at a constant temperature and gradually diminishing pressure has been used for effecting a partial separation of the constituents of a liquefied cracked gas.[4] Methods involving fractional condensation have also been employed.[5]

A recent development is fractionation in the presence of a third substance which forms azeotropes. Sulphur dioxide has been proposed for this purpose. By adding sulphur dioxide to a mixture of C_4 hydrocarbons in an amount equivalent to the azeotropes of the butanes present, and then subjecting the mixture to fractional distillation, the butenes can be separated from the butanes.[6]

373. (b) Absorption with Selective Solvents.—A partial separation of the various lower olefines from one another, and from the corresponding paraffins, can be effected by taking advantage of their different solubilities in various liquid solvents. The dissolved gases can be liberated from solution by heating. Generally, the solubility of the olefines in neutral solvents increases with increasing molecular weight and, possibly on account of their greater reactivity, they are sometimes more soluble than the corresponding paraffins.

The following types of solvents have been suggested:

(1) Certain organic solvents such as mineral oil fractions in which the higher olefines are preferentially soluble, but which also tend to absorb relatively large proportions of the paraffins.

(2) Certain solvents which dissolve the gaseous olefines by forming loosely bound addition compounds, but which do not dissolve saturated hydrocarbons.

In scrubbing with solvents such as mineral oil fractions, the use of elevated pressures is desirable, since the solubilities of the gas constituents are approximately proportional to their partial pressures. This

method is only suitable for giving rough separations, but is used to a considerable extent. Some figures for the solubility of the lighter hydrocarbons in various hydrocarbons and oils are given in Table 2.

TABLE 2. SOLUBILITY OF GASEOUS HYDROCARBONS AND HYDROGEN IN VARIOUS LIQUID HYDROCARBONS AT 20° C.

(Volumes dissolved at N.T.P. in 1 volume of solvent per atmosphere partial pressure = Bunsen absorption coefficient)

Solvent	H_2	CH_4	C_2H_6	C_2H_4
Hexane	—	0·57	3·15	2·91
Heptane	—	0·69	4·25	3·15
Gasoline (sp. gr. 0·771)	0·086	—	—	—
Kerosene (sp. gr. 0·839)	0·052	—	3·55	2·20
Benzene	0·066	0·47	—	2·95
Toluene	0·077	0·46	—	—
Xylene	0·073	0·49	—	—

As an example of what may be accomplished by scrubbing a cracked gas with kerosene, the following figures by Horsley[7] may be mentioned. Such a gas was washed at 22°C. in counter-current with 60 litres per hour of kerosene (B.P.200–300°C.) in an unpacked tower 2-in. diameter and 12 feet high, having an effective washing surface of 6·3 sq. ft. The gas was compressed before scrubbing to a pressure of 21 atmospheres, and the gases dissolved in the kerosene were substantially regenerated by reduction of pressure, firstly to 7 atmospheres and subsequently to atmospheric pressure. The two gas fractions evolved were collected separately. Under these conditions the following gases were obtained, volumes referring to normal temperature and pressure :—

TABLE 3

	Ethylene	Propylene & Higher Olefines	Methane	Ethane & Higher Saturated Hydrocarbons	Hydrogen & Inert Gases
Initial gas.					
9000 litres./hr.	26·5%	17·1%	29·9%	20·8%	5·7%
Residual gas.					
5820 litres./hr.	28·2%	2·4%	42·8%	18·1%	8·5%
1st stage let-down gas.					
1000 litres./hr.	36·4%	23·6%	16·4%	22·4%	1·2%
2nd stage let-down gas.					
2180 litres./hr.	17·6%	53·2%	1·7%	27·2%	0·3%

It is evident that the gas dissolved in the kerosene and evolved on reducing the pressure on the solvent to 7 atmospheres contains a much higher concentration of ethylene than initially. Similarly, it contains less methane and hydrogen. The second stage let-down gas is a concentrated source of propylene.

Acetone has been suggested as a solvent for ethylene[8] and also 95% ethyl alcohol.[9] For the separation of butylene from butane, ammonia has been proposed.[10]

The removal of acetylene from gaseous mixtures by scrubbing with esters or ethers of high boiling point has also been suggested. Suitable solvents are said to be glycol mono-formate, glycol mono- and di-alkyl ethers, esters of the mono-alkyl ethers of ethylene glycol,[11] and also poly-glycols, their ethers, esters and mixed ester-ethers.[12]

374. (c) **Chemical Processes.**—Perhaps the most obvious method for the separation of olefines from gaseous mixtures is absorption in a reagent capable of combining more readily with the olefines than with the other hydrocarbons present. Such methods include direct hydration to the corresponding alcohols, esterification with sulphuric acid or with the hydrogen halides and also selective polymerisation. These reactions, described in considerable detail by Ellis,[13] suffer from the great disadvantages that the absorbed olefines are not recoverable and therefore they need not be considered here.

Aqueous solutions of silver, cuprous and mercury salts are known to dissolve the gaseous olefines readily, probably by forming complex compounds. The olefines can be recovered from these solutions by warming with or without reduction of pressure. Thus, Horsley[14] has proposed the use of an acid solution of silver nitrate for the removal of ethylene from coal gas, and the use of solutions of mercury salts for the separation of olefines has also been suggested.[15] Cuprous salts are much more popular, e.g., ammoniacal cuprous formate, acetate or carbonate.[16]

A typical liquor composition is as follows :—[7]

Ammonia	.. .. ..	7·5 gram moles per litre.
Copper	.. .. ..	1·75 gram atoms per litre.
Formate	.. .. ..	1·5 gram moles per litre.
Carbonate	.. .. ..	1·8 gram moles per litre.

This is preferably used at high pressures, e.g., 250 atmospheres.

Recently the following figures have been given to show that the solubility of ethylene is greater in ammoniacal solutions of cuprous nitrate, salicylate, phenolate and cresolate.[17]

	Solubility of Ethylene Volumes per volume
Amm. cuprous formate	5·43 at 24·0°C.
,, ,, acetate	4·27 at 24·0°C.
,, ,, carbonate	3·33 at 23·5°C.
,, ,, nitrate	9·1 at 24·2°C.
,, ,, salicylate	14·1 at 19·0°C.
,, ,, cresolate	8·5 at 20·5°C.
,, ,, phenolate	9·5 at 21·5°C.

Solutions of cuprous salts in aqueous hydroxy-alkylamines have also been proposed as selective solvents for the removal of olefines from gas mixtures, from which the olefines may subsequently be recovered by heating or by reducing the pressure. A satisfactory solution of such a composition may be prepared by dissolving 100 grams of cuprous chloride in a mixture of 300 grams of water, 75 ccs. of hydrochloric acid (d = 1·16), and 200 grams of mono-ethanolamine.[18]

The following are solubilities of the lower olefines and hydrogen in this solution—expressed in litres at N.T.P. per kilogram of solvent.

Absolute Pressure Atmospheres	1	5	10	20
Ethylene	8·4	15·8	21·2	24·2
Propylene	1·1	4·3	6·1	—
Butylene	1·0	—	—	—
1-3 Butadiene	11·0	—	—	—
Hydrogen	—	—	0·08	0·17

The removal of diolefines from mixtures containing also mono-olefines by contacting the mixture in the liquid phase with finely divided cuprous chloride dispersed in an aqueous solution has also been patented.[19]

375. (d) Adsorption.—Olefines can be preferentially adsorbed from gaseous mixtures on active carbon, silica gel, Fuller's earth, or other highly adsorptive materials, and subsequently recovered by heating the adsorbent, with or without the use of superheated steam. The olefines appear to be much more readily adsorbed than the corresponding paraffins, and methane and hydrogen are adsorbed to only a small extent. Olefines of higher molecular weight are more easily adsorbed than ethylene, and hence this method allows ethylene to be separated from its homologues.[20] The adsorption may be carried out under pressure.[21]

376. The Gaseous Paraffins as a Source of Olefines.—Owing to the ease with which the lower olefines enter into polymerisation reactions to give valuable anti-knock gasolines and also because of the valuable nature of the olefines as raw materials in organic chemical synthesis, many attempts have been made to produce them from the gaseous paraffins.

Two methods are available for converting the lower paraffins into olefines.

(1) Thermal non-catalytic decomposition, and

(2) Catalytic dehydrogenation.

Theoretically it is feasible to obtain high yields of olefines from the corresponding paraffins by heat treatment—the reaction involved being a simple dehydrogenation.

$$C_nH_{2n+2} \rightleftharpoons C_n\,H_{2n} + H_2$$

Methane is not amenable to such dehydrogenation because the production of ethylene from it involves a synthesis process in which two carbon atoms must become linked together.

Unfortunately heat treatment alone does not have the desired results because, as already shown, the gaseous paraffins decompose in a variety of ways, each C-C linkage being broken in addition to the elimination of hydrogen from a terminal alkyl radical. Consequently the thermal treatment of a gaseous paraffin results in the formation of both paraffins and olefines containing fewer carbon atoms per molecule than the parent substance, and the yields of olefines are, as a result, low. As far as can be ascertained the highest yield of olefines yet obtained by the thermal treatment of either propane or butanes is about 60% by weight, the production of lower paraffins and hydrogen being about 40% by weight.

377. Methane.—Most of the work reported on the thermal decomposition of methane is concerned with either the decomposition into carbon and hydrogen or with the production of aromatic liquids, and no work has apparently been carried out to determine the optimum yield of gaseous olefines obtainable. The production of acetylene from methane is dealt with later.

Whenever liquid hydrocarbons are produced from methane by thermal treatment, the exit gas is found to contain small amounts of ethylene and/or higher olefines in addition to varying quantities of acetylene. For example, Hague and Wheeler,[22] in experiments at 900–1,050°C. obtained an exit gas, after condensation of higher hydrocarbons, containing 0·3–0·9% of higher olefines and 2·1–3·7% of ethylene. Similarly, Stanley and Nash,[23] in experiments on highly purified methane at 1,000°C., obtained an exit gas containing up to 1·1% ethylene

and 0·8% acetylene. In these tests the space velocity was varied from about 24 to 143 volumes of inlet methane per volume of reaction space per hour.

Cambron[24] has described detailed tests on a natural gas fraction of the following analysis :—

Methane	89·7%	volume
Ethane	4·8	,,
Propane	3·4	,,
Butanes	1·5	,,
Pentanes + ...	0·6	,,

These tests were made in quartz and porcelain tubes containing a centrally-disposed electrically-heated carbon rod. Temperatures ranging from 990–1,200°C. were employed, and the effects of temperature and contact time variables were investigated.

Cambron found that yields of ethylene and acetylene equivalent to 13·5% and 3·0% respectively, could be obtained from the above natural gas fraction at 1,020°C., using a suitably short contact time. Under more severe conditions the yield of ethylene decreased while that of acetylene increased.

It is evident from these results that the production of ethylene and higher olefines from methane by thermal treatment is not a commercial feasibility. As far as is known, the use of catalysts has not yet given any greater yields than those mentioned above. As a source of olefines, therefore, methane may, at the present time, be disregarded.

378. Ethane.—Ethane is a very convenient source of ethylene. As already mentioned, the main reaction involved in thermal treatment even at temperatures considerably higher than the initial decomposition temperature, is dehydrogenation, although other reactions take place to minor extents. In the following correlation of the published work on the production of ethylene from ethane by non-catalytic thermal treatment, experiments made by heating ethane statically in a closed system have been ignored because, while they have given valuable information on the reaction mechanisms involved, they are far removed from industrial practice, and give no indication of what may be realised in commercial operation.

Among the earliest work on the thermal decomposition of ethane to ethylene that is of any value is that of Hague and Wheeler,[22] whose results are reproduced in Table 4. These investigators used silica and porcelain tubes, 2·2 cms. diameter and 70 cms. long. The heated length of the tube was 42·5 cms., but the volume of the constant temperature zone is unknown. The total heated reaction volume is thus 162 c.cs., and the constant temperature volume must have been at

least half this, i.e., 81 c.cs. These figures ignore the volume of an internal thermo-couple pocket which was used. A constant inlet gas rate of 4 litres per hour (measured at N.T.P.) was used in all the tests reported, and therefore the space velocity (volumes of inlet gas per volume of reaction space per hour) was $\frac{4{,}000}{81} = 49{\cdot}4$, based on the assumed constant temperature zone volume. Under these conditions, Hague and Wheeler obtained the optimum conversion of ethane to ethylene (as shown in Table 4) at 750° C., when the olefine content of the exit gas was 33·3%, and the increase in gas volume due to reaction was 63%. Assuming the olefines formed to consist entirely of ethylene, these figures correspond to an ethylene yield of $33{\cdot}3 \times \frac{163}{100}$ = 54·2% by volume or 50·5% by weight. Under these conditions the reaction time was about 20 seconds.

TABLE 4. PRODUCTION OF ETHYLENE BY THE PYROLYSIS OF ETHANE (Sullivan, Ruthruff and Kuentzel)[25]

Run No.	Mean Reaction Temp. °C.	Mean Reaction Temp. °F.	Inlet Gas, Litres per minute	Reaction Time seconds	Space Velocity	Exit Gas: Litres/minute	Exit Gas: % Unsaturateds	Exit Gas: Mol. wht.	Volume Increase %	Conversion to Ethylene: Volume %	Conversion to Ethylene: Weight %
55	780	1436	3·98	0·80	950	5·59	28·1	20·9	40·5	39·5	36·9
50	782	1440	3·83	0·85	914	5·60	29·6	21·0	46·2	43·3	40·4
58	780	1436	2·22	1·38	529	3·35	31·9	20·0	50·7	48·1	44·9
54	777	1430	2·12	1·47	504	3·11	31·5	19·8	46·8	46·2	43·1
53	785	1445	2·13	1·48	484	3·18	34·2	19·5	49·0	51·1	47·6
51	780	1436	1·82	1·69	434	2·88	32·6	19·0	58·0	51·5	48·1
56	772	1421	1·28	2·5	305	1·83	30·2	19·3	42·5	43·0	40·3
52	785	1445	1·14	2·6	272	1·94	28·2	17·5	70·0	47·8	44·6
57	773	1423	1·17	2·6	279	1·81	31·2	19·4	55·0	48·3	45·1
42	812	1494	6·06	0·50	1440	9·60	33·2	20·0	58·0	52·6	49·1
40	817	1502	4·94	0·54	1175	8·15	34·1	19·8	65·0	56·2	52·4
59	812	1494	4·55	0·65	1080	7·06	33·6	19·5	55·0	52·1	48·6
43	810	1490	4·04	0·73	961	6·66	35·5	—	64·6	58·5	54·6
49	813	1496	3·78	0·76	900	6·44	34·9	18·8	70·5	59·5	55·6
39	816	1500	3·32	0·85	790	5·54	35·6	—	66·5	59·3	55·3
44	813	1496	1·94	1·42	461	3·51	37·5	17·5	80·5	67·7	63·0
45	843	1550	5·89	0·47	1400	10·42	39·2	18·3	77·0	69·4	64·9
47	844	1552	4·00	0·65	953	7·60	39·0	16·6	90·0	74·1	69·1
46	832	1530	4·06	0·66	967	7·45	38·8	17·7	83·0	71·3	66·6
48	853	1571	1·99	1·27	474	3·89	32·2	15·4	96·0	63·1	59·0

Other workers have employed reaction time and space velocity conditions more in accord with industrial operations, in which high gas linear velocity is essential in order to obtain good heat transfer rates. Thus, Sullivan, Ruthruff and Kuentzel[25] have studied the pyrolysis of ethane for olefine production in a helical coil of KA2S tubing (18/8 Cr-Ni steel) of 14 feet total length and 5/16-in. I.D. Reaction times of 0·5 to 2·6 seconds, and space velocities of 270–1,440 were employed. The detailed results of these investigators are reproduced in Table 4, and the effects of the more important variables are shown in Figs. 1, 2 and 3.

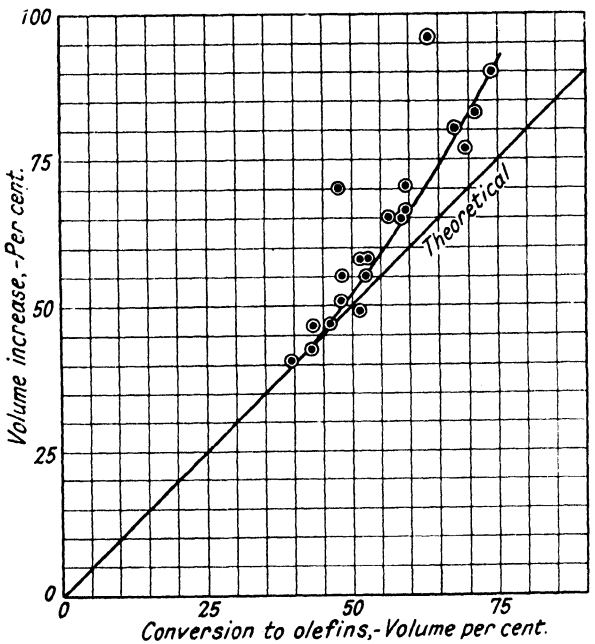


FIG. 1

In Fig. 1 the volume per cent. conversion of ethane to ethylene is plotted against the per cent. volume increase. In the absence of any secondary reactions, the volume increase should be numerically equal to the volume yield of olefines, and as Fig. 1 shows, the deviation of experimental points from the theoretical curve is quite small but increases with increasing conversion. This figure also demonstrates that temperature, per cent. conversion and reaction time *per se* have little influence on the course of the reaction. The curve in Fig. 1 represents all the data obtained in the temperature range 1,400–1,550°F. (782–843°C.), and at reaction times varying from 0·5 to 2·6 seconds.

In Fig. 2 the olefine content of the exit gas is plotted against reaction

time, and it is apparent that the greatest olefine concentration is obtained by operating at high temperatures and short reaction times.

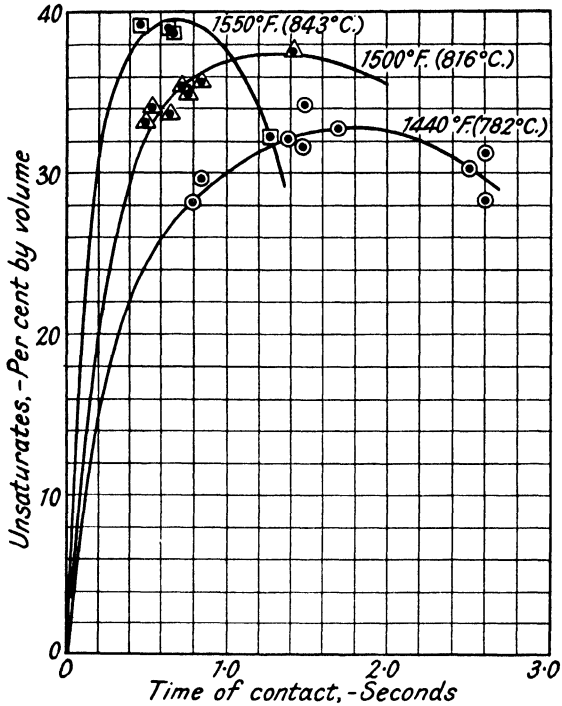


FIG. 2

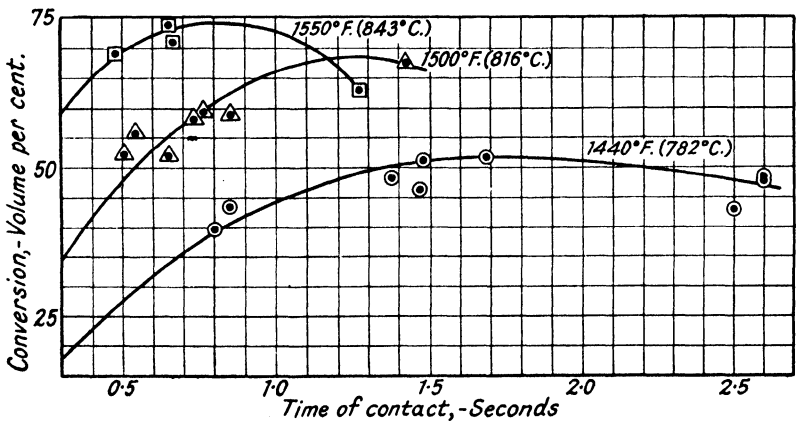


FIG. 3

Volume per cent. yield of olefines is plotted against reaction time in Fig. 3. Under optimum conditions 74 per cent. of the ethane treated was converted into olefines in one pass. These figures demonstrate

that olefine yield and olefine content of the cracked gas increase at any given temperature with increasing reaction time until optimum conditions are reached, after which a further increase in reaction time results in decreased olefine yield and lower olefine concentration in the cracked gas. This decrease is due to the destruction of ethylene through secondary reactions giving carbon, hydrogen and methane and also aromatic liquids.

Further important work on the production of ethylene from ethane by pyrolysis has been carried out by Cambron and his co-workers,[26, 27] using reaction tubes internally heated by glowing carbon rods. No details are, however, available for the calculation of reaction times and space velocities obtained in these experiments. Results obtained by Tropsch and Egloff[28] on the pyrolysis of ethane and other gases at 1,100–1,400° C. are considered later.

A possible method of obtaining greater yields of ethylene from ethane than those mentioned above is to operate at a sufficiently low temperature to obtain a low conversion of ethylene per pass, and to remove the ethylene before recycling the residual ethane. In this way the production of methane and hydrogen would be considerably decreased.

The data of Sullivan, Ruthruff and Kuentzel give the following rates of ethylene production under the optimum conversion conditions :—

	780°C.	813°C.	844°C.
Cu. ft. ethylene per cu. ft. reaction space per hour ..	223	535	704
Lbs. ethylene per cu. ft. reaction space per hour ..	16·5	39·6	52·1
Grams ethylene per litre reaction space per hour ..	264	633	833

379. Propane.—As already mentioned, it is not feasible to convert propane exclusively into propylene and hydrogen to an extent sufficiently attractive for large scale operation by thermal non-catalytic decomposition, because lower paraffins and olefines are both formed. The work of Hague and Wheeler[22] shows this very clearly. For example, at 700°C. propane gave an exit gas containing 14·2% higher olefines and 23·1% ethylene plus acetylene. At 850°C. the higher olefine content of the exit gas was only 2·3%, while that of ethylene was 14·5% Under these conditions the volume % yield of higher olefines (presumably propylene) was 21·7% and 4·8%, respectively, at these two temperatures. In order to obtain high yields of propylene without the concurrent formation of ethylene, methane and ethane, resource must be made to catalytic dehydrogenation (see later).

Similar results have been described by Frolich and Wiezevich.[29]

These are given in Fig. 4. Using a quartz reaction tube, a contact time of 0·4 seconds and a space velocity of *circa* 7,500, the maximum concentration of propylene in the exit gas was 13·2%, and this occurred at a lower temperature (810°C.), than the maximum concentration of ethylene (29·4%), which occurred at 890°C. The ratio of ethylene to propylene in the cracked gas was roughly 2 to 1, increasing slightly with temperature, because presumably, the propylene initially formed enters more readily into secondary reaction than does the ethylene. However, if the cracking of propane is carried nearly to completion, the sum of ethylene and propylene in the exit gas is close to 40 per cent. over a wide temperature range. Since the volume of gas is practically doubled by the cracking process, this means that the yield of ethylene plus propylene is of the order of 80% (by volume) on the basis of entering propane. This is equivalent to 56% by weight.

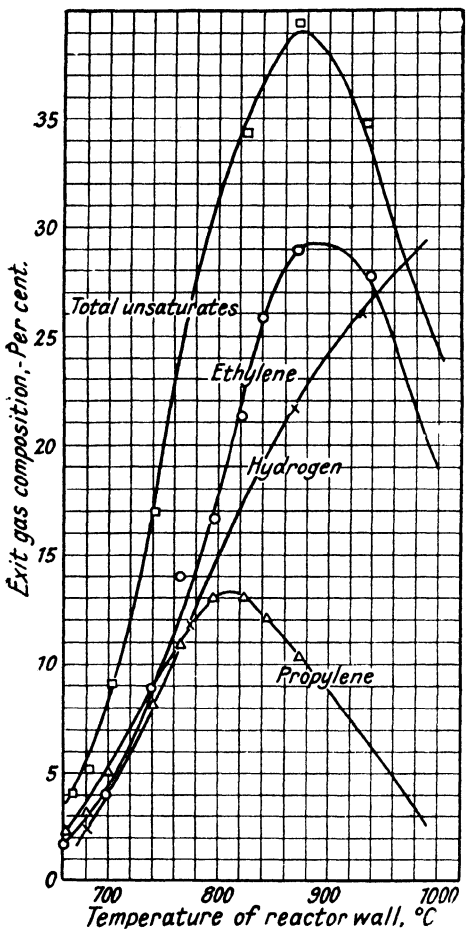


FIG. 4

Tests made by Ebrey and Engelder[30] at a constant space velocity of 98 volumes of inlet gas per volume of reaction space per hour, gave an ethylene + propylene concentration in the exit gas of 33·7% by volume, at a temperature of 760°C. The maximum propylene concentration in the exit gas was 10·7% by volume—obtained at 660°C. At 760°C. the yield of ethylene + propylene was 42·5% by weight of the propane treated. This low yield may be attributed to the low space-velocity employed.

One of the most complete published accounts of the pyrolysis of propane for the production of olefines is that by Sullivan, Ruthruff and Kuentzel.[25] Qualitatively, the results obtained are similar in all respects to those obtained by the same workers on ethane (see above).

A plot of volume per cent. conversion of propane to olefines against per cent. volume increase is satisfied by one curve, regardless of the time and temperature conditions employed to obtain the individual points. The deviation of this curve from the theoretical is small but increases rapidly as conversion increases. This is reproduced in Fig. 5. As shown in Figs. 6 and 7, the volume olefine yield and the olefine content of the cracked gas are both at a maximum when operating at high temperatures and short contact times. On increasing the time of contact beyond that necessary for optimum results, the olefine content of the cracked gas and the olefine yield both decrease because of destruction of the olefines through secondary reactions. The highest weight per cent. conversion of propane to olefines obtained was 55%. The detailed results of Sullivan, Ruthruff and Kuentzel on the pyrolysis of propane are reproduced in Table 5.

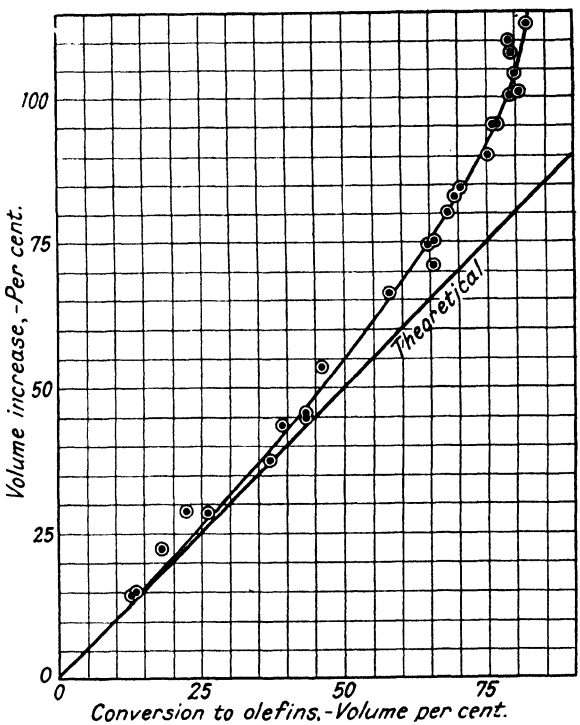


FIG. 5

Further work of value on the production of olefines by the pyrolysis of propane is that by Cambron and Bayley. These workers found that when pyrolysis is carried out under conditions of turbulent flow, the yields of olefines obtained at a given temperature are greatly increased over those obtained under conditions of streamline flow. They also found that under conditions of turbulent flow higher rates of conversion to olefines are possible since the temperatures at which side reactions begin to be noticeable are considerably higher under these conditions. Cambron and Bayley obtained turbulent flow conditions by inserting suitable baffles in their reaction tubes.[31] Space velocities up to 4,000 and temperatures of 800–1,087°C. were employed. Under these conditions the optimum results obtained were as summarised below (Table 6).

The production of olefines by the thermal pyrolysis of propane at super-atmospheric pressure has been studied by Tropsch, Thomas

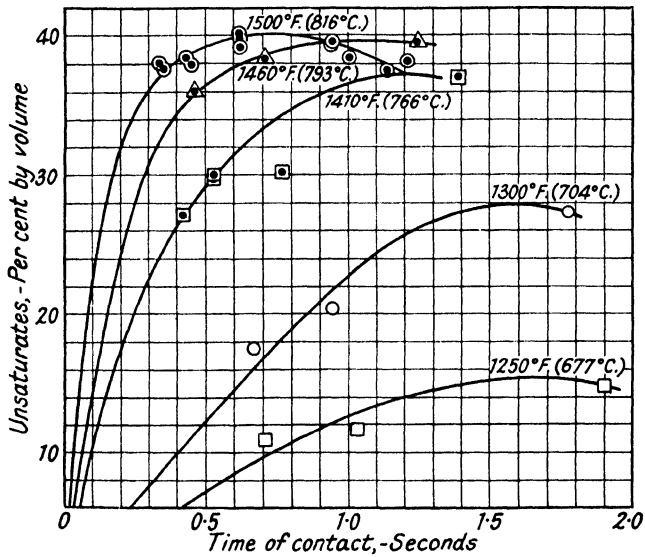


FIG. 6

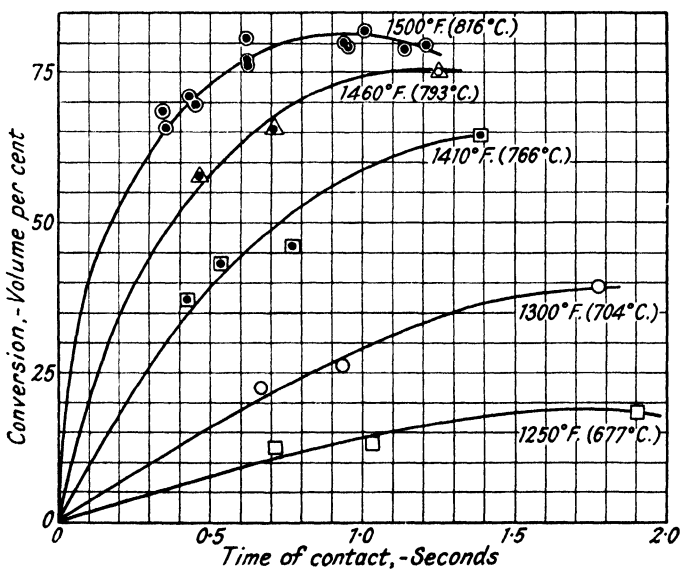


FIG. 7

and Egloff,[32] whose results may be summarised as shown below (Table 7).

TABLE 5. PROPANE PYROLYSIS IN KA2S COIL[25] (SULLIVAN, RUTHRUFF AND KUENTZEL)

Run No.	Mean Reaction Temp. °F.	Mean Reaction Temp. °C.	Inlet Gas ltrs./min.	Reaction Time seconds	Space Velocity	Exit Gas: Litres per minute	Exit Gas: % Unsaturateds	Exit Gas: Mol. wht.	Exit Gas: Mol. wht. Olefines	Volume Increase %	Conversion: Volume %	Conversion: Weight %	Grams of Olefines per litre of Reaction Space per hour
3	1260	682	5·96	0·71	1420	6·82	11·0	35·7	34·6	14·5	12·6	9·9	—
2	1246	674	3·98	1·03	950	4·61	11·7	35·8	—	14·8	13·6	—	—
1	1247	675	2·01	1·90	476	2·46	15·0	40·0	—	22·2	18·3	12·7	—
4	1310	710	5·72	0·67	1365	7·36	17·4	—	31·6	28·6	22·4	16·1	—
5	1305	707	4·02	0·94	957	5·16	20·4	—	31·6	28·5	26·2	18·8	—
6	1313	712	1·96	1·78	467	2·81	24·4	—	32·1	43·4	39·3	28·7	236
7	1407	764	8·30	0·42	1980	11·4	27·1	30·0	32·8	37·5	37·2	27·7	—
8	1412	767	6·30	0·53	1500	9·18	29·7	28·5	32·2	45·6	43·3	31·7	—
9	1410	766	6·34	0·53	1510	9·14	29·9	28·5	32·2	44·6	43·3	—	—
10	1403	762	4·20	0·77	1000	6·4	30·1	27·0	33·5	53·5	46·2	35·2	—
11	1412	767	2·13	1·39	508	3·72	37·0	23·8	31·6	74·5	64·6	—	—
12	1466	797	6·59	0·46	1560	10·62	36·0	25·0	30·3	61·1	58·0	40·0	—
13	1465	796	4·13	0·71	997	7·06	38·5	24·3	32·4	71·0	65·8	48·5	—
14	1460	793	2·17	1·25	517	4·13	39·6	22·5	31·5	90·2	75·2	53·4	552
15	1498	814	8·28	0·35	1960	14·48	37·6	25·5	32·3	75·0	65·8	48·3	1880
16	1494	812	6·36	0·43	1520	11·71	38·4	24·8	34·1	84·3	70·8	54·8	—
17	1495	813	4·24	0·62	10'0	8·29	39·5	22·6	30·2	95·4	77·1	53·0	—
18	1497	814	2·07	1·21	492	4·31	38·2	20·4	30·4	108·0	79·5	55·0	—
19	1491	811	2·73	0·95	650	5·47	39·6	21·6	29·8	100·2	79·3	—	—
32	1503	817	8·16	0·34	1945	14·7	38·0	25·0	—	80·0	68·4	—	—
33	1497	813	4·23	0·62	1010	8·26	39·2	22·2	—	95·2	76·4	—	—
34	1505	818	2·71	0·94	644	5·54	39·4	20·6	—	104·0	80·1	—	—
35	1505	818	2·17	1·14	517	4·56	37·6	19·8	—	110·0	79·0	—	—
36	1486	808	6·19	0·45	1480	11·33	37·9	*Ca.*25	—	83·0	69·4	—	—
37	1499	815	4·13	0·62	997	8·30	40·2	23·0	—	101·0	80·8	—	—
38	1508	820	2·43	1·01	580	5·18	38·5	*Ca.*22	—	113·0	82·1	—	—

TABLE 6. OPTIMUM RESULTS OBTAINED BY CAMBRON AND BAYLEY IN THE PYROLYSIS OF PROPANE FOR OLEFINE PRODUCTION

Expt. No.	Temp. °C.	Space Velocity	Conditions of Flow	Reactor	Expansion % vol.	Yield of Olefines		Olefines in exit gas % vol.		Olefine Production Rate	
						% Wht.	% Vol.	Ethylene	Propylene	Grams/ltr. Reaction Space/hr.	Lb./cu. ft. Reaction Space/hr.
15	1050	3560	Streamline	Quartz	78·3	31·7	47·4	21·8	4·8	2110	132
18	950	3560	Turbulent	Quartz	99·6	54·7	78·0	30·4	8·8	3630	227
36	1087	4100	do.	do.	76·4	50·0	65·8	—	—	3920	245
84	977	1236	Streamline	KA2S	66·9	38·8	54·0	22·5	9·8	895	55·8
81	949	1250	Turbulent	KA2S	81·2	50·2	70·0	28·0	9·6	1160	69·5
97	860	1295	do.	28% Chromium Alloy	84·0	50·2	72·8	28·3	11·4	1320	82·0

TABLE 7. THE PRODUCTION OF OLEFINES BY THE PYROLYSIS OF PROPANE AT SUPER-ATMOSPHERIC PRESSURE—725 LBS/SQ. IN. GAUGE

Run No.	A	B	C	D
Temp. °C.	555	555	585	585
Reaction time (secs.)	95	144	52·5	86·8
% Inlet propane decomposed	13·0	17·6	21·6	39·9
Liquid Product				
U.S. gallons/1000 ft. input	0·1	0·4	0·5	0·9
Imp. „ „ „ „	0·08	0·33	0·42	0·75
Gaseous Products				
% by vol. of propane decomposed.				
H_2	6·1	4·9	9·8	6·6
CH_4	48·4	50·5	83·5	57·9
C_2H_6	36·3	20·5	20·5	30·8
C_2H_4	25·2	32·3	27·8	16·3
C_3H_6	32·4	28·8	35·6	23·5
Total olefines	57·6	61·1	63·4	39·8
Mean molecular weight of olefines produced	35·9	34·6	35·9	36·4
Yield of Olefines				
% Volume on propane decomposed	57·6	61·1	63·4	39·8
% „ „ input	7·48	10·75	13·65	15·9
% Wht. on propane decomposed	47·0	48·1	51·8	33·2
% „ „ input	6·1	8·47	11·2	13·2

These results are of particular interest in view of the high mean molecular weight of the olefines produced.

380. Butanes.—The olefines produced by the non-catalytic pyrolysis of *n*-butane and *iso*-butane comprise ethylene, propylene and butylenes—the more severe the conditions the lower the average molecular weight of the olefines produced. That is, the behaviour of butanes is similar to that of propane in this respect.

The effect of temperature on the products obtained from *n*-butane as determined by Frolich and Wiezevich is shown in Fig. 8. In these experiments the contact time was 0·4 seconds, and the space velocity *circa* 340; and, under these conditions, the temperature (650°C.) at which maximum propylene concentration occurs (11·1%) is somewhat lower than the temperature (730°C.) for maximum ethylene (29%). The highest concentration of butylene (8·1%) was reached at about 670°C. For maximum total unsaturateds in the exit gas, a temperature of about 690°C. was required.

The experimental results of Hague and Wheeler[22] on butane have

already been mentioned. These were obtained at very low space velocities (*circa* 49), i.e., long times of contact. The highest total olefine content in the exit gas was 42·5% vol. (i.e., 19·7% higher olefines, 2·4% C_2H_2 (probably C_2H_4), and 20·4% C_2H_4), at a temperature of 700°C. Under these conditions a 2·3% oil yield was obtained simultaneously and higher temperatures gave decreased olefine yields, but higher liquid

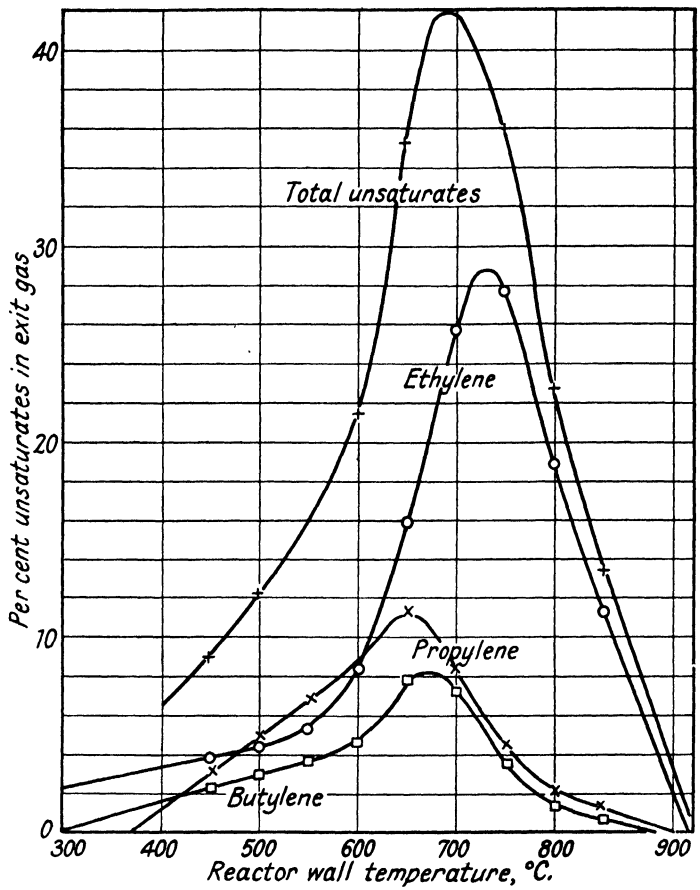


FIG. 8.—PYROLYSIS PRODUCTS OF NORMAL BUTANE (FROLICH AND WIEZEVICH)

yields. Valuable results at higher space velocities—i.e., under conditions much nearer to commercial scale practice than those of Hague and Wheeler, have been obtained by Cambron and Bayley.[27] These results, together with figures derived therefrom, are detailed in Table 8. It will be observed that the high space velocities used by Cambron and Bayley necessitated the use of temperatures up to 990°C., but under these conditions the output of olefines per unit of reaction space was very high.

Table 8. Pyrolysis of *n*-Butane (Cambron and Bayley)[27]

Reactor	Expt. No.	Inlet Gas Rate litres/hour	Size of Reactor cms.	Reaction Volume ccs.	Space Velocity Inlet gas	Temp. °C.	Exit Gas Anal. % Vol.				Expansion %	Yield of Olefines		Olefine Prodn. Rate			Remarks
							C_2H_4	C_3H_6	C_4H_8	Total Olefines		% Wht.	% Vol.	Olefines g/hr.	lb./cu. ft. reaction vol/hr.	grams/litre reaction vol/hr	
Empty Quartz	21	203·8	18·5 x 2·0	58	3520	852	9·3	10·2	1·4	20·9	24·2	17·0	26·0	84·4	94	1475	
do.	22	204·6	do.	58	3525	910	13·0	10·9	1·7	25·6	45·2	18·8	37·1	94·7	104	1630	Formation of liquid products observed.
do.	23	202·1	do.	58	3480	950	16·7	10·5	2·7	29·9	63·0	30·6	4[illegible]·7	152·1	168	2625	
do.	23A	204·6	do.	58	3525	990	20·7	10·0	2·2	32·9	78·4	34·8	58·8	175·7	193	3020	
Baffled Quartz	24	205·4	do.	58	3550	840	12·2	13·9	2·9	29·0	43·1	27·9	41·5	141·5	156	2440	
do.	25	202·1	do.	58	3480	868	14·2	15·1	2·6	31·9	56·3	32·9	49·9	164·2	181	2830	
do.	26	203·8	do.	58	3520	895	15·7	17·0	1·8	34·5	67·6	37·5	57·8	189·2	208	3260	Formation of liquid products observed.
do.	27	203·8	do.	58	3520	922	19·6	15·0	2·1	36·7	83·3	41·7	67·1	210·4	232	3630	
do.	53	396·5	40 x 2·5	196	2020	881	14·7	16·8	5·0	36·5	61·9	40·7	59·0	399·0	130	2030	
do.	54	399·0	do.	196	2030	913	17·2	18·4	4·3	39·9	80·8	48·0	72·0	473·0	154	2420	
do.	55	397·5	do.	196	2025	940	19·8	18·4	3·1	41·3	97·6	52·5	81·2	515·0	168	2630	
do.	56	808·0	80 x 2·5	392	2060	827	9·4	12·6	4·4	26·4	41·0	27·4	37·2	545·0	88·5	1390	
do.	57	812·0	do.	392	2080	858	11·7	14·7	5·0	31·4	58·0	34·8	50·2	700·0	114	1785	
do.	58	808·0	do.	392	2060	898	14·6	16·3	5·8	36·7	73·7	44·1	63·8	879·0	143	2240	
do.	59	808·0	do.	392	2060	915	16·4	17·3	5·3	39·0	88·1	50·0	73·4	995·0	162	2540	

The production of gaseous olefines and liquid products by the pyrolysis of butanes at 725 lbs./sq. in. (51 Kgs./cm.^{2}) has been studied by Tropsch, Thomas and Egloff.[32] At these pressures the temperatures required (525–550°C.) for olefine production are much lower than those necessary at substantially atmospheric pressure, but the reaction times (40–120 seconds) are correspondingly longer. Under these conditions it was found necessary to limit the per cent. decomposition per pass in order to reduce carbon formation, and in all tests liquid products were produced. The results obtained by Tropsch *et al.* have been used to calculate the data pertaining to them given in Table 9.

TABLE 9. PRESSURE PYROLYSIS OF BUTANES (TROPSCH, THOMAS AND EGLOFF)

Material treated	Normal Butane				Iso-Butane		Commercial Butane		
Run No.	E	F	G	H	I	J	3	4	5
Temperature °C.	525	525	555	555	555	555	350	550	550
Reaction time (seconds)	99	173	82·3	47	51	86·5	115	96	82
Pressure, lbs./sq. in.	725	725	727	725	725	725	725	725	725
% of inlet gas decomposed	25·6	38·6	55·4	43·3	21·6	25·8	51·2	44·5	41·7
Liquid produced									
U.S. gallons/1,000 cu. ft. input	0·75	1·3	2·2	1·3	0·3	0·4	3·1	2·3	2·3
Imp. gallons/1,000 cu. ft. input	0·62	1·08	1·83	1·08	0·25	0·33	2·58	1·92	1·92
Gaseous Products									
% vol. of C_4H_{10} decomposed.									
H_2	1·5	1·9	2·2	nil	5·5	6·4	—	—	—
CH_4	35·1	58·5	52·5	45·8	45·8	42·2	—	—	—
C_2H_6	45·8	29·5	30·6	27·7	1·3	5·0	—	—	—
C_3H_8	19·6	16·7	14·4	13·1	19·2	20·7	—	—	—
C_2H_4	12·5	6·9	7·4	10·3	2·9	4·5	—	—	—
C_3H_6	18·2	21·3	25·1	31·0	19·2	20·7	—	—	—
C_4H_8	23·2	18·3	17·8	16·0	20·3	20·9	—	—	—
Mol. wht. of Olefines produced	44·8	45·4	45·1	43·4	49·3	48·4	—	—	—
Yield of Olefines									
% *volume on*									
C_4H_{10} decomposed	53·9	46·5	50·3	57·9	42·4	46·1	50·2	57·5	61·4
C_4H_{10} input	16·35	17·9	27·8	25·0	9·15	11·9	25·7	25·6	25·6
% *weight on*									
C_4H_{10} decomposed	41·7	36·4	39·2	43·4	36·1	38·4	—	—	—
C_4H_{10} input	12·65	14·0	21·7	18·7	7·8	9·9	—	—	—

It is noteworthy that the olefines produced under these conditions had average molecular weights ranging from 43 to 48 (i.e., approximating to propylene) (see later). A suitable recycling arrangement would allow the production of *circa* 50% by weight of such olefines, plus 1–4 Imp. gallons of liquid product per 1,000 cu. ft. of butane treated. These yields are very promising.

381. General Considerations on the Production of Olefines by non-Catalytic Pyrolysis.—The above account of the more important published work on the production of olefines by the pyrolysis of the gaseous paraffins may be briefly summarised as follows :—

1. Olefines may conveniently be produced by this means. Yields up to 50–60% by weight may be realised.

2. The temperature and reaction time conditions required are less severe than those necessary for liquid hydrocarbon formation.

3. Olefines may be produced over a very wide temperature range (i.e., 600–1,000°C.) by proper choice of the reaction times.

4. The shorter the reaction time—i.e., the higher the space velocity employed—the higher is the temperature required for a given conversion.

5. The olefines produced are invariably of considerably lower molecular weight than the parent paraffins, i.e., olefines are produced by the splitting of carbon chains in preference to simple dehydrogenation.

6. The more severe the conditions employed the lower is the molecular weight of the olefines produced, i.e., ethylene is the predominating olefine product under severe pyrolysis conditions. (Acetylene is also an important high temperature product—this is dealt with later.)

7. The higher the molecular weight of the paraffin treated, the milder the reaction conditions required for a given conversion, or alternatively, the greater the conversion under given reaction conditions.

The reaction conditions and the results obtained by selected workers in this field are summarised in Table 10. These refer to experiments in which conditions were controlled so as to prevent the formation of oils and substantial amounts of coke.

382. Thermal Considerations.—The pyrolysis reaction for the production of gaseous olefines is markedly endothermic, as shown by the following typical examples :—

$C_2H_6 \rightarrow C_2H_4 + H_2$	— 32,000	cal.	/gram mole.	(1920	B.T.U. /lb.)
$C_3H_8 \rightarrow C_3H_6 + H_2$	— 32,000	,,	,,	(1309	,,)
$C_3H_8 \rightarrow C_2H_4 + CH_4$	— 16,100	,,	,,	(658·6	,,)
$n.C_4H_{10} \rightarrow C_4H_8 + H_2$	— 32,000	,,	,,	(993·1	,,)
$n.C_4H_{10} \rightarrow C_2H_4 + C_2H_6$	— 17,000	,,	,,	(527·6	,,)
$n.C_4H_{10} \rightarrow C_3H_6 + CH_4$	— 17,600	,,	,,	(546·2	,,)

TABLE 10. SUMMARY OF PUBLISHED RESULTS ON OLEFINE PRODUCTION BY THERMAL PYROLYSIS

Investigators	Material treated	Temp. °C.	Reaction Time, secs.	Space Velocity	Wht. % yield of Olefines	Pressure lbs./sq. in. gauge	Olefine Production Rate		Remarks
							Grams/litre reaction space/hr.	Lbs./cu. ft. reaction space/hr.	
Dunstan & Howes[33]	Natural & Refinery Gases	750–900	—	200–2500	50–60	0–30	3200–16,000	200–1000	
Sullivan, Ruthruff & Kuentzel[35]	Ethane	780–855	0·5–1·7	270–1440	36·9–69·1	Atm.	264–834	16·5–52·1	
Hague & Wheeler[22]	Ethane	750	—	49	50·5	Atm.	33·7	2·1	Assumption made that the olefines produced had a mol.wht. of 28
Sullivan, Ruthruff & Kuentzel[35]	Propane	674–820	0·43–1·9	467–1980	up to 55	Atm.	3776–30,080	236–1880	
Cambron & Bayley[27]	Propane	860–108	—	1236–3560	31·7–54·7	Atm.	893–3920	558–245	
Tropsch, Thomas & Egloff[32]	Propane	555–585	52·5–144	—	6·1–13·2	725	—	—	% Decomposition per pass limited to avoid coke formation
Hague & Wheeler[22]	Propane	750	—	49	57·2	Atm.	55·9	3·49	
Cambron & Bayley[27]	*n*-Butane	827–990	—	2020–3550	17–52·5	Atm.	1504–3712	94–232	
Hague & Wheeler[22]	*n*-Butane	700	—	49	49·0	Atm.	62·8	3·9	
Tropsch, Thomas & Egloff[32]	*n*-Butane	525–555	47–175	—	12·6–21·7	725	—	—	% Decomposition per pass limited to avoid coke formation
do. do.	*i*-Butane	555	51–86·5	—	9·15–11·9	725	—	—	do. do.
do. do.	Comm. Butane	550	82·115	—	*ca* 25% (vol.)	725	—	—	do. do.

As a result a large quantity of heat at a high temperature level must be transmitted to the reacting gas. It is, therefore, essential to employ highly turbulent flow of the gas within the reaction tubes so as to obtain a heat transfer rate as high as possible. Without such highly turbulent flow, side reactions occur leading to the formation of coke and aromatic liquids, and the throughout capacity of the plant is considerably reduced.

383. Plant Arrangement.—It is evident that the reaction coil must be heated, and the plant arrangement is simple. A gas-fired furnace, designed on conventional lines, serves for both preheat and reaction heat duties, but care must be taken in the choice of suitable furnace tube materials. Such steels as Krupps **NCT3**, and Hadfields **HR3** (both containing 25% chromium and 20% nickel), are satisfactory for use at temperatures up to 1,000°C., while for lower temperatures there is a wide range of suitable tube steels—including austenitic stainless steels and molybdenum and chromium steels.

It is frequently found that steels of different chemical composition have appreciably different catalytic effects upon the reactions involved. The use of steels containing large quantities of nickel (but only a little, or no, chromium) is to be avoided because they accelerate carbon formation.

384. Large Scale Installations.—As far as is known, the only large scale plants in operation for the manufacture of olefines by the pyrolysis of gaseous paraffins are those of certain American chemical manufacturers, who utilise the olefines produced, particularly ethylene, for the production of synthetic organic chemicals. The reason for the non-adoption of this process on any scale by the petroleum industry is the rapid development of combination pyrolysis—polymerisation plants by which paraffins are converted into olefines and the olefines then polymerised in one and the same plant. These plants obviate the necessity of segregating the olefines produced before subsequent polymerisation.

385. The Production of Gaseous Olefines by the Dehydrogenation of the Lower Paraffins.—It has already been mentioned that the low yields of olefines obtainable from the gaseous paraffins by pyrolysis processes, due mainly to the fact that cracking (i.e., formation of hydrocarbon containing a smaller number of carbon atoms), is the predominating reaction, may be considerably improved in processes of catalytic dehydrogenation. Thus the highest yield of olefines yet obtained from butane by pyrolysis is about 60 per cent. by weight, whereas by dehydrogenation it is theoretically possible to obtain an olefine yield of 96·5 per cent. by weight consisting entirely of butylenes.

This high yield of olefines is not obtainable in single-pass operation, for reasons which are given later, but such a process offers other attractions (e.g., production of hydrogen for hydrogenation).

The equilibrium

$$C_n H_{2n+2} \rightarrow C_n H_{2n} + H_2$$
Paraffin — Olefine + Hydrogen

lies well over to the left at temperatures below 350°C., but the extent of dehydrogenation increases with rise in temperature and proceeds extensively above 450°C. Of particular interest is the work by Frey and Huppke,[34] on the experimental determination of the dehydrogenation equilibrium in the case of ethane, propane and the butanes, whose results are presented in Fig. 9. These results enable the percentage conversions of the lower paraffins into the corresponding

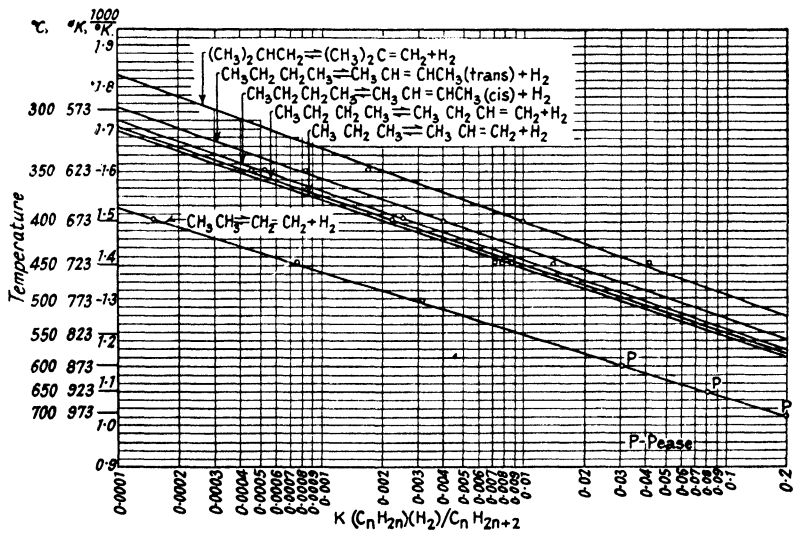


FIG. 9.—EQUILIBRIUM CONSTANTS DEHYDROGENATION OF PARAFFINS (FREY & HUPPKE)

olefines to be calculated for any particular temperature. From the values of K given in Fig. 9, the extent of dehydrogenation theoretically possible has been calculated—as reproduced in Table 11—while the corresponding concentrations of olefines in the exit gases are set out in Table 12.

According to Frey and Huppke (*loc. cit.*) no molecular rearrangement occurs in dehydrogenation in the presence of suitable catalysts, with the result that *n*-butane yields *n*-butylenes only and iso-butane gives exclusively iso-butylene.

TABLE 11. MAXIMUM CONVERSION TO OLEFINES BY DEHYDROGENATION OF PARAFFINS AT 350–700°C. FROM THE DATA OF FREY AND HUPPKE[34]
(Percentage Conversion to Olefines (volume))

	350°C.	400°C.	450°C.	500°C.	550°C.	575°C.	600°C.	650°C.	700°C.
Ethane ..	—	1·0	2·8	5·8	9·5	13·0	17·8	28·2	40·8
Propane ..	1·9	4·7	8·7	16·3	28·2	37·0	43·9	—	—
n-Butane ..	3·8	9·4	19·1	32·5	52·3	—	—	—	—
Iso-Butane ..	4·2	10·0	20·1	32·8	—	—	—	—	—

TABLE 12. MAXIMUM CONCENTRATION OF OLEFINES IN EXIT GAS BY DEHYDROGENATION OF PARAFFINS (% VOLUME)[34]

	350°C.	400°C.	450°C.	500°C.	550°C.	575°C.	600°C.	650°C.	700°C.
Ethane ..	—	1·0	2·7	5·5	8·7	11·5	15·0	22·0	29·0
Propane ..	1·9	4·5	8·0	14·0	22·0	27·0	30·5	—	—
n-Butane ..	3·7	8·6	16·0	24·5	34·3	—	—	—	—
Iso-Butane .	4·0	9·1	16·7	24·7	—	—	—	—	—

It is evident from the above figures that it is thermodynamically possible to obtain from *n*- or iso-butane, for example, an exit gas containing *circa* 30 per cent. butylenes by dehydrogenation at 550°C., the other constituents being 30 per cent. hydrogen and 40 per cent. undecomposed butane. In practice, however, there are various conditions which must be realised before the reaction involved can proceed satisfactorily. The most important requirement is a suitable catalyst to speed up the dehydrogenation reaction so that it may proceed at a much greater rate than any cracking reactions. Figures already presented show that in the absence of such a catalyst dehydrogenation proceeds only to a slight extent. Other important requirements are choice of pressure and temperature conditions, and also choice of catalyst such that there is complete prevention of any cracking reactions which cause the deposition of cracked products and carbon on the catalyst and so reduce its activity. Polymerisation of the olefines formed must also be prevented, because this also causes the deposition of deleterious products on the catalyst.

386. Catalysts.—Various catalysts have been used in the dehydrogenation of the lower paraffins. According to Peace[35] copper is active in this direction, but loses its activity rapidly, while nickel, platinum and palladium have been reported to bring about complex decomposition in addition to simple dehydrogenation.

The I. G. Farbenindustrie[36] claim the production of amylene by passing pentane over active carbon at 450–500°C., and Tausz and Putnoky[37] have dehydrogenated pentane, hexane, heptane and octane over palladium at 300°C. In their work on the determination of equilibrium constants, Frey and Huppke[34] used a chromic oxide gel catalyst prepared by precipitation from a chromic nitrate solution by ammonia in the presence of ammonium acetate. The gel was black in appearance and vitreous in texture. At temperatures above 450°C., however, this catalyst suffers from deterioration in activity. Chromic

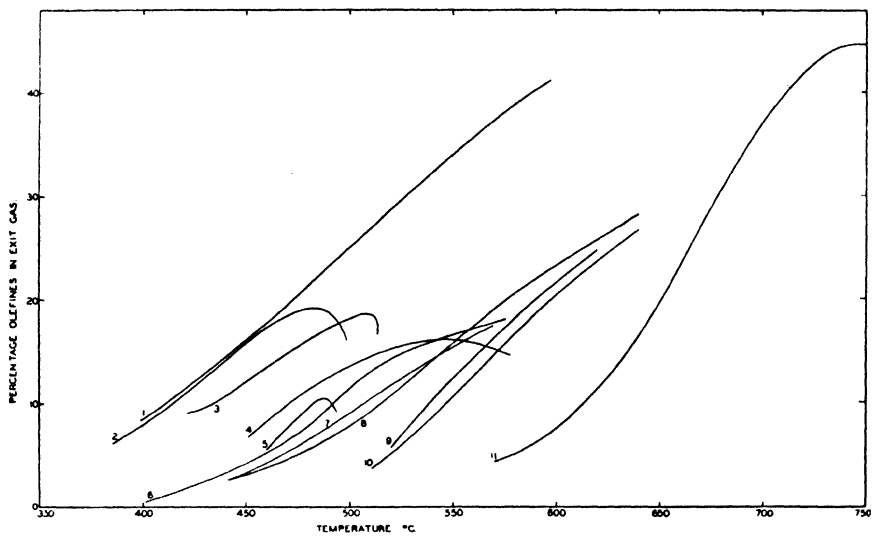


FIG. 10.—DEHYDROGENATION OF NORMAL BUTANE (DUNSTAN & HOWES)

oxide catalysts not in the gel form are reputed to give inferior results,[38] while the best results are claimed to be obtained from chromic oxide gel catalysts made by precipitation from chromic nitrate solution by caustic soda or caustic potash. Such gels retain their gel structure on drying and heating. Catalysts of good catalytic activity may also be obtained by precipitation with ammonia in the presence of acetic acid, sulphuric acid, aluminium salts or soluble silicates.[38]

Mixtures of chromic oxide and zinc oxide have been claimed by Frolich and Boeckeler[39] as satisfactory catalysts for the dehydrogenation of paraffin hydrocarbons higher than methane. The temperature range is quoted as 450°C.–700°C. Catalysts containing zinc oxide and another oxide of a metal which has two or more valencies are favourably mentioned, such as 30 mole per cent. zinc oxide plus 70 mole per cent. chromium oxide, or other proportions of the same oxides, or zinc oxide and molybdenum oxide. According to Frolich and Boeckeler, the space velocities allowable with such catalysts are in the

neighbourhood of 780, but may range from 108 to 6,480. The catalysts must be reduced before use and it is often advantageous to dilute the ingoing paraffin hydrocarbon gases with nitrogen or water vapour—or else with hydrogen—which tends to prevent carbon deposition. A process has been described by Frolich[40] in which gaseous paraffin hydrocarbons are dehydrogenated to the corresponding olefines, using the chromium oxide–zinc oxide catalysts described above; the resulting hydrogen is then removed by treatment with reducible metallic oxides (such as copper oxide) and the olefine polymerised.

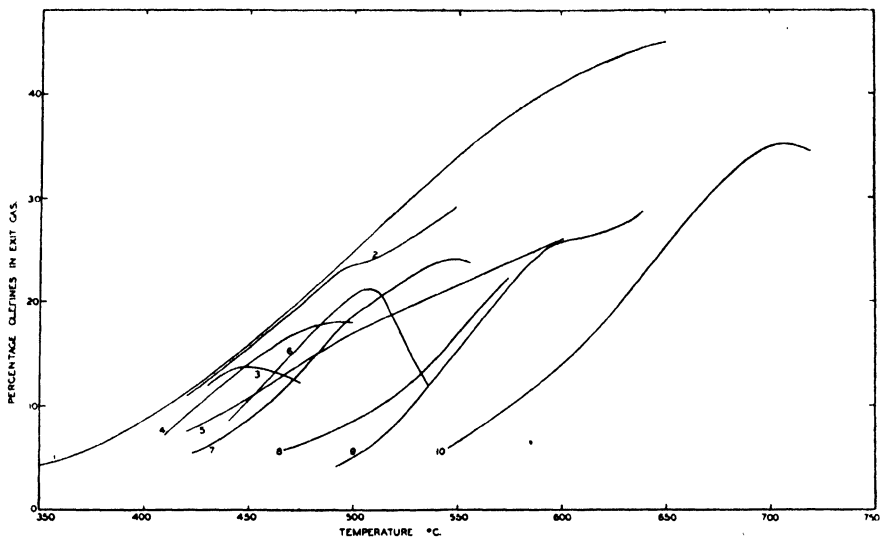


FIG. 11.—DEHYDROGENATION OF ISO-BUTANE (DUNSTAN & HOWES)

The removal of hydrogen before the polymerisation stage by treatment over a suitable catalyst with carbon monoxide has also been suggested.[41] In this case the reaction involved is

$$CO + 2H_2 \rightarrow CH_4 + H_2O$$

and the catalyst employed is nickel in various forms.

Dunstan and Howes[33] have described tests made on the dehydrogenation of *n*-butane and iso-butane. Their results on a variety of catalysts are shown in Figs. 10 and 11. With the most satisfactory catalysts equilibrium conditions were established at temperatures up to 450–500°C. In general, above this temperature cracking took place with the formation of methane and ethane, carbon was also deposited. The most effective catalysts examined by Dunstan and Howes comprised mixtures of molybdenum, zinc and magnesium oxides, and ammonium chromate deposited on carriers, such as silica gel and active carbon. In the temperature range 400–600°C., the allow-

able space velocities varied from 250 to 2,000, the higher throughputs being obtained with the more active molybdenum and chromium catalysts.

The patent literature contains several statements concerning effective catalysts for the dehydrogenation of ethane and higher gaseous paraffin hydrocarbons. The most important of these may be summarised as follows :—

Copper and porcelain catalysts.[42]

Various metals and alloys, also nickel, calcium and platinum.[43]

Reaction chambers constructed of chromium steel.[44]

Porous materials such as active carbon and silica gel.[45]

Zinc, aluminium and nickel oxides on supports.[45]

Heavy metals of group 1, e.g., gold, silver or copper or their alloys.[46]

Stainless steels coated with tin, zinc, lead, aluminium and chromium, with free elementary silicon.[46]

Silicates, phosphates and borates of copper, manganese, lead and copper.[47]

Vapours of mercury, lead, tin and zinc.[48]

High-temperature cokes.[49]

Silicon carbide.[50]

387. Large Scale Plant Operation.—Because dehydrogenation is an equilibrium reaction and because temperatures high enough for substantially complete conversion per pass are not allowable—due to secondary reactions—a recycle operation is necessary. It is usually undesirable, with the catalysts at present available, to operate at temperatures in excess of 500°C. This limits the extent of dehydrogenation as follows :—

Ethane	..	9·5%
Propane	..	28·2%
n-Butane	..	52·3%
Iso-Butane	*circa*	60%

Moreover, it is usually preferable to employ catalysts which do not give the theoretical conversion, and in practice, on C_3–C_4 paraffin mixtures the decomposition per pass rarely exceeds 35 per cent. This necessitates the use of a recycle ratio of 65 /35, i.e., the feed consists of 65 parts of recycle material and 35 parts fresh feed. The olefines and hydrogen must be separated from the exit gas before returning this to the system, and a convenient arrangement is that shown diagrammatically in Fig. 12, which relates to a typical treatment of butane.

It is desirable to operate the dehydrogenation process at such a

pressure that the feed to it may be handled in the liquid state—thus avoiding compressors—and also at such a pressure that simple separation or fractionation may be employed for the separation of the hydrogen from the paraffin-olefine mixture before passing the latter to polymerisation.

The plant requirements are not stringent. Because of the fairly low temperatures required, the catalyst tubes may be constructed of normal carbon steels or the well-known steels containing small amounts of molybdenum and/or chromium. The dehydrogenation reaction is

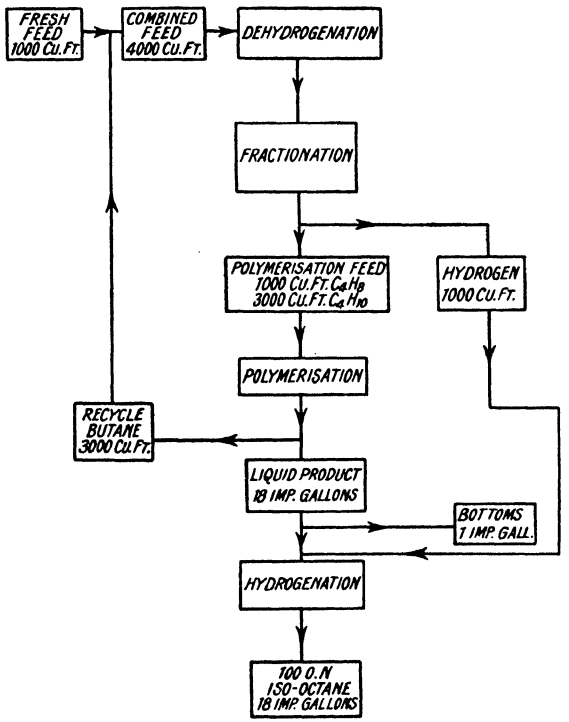


FIG. 12.—FLOW DIAGRAM. DEHYDROGENATION OF ISO-BUTANE

markedly endothermic (990 B.T.U./lb. of paraffins reacting in the case of butane), and arrangements must be made for supplying this heat to the catalyst without danger of overheating. This is the only important factor in the design of the equipment and must be given adequate attention.

The dehydrogenation of the gaseous paraffins is receiving considerable attention in the petroleum industry at present, because it provides large quantities of raw materials for the manufacture of 100 octane number aviation fuels. Thus butane fractions may be converted by this means into butylenes. The latter may then be polymerised, by

methods which are described later, into di-butenes, which, when hydrogenated, become converted into branched chain octanes of very high anti-knock value. The following figures illustrate the yields obtainable in commercial operation :—

TABLE 13

Feed Material to Dehydrogenation Plant	Propane	Butanes	Iso-butane
Olefine yield (80% theory).			
Tons/100 tons feed	76·4	77·3	77·3
Cu. ft./100 cu. ft. feed	80·0	80·0	80·0
Hydrogen yield (90% theory).			
Tons/100 tons feed	4·1	3·1	3·1
Cu. ft./100 cu. ft. feed	90·0	90·0	90·0
Polymer yield (95% theory).			
Tons/100 tons feed	72·6	73·4	73·4
Gallons/1,000 cu. ft. feed	11·0	15·0	15·0
Polymer spirit, 200°C. E.P.			
Tons/100 tons feed	64·3	66·1	66·1
Gallons/1,000 cu. ft. feed	9·9	13·5	13·5
Hydrogenated polymer spirit. 200°C. E.P. 100 octane number.			
Tons/100 tons feed	—	—	66·0
Gallons/1,000 cu. ft. feed	—	—	14·2

388. The Production of Acetylene by the Pyrolysis of the Lower Hydrocarbons.—Acetylene is produced in the pyrolysis of all hydrocarbons, but is mainly a high temperature product. For this reason the production of acetylene by pyrolysis has not received its due attention, and moreover, the polymerisation of acetylene to liquid hydrocarbons of gasoline boiling range has not yet been fully explored. Considerable data have been published on the synthesis of acetylene from methane by means of an electric discharge through the gas,[51] or by passing methane through an electric arc.[52] Cost estimates made by Storch[53] (based on a power cost of 0·25 cents./K.W.H.), indicate, however, that such processes cannot compete with the production of acetylene from calcium carbide, with the latter at its present low price. There are also several patented processes,[54, 55] for the production of acetylene by the partial oxidation of methane, but so far these have made no headway.

In 1932, Fischer and Pichler[56] published some data on the dehydrogenation of ethylene at temperatures from 1,000°C. to 1,400°C.,

and at reaction times varying from 0·004 to 0·005 seconds. Under these conditions the formation of hydrocarbons of higher molecular weight was always appreciable. On the other hand, little or no carbon was formed. The results obtained by these workers are summarised in Table 14, reproduced from a paper by Storch.[53] It is evident from

TABLE 14. PRODUCTION OF ACETYLENE BY THE PYROLYSIS OF ETHYLENE (FISCHER AND PICHLER)

Expt. No.	Temp. °C.	Pressure (Atm.)			% Ethylene decomposed	Products as % of Ethylene decomposed			% Acetylene in Exit Gas
		C_2H_4	H_2	N_2		Acetylene	Polymers	Methane	
8	1000	1·0	—	—	8·5	16·5	83·5	—	1·3
2	1000	0·1	—	—	13·0	32·3	53·1	8·5	3·6
11	1000	0·5	0·5	—	6·4	12·5	45·3	42·2	0·4
19	1000	0·5	—	0·5	9·9	30·3	51·6	19·2	1·4
9	1100	1·0	—	—	20·9	23·9	64·2	9·6	4·3
3	1100	0·1	—	—	26·0	95·0	—	2·3	18·8
12	1100	0·5	0·5	—	20·0	43·0	38·0	19·0	3·9
20	1100	0·5	—	0·5	27·0	43·4	49·6	7·0	5·2
10	1200	1·0	—	—	46·2	29·4	60·3	9·5	10·6
4	1200	0·1	—	—	54·4	67·4	25·2	7·3	23·6
13	1200	0·5	0·5	—	45·1	47·5	36·7	15·8	9·4
21	1200	0·5	—	0·5	54·4	42·0	48·7	9·4	9·3
5	1300	0·1	—	—	82·2	72·0	22·6	4·6	31·8
7	1300	0·017	—	—	93·4	66·3	30·2	3·5	32·0
10	1320	0·05	0·05	—	80·6	74·5	19·4	4·3	24·4
12	1300	0·0085	0·0085	—	85·8	76·3	17·1	5·6	23·5
14	1280	0·025	0·075	—	62·8	84·8	2·9	8·9	10·9
18	1300	0·0143	0·0857	—	61·6	81·2	13·2	5·6	6·8
9	1400	0·017	—	—	98·5	59·0	39·0	2·0	28·8
11	1380	0·05	0·05	—	95·2	74·0	22·3	3·7	27·0
13	1400	0·0085	0·0085	—	98·7	73·5	23·5	2·7	24·6
16	1400	0·025	0·075	—	97·0	87·4	11·1	1·5	16·4
19	1400	0·0143	0·0857	—	91·1	92·3	3·1	4·6	11·1
20	1410	0·0143	0·0857	—	100·0	90·0	2·0	8·0	11·2

these results that concentrations of acetylene in the exit gas as high as 32% were obtained, corresponding to ethylene conversions to acetylene as high as 92%. The percentage of ethylene decomposed is fairly constant, under the above-mentioned conditions, for any particular temperature, but there is a definite trend towards somewhat higher conversions at low ethylene partial pressures. The presence of hydrogen appears to retard the dehydrogenation rate. Pressure

seems to affect the distribution of the products markedly, a lower partial pressure of ethylene resulting in a higher conversion to acetylene. Fischer and Pichler[56] have also given some results on the conversion of ethane to acetylene. These data are practically identical with those obtained for ethylene under the same conditions and indicate that the dehydrogenation of ethane to ethylene is much more rapid at 1,000°C. to 1,400°C. than is the dehydrogenation of ethylene to acetylene. Acetylene was also produced in quantity by the pyrolysis of various petroleum fractions at 700–1,260°F.,[57] and 50–75% conversions of methane to acetylene realised by the pyrolysis of coke oven gas at 1,500–1,600° and 0·004–0·005 seconds reaction time.

Recently valuable contributions have been made by Egloff and his co-workers[58, 59] on the pyrolysis of the gaseous olefines and paraffins at 1,100–1,400°C. and 50 mm. total pressure. Acetylene was in most cases an important reaction product. Considering their results on the gaseous paraffins first, it was found that at 1,100°C. and 50 mm. total pressure, the highest yields of acetylene, expressed as per cent. by volume, were as follows, over a reaction time range of 0·8 to 100×10^{-3} seconds.

Ethane	..	10·0
Propane	..	25·0
n-Butane	..	30·0

At 1,400°C. it was found that methane required from ten to twenty times longer reaction time than ethane and propane to obtain maximum acetylene yields. A maximum of 12% by volume of acetylene was obtained from methane at $14{\cdot}1 \times 10^{-3}$ seconds reaction time. De Rudder and Biederman[60] have reported yields of 22% by volume, which they obtained using a reaction time of *circa* 100×10^{-3} seconds. The pyrolysis of ethane and propane proceeded similarly at 1,400°C. as at 1,100°C. The maximum yields of olefines obtained at 1,400°C. were as follows :—

TABLE 15

	Ethylene	Propylene	Acetylene
From Ethane.			
Vol. %	67	5·00	53
Reaction time 10^{-3} secs.	0·4	0·33	5·5
From Propane.			
Vol. %	72	14·5	76
Reaction time 10^{-3} secs.	0·5	0·39	5·5

With regard to the pyrolysis of olefines, the results obtained at 1,100°C. and 50 mm. total pressure were as follows :—

TABLE 16

	Ethylene	Propylene	Butene-1	Butene-2	Iso-Butene
Acetylene.					
Volume %	21·0	21·8	35·0	26·0	40·3
Contact time 10^{-3} secs. ..	44·0	12·0	13·0	3·0	4·9
Ethylene.					
Volume %	—	28·5	42·6	32·6	20·1
Contact time 10^{-3} secs. ..	—	12·0	13·0	5·8	4·0
Propylene + Butylene.					
Volume %	3·0	—	—	—	22·6
Contact time 10^{-3} secs. ..	2·2–44·0	—	—	—	2·8
Butadiene.					
Volume %	1·5	2·6	17·4	23·3	10·9
Contact time 10^{-3} secs. ..	0·7–44·0	2·5–12·0	3·7	2·5	2·8

The highest yields of acetylene and ethylene obtained at 1,400°C. and 50 mm. pressure were as follows :—

TABLE 17

	Ethylene	Propylene	Butene-1	Butene-2	Iso-Butene
Acetylene.					
Volume %	76·6	59·3	64·5	64·1	57·8
Contact time 10^{-3} secs. ..	2·3	2·2	0·9	1·9	1·8
Ethylene.					
Volume %	—	26·4	38·2	9·9	10·3
Contact time 10^{-3} secs. ..	—	0·9	0·9	1·9	0·8

It is thus evident that acetylene can be produced by the pyrolysis of gaseous paraffins and olefines—particularly the latter—in attractive yields.

The high temperature required is a great disadvantage, however, especially when combined with sub-atmospheric pressure operation. Metal reaction tubes are out of the question, and the only suitable materials for fabrication appear to be alundum and silicon carbide.

389. Pyrolysis Processes for the Production of Liquid Fuels from Gaseous Hydrocarbons.—It is necessary to make a distinction between " pyrolysis " and " polymerisation " processes, because recent American publications refer to all processes by which liquid hydrocarbons are obtained from natural and refinery gases as " Poly " processes. In this book, polymerisation processes are classed as those in which polymerisation of olefines takes place as a major reaction, whereas processes in which chemical degradation is predominant and the liquids produced (if any) are essentially aromatic in character, are termed " pyrolysis " processes. Processes in which both reactions occur—either in sequence or simultaneously, are called " combination " pyrolysis-polymerisation processes.

Pyrolysis processes have been adopted for the conversion of the gaseous olefines and paraffins into liquid products boiling essentially in the gasoline range and of a pronounced aromatic character. This type of operation is frequently referred to as " benzole pyrolysis," because the liquid produced contains a considerable proportion of benzole.

390. Among the most valuable work done on this application of pyrolysis is that of Hague and Wheeler.[22, 61] The yields of liquid products obtained are shown in Fig. 13, and are also detailed below.

TABLE 18.—YIELDS OF PRODUCTS OBTAINABLE BY THE BENZOLE PYROLYSIS OF PURE HYDROCARBONS

ATMOSPHERIC PRESSURE OPERATION. CONSTANT REACTION TIME
Space Velocity = *circa* 49·0

Hydrocarbon	Temp. (°C.)	Total Liquids		200° E. P. Benzole		Residue above 200°C.	
		Imp. Gal./ 1,000 cu. ft.	Per cent. weight	Imp. Gal./ 1,000 cu. ft.	Per cent. weight	Imp. Gal./ 1,000 cu. ft.	Per cent. weight
Paraffins:							
Methane	1050	0·44	8·8	0·3	4·7	0·14	4·1
Ethane	900	2·1	21·9	1·5	16·9	0·6	5·0
Propane ..	850	3·25	23·09	2·4	18·4	0·85	4·69
Butanes ..	850	4·6	24·55	3·4	19·8	1·2	4·75
Olefines:							
Ethylene ..	800	3·15	36·1	2·4	28·8	0·75	7·3
Propylene ..	800	5·32	40·6	4·0	31·2	1·32	9·4
Butylenes ..	800	6·85	39·6	5·1	30·7	1·75	8·9

It will be observed that the liquid yield increases with rise in molecular weight of the gas treated in the case of both paraffins and olefines, and also that the yield is greater for an olefine than the corresponding paraffin.

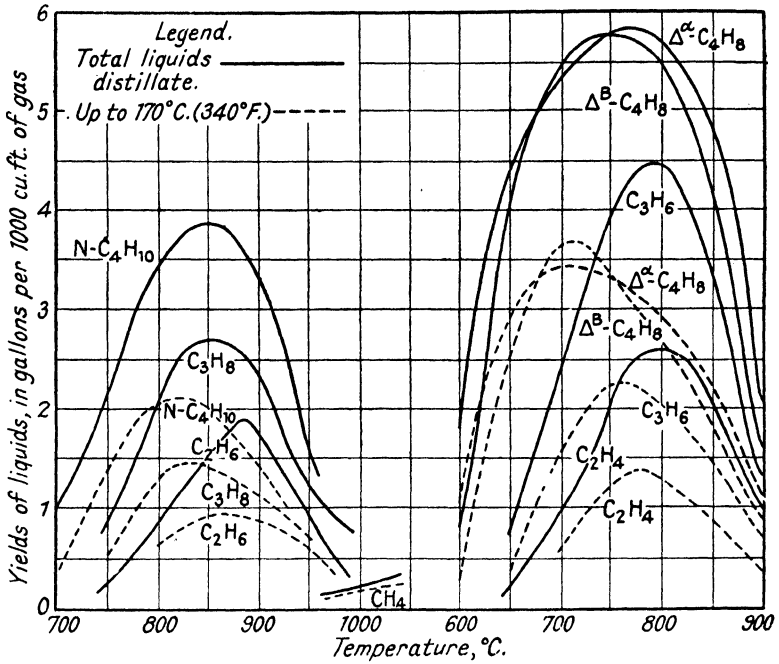


FIG. 13.—YIELDS OF LIQUID HYDROCARBONS OBTAINABLE BY THE HIGH TEMPERATURE PYROLYSIS OF THE GASEOUS HYDROCARBONS (HAGUE & WHEELER)

It is of interest to compare the above gallonage yields with those theoretically obtainable from the relationship

$$\text{Imp. gallons per 1,000 cu. ft. of gas treated} = \frac{\text{lbs. per cu. ft. of gas treated} \times 1{,}000}{\text{sp. gr. of liquid product} \times 10}$$

which is graphed in Fig. 14.

To obtain products rich in benzene, the temperature conditions are necessarily severe, but the yields obtainable are sufficiently high to attract attention. The temperatures required at substantially atmospheric pressure operation vary from 1,000 to 1,200°C. (1,832–2,192°F.) in the case of methane to 800 to 850°C. (1,472–1562°F.) in the case of butane, although with suitable adjustment of space velocity (or reaction time) these temperature ranges may be extended somewhat in an upward direction.

By operating under temperature, pressure and throughput conditions less severe than those required for the production of benzole,

the liquids obtained are essentially unsaturated in character, and are of lower octane number than benzoles. Under reaction conditions suitable for benzole production, by making small variations in operating conditions, the freezing point, boiling range and unsaturated content of the product may be varied at will, and under the most severe conditions employed, 200°C. E.P. distillates consisting largely of benzene (C_6H_6, b.p. 80·8°C.) can be obtained.

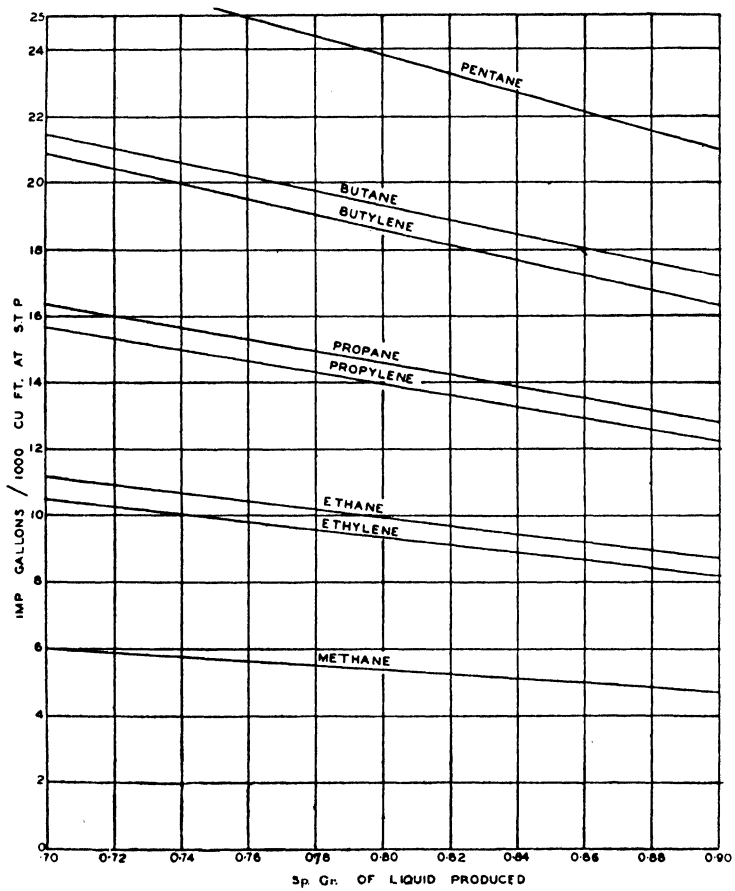


FIG. 14.—THEORETICAL YIELDS OF LIQUID HYDROCARBONS OBTAINED FROM GASEOUS PARAFFINS AND OLEFINES

In the benzole pyrolysis process the variables, temperature, pressure and throughput rate are to a large extent complementary, although there is a minimum temperature below which benzole formation is not obtained. If super-atmospheric pressure is employed as a means of increasing plant throughput, the temperature remaining the same as in atmospheric pressure operation, then the same type of product

TABLE 19. PROPERTIES OF PYROLYSIS BENZOLES. EFFECT OF VARIATION IN REACTION CONDITIONS

INLET GAS. STRAIGHT-RUN GAS. $C_2H_6 = 15\%$, $C_3H_8 = 20\%$, $C_4H_{10} = 45\%$, $C_5H_{12} = 20\%$

Temperature (°C.)	700	750	800	850	870	800	850	850
Inlet pressure (lb./sq. in.)	30	30	30	30	5	5	5	15
Space velocity (vol. inlet gas/vol. reaction space/hr.)	209	209	209	209	210	182	182	400
Properties of Product :—								
Sp. gr. at 60°F.	0·796	0·849	0·873	0·875	0·880	0·845	0·873	0·875
Initial b. pt. (°C.)	39	51	69	70	69	66·5	67·5	63
10 per cent. distillate at	55	70·5	79	80	80	80	78·5	76·5
20 „ „	62	77	81	82	82·5	84	81	79·5
30 „ „	68·5	81	82·5	83	84	87·5	82	81
40 „ „	75	84	84	84	86	91	83·5	83
50 „ „	81	87	85	85	87·5	96·5	85	84
60 „ „	87	90	87	86·5	89·5	107	86	86
70 „ „	94·5	94·5	89·5	89	94	133·5	88·5	88·5
80 „ „	109	102·5	95	93·5	102	169	93	93
90 „ „	153	125	113	110	130	188·5	109·5	109
Final b. pt. (°C.)	211	190	187	200	200	200	200	195
Aniline point (°C.)	<0°C.	<0°C.	<0°C.	<0°C.	<0°C.	<0°C.	<0°C.	<0°C.
Bromine number (grm./100 g.)	74	56	25	22	—	—	—	30
Octane number (C.F.R. Motor)	84·4	95·6	96·1	104·1	102	87·7	101·5	99
Freezing point (Air Ministry test) (° C.)	−38	−19	−17	− 7	—	—	—	−15
Blending Octane Number :—								
20 per cent. in 52·5 octane number base	104·8	—	—	—	100·2	—	—	—
30 „ „ 65 „ „ „	91·6	93	—	—	92	—	—	—
30 „ „ 70 „ „ „	87·3	90·3	—	—	88·6	—	—	—

will be obtained, but if, by the use of pressure, a lower reaction temperature is used, then the product will only be substantially benzene if the temperature is above about 800°C. At lower temperatures products containing toluene, xylene and higher aromatics are obtained. Data are given in Table 19 showing how variation of reaction conditions affects the properties of the 200°C. E.P. distillates produced.[33]

391. Exhaustive tests[33] have shown that the benzoles obtained by the pyrolysis of gaseous hydrocarbons may be easily refined to yield spirits of good colour and of very satisfactory gum stability in conventional refining plant. Sulphuric acid may be used as the refining agent. The amount required is only in the order of 0·3 per cent., a quantity not greater than that required in the refining of many cracked spirits. The refined spirits have been subjected to prolonged engine tests in which gum formation has been encouraged, but the amount of gum deposition in the inlet manifold and on the inlet valves is negligible.

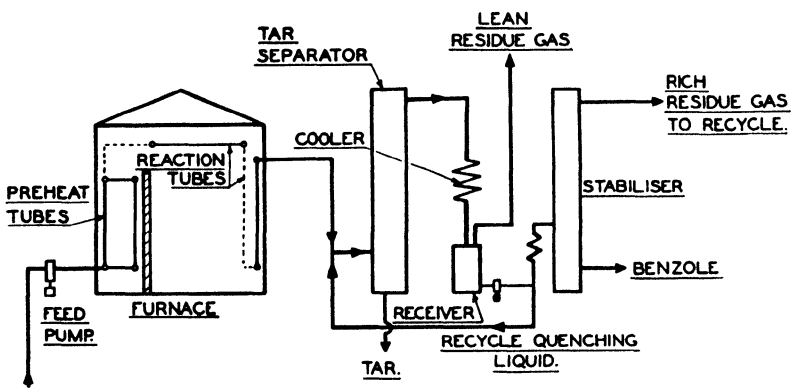


FIG. 15.—SIMPLIFIED FLOW DIAGRAM. BENZOLE PYROLYSIS OPERATION

The product may thus be described as a fully satisfactory benzole of natural gas origin.

With regard to the knock ratings and blending properties of benzoles produced by pyrolysis, these are very similar to those of pure benzene and are referred to in detail later.

392. Plant for Pyrolysis Benzole Production.—The plant required for the production of benzole by the pyrolysis of gaseous hydrocarbons is very simple, and only consists of conventional refinery equipment, although the choice of materials and reaction conditions is important. A typical flow diagram is reproduced in Fig. 15.

It is usually convenient to avoid the use of feed stocks in the gaseous state and to liquefy in normal stabilising equipment. This

allows the use of inlet feed pumps and the avoidance of compressors with their attendant high running and maintenance costs. Modern stabilising equipment operates at pressures up to 500 lb. /sq. in., and there is usually no difficulty in obtaining feed stocks in the liquid state, except in the case of those containing large amounts of non-condensable gases such as ethylene. In such cases compressors must be used. The plant required comprises a preheat furnace, reaction coil (either heated or unheated), cooling device, tar separator, product receiver and product stabiliser.

Furnaces.—The preheat furnace may follow conventional pipe-still practice, although the selection of the furnace tubes and furnace insulation for use at temperatures above 500°C. (932°F.) and up to 880–900°C. (1,616–1,652°F.) needs care. Up to temperatures of 500°C. ordinary cracking-furnace tubes may be employed, fabricated in mild steel, 0·5 per cent. molybdenum steel or 6 per cent. chromium steel, but, for the higher temperatures, steel containing higher percentages of nickel and chromium are required. Stainless steels of the 18/8 chromium-nickel type are satisfactory for temperatures not exceeding 650°C., but reasonable life at temperatures up to 900°C. (1,652°F.) is only obtained by the use of 25/20 chromium-nickel steels, examples of which are Hadfields H.R.3 and Krupps N.C.T.3. Tests carried out on semi-commercial plant over an extended period have demonstrated that such steels are perfectly satisfactory for continued service because of their excellent mechanical properties and resistance to decarburisation and scaling.

The reaction coil is preferably heated in pyrolysis processes as markedly endothermic as that involving benzole production, and is normally placed in the same furnace as the preheating tubes. The reaction coil may, however, be unheated when handling olefinic feed stocks and mounted on an independent structure; in this case it is desirable to provide means for fairly rapid cooling, such as controlled induced or forced-air circulation. In the production of benzole from saturated gases such as propane or butane the heat absorbed by reaction is approximately 1,000 B.Th.U. per lb. of inlet gas, excluding the heat in preheating the feed to reaction temperature. This figure is materially lower in the case of feed stocks containing unsaturateds because the latter undergo exothermic reactions during the initial stages of the pyrolysis process. To avoid sagging of furnace tubes, these may be mounted vertically and supported only from the top.

The formation of coke and carbon in the furnace tubes may be reduced to that normally met with in cracking plant practice by careful attention to the flow conditions of the gases being treated. Highly turbulent flow and short heating periods are necessary. Values

of $\frac{vD}{\nu}$, where v = gas velocity (cms. /second), D = diameter of tube, cms., ν = kinematic viscosity (stokes), should be at least 10,000–20,000 for efficient heat transfer and to avoid coke deposition. Recycle operation is also favourable with regard to prevention of coke formation.

Various patents cover the use of linings for pyrolysis furnace tubes which inhibit carbon formation. Such linings are effective for short periods, but eventually become coated with a thin layer of carbon and coke, and so lose their efficacy. Similarly, any differences which exist between different furnace-tube materials with regard to catalytic or auto-catalytic effect on carbon deposition disappear after a comparatively short period when the inside of the tube acquires a thin coating of carbon.

Proposals have been made from time to time to employ, as furnace-tube materials for pyrolysis processes, cheap steels, such as mild steel, treated in various ways to give an outside surface of heat-resisting alloy. Such composite materials rarely possess adequate mechanical strength, and often given trouble due to excessive creep.

Coolers and Tar Separators.—The exit gases from the preheat and reaction furnaces must be cooled to a temperature suitable for tar removal and stabilisation. This is conveniently accomplished by injection of cold oil, by heat exchange with the inlet feed to the furnaces or by a combination of atmospheric coolers and conventional water coolers. Tar separation may be effected by flashing into a separator under suitable temperature and pressure conditions or by the use of electrostatic detarrers at temperatures about 100°C.

Product stabilisers follow normal refinery practice.

393. Composition of Residue Gases from Benzole Pyrolysis Processes.—By the treatment of C_3 and C_4 hydrocarbons at pressures of 5–100 lb. /sq. in. and temperatures of 750–900°C. at suitable throughput rates, single-pass treatment is sufficient and recycling can be avoided. Under these conditions the exit gas from the product stabilisers has the following average composition :—[33]

Hydrogen	..	10–25% volume
Methane	..	50–65% ,,
Ethylene	..	20–25% ,,
Ethane	..	0–10% ,,

This gas is a refractory pyrolysis stock, but the ethane-ethylene fraction may be treated in this way after separation, or it may be subjected to polymerisation. The hydrogen-methane fraction constitutes an ideal feed for hydrogen manufacture by well-known processes.

394. Properties of Tars Produced (i.e., Liquids Boiling above 200°C.)—The tars produced in the benzole pyrolysis reaction consist almost entirely of polynuclear aromatic hydrocarbons, napthalene and anthracene predominating, and are solid crystalline masses at ordinary temperatures. They constitute valuable sources of the higher aromatic hydrocarbons, and by destructive hydrogenation may be converted, with good yield, into gasolines of 90–100 octane number having very low freezing points and good blending properties.[33]

395. Work by Other Investigators.—Of the work conducted by other investigators on the production of aromatic hydrocarbons by the pyrolysis of gaseous hydrocarbons, the most important is that reported by H. M. Smith *et al.*,[62] Cambron and Bayley,[63] Stanley and Nash,[23] Frolich and Wiezevich,[29] Podbielniak,[64] and Wagner.[65]

The last named has described the production of liquid aromatic hydrocarbons by rapidly heating olefine-containing gases to 1,100°F. (594° C.) or higher, and then allowing them to rise in temperature due to the exothermic nature of the reaction until a final temperature of 1,200–1,300°F. (649–705°C.) is reached. In this manner it is possible to obtain a highly aromatic distillate from which gasoline having an octane number of approximately 100 can be produced. It is also possible to produce relatively pure aromatic hydrocarbons (benzene, toluene and naphthalene), by simple fractionation after a light acid refining treatment.

Podbielniak[64] conducted pilot plant tests on the pyrolysis of stabiliser gases. The plant used comprised a furnace, having separate convection and radiant sections, a water spray cooler for cooling the pyrolysed gas, a scrubber for the removal of carbon and suspended tar, and a compressor installation for the recovery of the light oils produced. The maximum capacity of the furnace was 25,000 cu. ft. per day. For the optimum yield of benzole and heavier aromatics from gases consisting mainly of propane, outlet temperatures of 1,650–1,700°F. (899–927°C.), were necessary. No details regarding reaction times or space velocities employed are available. The yields of total oils realised ranged from 0·99 to 2·7 U.S. gallons per 1,000 cu. ft. (= 0·825–2·25 Imp. gallons/1,000 cu. ft.).

A gas containing 77·6% CH_4, 6·9% C_2H_6, 10·1% C_3H_8 and 5·4% C_4 +, gave an oil yield of 0·41 Imp. gallons per 1,000 cu. ft. at 899°C.

The published work of Stanley and Nash[23] is concerned entirely with the pyrolysis of methane. Temperatures of 1,000–1,200°C. were employed and the space velocities ranged from *circa* 500 to 10,000. The best yields of higher hydrocarbons were obtained at a temperature of 1,150°C., a reaction time of *circa* 0·6 seconds and a space velocity of

6,400. Under these conditions the best yield of light oil and tar was 11%, which compares well with Hague and Wheeler's figure of 8·8%.

The work of Smith *et al.*[62] is also concerned entirely with methane. The best results obtained, over a temperature range of 1,000 to 1,260°C. (space velocities not stated) averaged 0·3 gallons of light oil plus 0·25 gallons of tar per 1,000 cu. ft. of methane treated. This is approximately equivalent to a 9·8% total oil yield. The light oil contained about 86% benzene, and about 2% of liquid boiling below 73°C.—probably consisting partly of unsaturated hydrocarbons. The tar contained naphthalene, anthracene and pyrene.

Frolich and Wiezevich[29] have described tests on propane at 880°C. in which the maximum oil yield was 3·7 Imp. gallons per 1,000 cu. ft. of gas treated. Of this the yield of light oil was 1·27 Imp. gallons. The corresponding yields of Hague and Wheeler[22] were 3·25 and 2·4 Imp. gallons, respectively. A gas containing 60% propane, 18·6% ethane and 13·4% propylene gave, at 900–960°C., a total oil yield of 1·4–1·5 Imp. gallons per cu. ft., of which 70–75 per cent. boiled below 220°C. and slightly less than 50% of the total product was benzene. The exit gas increased in volume by 60 to 70 per cent. and contained 30–40 per cent. unsaturated hydrocarbons. Frolich and Wiezevich found that increasing pressure caused a change in chemical composition from the aromatic type obtained at substantially atmospheric pressure to a decidedly non-aromatic material resulting from operation at higher pressures.

The work of Cambron and Bayley[63] was also concerned with the treatment of propane. These investigators used temperatures ranging from 350 to 1,046°C., and space velocities from *circa* 280 to 1,230. The best liquid yield was obtained at 950°C. (space velocity *circa* 800), and amounted to 29 per cent. by weight, of which 70% boiled within the gasoline range. By recirculating the exit gas and using turbulent flow conditions approximately the same liquid yields were realised at 800–810°C. The gasoline fraction contained about 64% benzene, 14% toluene, 7·8% styrene and small amounts of cyclopentadiene, xylenes and higher aromatics. The liquids boiling above 200°C. contained about 25% naphthalene and 12·6% anthracene together with smaller amounts of mono- and di-methyl naphthalene, acenaphthene and phenanthrene.

396. The Alco Pyrolysis Process for the Production of Aromatics.—Alco Products, Incorporated, are licensing agents for so-called " Polymerisation " processes developed by the Pure Oil Company, Chicago. One of these processes is, according to the nomenclature adopted in this article, a pyrolysis process, and the products obtained consist primarily of aromatic hydrocarbons. The process has been

described[66] as a high-temperature—low-pressure operation, the conditions being 1,150–1,800°F. (621–704°C.) and pressures of the order of 50–250 lbs. per sq. in. gauge. Feed stocks of a saturated or unsaturated nature may be processed.

A flow diagram of the process is reproduced in Fig. 16. A liquid feed is shown, but a gaseous feed could be handled by substituting compressors for the feed pump. A feature of the process is that the reaction coil is unheated and situated outside the furnace, the operation being the same as that described by Wagner.[65] The exit gases from the reaction coil are suddenly quenched by the recycling of overhead material from the tar separator, and the plant includes conventional product stabiliser equipment and an absorber operating on the residue gas. Recycle material to the furnace is drawn from the reflux accumulator on the product stabiliser.

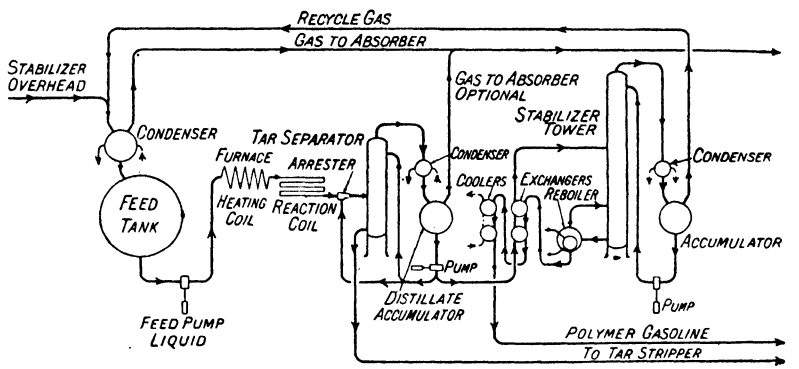


FIG. 16.—FLOW DIAGRAM. ALCO PYROLYSIS PLANT

The yields of distillate obtained by this process are shown in the results reproduced in Table 20. Saturated feed stocks are claimed to behave similarly and give similar products.

Figures included in Table 20 indicate that this process gives a product, the amount of which corresponds closely with the amount of olefines destroyed (i.e., olefines in, minus olefines out). On the other hand completely saturated feed stocks, consisting of propane and butanes, may be satisfactorily handled by this process.

Regarding the products obtained, the octane numbers are high, ranging from 85 to 105 (C.F.R. Motor method). The blending octane numbers in low octane number base spirits range from 105 to 125. The products are aromatic in character and therefore of rather low volatility. Fig. 17 shows a true boiling point distillation curve of the product and also specific gravities and refractive indices of 5% fractions.[67] The benzene content is approximately 30%, and the content of toluene approximately 24%.

TABLE 20. TYPICAL RESULTS OF ALCO PYROLYSIS PROCESS[66]
ONCE-THROUGH OPERATION—NO RECYCLE

FEED	Absorber Residue Gas	Stabiliser Overhead Gas
Properties of feed.		
Sp. gr. (Air = 1)	0·79	1·352
Unsaturateds %	39·4	79·6
Conditions of operation.		
Coil outlet °F.	1265 (685°C.)	1175 (635°C.)
,, ,, lbs./sq. in.	60	55
Residue gas.		
Sp. gr. (Air = 1)	0·72	0·86
Unsaturateds %	29	34·5
Cu. feet per cu. ft. input	0·85	0·46
Distillate produced.		
U.S. gallons/1000 cu. ft.	1·75	9·8
Imp. gallons/1000 cu. ft.	1·46	8·15
Gravity ° A.P.I.	21·6	26·4
Sp. gravity	0·929	0·896
% Boiling to 350°F. (176·7°C.)	76	68
Properties of 350°F. E.P. distillate.		
Octane number (C.F.R. Motor)	102	86
I.B.P. °C.	—	49
10% distillate at °C.	—	78
30% ,, ,, ...	—	88
50% ,, ,, ...	—	96
70% ,, ,, ...	—	107
90% ,, ,, ...	—	131
Final boiling point °C.	—	178
Estimated distillate yield by recycle operation—		
Imp. gallons/1000 cu. ft.	3·3	9·1
Figures calculated from above data.		
Feed.		
Mean molecular weight	22·9	39·2
,, ,, ,, of olefine content ..	28 (assumed)	39·2 (assumed)
Residue gas.		
Mean molecular weight	20·8	25
,, ,, ,, of olefine content ..	28 (assumed)	28 (assumed)
Per 1000 cu. ft. input.		
Olefines in —cu. ft.	394	796
,, —lbs.	29·2	82
Olefines out —cu. ft.	247	159
,, —lbs.	18·3	11·8
Distillate, lbs.	13·6	73·0
Distillate yield, % of olefines destroyed (wht.)	125	104
Distillate yield, % on input (wht.)	22·0	71·0
Estimated distillate yield on recycling as % (wht.) of olefines in change	105	100

397. Thermal Processes for the Polymerisation of Olefines.—The Alco Polymerisation Process.—The most important thermal polymerisation process in use at present is that developed by the Pure Oil Co., Chicago, and licensed by Alco Products, Inc., and recently described by Cooke, Swanson and Wagner,[66] and independently by Wagner.[65] The temperature range employed is 900–1,000°F. (482–538°C.), and the pressure 600–800 lbs. The feed is heated under these conditions in a conventional pipe heater and discharged into a reactor, which is cooled in order to absorb the exothermic heat of reaction, and the products are then chilled by injection of either cold gas or oil. The reaction is normally checked at about 60–70 per cent. conversion per pass, necessitating a recycle ratio of about 1·5 to 1.

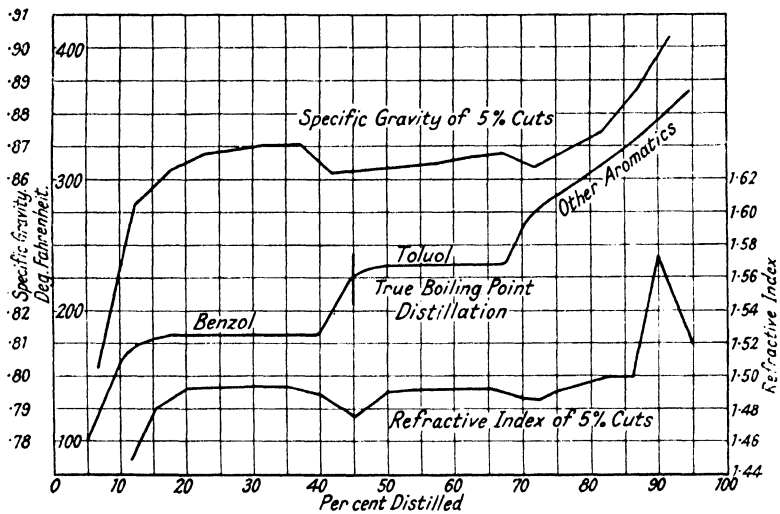


FIG. 17. PROPERTIES OF LIQUID PRODUCT FROM ALCO PYROLYSIS PLANT

A typical flow diagram is shown in Fig. 16. It is usually preferred to operate on a liquefied gas feed, to eliminate methane and ethane from the feed as far as possible, and to concentrate the active olefines (propylene and butylene). Many advantages result from this procedure: (1) lower power costs due to the large reduction in horse power required for the compression of the gaseous feed, (2) reduction in plant capital due to reduction in size of the several pieces of plant equipment as a result of eliminating the inactive gas from the cycle, (3) uniform control of the reaction is simplified. The process of preparing the feed stock consists either in absorbing the higher molecular weight constituents of cracked gas and recovering them from the absorbing medium under high pressure in the liquid state, or in separating and fractionating directly under pressure, this requiring compression of the cracked gas and fractionation of the condensed portion. When

using these methods, the amount of ethylene in the charging stock is relatively small. Typical results obtained in the Alco Thermal Polymerisation process are detailed in Table 21.

The following product properties have been given by Wagner.[65] Octane ratings are referred to again later.

	Condensate	Gasoline
Gravity °A.P.I.	53·7	56·5
Specific gravity	0·768	0·753
I.B.P. °C.	29	33
10% distillate at	43°C.	53
20% ,,	58	63
30% ,,	73	74
40% ,,	86	83
50% ,,	98	94
60% ,,	113	106
70% ,,	126	120
80% ,,	164	138
90% ,,	213	164
Final boiling point	—	203
Residue %	8·7	1·0
Reid Vapour pressure, lb./sq. in. at 100°F.	11·5	10·0
Octane No.		
C.F.R. Research method	—	96
C.F.R. Motor method	—	78

Wagner has described tests on various cracked gases at 600–1,000 lb. pressure and 647–951°F. (342–511°C.).

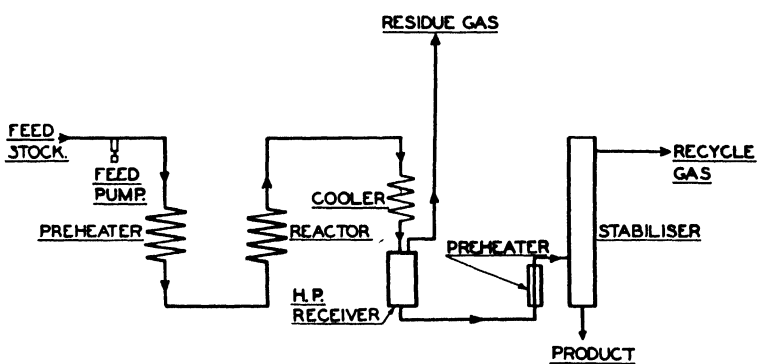


Fig. 18.—Flow Diagram. Semi-Commercial Thermal Polymerisation Plant. Anglo-Iranian Oil Company

398. Work Conducted by the Anglo-Iranian Oil Company.[33]— A flow diagram of the semi-scale plant employed by the Anglo-Iranian Oil Company in their investigations of the non-catalytic polymerisation

process is reproduced in Fig. 18. The feed stocks examined ranged from vapour-phase cracked gases to stabiliser overheads. These were fed to the plant by compressor and pump, respectively, and passed through a preheat coil and reactor in series, and thence to a cooler, high-pressure separator and product stabiliser. The plant designed was capable of operation at temperatures up to 650°C. and at pressures up to 4,500 lb./sq. in., so that the reaction variables could be studied over a wide range.

TABLE 21. TYPICAL RESULTS—ALCO POLYMERISATION PLANT[66]

FEED	Gyro Residue Gas	Liquid Feed
Properties of Feed.		
Sp. gr. (Air = 1)	1·06	1·51
Unsaturateds %	47·2	49·4
Recycle ratio	Once-through operation	1·75
Residue Gas.		
Sp. gr. (Air = 1)	0·87	1·01
Unsaturateds %	18·4	22·0
Cu. feet per cu. ft feed	0·80	—
Liquid Products.		
U.S. gallons/1000 cu. ft. charge	4·4	11·8
Imp. „ „ „ „	3·67	9·83
E.P. Gasoline.		
U.S. gallons/1000 cu. ft. charge	3·7	8·8
Imp. „ „ „ „	3·08	7·33
Gravity °A.P.I.	52·4	55·0
Sp. gravity	0·769	0·759
% of total liquid	84·0	75·0
I.B.P. °C.	35·6	32·2
10% distillate at	57°C.	41°C.
30% „	—	63
50% „	104	83
80% „	150	—
90% „	—	162
Final boiling point °C.	215·6	203
Octane No. (C.F.R. Motor)	–	76
Fuel Oil.		
Gravity °A.P.I.	—	8·0
Specific gravity	—	1·04
U.S. gallons/1000 cu. ft.	0·7	3·0
Imp. gallons/1000 cu. ft.	0·58	2·5
Conversion of unsaturateds to total liquids, %	78·0	86·7
Ditto to gasoline, %	63	—

As in the case of pyrolysis to benzole, it was found that desulphurisation of the feed stock was desirable in order to avoid corrosion and

the fixation of the sulphur in the product in the form of mercaptans and sulphides, with resultant increased refinery difficulties.

It was not found necessary to heat the reactor, in fact, when operating at high conversions per pass, considerable difficulty was experienced in preventing the reactor temperatures getting out of control, and means for sudden chilling were adopted. Careful temperature control was found necessary to avoid the formation of coke. Another factor controlling the amount of coke deposition was the time of reaction. When this was prolonged to get high conversions per pass, coke formation readily occurred, but by limiting the conversion per pass to 60–70 per cent. this was prevented. This necessitates the use of a recycle system if the optimum yields are required, and agrees with the experience of Alco Products Incorporated.

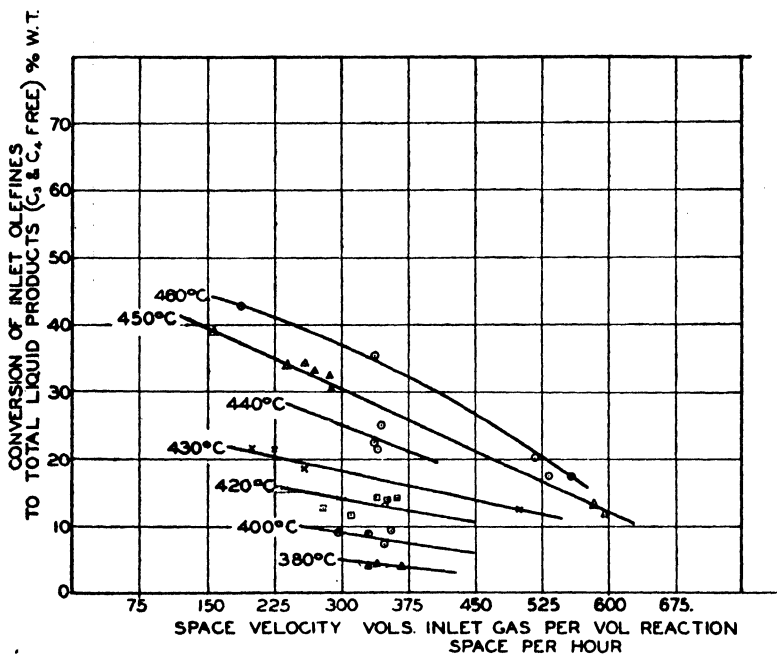


FIG. 19.—THERMAL POLYMERISATION OF STABILISER OVERHEAD. EFFECT OF INLET GAS RATE ON CONVERSION AT 800 LB. PRESSURE (DUNSTAN & HOWES)

A selection of typical results obtained are given in Figs. 19–21. These show the effect of pressure, temperature and reaction time on conversion, and refer to a stabiliser overhead feed stock.

The process is an easy one to operate. The reaction conditions are not unduly critical, and are determined by the nature of the product required and the capital and running costs of the plant. Under optimum conditions, the product contains about 80 per cent. by weight of 200 °C. end-point distillate, the remainder being a residue of little

value as a high-speed Diesel fuel, but a satisfactory stock for cracking or destructive hydrogenation. Unfortunately the gasoline produced

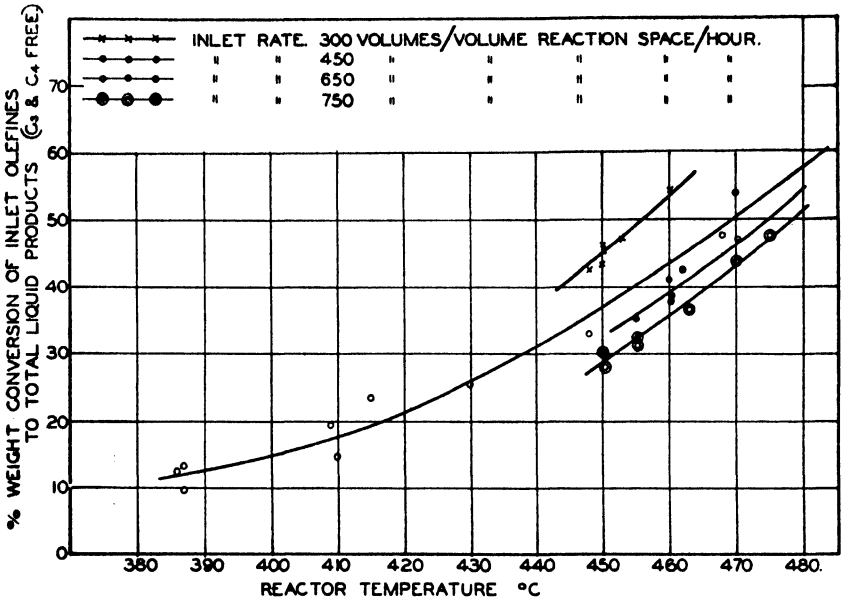


FIG. 20.—THERMAL POLYMERISATION OF STABILISER OVERHEAD. RESULTS OBTAINED AT 1300 LB. PRESSURE (DUNSTAN & HOWES)

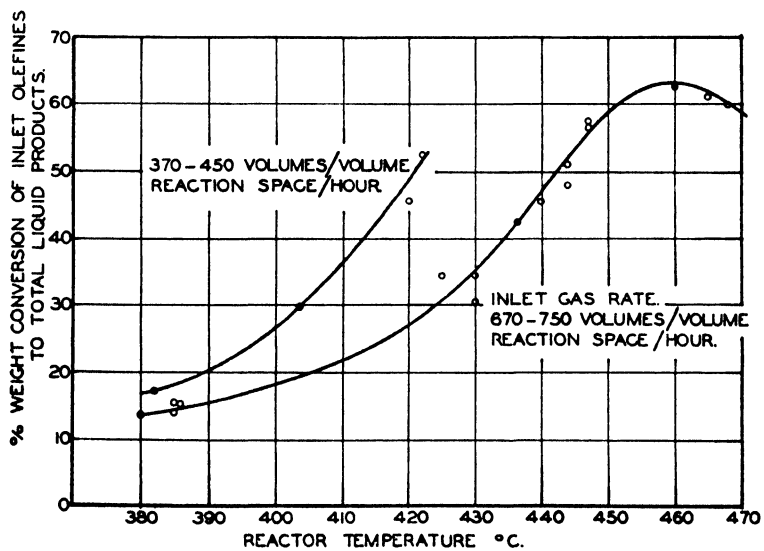


FIG. 21.—THERMAL POLYMERISATION OF STABILISER OVERHEAD. RESULTS OBTAINED AT 2000 LB. PRESSURE (DUNSTAN & HOWES)

under the most favourable conditions is little superior to normal cracked spirit in octane number, and has an optimum value of about

75 (C.F.R. Motor Method) when produced at 480–550°C. and 500–1,000 lb. pressure. In addition the lead responses are poor. At lower temperatures the gasoline octane numbers are lower.

The most important effect of pressure in the thermal polymerisation process is to increase the throughout capacity of a given size plant, but another valuable effect is a reduction in the temperature necessary to effect a given conversion per pass.

399. Typical properties of thermal polymers produced from stabiliser overhead gas at 1,000 lb. pressure and 510°C. are set out in Table 22.

TABLE 22

	Crude Polymer	Crude 200°C. E.P. distillate	Residue above 200°C.
Sp. gr. 60° F.	0·780	0·764	0·985
Initial b. pt. (° C.)	23	27	222
2% distillate at	—	35	—
5% ,, ,, ...	—	46	—
10% ,, ,, ...	60	58	236
20% ,, ,, ...	82	77	250
30% ,, ,, ...	95	91	266
40% ,, ,, ...	100	99	280
50% ,, ,, ...	110	103	297
60% ,, ,, ...	130	114	317
70% ,, ,, ...	150	123	335
80% ,, ,, ...	180	145	—
90% ,, ,, ...	230	178	—
Final b. pt.	320	198	—
% 100° C.	40	41	—
% 140° C.	64	77	—
% 200° C.	84	—	—
% 300° C.	—	—	52
Total distillate	97	98	75
Residue	1	1	25
Loss	2	1	—
Aniline point (°C.)	—	27	Below 15° C.
Bromine number	—	75	20
Freezing point (°C.)	—	Below −70	—
Gum actual mg./100 ml.	—	35	—
Reid vapour pressure at 100°F. ..	—	4·5 lb.	—
Octane number (C.F.R. Motor) ..	—	75	—
,, ,, (C.F.R. Research) ..	—	89	—
Cetene number	—	—	19

The gasoline fractions of thermal polymers produced from cracked feed stocks such as stabiliser overhead fractions, containing both

propylene and butylene, show no improvement in octane number on non-destructive hydrogenation. However, the polymer gasolines may readily be refined to marketable products of satisfactory quality.[33]

400. Combination Pyrolysis—Polymerisation Processes.—Two proprietary processes are in operation involving successive steps of pyrolysis and polymerisation to produce polymer products from saturated gases. When cracked gases are treated by these processes the yields of polymer products are higher than those that would be obtained from the olefine content alone, and it appears definite that, under the conditions employed, cracking of paraffins to olefines takes place at the same time as the olefines are polymerised. The olefines formed by pyrolysis are polymerised and the yield is thereby augmented.

The two processes concerned are :—

(1) The " Unitary " Process of Polymerisation Process Corporation—Licensing Agents, M. W. Kellogg Co.

(2) The " Multiple Coil " Process of the Pure Oil Co., Licensing Agents, Alco Products Incorporated.

401. The " Unitary " Process.—The idea of conducting two distinctly different reactions, governed by different laws, under identical conditions of temperature and pressure, is theoretically not attractive but the results claimed for the " Unitary " processes are of considerable interest, particularly the contention that, under the conditions employed, a certain amount of alkylation, i.e., direct union of paraffins with olefines, takes place.

The process is described in the literature[68] and a simplified flow diagram is reproduced in Fig. 22.

The practicability of the operation was demonstrated by experimental work carried out at the Alamo Refinery of the Phillips Petroleum Company at Borger, Texas, which has been conducted for an extended period. The operating schedule between shutdowns for cleaning varies from 50 to 60 days. The feed stocks which may be handled by the process vary from propane or butane, or any mixture of these, to a complex mixture of C_2, C_3 and C_4 hydrocarbons in which the unsaturated content may be as high as 80 per cent. The flow diagram shown in Fig. 22 is representative, but the gas recovery system, not shown in detail, varies with the type of feed handled and the recycle ratio required. According to the limited information available, the reaction conditions range from 800 to 1,100°F. (427–593°C.) and from 800 to 3,000 lb. pressure.

With regard to the results obtained by this process, in Table 23 are reproduced figures relating to tests made on a pilot plant on a

once-through basis (i.e., no recycle) and on cracked C_3–C_4 feed stocks. It is evident from these figures that the amount of liquid produced is greater than the amount of olefines converted, i.e., some of the liquid produced must have its origin in the paraffins in the feed. Keith and Ward[68] have assumed that, if the paraffins decomposed to give olefines, which subsequently polymerised, the yields of polymer from these paraffins would not be greater than 93·4%, 79·5% and 67·5% of the ethane, propane, and butane, respectively. The figures given in Table 23 for "Potential liquid yield from saturateds" are calculated on this basis. Because the liquid yields actually obtained from the saturated hydrocarbons in the feed are slightly greater than the calculated yields, obtained in this way, Keith and Ward have assumed that alkylation reactions proceed.

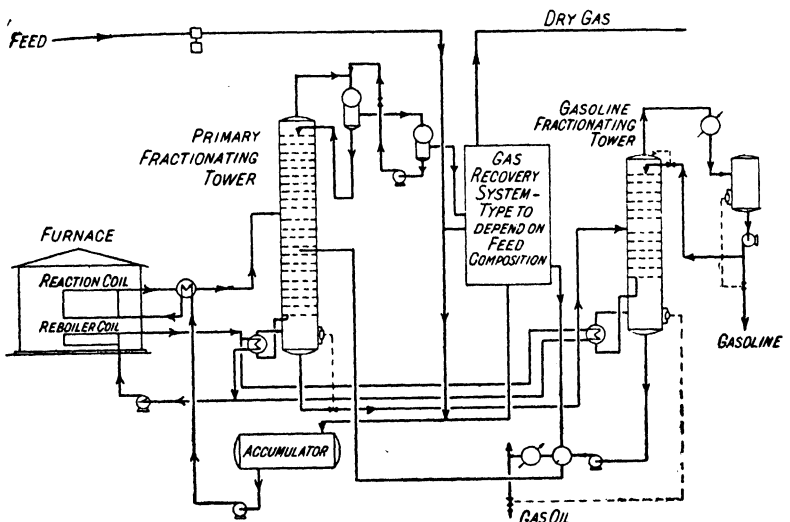


FIG. 22.—FLOW DIAGRAM. "UNITARY" POLYMERISATION PROCESS

This contention is not fully proved by the figures in Table 23. The assumptions regarding the maximum polymer yield from the saturated hydrocarbons are not strictly valid, because the primary or secondary products of the paraffin decomposition would certainly take part in the polymerisation reaction before they had time to be converted into stable lower paraffins. Keith and Ward[68] have also stated that the polymer products contain considerable quantities of *iso*-paraffins, but no evidence in support of this interesting statement has yet been presented.

Results obtained in recycle operation on stabiliser reflux feed are reproduced in Table 24. Of particular interest is the high yield of liquid product obtained, and also the high gasoline content of the liquid

TABLE 23. "UNITARY" POLYMERISATION PROCESS

ONCE-THROUGH OPERATION. PILOT PLANT RESULTS

Run No.	1217-1	1217-2	1217-3
1. *Reaction Conditions.*			
Pressure, lbs./sq. in. gauge	800	800	800
Temp. °F.	800	800	800
Temp. °C.	427	427	427
2. *Feed Stock*, grams/hour	667	635	1327
Analysis, grams/hour			
CH_4	1	1	2
C_2H_6	19	18	37
C_3H_8	170	162	339
C_4H_{10}	85	81	169
C_5+	19	18	39
C_2H_4	5	4	9
C_3H_6	155	148	309
C_4H_8	172	163	342
C_5H_{10}	41	39	81
3. *Liquid Products*, grams/hour	213	211	546
4. *Gaseous Product*, grams/hour	454	424	781
Analysis, grams/hour			
H_2	2	1	2
CH_4	6	5	12
C_2H_6	14	17	13
C_3H_8	120	113	161
C_4H_{10}	68	71	120
C_5+	19	18	39
C_2H_4	5	3	4
C_3H_6	92	79	123
C_4H_8	109	109	228
C_5H_{10}	19	8	79
5. Unsaturated hydrocarbons converted—grams/hour	148	155	307
6. Liquid production as % wht. of olefines converted	144	136	178
7. Liquid required from saturated hydrocarbons—grams/hour	65	56	239
8. Potential liquid yield from saturateds	55	46	197

product. With regard to the extent of decomposition of the paraffin constituents of the feed stocks listed in Table 24, it is noteworthy that the figures given by Keith and Ward for total liquid yield correspond very closely to those which would be obtained if the paraffins decomposed to olefines and these olefines then polymerised (together with the original olefines present in the feed), to give a 90% liquid yield. It can be assumed that all paraffins give a 60% wht. yield of olefines on pyrolysis.

TABLE 24. UNITARY PROCESS. RECYCLE OPERATION ON STABILISER REFLUX AND OTHER SIMILAR FEED STOCKS

Run No.	772	861	903	942	961	1191	—	1792	1803	1754-4
1. *Reaction Conditions.*										
Pressure, lb./sq. in.	800	1200	1200	1200	1200	1200	2200	2200	2200	2200
Temperature, °F.	1000	1000	1100	1030	1020	1035	1100	1050	1037	1025
,, °C.	538	538	593	554	557	593	566	566	558	552
2. *Feed Stock.*										
Net Feed, % wht.							C_2H_6 3·6			
C_3H_8	57	54	36·4	37·1	10·8	58·2	88·8	53	59·4	17·4
C_4H_{10}	—	—	24·3	22·8	75·5	41·2	(Iso) 7·6	47	15·7	59·8
C_3H_6	43	41·1	23·1	20·3	4·8	—	—	—	16·1	4·0
C_4H_8	—	4·9	16·1	19·8	8·9	—	—	—	8·8	18·8
Gross Feed, % vol.							CH_4 1·4			
C_2H_6	12·2	6·8	9·6	6·5	C_2 2·5	—	3·0	—	—	—
C_3H_8	46·3	49·8	38·8	39·6	14·4	—	83·0	—	—	—
C_4H_{10}	4·2	6·2	16·9	17·3	67·5	—	7·2	—	—	—
C_2H_4	3·4	1·9	2·4	2·0	—	—	0·7	—	—	—
C_3H_6	29·6	30·5	21·3	21·0	7·0	—	3·9	—	—	—
C_4H_8	4·3	4·8	11·0	13·6	8·6	—	0·8	—	—	—
3. "Net" Yield, % wht.	67·9	69·0	69·6	64·5	58·2	59·0	56·0	61·2	67·3	70·5
4. "Net" Yield, % wht. of unsaturateds in fresh feed	158	150	177	161	425	—	—	—	—	—
5. U.S. gallons of liquid product per 1000 cu. ft. net gaseous feed ..	12·78	13·10	14·40	13·5	14·29	—	11·7	14·07	13·28	16·1
6. Do., Imp. gallons/1000 cu. ft. ..	10·65	10·9	12·0	11·25	11·91	—	9·75	11·73	11·07	13·4
7. Yield, % wht. 392°F. E.P. gasoline	—	—	—	—	—	—	52·1	59·4	65·1	65·6
8. Theoretical yield calculated as follows:— Liquid yield = % olefines in feed × 0·9 + % paraffins in feed × 0·6 × 0·9	70·2	70·6	69·5	68·4	58·9	53·8	54	54	63·4	62·3

Calculated yield figures, on this basis, are given in Item 8 of Table 24. These do not support the opinion that alkylation reactions occur to any appreciable extent except at the higher pressures.

A recent paper by Frey[110] has shown that, under certain conditions, involving the use of pressures of 4,500 lbs., and temperatures of 505–520°C. (940–968°F.) iso-butane can be made to react with ethylene to give a product containing about 75 per cent. of isomeric hexanes, and similarly ethylene and propane give a product containing isomeric pentanes. At lower pressures polymerisation was evident.

402. Properties of Products.—The properties reported for the products obtained by the Kellogg Unitary Process are summarised in Table 25. The properties of the gasoline fractions vary widely as functions of feed stock composition and operating conditions. The use of a feed stock high in unsaturateds (65–70% by volume) at high conversions to liquid per pass appears to result in a product higher in specific gravity and lower in paraffin content than does one in which the unsaturated content lies between 15 and 35% by volume. Aromatics and mono-olefines appear to be predominant in products from highly unsaturated feed stocks. The material resulting from operation on stabiliser reflux feeds containing 30–38% of unsaturateds has a specific gravity of 0·724 to 0·739 when stabilised to a Reid vapour pressure of 10·5 lbs. Its composition is paraffinic rather than olefinic or aromatic. The products are very volatile, averaging 70–80% by volume boiling up to 100°C. The neat octane numbers (C.F.R. Motor method) are rather higher (79–82) than those normally obtained by olefine polymerisation, but this is no doubt due to the low average boiling point and molecular weight of the " Unitary " products.

403. The Alco Combination Pyrolysis-Polymerisation Unit—i.e., " Multiple Coil " Process.—In contradistinction to the Kellogg "Unitary" Process, the process developed by the Pure Oil Company and Alco Products, Incorporated, for the treatment of both saturated and unsaturated gaseous feed stocks, involves separate pyrolysis and polymerisation steps in separate furnaces and reaction coils, each step being carried out under its own optimum conditions.[66]

For example, in the treatment of a stabiliser overhead gas containing about 30 per cent. of olefinic constituents, the gas is first of all subjected to a polymerisation reaction under the most favourable conditions for the conversion of propylene and butylene to polymer gasoline. In this step the charge—normally available in the liquefied state—is heated to the proper temperature, and enters the reaction coil which is designed to give the required temperature-reaction time effect. Cooling means are provided to keep the temperature within the proper limits. The reaction products, immediately upon leaving

TABLE 25.—PROPERTIES OF PRODUCTS. "UNITARY" POLYMERISATION PROCESS

	Pilot-plant Products Stabiliser Reflux Feed		Comm. Plant Product Butane Feed (Clay-treated)	Total Product Propane Feed 2200 lb. 593°C.	Gasoline Fractions		
	Raw Product	Clay-treated Gasoline Fraction			2200 lb. Pressure 552–566°C. Various Feed Stocks		
Gravity ° A.P.I. ..	65·1	66·5	61·4	64·8	69·9	69·7	66·4
Sp. gravity	0·72	0·7146	0·7335	0·7208	0·7025	0·7032	0·715
Initial boiling point °C.	38	41	35	34	34	38	40
5% distillate at °C. ..	47	49	46	44	45	47	52
10% ,, ,, ..	51	52	49	47	48	49	56
20% ,, ,, ..	57	57	56	50	52	53	63
30% ,, ,, ..	63	61	64	56	56	57	68
40% ,, ,, ..	69	67	73	62	61	62	75
50% ,, ,, ..	73	72	82	68	67	68	82
60% ,, ,, ..	81	78	95	78	74	77	91
70% ,, ,, ..	91	85	109	93	86	88	103
80% ,, ,, ..	108	98	133	117	103	103	119
90% ,, ,, ..	147	126	183	162	134	134	151
95% ,, ,, ..	192	148	218	211	169	169	186
Final boiling point °C.	212	157	232	253	204	199	210
Total distillate, % ..	—	—	—	97	98	98	98
Residue .. % ..	—	—	—	2·5	—	—	—
Loss .. % ..	—	—	—	0·5	—	—	—
% at 392°F. (200°C.) ..	—	—	—	94·5	—	—	—
Reid vapour pressure	10·7	—	—	11·7	—	—	—
Colour (Saybolt) ..	—	30 +	30 +	—	—	—	—
Colour after 8 hours in the sun	—	30 +	—	—	—	—	—
Copper dish gum, mgs./100 ccs. ..	—	10·4	—	—	—	—	—
Induction period (mins.)	—	—	120	—	—	—	—
Ditto after adding 1 lb. B.A.P. gum inhibitor per 100 bbls. ..	—	—	+240	—	—	—	—
Octane number (C.F.R. Motor) ..	—	—	79	—	—	—	—
Ditto, blending value 50% in A.3 reference fuel of 43·6 octane number	92	90	—	91	—	—	—

the coil, are chilled to stop any further reaction, and simultaneously are cooled to a temperature low enough so that heavier products are dropped out in the tar separator. Gases, distillate vapours, and chilling medium forming the overhead from this separator are refluxed for end-point control. The total overhead passes to a cooler and

accumulator where the chilling medium, polymerised distillate, and a portion of the gaseous constituents are condensed. The uncondensed gases and vapours from the accumulator are passed directly to the gas-pyrolysis unit, where the saturated hydrocarbons are cracked to give the optimum yield of olefines.

A portion of the condensate from the accumulator is used as the chilling medium previously referred to; and the remainder, equivalent to the condensed products of reaction, is pumped to the fractionating unit. In this unit the polymer distillate is stabilised to desired specifications, and all gaseous compounds—including excess C_4 constituents not desired in the finished distillate—are taken overhead and form additional feed to the gas-pyrolysis coil.

In the gas-pyrolysis coil the charge as recovered in the primary polymerisation step is heated to a temperature in excess of 1,300°F. A reaction time as short as possible is desired to prevent the unsaturateds once formed from entering into secondary reactions leading to the formation of tar. The products of reaction are chilled to a temperature low enough to liquefy compounds in the fuel-oil and tar range. Gases, distillate vapours, and vaporised chilling oil pass overhead from the tar separator to a condenser and accumulator, where the chilling material is condensed. The gas remaining after compression and cooling is charged to the secondary polymerisation coil, and submitted to a high-temperature—low-pressure reaction. The chilling of the conversion product, tar separation, condensing of chilling medium, is analogous to the method used in the primary polymerisation step. Since the reaction products contain a high percentage of hydrogen and methane, recovery of polymer distillate cannot be effected by condensation under the low operating pressure. Recovery may be accomplished by compression and subsequent condensation. However, in most cases it is believed that absorption is more economical. All polymer distillate distilled from the absorption oil is accumulated and fed, together with the pyrolysis distillate, to the secondary fractionator. The bottoms product from this unit is stabilised to desired specifications, and the light overhead material is passed directly under its own pressure to the primary polymerisation unit as re-cycle.

The bottoms from the various tar separators are combined, heated, and then stripped of all fractions of gasoline boiling range.

A unit of the type described above is very flexible, and gives a high yield of distillate for charging stocks varying widely in composition.

A flow diagram of the Alco Multiple Coil Unit is reproduced in Fig. 23. No details of the products are available, but it may be assumed that the gasolines produced in each separate step are the same as those

produced in the Alco polymerisation and pyrolysis units, respectively. These have already been described.

404. Catalytic Polymerisation Processes.—A recent development of considerable importance is the growth of catalytic polymerisation processes for the production of gasolines and lubricating oils. These are now in commercial operation. The former application is alone considered here.

In general, it may be said that the use of an efficient catalyst enables lower temperatures and pressures to be employed, and as a result of this, secondary reactions by which the polymerised olefines

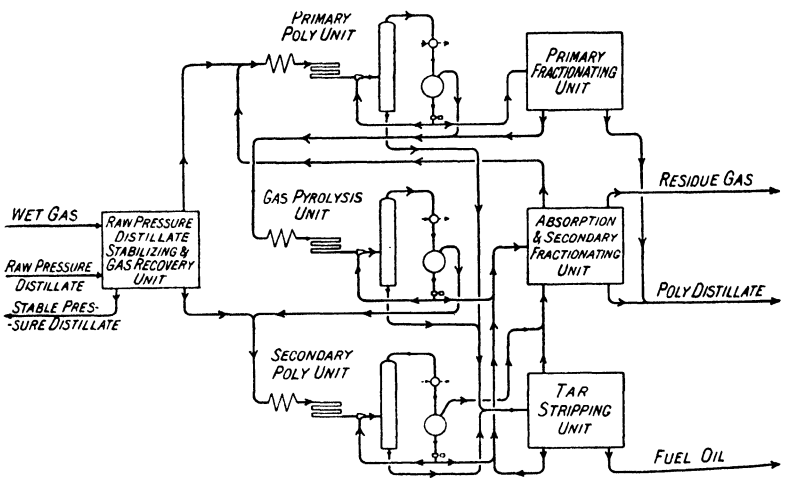


FIG. 23.—ALCO MULTIPLE COIL COMBINATION PYROLYSIS-POLYMERISATION PLANT

are converted into non-olefinic hydrocarbons are often suppressed. On the other hand, some catalysts, particularly aluminium chloride, have pronounced isomerisation activity, and yield products which are predominantly saturated in character.

The action of various polymerisation catalysts is described in detail in the literature, to which reference should be made. A short bibliography is given at the end of this Chapter.

405. Phosphoric Acid as an Olefine Polymerisation Catalyst.—Phosphoric acid is the most successful polymerisation catalyst yet developed, and is the only one known to be in commercial use on a large scale in the production of high octane number polymer gasolines from cracked gases. The development has been carried out by Universal Oil Products Co.,[69] and also independently by the Anglo-Iranian Oil Company.[33]

The polymerising action of the phosphoric acids has been known

for some time, but the application of such substances to the production of higher boiling hydrocarbons from gaseous olefines was probably first mentioned in patents of the I.G. Farbenindustrie bearing application dates between 1926 and 1929.

These make the following claims :—

(1) The polymerisation of olefines under pressure in the presence of salts and oxy-acids of phosphorus, giving as examples calcium phosphate, di-potassium phosphate, calcium pyrophosphate and also phosphorus pentoxide on a pumice support.[70]

(2) Polymerisation of olefines by heat treatment under any suitable pressure in the presence of salts of the oxygen acids of phosphorus, boron and antimony, with alkali metals or other metals as the basic constituent, or their reduction products, or the free acids themselves, in the solid form, or in the form of their anhydrides on carriers.[71]

(3) A process for the polymerisation of lower olefines, which comprises treating the said olefines with catalysts comprising phosphoric acid, metaphosphoric acid or other acids of phosphorus, as such or in the form of their salts, and in a solid or semi-solid state, and operating at temperatures below 400°C.[72]

These patents caused much interest in that they revealed the possible use of salts of phosphoric acid as polymerisation catalysts, and they stimulated further research.

In 1932 a patent[73] was issued covering a process involving the selective polymerisation of propylene and higher olefines in gaseous mixtures containing ethylene, by passing the mixtures at atmospheric pressure over a metallic salt of phosphoric acid at elevated temperatures, e.g., 200°C. The preferred catalyst mentioned was cadmium metaphosphate of the composition CdP_2O_6. The following year a proposal[74] was made to utilise as a motor fuel the mixture of polymers and alcohols obtained by passing a mixture of cracked gas and steam over phosphate catalysts, e.g., boron phosphate, at 200–350°C., and at high pressures, e.g., 30 atmospheres.

Patents by Universal Oil Products on the use of phosphoric acid and phosphate catalysts for the polymerisation of olefines did not appear until May 1934, when several novel features were disclosed. A proposal[75] was made to effect polymerisation of olefines at temperatures between 50° and 200°C. in the presence of an acid selected from the group consisting of orthophosphoric and orthophosphorous acids. Orthophosphoric acid was preferred.

This proposal was followed in 1935 by patents covering the use of so-called " solid phosphoric acid " catalysts, these consisting of solid mixtures of phosphoric acid and various phosphates. Examples of

such catalysts are mixtures of phosphoric acid with a chloride and/or an oxide of an alkaline earth metal,[76] and also mixtures of phosphoric acid with adsorbent materials of a siliceous nature such as kieselguhr.[77] Further patents disclosed the use of catalysts of the above general compositions calcined prior to use at temperatures between 180° and 300°C., without any substantial heating above 300°C.,[78, 83] and also the use of catalysts comprising phosphoric acid, zinc oxide and zinc chloride.[79] The catalytic polymerisation of ethylene, which is normally resistant to the action of the above catalysts, in the presence of readily reacting olefines, is also mentioned.[80]

Recent I. G. patents have included catalysts comprising solutions of an anhydride of an acid of phosphorus in a liquid acid of phosphorus,[81] and also acid esters of phosphoric acid, e.g., monocresyl phosphate, either in the presence or absence of copper or silver salts.[82]

406. The development of phosphoric acid catalysts for polymerisation is very closely connected with the catalytic vapour-phase hydration of olefines to the corresponding alcohols in the presence of steam, for which reaction practically identical catalysts have been proposed. This is evident from the following summary of the most important patents dealing with this reaction :—

E.P. 368,668. J. Y. Johnson and I.G. 1932.
The production of ethyl ether by passing ethylene and steam over phosphate catalysts—particularly phosphates of the rare earths.

E.P. 346,288. G.F. Horsley and I.C.I., Ltd. 1931.
Hydration of acetylene to acetaldehyde and crotonaldehyde by treating with cadmium phosphate catalyst (P_2O_5 : CdO = 0·4–0·6) in the presence of steam.

E.P. 369,216. 1932. I.C.I., Ltd.
Catalyst comprising a phosphate of cadmium, beryllium, zinc, aluminium, tin or lead. The preferred composition of cadmium phosphate is

$$P_2O_5 : CdO = 0{\cdot}9\text{–}0{\cdot}725.$$

Figures are given to show that cadmium phosphate is more active in this reaction than the phosphates of lead, zinc, aluminium or tin.

E.P. 378,865. Appl. date 1932. I.C.I., Ltd.
Catalytic hydration of olefines using boron phosphate catalyst.

E.P. 392,289. 1933. Distillers Company, Ltd.
Catalytic hydration using phosphates of uranium, iron or cobaltous cobalt—the amount of phosphoric acid being in excess of that required to form the orthophosphate, but not in excess of about 95 per cent. of the composition.

E.P. 392,685. 1933. Distillers Company, Ltd.
Catalysts for hydration of olefines—compounded from phosphoric acid and either or both of the metals copper or manganese or their oxides . . . the amount of phosphoric acid present being in excess of that required to form the orthophosphate but not in excess of about 95 per cent. of the composition.

E.P. 394,389. 1933. H. Dreyfus.
Phosphoric acid as a hydration catalyst—initially in the anhydrous condition.

E.P. 396,724. 1933. Distillers Company, Ltd.
Boron phosphate as a hydration catalyst. The amount of phosphoric acid

being at least 10 per cent. in excess of that required to form the orthophosphate, but not in excess of about 95 per cent. of the composition.

E.P. 404,115. 1934. Distillers Company, Ltd.
Catalysts for hydration reactions—containing a drying oil to improve mechanical strength.

E.P. 407,722. 1934. H. Dreyfus.
Alkali and alkaline-earth metaphosphate catalysts.

E.P. 407,944. 1934. I.C.I., Ltd.
Strontium metaphosphate catalyst.

E.P. 408,313. 1934. I.C.I., Ltd.
A catalyst comprising ferric metaphosphate associated with a metaphosphate of a divalent metal—e.g., barium, strontium, cadmium, copper or ferrous iron.

E.P. 408,982. 1934. Distillers Company, Ltd.
The production of *iso*propyl alcohol using a solid catalyst compounded from phosphoric acid with one or more of the metals manganese, copper, iron, cobalt or uranium with or without boron, or their oxides or compounds, the amount of phosphoric acid being in excess of that required to form the orthophosphates, but not in so great a quantity as to depart from the solid nature of the catalyst.

E.P. 413,043. 1934. Distillers Company, Ltd.
A catalyst rendered mechanically stable by incorporating with an organic substance or substances capable of forming true or colloidal solutions in water and which, after subjection to relatively elevated temperatures (of the order of 200°C.) leaves or leave as residue in the catalyst substantially carbon only, e.g., starch, glucose, gelatin, glycerol, etc.

E.P. 415,426. 1934. Distillers Company, Ltd.
Catalysts compounded from phosphoric acid with calcium and/or barium and/or strontium, magnesium, the amount of phosphoric acid present being in excess of that required to form the metaphosphates of the elements employed.

E.P. 415,427. 1934. Distillers Company, Ltd.
Catalysts compounded from phosphoric acid with calcium, barium, strontium and/or magnesium oxides—the amount of phosphoric acid being materially in excess of that required to form the orthophosphate, but materially less than that required to form the metaphosphate.

E.P. 422,635. 1935. Distillers Company, Ltd.
Catalysts rendered mechanically stable by incorporating, during preparation, a non-drying oil such as castor oil, anhydrides, aldehydes, ketones, etc.

E.P. 423,877. 1935. I.C.I., Ltd.
A catalyst consisting of cadmium phosphate together with a small quantity of one or more of the metaphosphates of barium, strontium, titanium, chromium and tellurium.

E.P. 435,769. 1935. I.C.I., Ltd.
Catalysts comprising one or more molecular proportions of aluminium metaphosphate associated with about one molecular proportion of a metaphosphate of calcium, cadmium, zinc, divalent copper, nickel, tin or lead.

U.S.P. 2,052,095. 1936. Distillers Company, Ltd.
Catalysts comprising phosphoric acid and the phosphates of a metal taken from the group *Mn*, *Cu*, *Fe*, *Co* and *Ur*, the amount of phosphoric acid being in excess of that required to form the orthophosphates of the metal or metals selected.

In addition to being similar with regard to catalyst requirements, the processes of catalytic hydration and polymerisation are also closely

similar with respect to optimum temperature and influence of pressure, although the products are different. It has been observed many times in the literature that, in the hydration reaction, if the olefine partial pressure or the total working pressure is increased, the rate of alcohol formation is augmented, but polymer formation becomes troublesome, because this also is favourably affected by increase in pressure. In order to prevent polymer formation and still cause the reaction to occur in the desired direction, it is necessary to increase the partial pressure of the steam and maintain the partial pressure of the olefines at a relatively low value. By this means good yields may be obtained.

The proper choice of catalysts for the vapour-phase hydration of olefines under pressure to form alcohols is a very important factor because, as stated by Marek and Hahn[84] in 1932, " catalysts active in promoting the hydration reaction are likewise active toward promotion of the undesirable polymerisation reactions, since the latter reactions often proceed at a more rapid rate."

The following statement is also made by Marek and Hahn :—

" In contemplating the use of high ratios of steam to olefine in vapour-phase hydrations for the purpose of restricting olefine polymerisation, sight must not be lost of the fact that excessive steam ratios may impair catalyst activity by flooding the active surface with water molecules. For this reason a mean should be struck between high ratios of steam to prevent polymerisation and low ratios to prevent loss of catalyst activity."

407. To complete the comparison between polymerisation and hydration reactions it is necessary also to consider the reverse of hydration of olefines to alcohols—namely, the dehydration of alcohols to the corresponding olefines.

Phosphoric acid has been used for the preparation of ethylene from ethyl alcohol since this use was first discovered by Pelouze.[85] In 1933, Lindinger and Moser[86] found that a mixture of alcohol and phosphoric acid would give off ethylene when heated to 205°C. They concluded that the formation of ethylene was due to the action of the pyro-acid into which the ortho-acid was being dehydrated, and that a more complete conversion would be obtained at a higher temperature. By passing ethyl alcohol vapour over finely divided pumice soaked in phosphoric acid heated to 250–300°C., a yield of 90 per cent. ethylene was obtained, which was 99·5 per cent. pure. At a later date Newth demonstrated that syrupy phosphoric acid heated previously to 200°C. was more efficient than glacial phosphoric acid (meta-acid) or phosphorus pentoxide. Weber and Walton[87] have concluded that orthophosphoric acid previously heated to 250°C. for 4½ hours gave the best yields of ethylene.

It is thus evident that orthophosphoric acid (containing some pyro-acid) is an efficient catalyst for the dehydration of ethyl alcohol to ethylene and also for the hydration of ethylene to ethyl alcohol. In view of the marked similarities between hydration and polymerisation, it is also evident that phosphoric acid should also be a very effective catalyst for the latter reaction—a contention supported by the above-mentioned patents.

408. The choice of suitable phosphoric acid catalysts for polymerisation is helped somewhat by the above patent specifications. Some of these frequently mention the advantages of catalysts containing free, i.e., uncombined, phosphoric acid, whilst others mostly claim metaphosphates containing, presumably, no free acid. It should be noted here that the hydration reaction is invariably carried out in the presence of large quantities of steam, and that the effective catalysts may actually be orthophosphates, or possibly pyrophosphates, or the corresponding acids. The reaction conditions most in favour for the hydration of olefines are as follows :—

Temperature 200–300 °C. Pressure, atmospheric to 2,000 lb. Olefine–steam ratios 1 to 1 up to 3 to 1—but at atmospheric pressure may be as high as 10 to 1.

It may thus be expected that under the same conditions, but in the absence of steam, polymerisation of olefines would proceed at an attractive rate in the presence of a suitable phosphate or phosphoric acid catalyst. As already mentioned, the temperature should be kept as low as possible, to prevent secondary isomerisation reactions which lead to the formation of products of inferior knock-rating.

409. Chemical and Physical Properties of Phosphoric Acids.—There are many acids of phosphorus—differing widely in their physical and chemical properties—some stable and others either volatile or easily decomposed, and it is necessary, in order to produce a catalyst of long active life and a polymer product free of phosphorus compounds, to choose the particular phosphorus acid with some care.

Fortunately, as shown in Table 26, choice is limited to the hydrates of phosphorus pentoxide—namely, *ortho*-, *pyro*- and *meta*-phosphoric acids.

Of these the former is a regular article of commerce, and is cheaper than the *pyro*-acid whilst the *meta*-acid is inactive catalytically (see later).

The most suitable phosphoric acid to employ is therefore *ortho*-phosphoric acid, which may be obtained commercially in the anhydrous state, and in 50 per cent. or in 90 per cent. solutions in water.

The presence of phosphorus pentoxide in polymerisation catalysts is precluded because this substance sublimes at 180–250 °C., and its

vapour pressure may reach 760 mm. at 250°C. At higher temperatures, however, polymerisation of the oxide causes the vapour pressure to fall considerably. Phosphorus trioxide is of little use, because it boils at 175°C. at 760 mm. pressure, whilst phosphorus tetroxide sublimes at about 180°C.

TABLE 26. THE ACIDS OF PHOSPHORUS

Name	Formulae	M.pt. (°C.)	Action of Heat, etc.
Ortho-phosphoric	H_3PO_4 ($P_2O_5 \cdot 3H_2O$)	36·6–42·5	Dehydrates to mixture of meta- and pyrophosphoric acids.
Meta-phosphoric	HPO_3 ($P_2O_5 \cdot H_2O$)	Sublimes	Polymerises to give a polymer of lower vapour pressure.
Pyro-phosphoric	$H_4P_2O_7$ ($P_2O_5 \cdot 2H_2O$)	61	Dehydrates to metaphosphoric acid.
Permono-phosphoric	$H_3P_2O_5$	—	Unstable.
Di-permono-phosphoric	$H_4P_2O_8$	—	Unstable.
Hypo-phosphoric	$H_4P_2O_6$ or H_2PO_3 ($P_2O_4 \cdot 2H_2O$)	(H_2PO_3 55° $+\frac{1}{2}H_2O$ 80° $+H_2O$ 70°)	Phosphine evolved at 180°C. At temperatures above the melting point spontaneously decomposes.
Ortho-phosphorous	H_3PO_3 ($P_2O_3 \cdot 3H_2O$)	70·1–74·0	Evolves phosphine at 140°C.
Meta-phosphorous	HPO_2	—	Reacts with water to form orthophosphorous acid.
Pyro-phosphorous	$H_4P_2O_5$ ($P_2O_3 \cdot 2H_2O$)	—	Reacts with water to form orthophosphorous acid.
Hypo-phosphorous	H_3PO_2	17·4–26·5	Evolves phosphine at 100°C.

As shown in Table 26, *ortho*phosphoric acid is dehydrated by the action of heat to give both *pyro-* and *meta-* acids, both of which are much too volatile for commercial use. The dehydration of *ortho*phosphoric acid may be briefly summarised as follows:

When a dilute solution of orthophosphoric acid is evaporated at temperatures up to 150°C., a syrupy liquid is obtained which consists entirely of orthophosphoric acid and between 150° and 160°C. it loses water slowly.

At 240°C. orthophosphoric acid loses water so that the ratio P_2O_5:H_2O = 1:$2\frac{2}{3}$ to 1:$2\frac{1}{2}$—as compared with 1:3 for pure ortho-acid.

At higher temperatures more water is liberated until a product is obtained consisting mainly of metaphosphoric acid. The literature is not conclusive regarding the minimum temperatures required for the formation of pyro- and meta- acids, but it is generally supposed that the conversion to pyrophosphoric acid is not complete at 230°C.—whereas it is so at 260°C., and that meta-acid begins to form at about 290°C. It is probable that, during the dehydration of ortho-phosphoric acid, there is a state of equilibrium between the three acids—dependent on the temperature and the partial pressure of any water present. Thus dehydration is greatly suppressed by the presence of water vapour. A consequence of dehydration is the formation of lower acids more volatile than the original ortho-acid. Therefore, if dehydration is allowed to occur, greater loss of acid, due to volatility, might be expected, although experimental evidence is at variance with this deduction to some extent.

410. Prevention of Phosphoric Acid Dehydration.—It has been stated[33] that whereas catalysts of the above type are active when prepared from either ortho- or pyro-phosphoric acid, those incorporating the meta-acid are inactive. Furthermore, the activity of all phosphoric acid catalysts diminishes in use in polymerisation reactions unless special steps are taken, and all such used catalysts contain meta-acid (HPO_3).

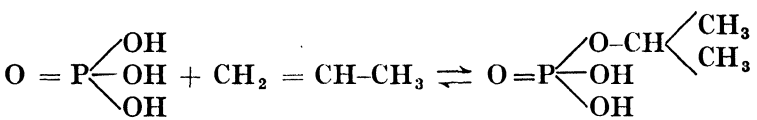
These observations show that, as is to be expected from the above comments on dehydration, the cause of catalyst decline is the formation of meta-acid, and the obvious way to prevent this is the admixture of small quantities of water vapour in the gas before passage over the catalyst. In this way it is possible to keep the water content of the catalyst substantially constant, the amount of water mixed with the inlet gas just compensating for that lost from the catalyst by dehydration. The amount of water required is approximately 2–10 per cent. by volume of the inlet feed, the water being measured in the form of steam. By injecting water or steam in this way catalyst deterioration by the formation of meta-acid is prevented. The amount of water should not exceed the above limits, otherwise alcohol formation is appreciable and often the mechanical strength of the catalyst is impaired.

With catalysts of high free acid content dehydration leads to the formation of large quantities of meta-acid, which change the catalyst from a hard cake to a wet pasty mass.

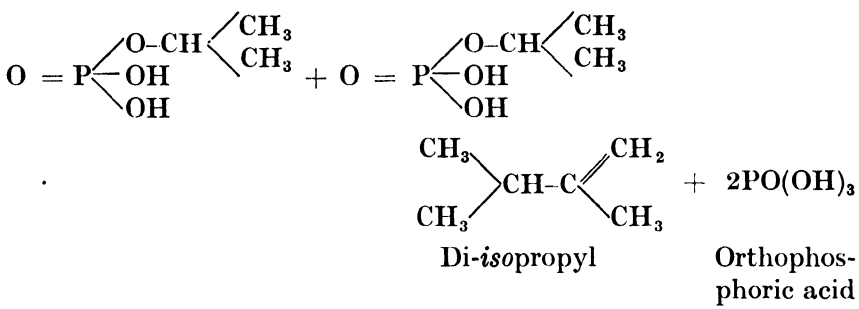
The use of steam to prevent phosphoric acid dehydration has been fully described by Dunstan and Howes,[33] and also by Ipatieff.[88] The scheme is, however, not novel, and was suggested in 1931 for maintaining sulphuric acid catalysts at constant strength at 140–160°C.[89]

411. Formation of Volatile Phosphorus Compounds.—A further consideration with regard to the use of phosphoric acid as a polymerisation catalyst is the possibility of the formation of volatile compounds by interaction of the phosphoric acid with the olefines being treated. This undoubtedly occurs with some phosphoric acid catalysts—particularly with catalysts consisting of phosphoric acid-impregnated active carbons and has also been observed by Sanders and Dodge[90] in the dehydration of ethyl alcohol to ethylene using phosphoric acid as catalyst at 300 °C. In this connection the mechanism of polymerisation suggested by Ipatieff[91] has a direct bearing. Ipatieff[91] postulates the formation of intermediate alkyl phosphates which break down again as soon as formed.

E.g., in the case of propylene, *iso*propyl phosphate is supposed to be formed—thus



which decomposes as follows :—



Di-*iso*propyl

Orthophosphoric acid

Ipatieff has demonstrated that when propylene is heated with phosphoric acid a homogeneous liquid is formed which contains esters such as the above, and that the liquid, on subsequent heating, liberates hydrocarbon polymers. It is believed that some such intermediates must be formed. When a phosphoric acid-active carbon catalyst is employed for the polymerisation of olefines in the presence of small amounts of added steam, to prevent dehydration, the condensed water contains a little free phosphoric acid and a considerable quantity of combined phosphoric acid.

Alkyl phosphates are volatile compounds as shown by the following figures :—

Dimethyl ethyl phosphate	..	B.pt. 203·3 °C.	at 760 mm.
Methyl diethyl phosphate	..	„ 208·2 °C.	„

Triethyl phosphate	..	„	215–216°C. at 760 mm.
Tripropyl phosphate	..	„	138°C. at 47 mm.
Tri-*iso*propyl phosphate	..	„	218–220°C. at 763 mm.
Tri-*iso*butyl phosphate	..	„	135–136°C. at 8–10 mm.

Experience indicates that loss of phosphoric acid from catalysts—presumably due to the formation of volatile phosphorus compounds—is more pronounced in the case of catalysts comprising phosphoric acid on inert carriers such as active carbon or coke than with other catalysts. Furthermore, loss of phosphoric acid occurs only when the concentration of phosphoric acid on the inactive support is more than 20 per cent.[33] The loss of phosphoric acid from catalysts comprising acid cadmium phosphate, kieselguhr and phosphoric acid, etc., is but slight.

412. The Composition of Phosphoric Acid Polymerisation Catalysts.—Of the various materials commonly used in catalyst masses only carbons and cokes have been found unreactive with phosphoric acids at temperatures up to 300°C., although even in the case of these substances there is the remote possibility of reduction of the phosphoric acid to phosphine, especially if the carbon or coke contains any oxides, such as ferric oxide.

When any other materials, such as oxides, aluminates, silicates, carbonates, etc., are mixed with phosphoric acid and heated to give a hard mass, chemical reactions occur to give phosphates. This even takes place in the case of silica, and in this case compounds of the type $(SiO_2)_x(P_2O_5)_y$ are formed—these are probably silicyl phosphates or silico-phosphoric acids and are very stable towards heat.

The literature evidence for the formation of stable compounds between siliceous materials and phosphoric acid is as follows :—

1. Phosphoric acid has practically no effect on glass at ordinary temperatures, but at 100–150°C. the attack is marked and silicyl phosphate and metaphosphates are produced.[92] At 400°C. phosphoric acid has a strong corrosive action on quartz glass.[93]

2. When a dried mixture of gelatinous silica and metaphosphoric acid is fused and extracted with hot water, transparent crystals are obtained, the composition of which corresponds to $SiO_2 \cdot P_2O_5$, which has been considered to be silicyl metaphosphate—$SiO(PO_3)$.[94]

3. Silica dissolves in orthophosphoric acid, and forms crystals of the composition $SiO_2 \cdot P_2O_5$.

Silicates and aluminates react with phosphoric acid as mixtures of the corresponding oxides and give mixed phosphates ; examples of such silicates are pumice and floridin.

The work described in the literature leads to the conclusion that

the catalytic activity of all phosphate catalysts is greatly affected by the presence of free phosphoric acid—probably in the ortho condition. Therefore, unless the acid is present in a quantity more than sufficient completely to combine with the support under the reaction conditions of temperature and water vapour pressure, an inactive, or only weakly active, catalyst is obtained.

On the other hand, the catalyst activity is to a large extent dependent upon the composition of the phosphates present, some being practically ineffective and others very efficient.[33]

There is, of course, a very definite upper limit to the amount of phosphoric acid which can be incorporated in a catalyst suitable for commercial use. As the amount of acid is increased the hardness of the catalyst diminishes, and a definite limit to the acid content is imposed for this reason. In the case of some catalysts, however, total acid contents as high as 75–80 per cent. can be tolerated.

The preparation and properties of phosphate catalysts of many types have been described in detail by Dunstan and Howes.[33] These include a wide range of metal phosphates containing various amounts of free phosphoric acid. As already mentioned, the patents of Universal Oil Products Company pay particular attention to catalysts comprising mixtures of phosphoric acid with the alkaline earth oxides and chlorides, and also with siliceous materials such as kieselguhr.

Typical compositions are as follows :—

(i) 73·7% wht. of 89% phosphoric acid,
6·3% ,, ,, zinc oxide,
10·4% ,, ,, zinc chloride,
9·6% ,, ,, aluminium hydrate.
Calcined at 180–200°C.

(ii) 72% wht. of 100% phosphoric acid,
6% ,, ,, magnesium chloride,
2% ,, ,, alumina,
5% ,, ,, magnesia,
5% ,, ,, starch,
10% ,, ,, kieselguhr.
Calcined at 250°C.

(iii) 82% wht. of 89% phosphoric acid,
18% ,, ,, kieselguhr.
Calcined at 250° C.

413. Regeneration of Phosphate Catalysts.—In use all phosphoric acid or phosphate catalysts become clogged with volatile high-boiling polymers, which, if allowed to stay on the catalyst, cause the

latter to become disintegrated and very soft. In addition to this volatile material, there is also formed on the catalyst a fairly large amount of practically non-volatile asphalt-like material which causes the catalyst volume to increase and also causes caking. This latter material is not so deleterious in its effect as the former, but at least partial removal is necessary after the catalysts have been in use for prolonged periods. A small amount of asphaltic material on the catalyst is beneficial in giving the catalyst greater activity and a higher degree of mechanical strength.

The first step in any regeneration is the removal of the volatile high-boiling polymers which tend to disintegrate the catalyst, and this is readily accomplished by flushing with a stream of nitrogen or flue gas at 300°C. for 4–12 hours. When asphaltic material has accumulated, this is conveniently removed by treatment with flue gas containing small amounts of oxygen at temperatures up to 350°C. In this manner the asphaltic material is removed by oxidation or partial combustion. Care is necessary in this step to prevent the development of local hot spots in the catalyst—otherwise acid is lost by volatilisation.

With regard to the frequency of such regeneration treatments Egloff and Nelson[95] have stated that when approximately 20 gallons of polymer gasoline per pound of catalyst has been produced, treatment with controlled amounts of air is applied to restore activity.

414. Plant Employed.—One of the attractions of the phosphoric acid catalytic polymerisation process is the mild conditions of temperature and pressure employed, and consequently the cheap and simple plant required. The temperatures employed vary from 150° to 300°C. (302–572°F.), and the pressures are normally those at which the gaseous or liquid feed stocks are available—generally 120 to 300 lbs. per square inch.

A flow diagram of a typical installation by Universal Oil Products Co. is reproduced in Fig. 24. The feed is preheated in a conventional furnace to a temperature of 204°C. (400°F.), mixed with the requisite amount of water or steam to prevent catalyst dehydration, and passed through a series of four catalyst towers, each 3ft. 6ins. diameter by 25ft. high, and containing the catalyst. Owing to the exothermic nature of the polymerisation reaction, a temperature rise of *circa* 70°C. (130°F.) occurs in the catalyst towers. The residue gas from the reactors, together with the polymer formed, passes through a condenser to a receiver where lean gas is separated and the polymer condensate is pumped to a conventional stabiliser, where the vapour pressure may be controlled to suit market requirements.

The pipe-work interconnecting the towers is arranged in such a way that any one may be taken off stream for regeneration treatment

and the towers may be used in any order of sequence. The reactivating line shown in the flow diagram is for flushing the catalyst with flue gas and also for treating with controlled quantities of air for burning off asphalt and carbon.

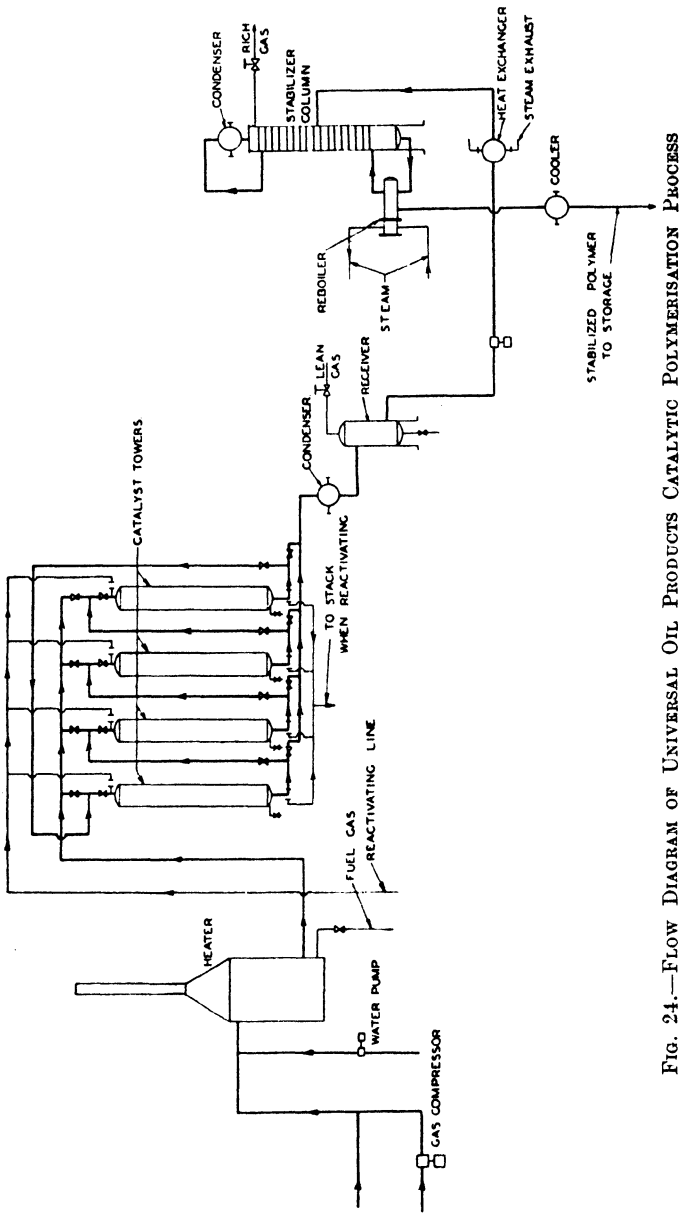


FIG. 24.—FLOW DIAGRAM OF UNIVERSAL OIL PRODUCTS CATALYTIC POLYMERISATION PROCESS

With reference to design figures, it is possible to obtain at least 90 per cent. conversion of olefines to total polymers in continuous

operation with an active catalyst at an inlet gas rate of 2–5 cu. ft. per lb. of catalyst per hour, measured at S.T.P.

An average figure for the 200°C. E.P. spirit content of the crude polymers is 85–90 per cent. by volume. Steam injection should be in amount equivalent to 2–10 per cent. by volume of the inlet gas (measured at N.T.P.).

415. The Polymerisation of Individual Olefines with Phosphoric Acid Catalysts.—Data is available in the literature on the polymerisation of all the lower olefines in the presence of liquid phosphoric acid or solid phosphoric acid catalysts. Of these isobutylene is the most reactive and ethylene the least.

Ethylene.— This has been polymerised under pressure in autoclave experiments in the presence of liquid phosphoric acid at 250–330°C.[96] and also with acid cadmium phosphate catalysts at 300–350°C.[33] Continuous plant tests have also been made using " solid phosphoric acid " catalysts at 520 lbs. pressure and 296–324°C.[97] In the presence of liquid phosphoric acid at 240–330°C. ethylene gives a product consisting of a mixture of paraffin, olefine, naphthene and aromatic hydrocarbons. The concentration of paraffins is greatest in the lowest boiling fractions, but aromatics only appear in fractions boiling above 225°C. Olefines are present in practically all fractions (*circa* 20–30% by volume) and naphthenes in those boiling above 110°C. The products obtained contain 60–65 per cent. by weight of spirit boiling up to 225°C.

An important product of the reaction was isobutane, the formation of which increased with rise in temperature. At 250°C., 2·5 per cent. by weight of the ethylene reacting was converted into isobutane, and at 330°C., 18·8 per cent. The difference between the polymerisation of ethylene in the presence and absence[96] of phosphoric acid consists in the presence of aromatic and paraffin hydrocarbons in the former, whereas no traces of aromatics, and only small quantities of paraffins were discovered in the latter. The first step in the process in contact with phosphoric acid appears to be the formation of ethyl phosphates, which, being unstable at elevated temperatures, decompose to give ethylene polymers and naphthenes (cf., polymerisation in the presence of aluminium chloride). The naphthenes become dehydrogenated to aromatics, and paraffins are formed by the hydrogenation of olefines, i.e., intermolecular hydrogenation and dehydrogenation reactions take place.

The results of continuous plant tests on the polymerisation of ethylene at 520 lb. pressure and 296–324°C. in the presence of a phosphate catalyst are detailed in Table 27. .The high gasoline octane number of 82 is noteworthy.

TABLE 27. POLYMERISATION OF ETHYLENE AT 520 LBS./SQ. IN. GAUGE PRESSURE

	A	*B*	*C*
Operating Conditions.			
Temp. ° C.	296 (565°F.)	324 (615°F.)	324 (615°F.)
Contact time, seconds	790	420	320
Inlet gas rate, cu. ft./hr./lb. catalyst	1·5	2·5	3·4
Ethylene Polymerisation to Liquid Polymer,	73	72	65
Polymer per 1,000 cu. ft. ethylene.			
U.S. gallons	8·0	7·9	7·1
Imp. gallons	6·67	6·6	5·92
200°C. E.P. gasoline per 1,000 cu. ft. ethylene			
U.S. gallons	4·7	4·7	4·6
Imp. gallons	3·92	3·92	3·8
Properties of Crude Polymer.			
Gravity °A.P.I. at 60°F.	48·8	48·7	48·8
Sp. gravity at 60°F.	0·7848	0·7852	0·7848
Initial boiling point °C.	37°C.	42°C.	44°C.
5% distillate at	48°C.	56°C.	61°C.
10% „ „	57°C.	63°C.	70°C.
20% „ „	74°C.	81°C.	87°C.
30% „ „	98°C.	100°C.	104°C.
40% „ „	133°C.	131°C.	127°C.
50% „ „	178°C.	169°C.	157°C.
60% „ „	209°C.	204°C.	184°C.
70% „ „	239°C.	234°C.	211°C.
80% „ „	267°C.	262°C.	241°C.
90% „ „	314°C.	303°C.	279°C.
95% „ „	337°C.	333°C.	311°C.
Final boiling point	340°C.	335°C.	329°C.
Reid vapour pressure at 100°F. (37·8°C.)	8·8	8·3	8·1

Properties of Steam Distilled Polymer.	
Gravity °A.P.I. at 60°F.	76·4
Sp. gravity at 60°F.	0·711
Colour (Saybolt)	30 +
Gum content, copper dish	10 mgs./100 mls.
Ditto + 0·025% wood distillate inhibitor	2 „ „
Octane number (C.F.R. Motor)	82
Blending octane number (25% in Reference Fuel A3 of 44 octane number)	96
Reid vapour pressure	6·5 lbs. at 100°F. (37·8°C.)
Initial boiling point	41° C.
5% distillate at	52° C.
10% „ „	58° C.
20% „ „	66° C.
30% „ „	74° C.
40% „ „	82° C.
50% „ „	93° C.
60% „ „	106° C.
70% „ „	121° C.
80% „ „	142° C.
90% „ „	163° C.
95% „ „	183° C.
Final boiling point	203° C.
Bottoms from Steam Distillation.	
Sp. gravity at 60° F. =	0·897
I.B.P. =	192°C.
F.B.P. =	369°C.

416. Propylene.—Propylene has been polymerised in contact with

liquid phosphoric acid at 204°C. and 51 atmospheres gauge pressure[98] and also at 330–370°C. and 100–40 atmospheres pressure.[99] At the lower temperature propylene polymerises to a liquid consisting almost entirely of mono-olefines, presumably of iso-structure. The liquid boils from 40°C. to 230°C. and is almost entirely gasoline. The evidence for the chemical nature is fourfold. The polymer is practically entirely soluble in 96 per cent. sulphuric acid at 0°C., the bromine numbers of fractions agree with those calculated for mono-olefines,

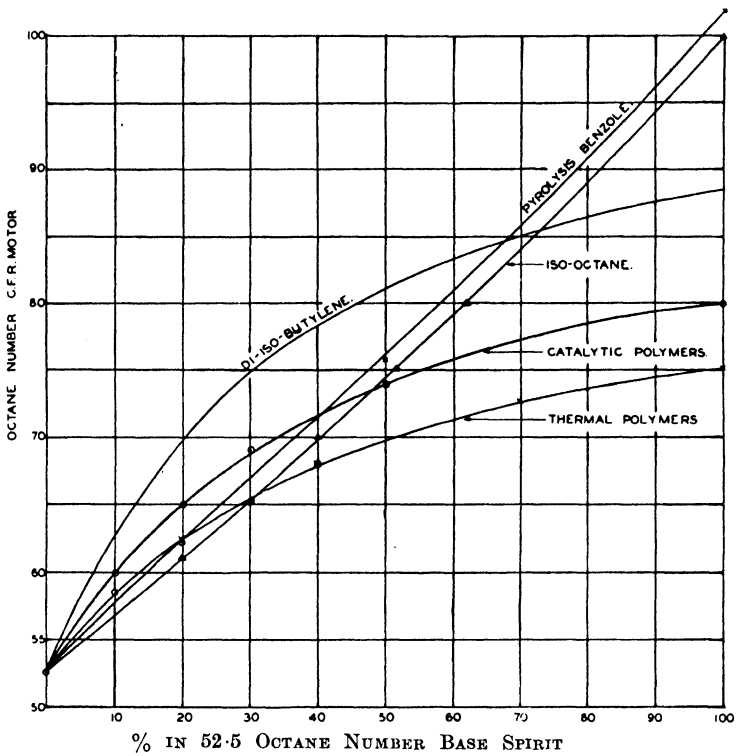


FIG. 25.—OCTANE NUMBERS OF BLENDS OF SYNTHETIC GASOLINES IN 52·5 OCTANE NUMBER BASE SPIRIT

the carbon-hydrogen ratios agree with the formula C_nH_{2n}, and non-destructive hydrogenation yields a product containing only paraffins.

At the higher temperatures (330–370°C.) secondary reactions take place resulting in a liquid product containing only 85 per cent. of unsaturated hydrocarbons. Paraffins are present in the lower boiling fractions (that boiling at 25–63°C. containing 80 per cent. paraffins), but the amount decreases with rise in boiling point. Cyclo paraffins occur in fractions boiling at 155°C. and above, while aromatics are found only in the very highest fractions. The degree of unsaturation

TABLE 28. CATALYTIC POLYMERISATION OF CRACKED GASES

	Residue Gas from Liquid-phase Cracking			Stabiliser Reflux from Liquid-phase Cracking			Stabiliser Overhead Gas from Vapour-phase Cracking			Stabiliser Reflux from Vapour-phase Cracking		
	1	2	3	4	5	6	7	8	9	10	11	12
Properties of Gas Treated.												
Propylenes and butylenes, % ..	17·3	18·6	16·8	37·5	37·5	37·5	43·9	42·6	42·7	70·4	69·2	69·4
Ethylene .. .. % ..	6·6	7·2	7·0	nil	nil	nil	20·2	21·6	21·2	—	—	—
Operating Conditions.												
Pressure, lb./sq. in. gauge	200	200	200	100	100	100	100	100	100	200	200	200
Temp., °C.	204	232	232	204	204	204	232	232	232	204	204	204
Inlet gas rate, cu. ft./hr./lb. catalyst	2·1	1·3	0·5	4·9	3·4	2·1	1·7	0·9	0·3	3·7	2·4	0·8
Olefine Polymerisation.												
Propylene and butylene, % ..	64	79	95	72	81	89	84	94	96	70·4	69·2	69·4
Ethylene .. .. % ..	13	16	31	—	—	—	9	25	32	—	—	—
Polymer Yield.												
Crude polymer :—												
U.S. gallons/1000 cu. ft. ..	2·9	3·8	4·0	6·0	6·9	7·2	7·6	8·5	8·4	12·4	14·2	15·0
Imp. gallons/1000 cu. ft. ..	2·4	3·16	3·3	5·0	5·7	6·0	6·3	7·1	7·0	10·3	11·8	12·3
Gasoline (*circa* 200°C. E.P.) :—												
U.S. gallons/1000 cu. ft. ..	2·7	3·5	3·7	5·4	6·2	6·5	6·3	7·1	7·0	9·7	11·1	12·0
Imp. gallons/1000 cu. ft. ..	2·25	3·9	3·1	4·5	5·2	5·4	5·25	5·9	5·8	8·1	9·2	10·0

of the products obtained from the catalytic polymerisation of propylene is much greater than in the case of thermal polymerisation.

417. Butylenes.—Of the three butenes, isobutylene polymerises the most readily and butene-1 the least, in the presence of liquid phosphoric acid. At 130 °C. the products obtained consist almost entirely

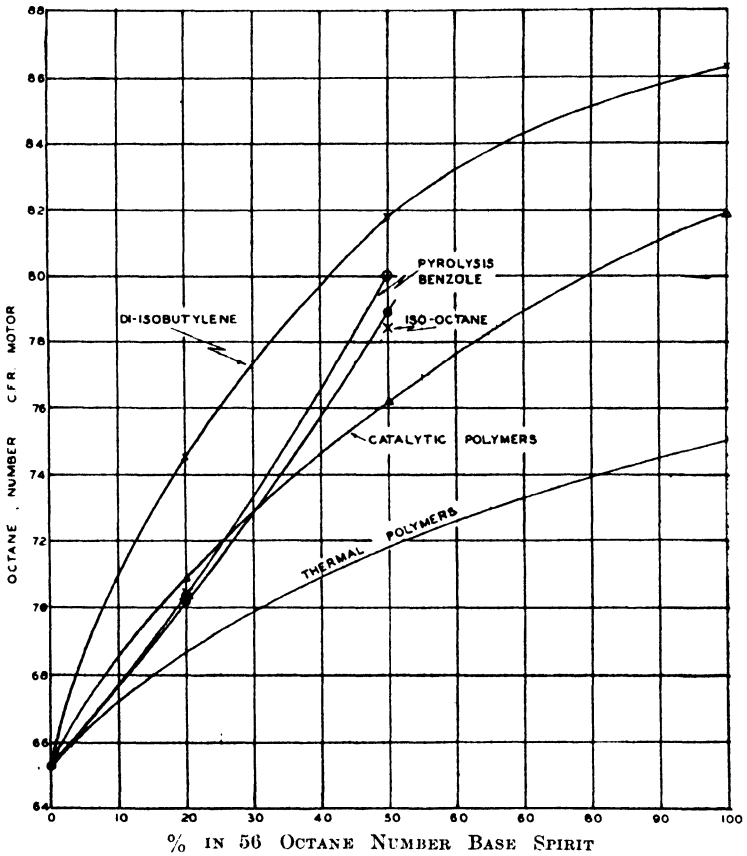


FIG. 26.—OCTANE NUMBERS OF BLENDS OF SYNTHETIC GASOLINES IN 65 OCTANE NUMBER BASE SPIRIT

of mono-olefines but the mixture is very complex. By reducing the polymerising temperature the complexity of the product is reduced, and at 30 °C. isobutylene gives a product containing only di-isobutylene and tri-isobutylene. It has been observed that butene-1 and butene-2 are polymerised much more readily in the presence of isobutylene than in its absence. Similarly, the butylenes exert a promoting effect in the polymerisation of propylene. The butylenes undergo isomerisation in the presence of phosphoric acid.[100]

418. Results Obtained on Cracked Gases.—Much information has been published by members of the staff of Universal Oil Products Co. concerning the polymerisation of cracked gases and their fractions, using catalysts of the type described above. The data summarised in Table 28 is typical of the results obtained on lean residue gas, stabiliser overhead and stabiliser reflux. The yields of polymers mentioned in Table 28 should be compared with the theoretical figures given in Fig. 14.

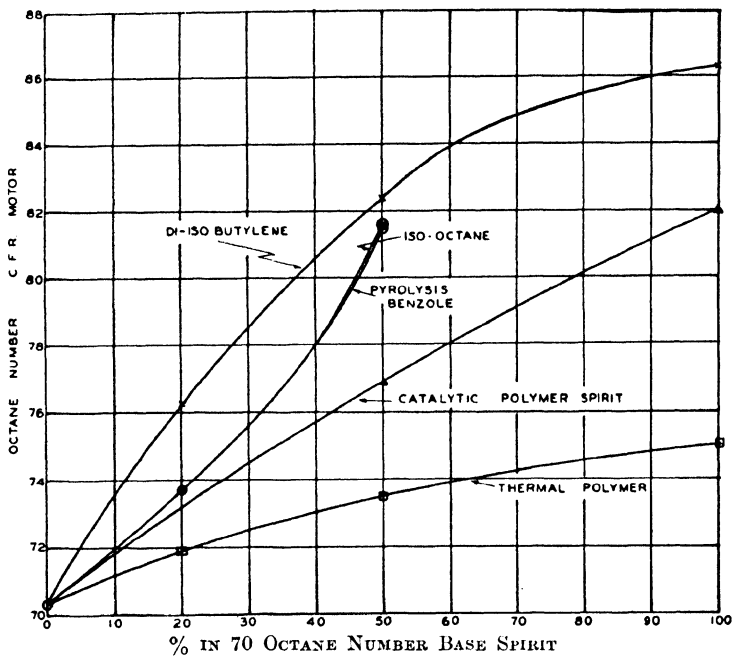


FIG. 27.—OCTANE NUMBERS OF BLENDS OF SYNTHETIC GASOLINES IN 70 OCTANE NUMBER BASE SPIRIT

419. Properties of Products.—It has previously been stated[33] that all phosphoric acid or phosphate catalysts, operating under the same conditions, give essentially the same product; the gasoline fractions are also of the same octane number (i.e., 78–82 C.F.R. Motor method). True boiling-point distillation curves of the products obtained from feed stocks containing both propylene and butylene show no decided flats corresponding to pure compounds, but, on the other hand, catalytic polymers obtained by the treatment of cracked C_4 fractions under mild conditions consist mainly of dibutenes and tributenes.

The anti-knock blending value of catalytic polymer spirit is of particular importance. In Figs. 25–27 are plotted the C.F.R. Motor

Method octane numbers of this material and other synthetic gasolines in three different base spirits.[33] The blending value of any polymer spirit expressed in terms of " blending octane numbers "* is naturally greatest in base spirits of low octane ratings, and Fig. 28 shows how the blending octane numbers of catalytic polymer spirit range from

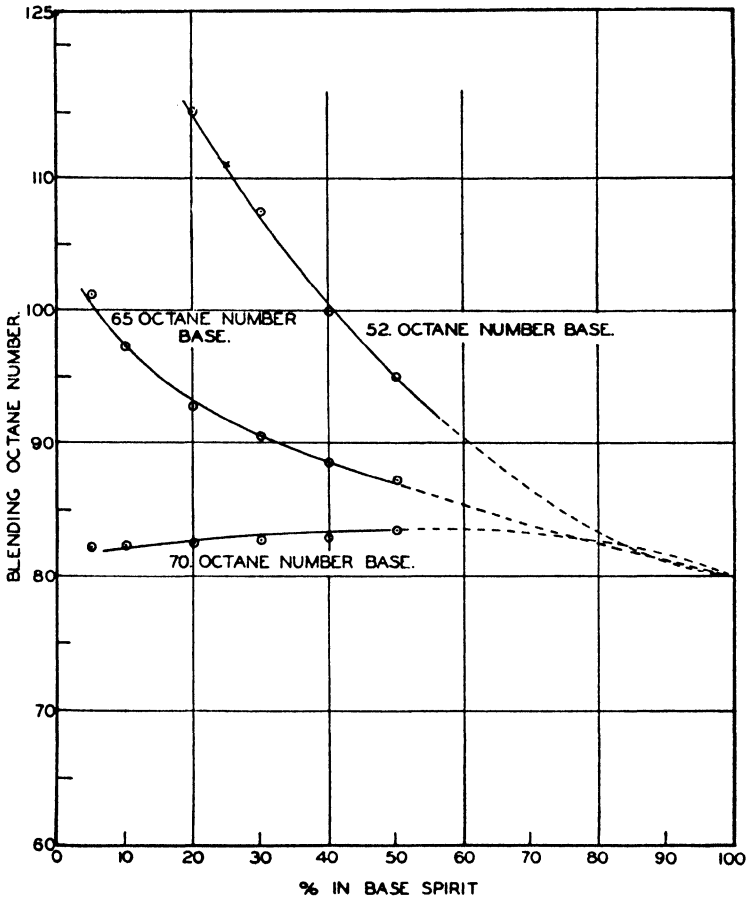


FIG. 28.—BLENDING OCTANE NUMBERS OF CATALYTIC POLYMER GASOLINES IN VARIOUS BASE SPIRITS

125 to 82 according to the nature of the base spirit and the concentration of polymer spirit used. The octane numbers of fractions

* The " blending octane number " of a spirit is calculated as follows:
Octane number of blend = Octane number of base × Concentration + Blending octane number of added spirit × Concentration. E.g., if a 50/50 blend of base spirit and a polymer spirit has an octane number of 74 and the base spirit alone has an octane number of 52·5, then the " blending octane number " of the polymer spirit at this concentration is given by:

$$74 = (52{\cdot}5 \times 0{\cdot}5) + (\text{Blending octane number} \times 0{\cdot}5)$$

$$\therefore \text{Blending octane number} = \frac{74 - 26{\cdot}25}{0{\cdot}5} = 95{\cdot}5$$

of catalytic polymer spirits show little variation with boiling point, as shown in the following figures referring to material produced from reflux liquid using granular acid cadmium phosphate catalyst :—

Fraction b. pt. (°C.)	C.F.R. Motor Method Octane Numbers		
	Neat	30% in 52·5 octane no. base spirit	70% in 52·5 octane no. base spirit
25–50	—	70·4	89·6
50–75	83·2	69·8	78·7
75–100	81·9	71·2	79·3
100–125	81·9	72·2	78·9
125–150	80·8	72·2	78·5
150–175	82·3	70·5	79·0
175–200	80·6	69·6	78·4
200–225	80·2	68·2	78·5

The octane number of the spirit produced from a cracked C_4 fraction is 78–82 and does not change from this value if the *iso*butene content of the feed (25 per cent. by volume) is removed prior to catalytic polymerisation.

Details of the properties of typical polymer products are given in Table 29.

420. The Refining of Catalytic Polymer Gasoline.—Polymer gasolines produced from desulphurised cracked gases using phosphate catalysts are normally suitable for the American market after re-running to the desired end-point and the addition of the requisite amount of gum inhibitor. To mask the slightly yellow colour, dyes are often added as well.

Conclusions arrived at as a result of refining tests may be summarised as follows :—

1. 200°C. E.P. distillates from the crude polymer are practically water-white, but very unstable to normal gum tests. A finished spirit of specification gum content and gum stability suitable for the English market has not been produced by the normal acid treatment applied to the total polymer. The potential gum content of the polymer spirit increases rapidly with boiling point.

2. 200°C. E.P. distillates from crude polymer spirit may be stabilised against gum formation to an extent satisfactory for normal conditions by the addition of inhibitors.

3. Blends of crude polymer with normal cracked spirit can be refined to give a finished product of good colour and gum stability by conventional acid treatment followed by redistillation and final neutralisation. The amount of acid required is very small.

TABLE 29. PROPERTIES OF TYPICAL CATALYTIC POLYMERS (PHOSPHATE CATALYSTS)

Feed	Stabiliser Reflux"	Cracked C_4 Faction"	Residue" Gas	Stabiliser Reflux"
Crude Product.				
Sp. gr. 60°F.	0·750	0·750	0·734	0·750
Reid vapour pressure at 100°F. ..	—	—	8·5	9·5
% distillate to 200°C. (392°F.) ..	82	83	*circa* 90	*circa* 80
Gasoline Fraction.				
Sp. gr. at 60°F.	0·750	0·740	0·732	0·738
I.B.P. °C.	44	27·5	57	61
10% distillate at	84	81·5	90	90
20% ,, ,, ...	96	111	100	102
30% ,, ,, ...	102	120	107	112
40% ,, ,, ...	115	125	114	122
50% ,, ,, ...	125	130	120	130
60% ,, ,, ...	136	144	127	140
70% ,, ,, ...	154	172	138	151
80% ,, ,, ...	168	185	151	162
90% ,, ,, ...	181	192·5	169	182
F.B.P. °C.	198	197	205	212
Loss %	2	4	—	—
Aniline point °C.	38	41	—	—
Colour, Saybolt	—	—	30	25
Octane No. (C.F.R. Motor) ..	80–82	82	82	82
Gum content (Copper dish), mgs./100 ccs.	—	—	5·0	72
Do. + 0·025% wood distillate inhibitor	—	—	—	0·02
Residue Fraction.				
Sp. gr. 60°F.	0·858	0·872		
I.B.P. °C.	215	222	—	—
10% distillate at	229	235	—	—
20% ,, ,, ...	234	240·5	—	—
30% ,, ,, ...	239	245·5	—	—
40% ,, ,, ...	243	250	—	—
50% ,, ,, ...	251	255	—	—
60% ,, ,, ...	260	262	—	—
70% ,, ,, ...	277	270	—	—
80% ,, ,, ...	305	286	—	—
90% ,, ,, ...	—	314	—	—
F.B.P.	348	320	—	—
% distillate at 300°C.	78	86	—	—
Aniline point °C.	47	53·8	—	—

Alternatively, the crude polymer may be fed to the cracking plant primary tower as reflux—in which case the polymer bottoms pass to

cracking stock and the polymer spirit is blended with cracked distillate for refining. The polymer bottoms crack readily to give a spirit of 80 octane.

Catalytic polymer bottoms (i.e., the fraction boiling above 200°C.) is at the moment of little use as a Diesel fuel, the cetene number being only about 35, and is obviously better employed as a depolymerisation stock.

421. Selective Catalytic Polymerisation.—A recent development is the catalytic polymerisation, using phosphate catalysts of the types referred to above, of C_4 fractions containing considerable amounts of isobutylene, whereby di-isobutylene and tri-isobutylene are produced. These, when hydrogenated under non-destructive (i.e., reducing) conditions, give iso-octanes and iso-dodecanes of *circa* 95–100 octane number, which are valuable constituents of aviation fuels, being saturated in chemical nature and gum-free.

It is not feasible to fractionate di-isobutylene from catalytic polymers produced from feeds containing ethylene and propylene in addition to isobutylene, because in this case the yield of di-isobutylene is low and its recovery uneconomic. The reason for this is that the isobutylene condenses with the lower olefines to give products other than di-isobutylene which do not give 100 octane number products on hydrogenation.

422. A Comparison of the Processes now available for the Production of Synthetic Gasolines from the Gaseous Hydrocarbons.—The processes described above for the production of synthetic gasolines from waste petroleum gases vary in their applicability and in the nature of the products they give. For the treatment of paraffinic gases containing no olefines there are four alternatives.

1. Pyrolysis to aromatics, e.g., the Alco Pyrolysis Process.
2. Pyrolysis to olefines, followed by polymerisation, these steps being carried out separately, e.g., the Alco Multiple Coil Process.
3. Simultaneous pyrolysis–polymerisation, e.g. the Kellogg Unitary Process.
4. Dehydrogenation to olefines followed by polymerisation.

Of these the only one not yet fully developed is No. 4, of which the dehydrogenation process is still in the experimental stage.

For the treatment of the olefine constituents of cracked gases, the following processes are available :—

1. Pyrolysis to aromatics, e.g., Alco Pyrolysis Process,
2. Thermal polymerisation, e.g., Alco and Kellogg Processes,
3. Catalytic polymerisation, e.g., U.O.P. process,

while the paraffin constituents of cracked gases may be handled by the processes listed above.

The gases amenable to treatment by these operations include ethylene and the higher gaseous olefines, and the paraffins propane and butane. No satisfactory methods for the treatment of methane and ethane are yet available, although active development work is in progress.

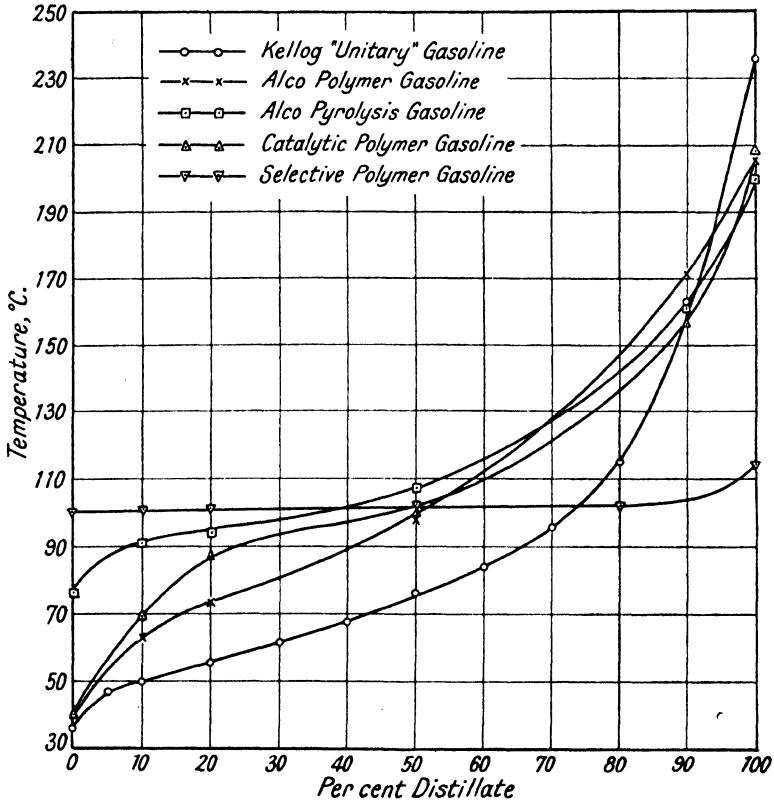


FIG. 29.—DISTILLATION CURVES (A.S.T.M.) OF PYROLYSIS AND POLYMERISATION GASOLINES

The greatest yields obtainable from a cracked or straight-run gas are realised by suitable combinations of dehydrogenation and catalytic polymerisation processes.

The products obtained by the various processes are compared, with respect to distillation range and anti-knock values, in Figs. 29–31.[101]

423. Hydrogenation of Catalytic Polymers.—The hydrogenation (i.e., reduction) of catalytic polymers to give saturated paraffinic materials is of considerable importance in view of the possible produc-

tion of materials similar to iso-octane, which is obtained by the hydrogenation of di-isobutylene.

As the result of experimental work in this connection[33] the following conclusions have been arrived at :—

1. Polymer spirit produced from cracked butylene feed, containing up to 20 per cent. *iso*butylene, is considerably improved by catalytic

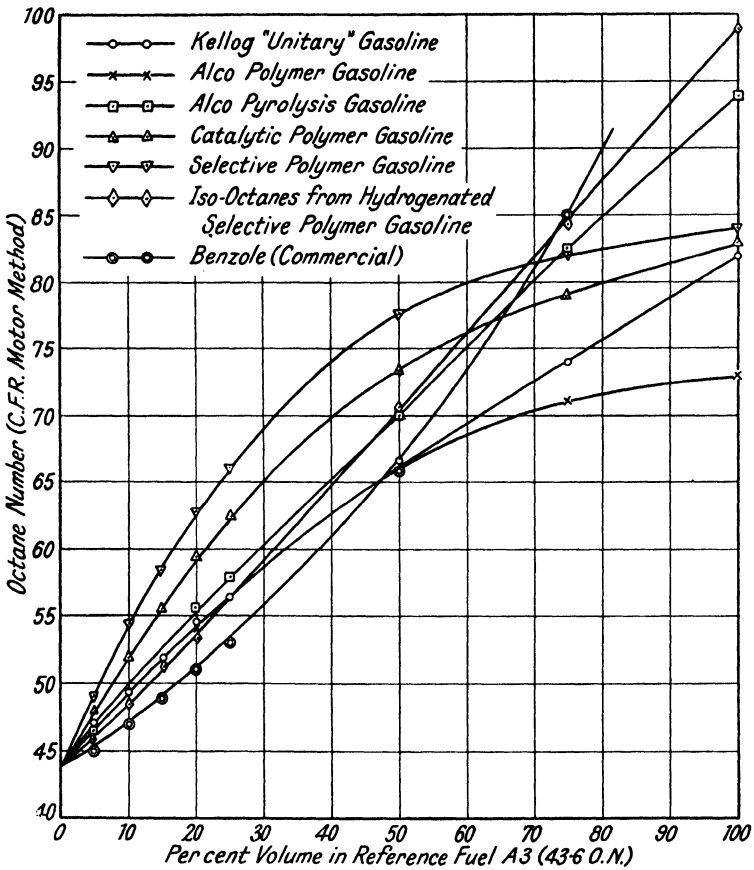


FIG. 30.—OCTANE NUMBERS OF BLENDS OF SYNTHETIC GASOLINES IN A3 REFERENCE FUEL

reduction—the octane number increasing from 80–82 to 95–100. The reduced spirit is absolutely gum stable, and constitutes an aviation fuel component of excellent quality.

2. Polymer spirit produced from cracked butylene feed, from which the *iso*butene content had previously been removed, was reduced in the presence of a suitable catalyst at 200–240 °C. and super-atmospheric pressure. By this treatment the neat octane number (C.F.R. Motor method) fell from 80·7 to 74·5.

3. Polymer spirit produced from stabiliser C_3–C_4 overhead (containing 8–10 per cent. *iso*butylene) at 150–200° C. was reduced and the octane number remained substantially constant (initial value 80·8; final value 80·4). The octane numbers of corresponding blends in base spirits fell considerably after reduction.

4. No appreciable improvement in octane rating can be achieved by hydrogen reduction of *fractions* from polymer spirit obtained by

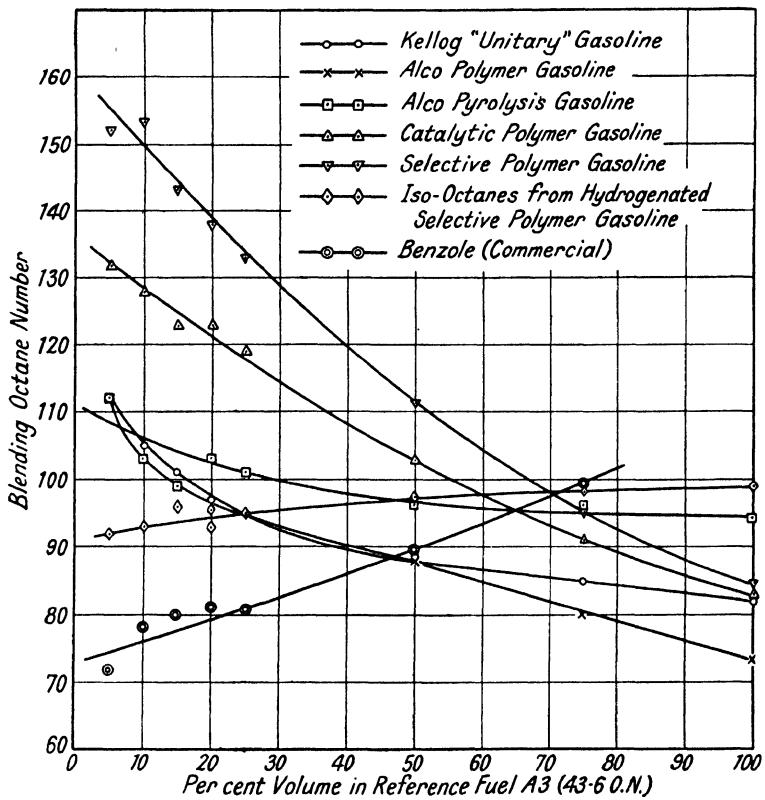


FIG. 31.—BLENDING OCTANE NUMBERS OF SYNTHETIC GASOLINES IN A3 REFERENCE FUEL

polymerisation of feed stocks containing both C_3 and C_4 olefines. The di-*iso*butylene fraction present in such polymers is very small and its isolation is definitely uneconomic.

It is evident that the only reasonable method of producing dibutenes by catalytic polymerisation, capable of being reduced to 100 octane material, is to treat a C_4 fraction rather than a C_2–C_3–C_4 mixture. In the latter case the C_4 components condense with both C_2 and C_3 hydrocarbons and the yield of dibutenes is therefore reduced.

424. Di-isobutylene and Iso-octane.—A recent development of

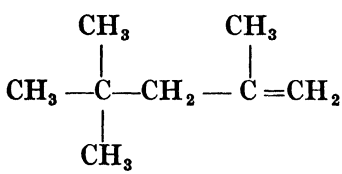
considerable importance is the polymerisation of isobutylene to di-isobutylene in the presence of sulphuric acid and the hydrogenation of the polymer to iso-octane.

Various catalysts have been proposed for the polymerisation of isobutylene; these include adsorbents and the inorganic halides such as aluminium chloride and boron trifluoride. When the lower polymerides are required, however, polymerisation is most conveniently effected by acid catalysts, either in the liquid phase, e.g., sulphuric acid, or in a supported form, e.g., orthophosphoric acid on charcoal.

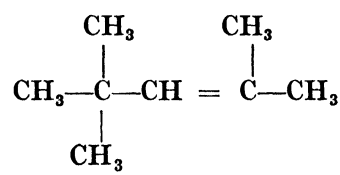
Numerous investigators have examined the reaction of isobutylene with sulphuric acid, and considerable quantities of di-isobutylene are now being produced by this method.

The reaction with sulphuric acid in the liquid phase takes place in two stages, absorption of the isobutylene with subsequent hydration to tertiary butyl alcohol being followed by dehydration and polymerisation. As the acid employed must be capable of promoting each of these several reactions, its concentration is obviously an important consideration. In the case of phosphoric acid polymerisation proceeds smoothly at 30°C. to give di- and tri-isobutylenes, but at higher temperatures the product becomes increasingly complex.

Little is known concerning the chemical composition of isobutylene polymers, although di-isobutylene is known to consist of two isomers, 2-2-4 trimethyl-pentene-1 and 2-2-4 trimethyl-pentene-2, the former being present in greater amount in the ratio 4 : 1.[103]



2-2-4 trimethyl-pentene-1



2-2-4 trimethyl-pentene-2

The properties of these isomers are as follows[104]:—

	B.P. at 760 mm. (Corrected)	d_4^{20}	n_D^{20}	Freezing Point °C.
2-2-4 trimethyl-pentene-	1101·2	0·7151	1·4082	— 93·6±0·1
2-2-4 trimethyl-pentene-2	104·5	0·7211	1·4158	—106·5±0·1

425. Isobutylene Absorption in Sulphuric Acid.—In the production of di-isobutylene from isobutylene by the use of sulphuric acid the following factors are important. While acids of medium concentration effect ready hydration of the olefine, stronger acid results in, immediate polymerisation accompanied by charring and consequent fouling of the acid. This is undesirable in any plant in

which the acid is continuously regenerated and recirculated. Furthermore it is necessary to limit the strength of the acid employed so that it does not react with hydrocarbons other than isobutylene, otherwise butyl sulphuric acid accumulates in the acid and the product becomes contaminated with secondary butyl alcohol and di-*sec*-butyl ether. Fortunately isobutylene is by far the most reactive of the C_4 olefines, as shown by the following figures of Davis[105] calculated from the data of Michael and Brunel.[106]

Olefine	Acid Concn. %	Temp. °C.	Absorption Coeff. K
Isobutylene (pure)	58·6	28–29	105×10^{-3}
„ (51·8%)	58·6	28–29	75×10^{-3}
2-Butene (pure)	58·6	28–29	$0{\cdot}54 \times 10^{-3}$
„ „	76	29–30	$10{\cdot}0 \times 10^{-3}$
1-Butene (pure)	76	29–30	$5{\cdot}0 \times 10^{-3}$

Butadiene is absorbed by 63 per cent. sulphuric acid at a rate intermediate between that of isobutylene and the normal butenes.[107] It is evident, therefore, that if an acid concentration is chosen such that the rate of absorption of *n*-butenes is low, the product should be substantially free from compounds derived from the normal butenes. It is possible, however, to identify traces of these products in crude di-isobutylene, e.g., 2-2-3 trimethyl-pentene and di-*sec*-butyl ether.

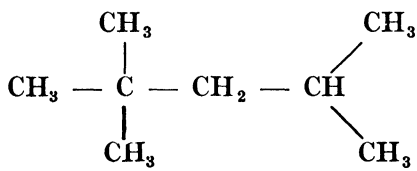
In commercial operation the strength of the sulphuric acid employed is generally 55–65 per cent. Higher strengths of acid give rise to the formation of appreciable quantities of the trimeride and higher polymers. The temperature of operation is preferably maintained at below 100°F., at which temperature, in the presence of 65 per cent. sulphuric acid, there is a tendency for di-isobutylene to be formed and carried away in the effluent hydrocarbon layer. The time of contact necessary is determined by plant considerations, but should in all cases be sufficiently long to enable equilibrium to be attained between the hydrocarbon and acid layers. The absorption reaction is markedly exothermic and is best conducted in a countercurrent continuous system.

426. Polymerisation.—The acid-alcohol mixture leaving the absorption vessel contains, in addition to sulphuric acid, water and tertiary-butyl alcohol with a small amount of hydrocarbons in solution. It is passed to a polymerising vessel and heated until polymerisation is complete, and the crude di-isobutylene layer formed is then withdrawn. Since the decomposition of the alcohol must regenerate completely the water consumed in its formation, it follows that when

polymerisation is complete the concentration of the recovered acid should be identical with that originally fed into the absorption plant. Actually there is a slight loss of water from the system due to the escape of very small amounts of tertiary butyl alcohol in the product.

In the polymerisation step a temperature of 69–90°C. is suitable, but the acid strength is again important in this stage as often the regeneration of isobutylene occurs. This, however, is negligible when 55 per cent. acid is employed, and the product normally formed under these conditions contains approximately 80 per cent. of the dimeride and 20 per cent. of the trimeride.

427. The Hydrogenation of Di-isobutylene to Iso-octane.—The preparation of iso-octane (2-2-4 trimethyl-pentane) by the hydrogenation of di-isobutylene using a nickel catalyst was first described by Edgar,[108] who suggested its use as a standard reference fuel for anti-knock measurements. Both isomers present in di-isobutylene hydrogenate to give the same product *i.e.*, 2-2-4 trimethyl-pentane.



which has the following properties:

Boiling point	99·37°C.
Freezing point	− 167·6°C.
Sp. gravity 20°/4°	0·6920
Refractive index 20°/D ..	1·3915

No published information is yet available concerning the production of iso-octane on a large scale, although sulphur-resistant catalysts, such as tungsten sulphide, have been claimed as being suitable.[109]

Typical properties of commercial di-isobutylene and iso-octane are given in Table 30.[33]

428. Isopropyl Ether.—Isopropyl ether has recently been suggested as an aviation fuel component of excellent anti-knock properties.[102] It may be produced from propylene *via* isopropyl alcohol by the action of warm moderately concentrated sulphuric acid—as follows:—

$$C_3H_6 \rightarrow C_3H_7OH$$
$$2C_3H_7OH \rightarrow (C_3H_7)_2O$$

Details regarding the manufacture of this material are not yet available. It would appear that the cost of production of iso-propyl ether is less than that of iso-octane and that its potential availability

is much greater, propylene being more plentiful in cracked gases than iso-butylene.

TABLE 30

	Di-isobutylene	Iso-octane
Sp. gr. 60'F.	0·7215	0·697
Initial boiling point	62°C.	80°C.
2% distillate at	—	94
5% ,, ,, ...	—	96·5
10% ,, ,, ...	98	97·5
20% ,, ,, ...	101	98·5
30% ,, ,, ...	101·5	99
40% ,, ,, ...	102	99·5
50% ,, ,, ...	103	99·5
60% ,, ,, ...	103·5	100
70% ,, ,, ...	104·5	100·5
80% ,, ,, ...	106·5	101
90% ,, ,, ...	112·5	103·5
Final boiling point	120	122
Bromine number	—	1·0
Gum content (actual + potential) mg./100 ml.	1·0	Below 1·0
Octane number (C.F.R. Motor) ..	87	99

The properties of isopropyl ether, with particular reference to its behaviour as an aviation fuel component, are considered in detail in Volume II (second edition).

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Chapter IX

MOTOR FUELS

Alcohol Fuels

430. Introduction.—The petroleum supplies of the world, though vast and seemingly unlimited, are not evenly distributed among the five continents and many countries occupying important positions in the conduct of world affairs are without a safe supply of this essential commodity. Thus, for example, the only plentiful sources of petroleum within the British Empire are those found in Burma, Canada and Trinidad. Other countries, such as France, Italy, Sweden, etc., are in a similar but even more unfavourable position and are entirely dependent upon foreign imports. Such a state of affairs is not a particularly happy one for the countries concerned even in times of peace, while in times of war their lack of fuel would severely limit their activities.

It is not surprising, therefore, to find, particularly among European countries, serious efforts being made to eliminate or largely reduce dependence upon foreign supplies. The extreme nationalistic tendencies of to-day have lent considerable weight to these efforts with the result that, at the present time, practically every European country encourages the use of home-produced alcohol fuels by the imposition of taxes upon all imported motor fuels. Such alcohol fuels are not popular because they have caused an increase in motor fuel prices and would for this reason not survive, in most cases, without government support. On the other hand, where they are sold at the same price as regular motor fuels, their peculiar properties appear to be appreciated.

431. The Production of Alcohols for Use as Fuels.—The only alcohols which have received much attention as possible internal combustion engine fuels are methanol (methyl alcohol) and ethanol (ethyl alcohol), while of the others only isopropanol and isobutanol appear to be commercial possibilities.

The Production of Alcohols by Wood Distillation.—As a method of producing methyl alcohol, wood distillation cannot compete with the newer synthetic process and has rapidly declined in importance during the last few years. At the present time it is of very minor importance in this respect. This process need not be considered as a means of producing

alcohols at a sufficiently low cost for satisfactory use as fuels. The rapid decline of the wood distillation industry has also been hastened by the development of synthetic processes for the production of acetic acid.

432. The Production of Methanol and Higher Alcohols from Water Gas.—The production of synthetic methanol began in 1925, when the I. G. Farbenindustrie completed the construction of their synthetic plant at Leuna,[1] which is still by far the largest plant of its kind in the world and which has an estimated capacity, at the present time, of 100 tons per day.[2] Production has, however, never reached this figure and since 1926[3] has remained at 20,000–25,000 tons per year. The production in 1927 was estimated at 60 tons per day or 21,000 tons per year.[4]

Synthetic methanol plants quickly followed in other countries, notably in France in 1927 when the Société des Mines de Lens erected a plant with a capacity of about 1½ tons per day (this has since been increased to about 5 tons per day [5, 6, 7]), and in America by the Du Pont Ammonia Corporation in the same year. In 1928 a synthetic methanol plant was erected and put into operation at the Billingham works of Imperial Chemical Industries, Ltd., in this country.

433. Raw Materials—(*i*) *Water Gas.* This is the most common source of carbon monoxide and hydrogen used for methanol synthesis. Its preparation from coke has already been mentioned in Chapter VIII.

The relative proportions of carbon monoxide and hydrogen in the gas employed for methanol synthesis may be varied from those in which these gases are found in water gas by means of the well-known "water-gas catalytic process," in which carbon monoxide is converted into the dioxide by the action of steam. The carbon dioxide may then be removed by simple water scrubbing. This process, described in detail in Chapter VIII, enables gas mixtures with any desired hydrogen / carbon monoxide ratio to be obtained ; in particular, those containing an excess of hydrogen.[12] Gases containing carbon dioxide may also be employed for methanol synthesis.[13]

For methanol synthesis, water gas is often purified and freed from sulphur compounds and volatile iron compounds.[10] Active carbon has been proposed for this purpose.[11]

434. (*ii*) *Coke oven gas.* Coke oven gas is commonly considered as a possible source of hydrogen. It may also be used as a raw material for methanol synthesis, as shown by Osterreith and Dechamps.[14] The high methane content of the gas may be converted into a mixture of carbon monoxide and hydrogen by partial oxidation processes, using promoted nickel catalysts.[15]

435. (*iii*) *Fermentation gases.* In the production of butyl alcohol and acetone by fermentation, the gases evolved contain carbon dioxide and hydrogen and may, therefore, be used for methanol synthesis. Such a source of raw material is being used by the Commercial Solvents Corporation at Terre Haute, U.S.A.[16] The gases concerned contain 60 per cent. carbon dioxide and 40 per cent. hydrogen and are stripped of their vapour content by passing through cooled activated coconut-shell charcoal. A certain amount of carbon dioxide is then removed from the gas, which passes to the methanol synthesis converters where the following reaction takes place :—

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

According to Ellis,[9] in two American works, 635 tons of corn are daily converted into about 55 tons of normal butanol, 27 tons of acetone and 9 tons of ethyl alcohol, while at one of the works 13 tons of methanol are simultaneously synthesised from the fermentation gases. The corn, containing about 8 per cent. of starch, is mixed with water at a temperature of 71°C. and sterilised with steam under pressure. It is then fermented by means of the micro-organism, clostridium aceto-butylicum, and allowed to stand about two and a half days, after which the mixture of alcohols and acetone is concentrated and fractionally distilled. The gaseous mixture evolved (60 per cent. carbon dioxide and 40 per cent. hydrogen) is washed with water under pressure in order to reduce the carbon dioxide content to 25%, compressed to 300 atmospheres, and passed over a catalyst consisting of 97–75 per cent. zinc. or magnesium oxide with 3–25 per cent. iron hydroxide. From the resultant mixture of 68% methanol and 32% water, pure methanol is obtained by distillation.

436. **The Methanol Synthesis Reaction.**—When a mixture of equal volumes of carbon monoxide and hydrogen is passed over a nickel catalyst at atmospheric pressure and at a temperature of 380°C., the product is a mixture of carbon dioxide, methane and hydrogen. A mixture of 3 volumes of hydrogen and 1 volume of carbon monoxide gives almost complete conversion to methane at 230–250°C., thus :—

$$CO + 3H_2 = CH_4 + H_2O$$

At higher pressures and temperatures, however, methanol is the chief product of the reaction if a suitable catalyst is employed. From purely thermodynamic reasoning, Kelley[17] concludes that the methanol synthesis, according to the reaction

$$CO + 2H_2 \rightarrow CH_3OH$$

is workable up to temperatures of 427°C., while Patart's[18] experiments give an optimum temperature between 327°C. and 627°C., at a pressure of 150 atmospheres. An I.G. patent specifies pressures preferably above 50 atmospheres and temperatures between 250°C. and 600°C., depending upon the efficiency of the catalyst employed; while the effective zinc-chromium catalysts, described by Cryder and Frolich,[19] have an optimum temperature of 370–390°C., at a pressure of 204 atmospheres.

Equilibrium Constants of the Methanol Reaction.—Much work has been published during the past few years dealing with the methanol equilibrium, notably by Kelley,[17] Audibert and Raineau,[20] Morgan, Taylor and Hedley,[21] Francis,[22] Smith and Branting[23] and Newitt, Byrne and Strong.[24] A résumé of this work has been recently compiled by Ellis.[9]

Kelley gave the following as the equation of the free energy change of the reaction :—

$$\triangle F = -21{,}300 + 32{\cdot}2T \log T - 0{\cdot}00825T^2 - 42{\cdot}5T$$

and also the value of the equilibrium constant :—

$$\log_n K_p = \frac{\triangle F}{-RT}$$

These results were derived from data which did not involve the specific heat of methanol in the gas phase, and it is probable that incorrect assumptions regarding the effect of temperature were made. Consequently, the results have been criticised by Morgan, Taylor and Hedley and by Francis, although it is admitted that such calculations are bound to be more or less inaccurate owing to the lack of adequate data. The limitations of any such calculations are shown by the fact that even if the heat of combustion of methanol was known to an error of only 0·10%, the value of K_p for the reaction at 298·1°K would still be in error to the extent of 33%.

Audibert and Raineau produced equations for the methanol equilibrium in the case of a gaseous mixture having the initial composition $CO + 2H_2$; thus, on the basis of partial pressures

$$\log K_p = \frac{P_{MeOH}}{P_{CO} \cdot (P_{H_2})^2} = \frac{27{,}000}{4{\cdot}571T} - 3{\cdot}5 \log T - 3{\cdot}6.$$

This equation is considered to be in close agreement with experimental results.[21]

Ellis[9] has compared the figures of Francis, Kelley and Audibert in the following table. Those of Francis and Kelley are of the same

order of magnitude, but they differ considerably from those of Audibert, which are generally considered to be the most satisfactory.

TABLE 1. METHANOL EQUILIBRIUM CONSTANT

Temperature		Equilibrium constant $K = \frac{CH_3OH}{CO \cdot (H_2)}$ according to		
°Absolute	°C.	Audibert	Kelley	Francis
300°	27°	$2{\cdot}65 \times 10^{7}$	$6{\cdot}7 \times 10^{7}$	
400°	127°	$1{\cdot}15 \times 10^{2}$	$20{\cdot}6 \times 10^{2}$	
500°	227°	$5{\cdot}75 \times 10^{-2}$	$316{\cdot}0 \times 10^{-2}$	417×10^{-2}
600°	327°	$3{\cdot}20 \times 10^{-4}$	$386{\cdot}0 \times 10^{-4}$	500×10^{-4}
700°	427°	$7{\cdot}55 \times 10^{-6}$	$1540{\cdot}0 \times 10^{-6}$	2100×10^{-6}

Smith and Branting give a value for K of $5{\cdot}57 \times 10^{-4}$ at 303·8°C., with a probable error of $\pm$ 5 per cent.

437. Catalysts for the Methanol Synthesis Reaction.—A study of the patent and other literature relating to suitable catalysts for the methanol reaction reveals the striking peculiarity of the necessity for excluding certain compounds of iron, nickel and cobalt from these substances, owing to the ease with which they catalyse undesirable side reactions, especially complete hydrogenation to methane. Carbonyls of these metals are particularly to be avoided. The catalysts which may be employed may consist of (*a*) mixtures of metallic oxides, (*b*) mixtures of metals and also alloys and (*c*) mixtures of oxides and metals, or a metal together with an oxide or salt as promoter. Alkalies are excluded if the product is to consist mainly of methanol, but if higher alcohols, such as the butanols and pentanols, are desired, then the presence of alkalies is beneficial.[13] Catalysts containing zinc and /or chromium appear to be those most generally employed.

Sabatier found that zinc oxide was a good catalyst for the decomposition of methanol and, bearing this in mind, Patart[25] examined its effect as a catalyst in the opposite reaction, i.e., the synthesis of methanol, but found that it possessed little, if any, activity. This catalyst has more recently been used in the methanol synthesis, but found to have low activity,[21] while Brown and Galloway[26] found it to be less effective than normal and basic zinc chromates, in that it was less active, gave poor yields at low temperatures and was short-lived. Brown and Galloway prepared their catalyst by precipitating basic zinc carbonate from hot solutions of zinc nitrate and sodium carbonate and washing it free from nitrates. The moist precipitate was pressed into threads 2·4 mm. diameter, air dried and then slowly heated

up to 300°C., under reduced pressure. The resulting oxide was used directly. According to British Celanese, Limited,[27] zinc oxide can be made into a very active catalyst if zinc carbonate is precipitated from a very dilute solution in the presence of protective colloids.

Zinc oxide—copper oxide mixtures have been used as catalysts by Morgan, Taylor and Hedley,[21] by Frolich, Fenske and Quiggle [28] and by Lewis and Frolich.[29] The second group of investigators prepared their catalyst by precipitating zinc and copper hydroxides together and found that this procedure gave a much more active catalyst than other methods, as shown in the following table in which the catalysts are compared with respect to their methanol decomposition efficiency.

TABLE 2. EFFICIENCY OF COPPER OXIDE—ZINC OXIDE CATALYSTS

Mode of Preparation	Decomposition Efficiency
Zinc hydroxide precipitated in suspended copper hydroxide	75
Copper hydroxide precipitated in suspended zinc hydroxide	67
Hydroxide gels mixed	83
Calcined nitrates	70
Co-precipitation of hydroxides ..	100

Frolich, Fenske and Quiggle also determined the effects of variations in the proportions of zinc and copper in these catalysts and found that the maximum decomposition of methanol and the formation of carbon monoxide occurs when the zinc oxide is present in excess.

438. Similar work on zinc-chromium catalysts has been reported by Cryder and Frolich,[19] who have also noted the close similarity between the decomposition of methanol and its synthesis by the aid of catalysts. These workers found that, at atmospheric pressure and 340°C., a maximum yield of carbon monoxide, equivalent to 85% of the methanol decomposed, occurred with a catalyst containing 75 mole. per cent. of zinc. Catalysts richer in zinc tend to produce methyl formate, while those richer in chromium give quantities of carbon dioxide and unsaturated hydrocarbons. The activity of the catalysts, as indicated by the amount of methanol decomposed in decomposition experiments, has also a sharp maximum at 78 mole. per cent. In synthetic experiments, conducted at a pressure of 204 atmospheres and a temperature of 350°C., a catalyst containing 77 mole. per cent. of zinc gave the highest methanol yield, equivalent to 18% conversion of the carbon monoxide. The optimum temperature for this particular catalyst composition was found to be 370–390°C., while the product

was found to be almost pure methyl alcohol. These observations are shown in Fig. 1.

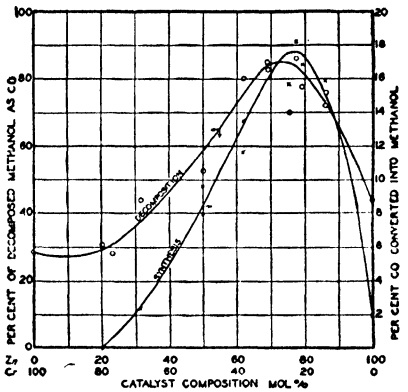


FIG. 1.—CURVES SHOWING THE COMPARISON OF METHANOL DECOMPOSITION AT 340°C. AND ATMOSPHERIC PRESSURE WITH SYNTHESIS AT 350°C. AND 204 ATMOSPHERES (CRYDER AND FROLICH) (Courtesy, Editor, *Industrial and Engineering Chemistry*)

Zinc chromium catalysts in the form of chromates are frequently quoted in the patent literature and have been examined by Brown and Galloway [26] and also by Morgan, Taylor and Hedley.[21] The results of these examinations are shown in the following Tables. The testing method employed by the latter investigators was to place 6 ml. of the catalyst in a reaction vessel, heated in a metal bath, which

TABLE 3. RESULTS OF BROWN AND GALLOWAY[26]

Catalyst: Reduced basic zinc chromate.
Pressure, 180 atmospheres. Temperature, 400°C.

Catalyst—Conditions of Reduction	Volume ml.	Weight grams	Zinc Oxide Content grams	Methanol Yield g./hour	
				Space Velocity	
				16,000	7,500
1. At 40 atmospheres of 1 : 2 mixture of CO : H_2. Slowly raised from 25°C. to 370°C.	250	165	112·5	129·3	—
2. Hydrogen at 1 atmosphere. Reduction began at 300°C., but temperature uncontrolled and allowed to rise to 450°C.	250	153	104·0	89·2	60·8
3. Reduced at 275-325°C. at 1 atmosphere with a mixture of 5% hydrogen and 95% carbon monoxide ..	250	170	115·5	106·4	94·5

was then rapidly filled with the hydrogen—carbon monoxide mixture at 200 atmospheres pressure. The activity of the catalyst was gauged by the time taken for a definite drop in pressure (10 or 20 atmospheres).

TABLE 4. RESULTS OF MORGAN, TAYLOR AND HEDLEY[21]
Pressure, 200 atmospheres

Catalyst	Time in minutes taken for a 10 atmospheres drop in pressure						
	290°C.	310°C.	330°C.	350°C.	370°C.	390°C.	410°C.
Zinc oxide	—	—	10·0	—	3·5	—	3·1
Basic zinc chromate ..	—	4·5	—	1·0	0·8	—	1·2
Zinc chromate	—	—	1·3	0·7	0·6	0·5	0·5
Basic zinc chromate and copper	6·0	1·5	0·8	0·6	0·6	0·9	—
Zinc manganate	—	—	—	5·2	—	—	1·6
Zinc oxide and zinc dust	—	—	—	7·0	—	—	1·5
	Time in minutes taken for 20 atmospheres drop in pressure						
Basic zinc chromate and copper	14·5	4·5	2·8	2·2	3·5	—	5·8

Morgan and his co-workers inferred from these experiments that (*a*) catalysts prepared from either of the two zinc chromates would probably prove efficient for methanol synthesis, (*b*) that the optimum temperature of the catalysts should be between 350° and 400°C., and (*c*) that a pressure of the order of 200 atmospheres should give a reasonable output of methanol. Experiments were then continued in a flow-through type of apparatus, using two volumes of hydrogen to one volume of carbon monoxide, at a rate of 1,600 litres per hour (measured at N.T.P.), over 60 ml. of a catalyst prepared from basic zinc chromate containing 5 per cent. of copper, and a pressure of 200 atmospheres. At 380°C., methanol was produced at the rate of 77 ml. per hour, whereas at 450°C. and 335°C., there were only obtained 38 ml. and 43 ml. per hour, respectively. The methanol had a density of 0·795 and 94% of the liquid distilled below 90°C. Experiments carried out in an apparatus allowing re-circulation of the reacting gases showed that the hydrogen content of these gases had a marked effect upon the yields of methanol obtained. As the hydrogen percentage fell below 66%, the yield rapidly decreased. At rates approximating to 2,000 litres per hour, through 60 ml. of catalyst, the hourly output was almost exactly twice the catalyst volume when zinc chromates were used as catalysts. When zinc oxide alone was used, the rate of methanol production was only 0·4 volumes per volume of catalyst per hour. In the above experiments, the reaction product had the following composition: methanol 91%, higher alcohols 2·5%, water 4·0%.

439. The use of zinc chromate catalysts containing 70–80 atomic proportions of zinc and 30–20 atomic proportions of chromium has been patented by Franklin and Synthetic Ammonia and Nitrates, Ltd.,[30] who give examples of the preparation of such catalysts by the reaction of soda ash solutions with :

(*a*) a mixture of sodium bichromate or chromate with sulphuric acid to which zinc has been added,
(*b*) the spent electrolyte of a bichromate electrolytic cell,
(*c*) commercial basic chrome liquor with added zinc sulphate.

The catalysts are preferably employed in pelleted form.

According to Smith,[31] catalysts prepared from a basic zinc chromate of the formula $4ZnO \cdot CrO_3$ are not poisoned by sulphur, although volatile compounds (e.g., carbonyls) of iron, nickel and cobalt should be excluded. Lazier (assignor to the Du Pont Ammonia Corporation)[32] has described catalysts for the methanol synthesis prepared by igniting a chromate or dichromate at 600–1,000°C., or by prolonged heating to redness of mixtures of chlorides and alkali dichromates or dichromates, etc.

TABLE 5. METHANOL AND DIMETHYL-ETHER FORMATION WITH NORMAL ZINC CHROMATE CATALYST

Pressure 180 atmospheres. 2 : 1 hydrogen : carbon monoxide

Run	Av. Temp. °C.	Space Velocity	Pure Methanol g./hour	Conversion CO to CH_3OH per pass	Dimethyl Ether			
					Total for Run grams	Liquid Products %	Equivalent Methanol g./hour	Conversion CO to Ether per pass %
A	300	3000	27·6	7·0	—	—	—	—
B	307	3000	29·7	9·1	1·0	1·65	0·7	1·0
C	311	3000	38·1	10·9	1·9	1·95	1·1	1·2
D	350	3000	83·3	22·5	4·8	2·95	3·34	1·7
E	350	7500	100·2	13·2	4·24	2·75	3·8	0·7
F	375	3000	95·6	28·94	8·0	5·45	7·4	3·3
G	375	7500	123·5	16·4	5·6	4·45	7·8	1·2
H	397	3000	68·0	21·4	7·5	8·6	8·4	5·2
I	398	3000	72·4	20·5	—	—	—	—

Dimethyl-ether has been shown by Brown and Galloway [33] to be a by-product in the methanol synthesis when normal zinc chromate catalyst is used. The amount of this substance formed is, however, very small, as shown in Table 5.

440. Catalysts for the Synthesis of Higher Alcohols by the Methanol Reaction.—The literature contains many statements to the effect that the catalysts for methanol production may be so modified

by the addition of alkaline substances that higher alcohols are produced.[12, 21, 34, 35]

Morgan, Taylor and Hedley [21] describe the preparation of such catalysts, of which the following is an example: zinc oxide, 15 parts by weight, potassium chromate, 23·5 parts, potassium carbonate, 11·5 parts. The catalyst was prepared in the form of granules and tested in a static plant at 370°C. The fall from an initial pressure of 200 atmospheres was 60 atmospheres in 75 seconds and 90 atmospheres in 6 minutes. In a circulatory apparatus and at low gas velocities, the product separated into two layers, and the lower the gas velocity the greater was the proportion of the upper layer of partially miscible alcohols and esters. An examination of the composition of this product showed it to contain methanol and higher alcohols mixed with esters and free acids. Morgan, Hardy and Proctor have dealt with alkalised catalysts in greater detail in a more recent publication.[35] A basic catalyst, containing a mixture of chromium and manganese oxides in molecular proportions, was impregnated with various amounts of the hydroxides of the five alkali metals, and these alkalised catalysts were tested in the methanol synthesis reaction. The results of these tests are reproduced in Table 6.

The percentages of carbon present as compounds other than methanol and the volumes of material insoluble in calcium chloride solution show that the percentage of higher alcohols in the liquid product increases as the alkali content of the catalyst is raised. Impregnation with lithium, sodium or potassium hydroxide diminished the yield of liquid product in amount proportional to the concentration of alkali in the catalyst, while rubidium or caesium hydroxide had little effect upon the output. From this it followed that catalysts containing rubidium or caesium gave the highest conversion to higher alcohols, and, as will be seen in Table 6, the catalyst containing 9·8% of rubidium gave the greatest yield of these compounds. These observations are in agreement with those of Fischer and Tropsch,[36] who found that rubidium hydroxide was the most efficient alkali for impregnating the iron chips which they used as catalyst for the production of "synthol." (See Chapter X.) These rubidia- and caesia-impregnated catalysts exhibited fairly long periods of initial activity during which the yield of product was as much as 20% higher than normal, but the initial high yields gradually decreased and, after a few hours, reached a steady value. A chromium-manganese catalyst containing 15% of rubidium was also used without giving any appreciable decrease in yield of liquid product, of which a large quantity was prepared and examined in detail. The products identified included methanol, a trace of ethyl alcohol, propanol and isobutanol, 2-methyl butanol, 2-methyl pentanol and 2-3-dimethyl pentanol. Aldehydes were also detected, including

TABLE 6

Impregnating Alkali expressed as combined metal	% by weight Impregnating Material	% Gas converted per passage	Yield of Product grams/hour	Density of Product	Carbon Content of Crude Product %	Methanol in Product %	Carbon present as Compounds other than Methanol %	Conversion of Carbon into Compounds other than Methanol grams/hour	Volume of Material insoluble in $CaCl_2$ solution (c.c. per 100 gm.)	Yield of material insoluble in $CaCl_2$ solution (c.c. per hour)
None	—	3·5	62	0·8235	34·7	80·5	13·0	2·8	0·3	0·2
Lithium ..	3·4	2·7	47	0·8265	36·8	76·9	21·7	3·8	3·55	1·7
	6·7	2·6	45	0·843	34·7	73·7	20·3	3·2	6·26	2·8
	10·1	2·3	40	0·834	35·8	71·7	24·9	3·6	4·42	1·8
Sodium ..	2·8	2·4	43	0·855.	35·7	63·9	32·9	5·0	12·8	5·5
	6·3	1·2	21	0·883	33·2	55·0	37·9	2·6	14·4	3·0
	9·8	1·0	17	0·893	31·0	50·1	39·4	2·1	14·05	2·4
Potassium ..	1·5	2·7	47	0·8175	36·7	81·8	16·4	2·8	0·63	0·3
	3·9	2·2	39	0·8505	37·0	60·8	38·4	5·5	12·8	5·0
	4·9	1·9	33	0·8775	37·0	50·7	48·6	5·9	21·5	7·1
	5·7	1·6	29	0·8815	34·8	53·0	42·9	4·3	18·6	5·4
	8·4	1·4	24	0·8985	34·6	52·2	43·4	3·6	17·5	4·2
	11·9	1·5	27	0·9085	34·2	49·0	46·3	4·3	23·0	6·2
Rubidium ..	2·3	3·4	61	0·8325	36·8	75·5	23·1	5·2	4·65	2·8
	4·4	3·5	62	0·847	37·7	67·2	33·1	7·7	17·8	8·8
	9·8	3·0	53	0·881	34·5	49·7	46·0	8·4	28·7	15·2
Caesium ..	1·8	3·5	62	0·825	35·3	79·5	16·2	3·6	1·53	1·0
	3·8	3·0	53	0·818	37·9	82·1	18·8	3·8	1·58	0·8
	8·9	3·3	58	0·849	38·2	63·7	37·5	8·3	16·4	9·5

formaldehyde, propaldehyde, hydroxy-aldehydes and unsaturated aldchydes.

Higher-alcohol-producing catalysts work at slightly higher temperatures (about 400°C.) than those producing mainly methanol.

441. Morgan, Taylor and Hedley[21] have also used cobalt-containing catalysts for higher alcohol production, since the successful use of this element by Fischer and Tropsch[37] in the production of hydrocarbons from carbon monoxide and hydrogen suggested that it had the special property of linking carbon atoms together. A catalyst prepared from cobalt nitrate and basic zinc chromate effected the production of a whole series of higher alcohols, although methanol remained the major portion of the product. Some results on cobalt catalysts are as follows :—

Catalyst	Temp. °C.	Products		
		Methanol %	Higher Alcohols %	Water %
Basic zinc chromate + 10% cobalt chromate	400	82	9·0	8·0
Basic zinc chromate + 10% cobalt chromate	450	90	1·6	8·4
Basic zinc chromate + 5% cobalt chromate	400	88·5	5·0	6·5

Fractional distillation of the higher alcohols produced with the first catalyst showed that four-fifths of this portion of the product consisted of *n*-propanol and isobutanol, the latter slightly predominating. The remaining fifth consisted of a mixture of alcohols boiling mainly at 115°–116°C. Experiments with a catalyst made from a mixture of 2 parts cobalt nitrate, 1 part zinc manganate, and 0·7 parts copper carbonate, gave a product of the following composition (on a water-free basis) : aldehydes 1·4, methanol 79·7, ethanol 11·6, higher alcohols 7·3. The amount of water formed was 40% of the crude product.

Using a catalyst made from a mixture composed of zinc oxide 10 parts, chromic acid 20 parts, cobalt nitrate 60 parts and copper carbonate 10 parts, a product was obtained containing 45% of water. Alcohols were present in the product in the following proportions :— methanol 77, ethanol 20·3, higher alcohols 2·7.

442. The Production of Ethyl Alcohol from Carbon Monoxide and Hydrogen.—The production of ethanol by the catalytic treatment of water gas has been a matter of some controversy, but recent work by Morgan and his connections at the Chemical Research Laboratory, Teddington, England and by others has demonstrated

that this very valuable material may be produced in quantity by this method. Taylor[86] has shown that, at 175–200 atm. pressure and 380–435°C., in the presence of a catalyst comprising 0·05 mole. cobalt oxide added to 1 mole. of copper oxide and 1 mole. of manganese oxide, 12% of the carbon monoxide reacting is converted into ethanol and at the same time 47% is hydrogenated to methane. Catalysts containing cobalt sulphide give the highest conversions to ethanol, the optimum catalyst composition being a 10 : 10 : 1 molecular mixture of copper oxide, manganese oxide and cobalt sulphide. At 400°C. and 200 atm. pressure this catalyst gave a product, the carbon distribution in which was—methanol 17%, ethanol 22%, higher alcohols 11% and methane 47%.

Klynkvin, Volnov and Karpinskii[87] have employed zinc oxide—cobalt oxide catalysts of 3–1 mole. ratio composition at 120 atm. and 320–330°C. and have claimed a 39% yield of ethanol, in addition to other alcohols, under these conditions.

443. Nature of the Higher Alcohols Produced from Carbon Monoxide and Hydrogen.—The nature of the higher alcohols produced by this process, as well as their quantity, is, of course, a function of both the catalyst employed and the operating conditions. Mittasch[38] states that the following alcohols are produced :—methanol, ethanol, *n*-propanol, isobutanol, "amyl" alcohol, B.P. 128°, hexanol, B.P. 148°, heptanol, B.P. 160–165° and octanol, B.P. 180°C. He also states that the predominant higher alcohols appear to be of the type $CHRR'-CH_2OH$.

The product from a 15% rubidium catalyst, operating at 400°C. and at 200 atmospheres, with a space velocity of 53,000 reciprocal hours and an inlet gas composition of 2 volumes of hydrogen to 1 volume of carbon monoxide, has been fully examined by Morgan, Hardy and Proctor[35] with the following results :—

The product was distilled and collected in two fractions after being refluxed with magnesium oxide to fix the acid constituents. In this way was obtained

B.P. up to 85°C.	67% by weight,	
B.P. above 85°C.	23% „ „	containing 45% non-aqueous material.

The distillate boiling up to 85°C. contained methanol, 62%, and ethyl alcohol, 2·1%. The residue boiling above 85°C. was fractionated after the removal of aldehydes, acetates, etc., with the following results :—

B.P. 80–103°C.	5·8%
103–112·5°C.	9·0%
112·5–122·5°C.	1·4%
122·5–127°C.	1·3%
127–131°C.	0·9%

131–133°C.	2·1%
133–136°C.	0·4%
136–142°C.	2·8%
142–145°C.	1·9%
145–150°C.	1·4%
72–88°C./40 mm.	10·2%
88–93°C./40 mm.	8·7%
80–105°C./10 mm.	10·5%
105–114°C./10 mm.	9·5%
114–122°C./10 mm.	3·2%
Residue	30·9%

The following alcohols were identified in the appropriate fractions :— isobutanol, *n*-butanol, 2-pentanol, 2-hexanol and 2-3-dimethyl pentanol.

The properties of the 85°–162°C. fraction of the higher alcohols produced at the Belle plant of the Du Pont Ammonia Corporation have been given as follows :—[39]

Boiling Range.

85–129°C.	3·5% by wht.	162–165°C.	0·3% by wht.
129–132°C.	25·1% ,, ,,	165–170°C.	1·0% ,, ,,
132–138°C.	18·7% ,, ,,	170–175°C.	1·0% ,, ,,
138–142°C.	11·1% ,, ,,	175–180°C.	1·4% ,, ,,
142–147°C.	20·1% ,, ,,	180–185°C.	0·3% ,, ,,
147–152°C.	5·9% ,, ,,	185–191°C.	1·0% ,, ,,
152–158°C.	3·1% ,, ,,	191–196°C.	0·3% ,, ,,
158–162°C.	5·9% ,, ,,	Residue	0·2% ,, ,,
			98·9%

The primary alcohols were separated by esterification with phthalic anhydride in benzene solution. The resulting monophthalates were saponified with caustic soda and the liberated primary alcohols removed by steam distillation. Of the crude product 48·5 per cent. consisted of primary alcohols, while the unesterified fraction was found to be quite free of acids, esters, ketones, olefines and other hydrocarbons and also tertiary alcohols, and, therefore, consisted of saturated secondary alcohols. The primary alcohols were separated by fractional distillation in a 4-foot column, 5/8 inches in diameter, packed with crystalline silicon carbide and operating at a reflux ratio of 10 to 1, and the substances detailed in Table 7 were identified.

The secondary alcohols distilled as follows :—

Below 120°C.	5·3%	153–160°C.	0·6%
120–134°C.	3·0%	160–161°C.	0·5%
134–139°C.	35·3%	161–165°C.	0·9%
139–144°C.	3·0%	165–169°C.	1·1%
144–153°C.	0·8%	169–174°C.	0·5%
			51·0%

TABLE 7. PRIMARY ALCOHOLS IN HIGHER ALCOHOLS PRODUCED BY THE DU PONT AMMONIA CORPORATION[39]

Substance	Boiling Point °C.		Neutralisation equivalents of 3-nitro-phthalate		Melting Point of 3-nitro-phthalate °C.		Mixed Melting Point °C.	Weight % of Higher Alcohol
	Found	Literature	Found	Calculated	of Substance	of known Material		
2-Methyl 1-Butanol ..	128·30	129·5	296	295	156	157	156·7	17·3
2-Methyl 1-Pentanol ..	145·7	146·5	300	295	141	145	143	16·6
2-4-Dimethyl 1-Pentanol	153·8	159–161	310	309	152–3	154–5	152–3	2·3
4-Methyl 1-Hexanol ..	162–4	165	312	309	140	144	141	3·3
2-4-Dimethyl 1-Hexanol	173–5	175–180	321	323	132	—	—	1·0
4- or 5-Methyl 1-Heptanol	180–3	182·7	327	323	133	—	—	0·3

The 134–139°C. fraction gave, on refractionation, a substance, B.P. 137–138°C., which analysis showed to be a heptanol (M.W. 113, 73·3% C, 13·1% H). Its identity was proved by comparison to be 2-4-dimethyl 3-pentanol. Iso-propanol was not isolated but identified by oxidation to acetone; it was only present in very small amounts. 2-methyl 2-butanol, 3-methyl 2-butanol, 3-pentanol, 2-pentanol and 2-methyl 3-pentanol were also identified.

444. Mechanism of the Formation of Higher Alcohols from Water Gas.—As may be expected, there is some divergence of opinion regarding the course of the reactions which would serve to explain the formation of alcohols of high molecular weight from mixtures of carbon monoxide or carbon dioxide and hydrogen. One of the earliest suggestions was that of Fischer and Tropsch,[40] who, in their early work on "synthol," isolated and identified, besides methanol and higher alcohols, various amounts of acetaldehyde, propionaldehyde, acetone, methyl-ethyl-ketone, diethyl-ketone and methyl normal propyl ketone, as well as esters and hydrocarbons. These investigators suggested that the higher alcohols are formed by reduction of aldehydes, which result from the reduction of acids, which in their turn result from the addition of carbon monoxide to the alcohol containing one-less carbon atom, thus :—

$$\begin{aligned} C_2H_5OH &\rightarrow C_2H_5COOH \\ C_2H_5COOH &\rightarrow C_2H_5CHO \\ C_2H_5CHO &\rightarrow C_2H_5CH_2OH \end{aligned}$$

This mechanism, however, only accounts for the formation of normal primary alcohols. Ketones were supposed to result from the loss of water and carbon dioxide from two molecules of fatty acid, thus :—

$$CH_3COOH + CH_3COOH \rightarrow CH_3COCH_3 + H_2O + CO_2$$

Ketones have also been regarded as dehydration products of secondary alcohols.[41]

A more recent hypothesis concerning the formation of higher alcohols is that involving the occurrence of a series of aldol condensations starting with formaldehyde.[42] According to this scheme, two molecules of formaldehyde condense to give $CH_2OH{\cdot}CHO$, which is hydrogenated to give acetaldehyde and water. The acetaldehyde is then reduced to ethyl alcohol or then condenses with a further molecule of formaldehyde or acetaldehyde to give hydroxy-aldehydes of higher molecular weight, which would, in turn, be hydrated and reduced. The series of reactions involved are as follows :—

$$\begin{aligned} 2\,HCHO &= H_2C(OH){\cdot}CHO \\ H_2C(OH){\cdot}CHO + H_2 &= CH_3CHO + H_2O \\ CH_3CHO + H_2 &= CH_3CH_2OH \\ HCHO + CH_3CHO &= CH_2(OH){\cdot}CH_2CHO \end{aligned}$$

$$CH_2(OH)CH_2CHO + H_2 = CH_3{\cdot}CH_2{\cdot}CHO + H_2O$$
$$CH_3CH_2CHO + H_2 = CH_3{\cdot}CH_2CH_2OH$$

and so on.

It will be noticed that, according to this scheme, straight-chain alcohols should be formed. Provision is made for the production of branched-chain alcohols by a condensation involving two molecules of formaldehyde and one of acetaldehyde to give the product $(H_2COH)_2$ CH·CHO, which after dehydration and reduction, would give isobutanol, thus :—

$$2\,H{\cdot}CHO + CH_3{\cdot}CHO = \begin{matrix} CH_2(OH) \\ CH_2(OH) \end{matrix}\!\!>\!CH{\cdot}CHO$$

$$\begin{matrix} CH_2OH \\ CH_2OH \end{matrix}\!\!>\!CH{\cdot}CHO + 3H_2 \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH{\cdot}CH_2OH + 2H_2O$$

The above aldol condensation mechanism for the formation of higher alcohols is widely accepted but the non-existence of normal butanol in the products examined by Graves,[39] has led this investigator to doubt its validity.

A mechanism involving progressive dehydration has also been proposed by Frolich,[43] suggesting that the dimethyl ether observed to be a reaction by-product,[33] represents an intermediate step in the production of its isomer ethanol. According to this mechanism, two molecules of methanol are dehydrated to form dimethyl ether, which rearranges to form ethanol. Similarly, methanol and ethanol would be dehydrated to ethyl methyl ether and this would rearrange to give normal propanol, thus :—

$$CH_3OH + CH_3OH \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!O \rightarrow CH_3CH_2OH$$

$$CH_3OH + C_2H_5OH \rightarrow \begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>\!O \rightarrow C_2H_5\,CH_2OH$$

Frolich has also pointed out that one would expect the aldehydes to be converted to esters by addition and rearrangement. Esters have actually been isolated in higher alcohol fractions.

Similar condensations of aldehydes to higher alcohols, to give a series of aldol condensations and hydrogenations, have been assumed to explain the formation of these bodies and also higher esters in the catalytic condensation of acetaldehyde in the presence of hydrogen, carried out by Adkins, Kinsey and Folkers[44] but, in these experiments, the yields of esters have always been greater than those of the higher alcohols.

The formation of these same higher alcohols by heating the lower alcohols with alkali has been reported by several investigators, including Guerbet,[45] who has reported that methanol does not condense in this way but that the higher alcohols react with increasing ease. It would appear that such condensations always involve a hydrogen atom attached to the β-carbon atom, giving a series of primary alcohols,[46] thus :—

$$CH_3 \cdot CH_2OH + CH_3 \cdot CH_2OH \rightarrow CH_3\,CH_2\,CH_2\,CH_2OH \text{ (}n\text{-butanol).}$$

445. The above hypotheses concerning the production of higher alcohols from carbon monoxide and hydrogen have recently been critically examined by Graves,[39] in the light of experience gained with the higher alcohols produced in the Du Pont Ammonia Corporation methanol plant, the compositions of which have already been given. According to Graves, the direct dehydration mechanism proposed by Guerbet (*loc. cit.*) offers a simple and satisfactory explanation of the formation of normal propanol, isobutanol and 2-methyl butanol, which are present in the Du Pont product, but the presence of esters has not been demonstrated therein, although the low boiling fractions contain traces of aldehydes and ketones. These latter compounds, however, have always been looked upon by Graves as dehydrogenation products of the alcohols rather than as residual intermediates produced by aldol condensations. The small amounts of saturated and unsaturated hydrocarbons which have been identified in the low boiling fractions are considered to be dehydration products of the alcohols. Compared with the higher alcohols themselves, all of these other materials are only found in traces.

Graves has, therefore, proposed the following :—

(1) Higher primary alcohols are formed by intermolecular dehydration of two lower alcohol molecules.

(2) Dehydration may involve a hydrogen atom attached to the carbon atom of methanol, thus :

(a) $CH_3OH + CH_3OH \rightarrow CH_3 \cdot CH_2OH$,

(b) $CH_3 \cdot CH_2OH + CH_3OH \rightarrow CH_3\,CH_2\,CH_2OH$,

but such a reaction is slow compared with one involving a hydrogen atom attached to the β-carbon atom.

Thus the reactions

(c) $CH_3OH + H \cdot CH_2\,CH_2OH \rightarrow CH_3\,CH_2\,CH_2OH$ (n-propanol),

and (d) $CH_3OH + CH_3 \cdot H \cdot CH \cdot CH_2OH \rightarrow CH_3 \cdot CH \cdot CH_3 \cdot CH_2OH$ (isobutanol)

take place, whereas the reactions

(e) $CH_3\,CH_2\,CH_2OH + H\,CH_2OH \rightarrow CH_3\,CH_2\,CH_2\,CH_2OH$ (n-butanol)

and (*f*) $CH_3CH(CH_3)CH_2OH + HCH_2OH \rightarrow CH_3CH(CH_3)CH_2CH_2OH$ (isoamyl alcohol)

do not occur,

(3) Condensation takes place with difficulty on a CH_3 group, as instanced by the failure of the reactions

(*g*) $CH_3 \cdot CH_2OH + HCH_2CH_2OH \rightarrow CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2OH$ (*n*-butanol)

and (*h*) $CH_3CH_2CH_2OH + HCH_2CH_2OH \rightarrow CH_3CH_2CH_2CH_2CH_2OH$ (*n*-pentanol)

and does not take place on a CH group, as instanced by the failure of the reaction

(*i*) $CH_3OH + CH_3CH(CH_3)CH_2OH \rightarrow (CH_3)C \cdot CH_2OH.$

Most of the higher alcohols result from a condensation on a CH_2 group. In order to explain the formation of secondary alcohols the hypothesis is extended to include a dehydration involving a hydrogen atom attached to the carbon atom holding the OH group.

446. Plant used in the Methanol Synthesis.—As already pointed out, the methanol reaction

$$CO + 2H_2 \rightarrow CH_3OH + 23{\cdot}9 \text{ cals.}$$

is carried out, using efficient catalysts, at pressures of about 200 atmospheres and at temperatures of 350–400°C. The plant used for such a reaction is, in essentials, very simple, and comprises a reaction chamber in which the actual synthesis takes place, mounted vertically and very similar in appearance to a coal or oil hydrogenation converter; compressors for supplying the mixed gases (carbon monoxide and hydrogen) to the reaction chambers, gas circulators to circulate the reacting gases through the reaction chambers, suitable condensers, etc., for condensing the methanol vapour formed in the reaction out of the circulating gas and suitable let-down drums and product receivers. The bare essentials of the plant commonly used are shown diagrammatically in Fig. 2, and closely resemble a vapour-phase oil hydrogenation process, except in so far as both the reacting materials are gases.

One point of particular interest is shown in the patent literature, namely that relating to the complete elimination of all metals which form volatile carbonyls by combination with carbon monoxide. Contact of this gas with iron, nickel or cobalt is particularly to be avoided because the carbonyls formed are volatile and find their way to the methanol catalyst. Here they are decomposed and deposit metal on the catalyst surface, thereby poisoning it and causing it to lose its

activity.[47] An English patent, granted to the Badische Co.,[48] states that the synthesis plant must be made of, or coated with, a metal or alloy which does not form carbonyls and which can resist the high temperatures used. Special steels, containing large amounts of chromium, manganese, tungsten, molybdenum or vanadium (e.g., steel V.2.A.) may be used, also copper, silver, aluminium and their alloys, etc. The reaction tube may also be protected against the action of hot hydrogen by making it in the form of a steel jacket with an inner wall of copper or some other suitable material. The use of non-carbonyl forming liners in the reaction vessel and all parts of the plant coming into contact with compressed carbon monoxide has also been patented.[49]

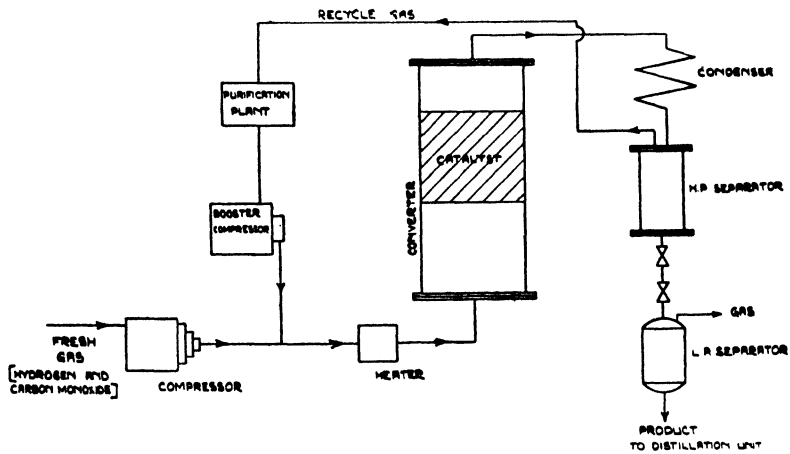


FIG. 2.—DIAGRAMMATIC FLOW SHEET OF METHANOL SYNTHESIS PLANT

Details of experimental scale high-pressure synthetic methanol plants have been given by Morgan, Taylor and Hedley,[21] while, for further details, reference should be made to " Hydrogenation of Organic Substances," recently published by Ellis, to the paper on this subject by Tongue,[50] and to " The Design and Construction of High Pressure Chemical Plant," H. Tongue, Chapman & Hall, Ltd. Details concerning the full scale methanol synthesis plants of the I.G. Farbenindustrie have been given by Bosch.[163]

447. Some Statistics concerning Methanol Production.—During the past thirteen years, the methanol industry has undergone a radical change. This comparatively short period, which began with the completion of the I.G. synthetic methanol plant in 1924, has seen the wood distillation industry driven from its former position of undisputed control to one of approximately equal importance to the synthetic industry by the end of 1928, and to one of considerably inferior importance at the present time. While the costs of production appear

TABLE 8. SYNTHETIC METHANOL PLANTS

Country	Location of Plant	Operating Company	Date of Starting	Source of raw materials ($CO + H_2$)	Capacity (Tons/year)	Production (Tons/year)	Reference
United Kingdom	Billingham	Imperial Chemical Industries, Ltd.	1929	Water gas	20,000	8653 (1934) 9657 (1935)	(*m*)
United States	Belle, W. Va.	Du Pont Ammonia Corporation	1927	Do.	6,000*	75,600 (1936)	(*k*)
	Peoria, Ill.	Commercial Solvents Corporation	1927	Fermentation of maize	7,500*		(*l*)
	Niagara Falls, N.Y.	Carbide and Carbon Chemicals Corporation	1930	—	—		
Belgium	Ougrée	Société Belge de l'Azote	1929	Coke oven gas	—		(*a*)
	Willibroeck	S. A. Ammoniaque Synthétique et Dérivés	1931	Do.	—		(*b*)
France	Lens	Société des Mines de Lens	1927	Do.	1,750		(*c*)
	Bully-Grenay	Société des Mines de Bêthune	1927	Do.	5,000		(*d*)
	Courrières	Société des Produits Chimiques Courrières Kuhlmann	1927	Do.	3,600		(*e*)
Germany	Leuna	I.G. Farbenindustrie, A.G.	1925	Water gas	35,000	21,000 (Oct. 1930)	(*f*)
Italy	Terni	Societa Italiana Recerche Industriale "Siri"	1928	—	2,100		(*g*)
	Nera Montora	Do.	—	—	14,000		(*i*)
Japan		Chosen Chisso Kaisha	—	—	3,500		(*j*)
		Gosei Koggo Kaisha	—	—	1,500		
		Tokyo Metanol Kaisha	—	—	1,500		
		Chrode-skiki Chisso Kaisha	—	—	500		

(*a*) Rev. prod. chim., 1929, 370, June 15. Report for year 1929.
(*b*) J. Comm. (N. York), September 2, 1929.
(*c*) Chem. Trade J., October 8, 1926, p. 423.
(*d*) Rev. prod. chim., December 15, 1929, p. 753.
(*e*) Oil, Paint and Drug Reporter, May 19, 1930, p. 76.
(*f*) Chemicals, October 27, 1930, p. 27.
(*g*) J. Comm. (N. York), December 17, 1929.
(*i*) Chem. Trade J., 1932, **91**, 528.
(*j*) Ind. Eng. Chem., News Edition, August 10, 1929, p. 9.
(*k*) Chem. and Met. Eng., 1930, 544.
(*l*) Ind. Eng. Chem., 1930, 789.
(*m*) R. Taylor, Gas World, Coking Section, 1936, April 4.

* As given in 1930—considerably greater now.

to be well below those of wood spirit methanol, there is little doubt that the simultaneous competition of synthetic acetic acid and fermentation acetone with the wood distillation products hastened the decline of the wood distillation industry. The growth of the synthetic methanol industry has been closely connected with that of synthetic ammonia, for the two industries share a raw material (water gas) and utilise very similar plants. Moreover, the carbon monoxide required for methanol production is a by-product at synthetic ammonia works using coke oven gas, and is a raw material at those works which use water gas.

The number of synthetic methanol plants now operating in various parts of the world is still relatively small and not much more than 100. Few of these plants are operating at full capacity, the limitation being market requirements.

Some details regarding known synthetic methanol plants are given in Table 8, together with what is known regarding their capacity.

Some statistics regarding wood spirit methanol production are given in Table 9.

TABLE 9. WOOD METHANOL PRODUCTION STATISTICS

Country	Production (Tons/year)	Country	Production (Tons/year)
United Kingdom	200	Russia ..	832 (1928–9)
India	1,000 (*f*)	Rumania ..	1,920 (1927) (*c*)
Yugoslavia ..	800 (1927) (*e*)	Poland ..	435 (1929) (*b*)
Spain	220 (*d*)	Czechoslovakia	5,000 (1928)
		Japan	516 (1930) (*a*)

(*a*) Chem. Trade J., 1935, Mar. 22, p. 219.
(*b*) Chem. Ind., February 15, 1930, p. 192.
(*c*) Chem. Ztg., October 29, 1930, p. 848.
(*d*) Oil and Colour Trades J., January 10, 1930, p. 140.
(*e*) U.S. Comm. Rep., February 3, 1930, p. 316–319.
(*f*) Chem. Trade J., April 15, 1927.

Indicating the present uses of methanol, the following figures, showing the domestic consumption in the U.S.A. in 1929, are of interest.[51]

For formaldehyde manufacture	41%
For denaturing	31%
For dimethyl aniline manufacture	5%
Miscellaneous and solvents	23%
	100·0%

The production of methanol in the U.S.A., during the past few years,

is shown in Table 10. The market price of methanol, in the U.S.A., has decreased rapidly in recent years and in 1930 was selling at the same price as denaturated ethyl alcohol.

TABLE 10. U.S. METHANOL PRODUCTION

	Millions of gallons	
	Methanol	
	Total	Synthetic
1922	5·2	—
1923	5·2	—
1924	5·6	—
1925	4·7	—
1926	6·4	—
1927	6·2	0·6
1928	8·0	2·4
1929	9·6	4·5
1930	15·3	10·0
1933	9·7	8·8
1934	16·26	12·5
1935 (First nine months)	14·7	11·5

448. The Production of Alcohols by Fermentation Processes.—The fermentation process for the manufacture of ethyl alcohol has been practised for many years. The raw materials are vegetable matter containing either sugar, starch (which has to be converted into sugar as a preliminary to fermentation) or cellulosic materials, the cellulose being converted by chemical treatment into fermentable sugars. In the manufacture of alcohol for potable purposes, of which the requirements are comparatively small as compared with those for a liquid fuel, and for which a higher price is obtainable, cereal grains, such as barley and rye, are employed, but in the production of power alcohol, molasses, maize, sugar beet and potatoes are more suitable raw materials. In the British Dominions, cassava, Nipa palm juice, sweet potatoes, grasses, straws and waste vegetable materials have also been considered in this direction.

In Great Britain, during the year ending 31st March, 1927, the alcohols distilled totalled approximately 22½ million imperial gallons of 95 per cent. alcohol, including 46,500 gallons for the manufacture of power methylated spirits, whereas, over the same period, the petrol consumption was 750,000,000 gallons. Nathan [52] has compared these figures and has shown (see Table 11) that for lack of acreage, irrespective of all other considerations, the production of any but an infinitesimal quantity of alcohol for power purposes would be an

impossibility in this country. The average total area under crops and grasses in Great Britain, for the years 1917–1926 was, in round figures, 14¾ and 16¼ million acres, respectively, or a total of 31,000,000 acres.

TABLE 11

Material	Area acres	Yield per acre tons	Total Produce tons	Alcohol		Approximate Requirements for 1,000,000,000 gallons	
				Gals. per ton raw material	Gals. per acre	Produce millions of tons	Area in millions of acres
Potatoes ..	1,256,000	5·6	7,049,000	20	112	50	9
Mangolds ..	473,000	18·8	8,922,000	8	150	125	7
Sugar beet ..	222,500	7·7	1,450,000	22	170	45·5	6
Jerusalem artichokes ..	negligible	11·0	negligible	18	198	56	5

449. Sources of Fermentation Alcohol.—The approximate yields of alcohol obtainable from various raw materials, under average conditions, are shown in Table 12. In one or two cases, these figures are based on the results of actual practice, but, in general, they are based on the average sugar or starch contents and on the assumption

TABLE 12. APPROXIMATE YIELDS OF ALCOHOL OBTAINABLE BY THE FERMENTATION OF VARIOUS RAW MATERIALS (AFTER COOK)

Material	Yield of 95 per cent. alcohol obtainable	Material	Yield of 95 per cent. alcohol obtainable
	Imp. gallons/ton		Imp. gallons/ton
Sugar molasses	65	Sweet potatoes	35
Sugar cane ..	20	Arrowroot	35
Sorghum stalks	12	Yams	35
Nipa palm juice	0·065 per gallon	Apples and pears	12
Maize	85	Apricots and peaches	11
Sorghum grains	87	Grapes	18
Wheat ..	83	Bananas	13
Barley ..	70	Zamia palm	18
Oats	68	Grass-tree	20
Potatoes ..	20	Prickly pear	2–5
Sugar Beet ..	20	Prickly pear fruit	19
Artichokes ..	18·5	Sisal hemp leaves	19
Cassava ..	39	Wood (dry)	Up to 75

of an average conversion into alcohol of 90 per cent. The evidence on which they are based has been discussed at length by Cook.[53]

In the case of Great Britain, the only raw materials that could be grown in this country for the production of ethyl alcohol for power purposes (apart from wheat and grain, which are out of the question), are potatoes, mangolds, sugar beet and Jerusalem artichokes, but the cost of the alcohol produced from either of these materials is very high. Nathan [52] has estimated the cost, as shown in Table 13, and has concluded that " the availability and price of raw materials would make it impossible to manufacture alcohol for power purposes in quantity in this country from indigenous raw materials." Further information on this subject will be found in the Interim and Third Memoranda on Fuel for Motor Transport issued by the Department of Scientific and Industrial Research in July 1920, and October 1924, respectively. The position has not greatly changed in recent years.

TABLE 13

Material	Yields of Alcohol in gallons per ton	Price per ton of Raw Materials £ s. d.	Price of Raw Material per gallon of alcohol s. d.
Potatoes ..	20	4 10 0	4 6
Mangolds ..	8	19 0	2 4½
Sugar beet ..	22	2 8 9	2 2½

In Germany, the potato has for many years been the main source of industrial alcohol, potato growing being inaugurated more than a century ago in order to improve the sandy soils of East Germany, where the conditions of soil and climate were so unfavourable that without some such encouragement the country would have been in serious danger of depopulation.

In 1922, Monier-Williams [54] summed up English conditions, as far as the production of ethyl alcohol from potatoes was concerned, by stating that such a development " would, undoubtedly, demand heavy State subvention and would not . . . be commercially practicable."

The commercial production of alcohol from beets has been practised for many years in France (and in Europe, generally), and a large proportion of the industrial alcohol now produced in that country is manufactured from these roots. In Great Britain, subsidies are given to sugar beet production as an assistance to agriculture.

Details regarding the fermentation process for the production of ethyl alcohol may be found in other publications. The production of industrial alcohol from molasses at the Dagenham works of Solvent Products, Limited, has been described.[55]

The production of ethyl alcohol from potatoes in Europe has been fully described by Williams.[88] After cooling, the tubers are steamed

under a pressure of 2–3 atm. for 1–2 hours in order to gelatinise the starch. The resulting pulp is cooled to about 50°C., an equal volume of water added, the temperature raised to 40°C. and 10 per cent. malt added. The mixture is allowed to stand for 10–15 minutes while the starch is converted to dextrin. The temperature is then gradually raised to 55°C. when the dextrin is converted to maltose, which in turn is partially transformed into dextrose. The mash is subsequently diluted with hot water at 80°C. to prevent the growth of bacteria and the bulk of the solid matter is separated by centrifuging. Fermentation is begun at a temperature of 18°C., but the temperature rises soon after the addition of the yeast and must be held at about 28°C. by circulation of cold water. The fermentation process occupies 3–4 days and the yield obtained commercially is 50–51% of the starch content of the potatoes. The alcohol content of the wash may reach 9–10% as compared with about 4% in wash from sugar molasses. It is possible to produce 96–97% alcohol from the wash in one operation by the use of modern distillation plant. A certain amount, usually about 1% of the original starch content, of a low boiling mixture, chiefly aldehydes, is obtained on primary distillation and this is unsuitable as a motor fuel constituent. About 1–2% of fusel oil, calculated on the weight of potato starch, is also produced, this containing about 65% amyl alcohol, 20% isobutyl alcohol and 5% normal propyl alcohol and having a boiling range of 95–135°C. The removal of fusel oil from ethyl alcohol intended for use as motor fuel by adsorption on active charcoal is now practised.[89] It is necessary, in order to avoid oxidation and the formation of aldehydes, for the adsorption to be carried out at a maximum temperature of 30°C. and also in a vacuum. For alcohol containing 0·1% fusel oil, 1 ton of active carbon is said to be sufficient for the treatment of 4,000 tons of alcohol.

The production of ethyl alcohol in the U.S.A. is given in the following table.[56]

Fiscal Year	*Alcohol produced* *Proof gallons*
1922	79,906,101
1923	122,402,849
1924	135,897,725
1925	166,165,517
1926	202,271,670
1927	184,333,016
1928	169,149,904
1929	200,832,051
1930	191,859,342
1931	166,014,846
1932	146,950,812

In 1932, 84·75 per cent. of the total alcohol was made from molasses, while 10 per cent. of the total production was by synthetic processes.

450. The Production of Alcohols from Olefine Gases.—The aliphatic alcohols, with the exception of methanol, may be produced synthetically from olefine-bearing gases and, during the past few years, much work has been done on this new development. Two methods have been investigated: (*a*) the sulphuric acid process and (*b*) the direct hydration process.

(a) **The Sulphuric Acid Process.**—When ethylene is absorbed in concentrated sulphuric acid and the resulting liquid diluted and distilled, ethyl alcohol is produced according to the equations:

$$CH_2{=}CH_2 + H_2SO_4 \rightarrow CH_3{\cdot}CH_2{\cdot}HSO_4$$
$$CH_3{\cdot}CH_2{\cdot}HSO_4 + H_2O \rightarrow CH_3{\cdot}CH_2OH + H_2SO_4$$

In 1919, the results of experimental work on the production of ethyl alcohol from the ethylene contained in coke oven gas was described by Bury,[57] but the process was not applied to large scale operations until some years later. Two years later, in 1921, Tidman [58] published further details. The coke oven gas was passed through the usual plant for the removal of tar, ammonia, naphthalene and benzole and desulphurised in iron oxide purifiers. The gas was then scrubbed with 80 per cent. sulphuric acid in order to remove moisture and the higher olefines, such as propylene and butylene. After this treatment, the gas was passed through towers of sheet lead packed with broken fused silica and sulphuric acid, where it met a counter current of 95·4 per cent. sulphuric acid. At temperatures lower than 60–80°C., absorption was slow, while at higher temperatures decomposition occurred. The resulting acid liquor was treated in two ways. According to one procedure, it was distilled in a column with a counter current of steam, when the ethyl sulphuric acid was hydrolysed and the resulting acid simultaneously reduced to 75 per cent. strength. This method was abandoned because of the excessive frothing which occurred. The second method was to dilute the liquor with water under reduced pressure, after which it was distilled. At this time, it was estimated that a plant processing 5,800 tons of coal per week should produce 9,280 gallons of absolute alcohol, i.e., 1·6 gallons of alcohol per ton of coal. This was based on a 70 per cent. absorption of ethylene in the sulphuric acid and a 70 per cent. conversion of the absorbed ethylene into ethyl alcohol. The cost of the alcohol produced was estimated at two shillings per gallon.

The main obstacle in the way of developing this process for making ethyl alcohol from coke oven gas, appears to have been the large amount of concentrated acid required and the need for continued re-concentration. Tidman (*loc. cit.*) stated that the amount of sulphuric acid required was six to seven times the weight of the alcohol produced. These difficulties appear to have been surmounted in other localities and in 1927 it was reported[59] that, at the coke oven works of the Compagnie des Mines de Bêthune in Northern France, ethyl alcohol was being produced there to the extent of 2·7 gallons per ton of coal processed, at a rate of 4 tons (1,120 gallons) per day. In this case, the diluted sulphuric acid, after recovery of the alcohol, was used for the manufacture of sulphate of ammonia and hence could be disposed of economically. Later details of the process used by the Compagnie de Bêthune have been given by Osterreith and Dechamps.[14] The process now embodies absorption of ethylene in sulphuric acid in a series of towers at a pressure of 10 atmospheres. The ethyl hydrogen sulphate so produced is then diluted with a certain small proportion of water in order to separate resinous compounds which are formed by polymerisation or decomposition side-reactions, and is then admitted to lead plate fractionating columns heated with open steam. The regenerated sulphuric acid leaves the column at the bottom, while the alcohol vapour escapes from the top of the column and is subsequently rectified. In the installation erected by this concern at Ougrée (Belgium), the efficiency of the absorption of ethylene exceeds 95 per cent., so that about one litre of concentrated acid is consumed per litre of alcohol produced. The dilute sulphuric acid is still used in the production of ammonium sulphate, an economic means of disposal only available in certain circumstances. The alcohol produced is said to contain oily impurities and appreciable quantities of isopropyl alcohol and ethers, which are removed by a nitration process, developed by the Société des Distilleries des Deux-Sèvres. It is of interest to note, in this connection, that it is practically impossible completely to separate by simple means isopropyl alcohol from ethyl alcohol and that if pure ethyl alcohol is to be obtained (this is not essential if the alcohol is to be used as a fuel constituent), the propylene must be separated from the ethylene before the latter is absorbed into sulphuric acid. The process adopted for this by the Société d'Ougrée-Marihaye consists of the selective absorption of propylene in sulphuric acid already containing a definite amount of ethyl hydrogen sulphate.

451. The production of ethyl alcohol from ethylene by means of the sulphuric acid process is also carried out in America, where the Carbide and Carbon Chemical Co. has erected a plant capable of producing 8–10 million gallons of alcohol per year. The source of the ethylene

used is Gyro cracking gas. The gas is compressed and refrigerated in order to separate the olefines and these are then separated from each other by fractionation under pressure, thus producing ethylene of high purity. The use of pure ethylene has contributed largely to the success of the process, other methods having been handicapped by the use of impure gaseous raw materials. A process developed by the National Research Council at Ottawa is estimated to be capable of producing 10 million gallons of industrial alcohol per year from the waste gases of the Turner Valley field in Alberta, but no public disclosures of the process involved have yet been made.[60] A survey of the patent literature indicates that the Petroleum Chemical Corporation, the Standard Oil Company of New Jersey, the Shell Oil Corporation and the Empire Refineries Company in America, the Distillers Company and Imperial Chemical Industries, Ltd., in England and the N. V. de Bataafsche Petr. Maat in Holland are also actively interested in the process.

452. The olefines higher than ethylene react with sulphuric acid to give alcohols much more readily than ethylene itself and less concentrated sulphuric acid is required.[61, 62] The first production of isopropyl alcohol was undertaken by the Standard Oil Company of New Jersey in 1919 by the Ellis process.[63] The gas used was obtained from Burton cracking stills and, after being purified, was passed through 87 per cent. sulphuric acid, the temperature being maintained below 20°C. The product was diluted with several volumes of water and distilled, a crude 20 per cent. aqueous isopropyl alcohol thus being obtained. Complete details of the process, as applied to mixtures of propylene, butylenes, and other olefines, have been given by Davis and the Petroleum Chemical Corporation in their various patents,[64] which should be consulted for further details. The process is briefly as follows :—

The gases are first desulphurised and separated into fractions by washing with cooled gas oil, in which the butylenes and higher olefines are dissolved. The stripped gas, containing propylene and ethylene, is converted into isopropyl alcohol by solution in 93–100 per cent. sulphuric acid, the temperature of the acid being kept below 30°C., to prevent polymerisation. The gas oil from the scrubbers is stripped of its higher olefine content in two or more stages, at different temperatures and pressures, whereby the amylenes and butylenes are separated from each other. The butylene and amylene fractions are treated with 60 per cent. sulphuric acid to convert the iso-hydrocarbons into tertiary alcohols, while a further treatment with 75–83 per cent. acid suffices to convert the unabsorbed butylenes and amylenes into secondary alcohols.

453. In the sulphuric acid absorption of ethylene and its homologues, it has been found that catalysts can be employed to advantage, since working temperatures and /or the concentration of the acid may be reduced. For example, Damiens[65] has shown that cuprous oxide is an effective catalyst, while silver sulphate has been proposed by Glaud,[66] Gerr and Popov[67] and by the Distillers Company, Joshua and Stanley.[68] Patents by the N. V. de Bataafsche Petr. Maat have protected the following substances as catalysts :—

(*a*) Metallic cyano complexes, such as ferricyanic or ferrocyanic acids or salts or compounds, etc., derived from them.[69]

(*b*) Double compounds or complexes of unsaturated hydrocarbons and metallic cyano complexes.[70]

(*c*) The elements platinum, palladium, osmium, iridium, ruthenium or rhenium or their compounds in a finely divided condition and preferably on a carrier.[71]

The use of heavy metal sulphates, particularly ferrous and copper sulphates[72] and the use of sub-oxides of salts of metals possessing several oxides,[73] has also been proposed in very early patents by Damiens and Piette. The results of experimental work on the absorption of ethylene into sulphuric acid of density 1·84, containing small amounts of iron and silver, have been described,[74] while the addition of solvents, such as nitrobenzene, ether and ethyl alcohol to sulphuric acid to increase the solubility of olefines has been mentioned.[71] The use of sulphuric acid deposited on a carrier for the vapour-phase hydration of ethylene in the presence of steam, is the subject of a very interesting patent by the Distillers Company, Joshua and Stanley.[75] Sulphuric acid of 60–85 per cent. strength is supported on a porous carrier and maintained at a temperature, preferably of 140–160°C., but not above 200°C. Ethylene and steam are then passed over this mass at atmospheric or super-atmospheric pressure, the amount of steam used being such that there is sufficient, on the one hand, to take part in the reaction, and, on the other hand, to maintain the acid concentration at the temperature employed. The idea expressed in this patent is a very ingenious one as it makes use of sulphuric acid in the most efficient manner possible and eliminates any need for concentration, but it would appear that, for any given working temperature, the range of steam space velocities allowable is somewhat limited. No information regarding the extent of polymerisation reactions in this process is available.

454. (b) Direct Hydration Processes.—Considerable work is being carried out, particularly in this country, on the reaction whereby

ethylene and higher olefines are directly combined with steam in the presence of suitable catalysts. The general reaction involved is

$$C_nH_{2n} + H_2O \rightleftarrows C_nH_{2n+1}OH$$

the reverse of which, the dehydration of alcohols, has been practised for some years as a means of preparing the corresponding olefines.

Very complete data on the experimental determination of the equilibrium constants for the vapour-phase hydration of the various gaseous olefines have been published by Stanley, Youell and Dymock,[90] who determined the equilibrium in both hydration and dehydration using catalysts comprising phosphoric acid, manganese oxide and boric oxide, of the general formula $MnO–BO–xH_3PO_4$, where x varied between 2·4 and 3·6. The determinations were made at atmospheric pressure and the results obtained were as follows :—

TABLE 14.—MEAN VALUES OF EQUILIBRIUM CONSTANT

$$K_p = \frac{pC_nH_{2n+1}OH}{pC_nH_{2n} \cdot pH_2O}$$

Temp. °C.	Ethylene	Propylene	*n*-Butylenes	Iso-Butylene
145	$6·8 \times 10^{-2}$	—	$9·4 \times 10^{-3}$ (150°C)	$3·64 \times 10^{-2}$ (150°C)
175	$3·6 \times 10^{-2}$	$1·91 \times 10^{-2}$	$4·58 \times 10^{-3}$	$1·98 \times 10^{-2}$
200	$1·65 \times 10^{-2}$	$1·19 \times 10^{-2}$	$3·36 \times 10^{-3}$	—
225	$1·07 \times 10^{-2}$	$7·92 \times 10^{-3}$	$1·96 \times 10^{-3}$	—
250	$6·7 \times 10^{-3}$	$4·63 \times 10^{-3}$	$1·39 \times 10^{-3}$	—

Appleby, Glass and Horsley[175] have investigated the hydration of ethylene using a cadmium metaphosphate catalyst and determined the equilibrium constant at atmospheric pressure. The equilibrium was approached from both sides at five different temperatures and the following results were obtained :

Temp. °C.	K_p		
	Approached from Synthesis Side	Approached from Decomposition Side	Mean
175	$2·57 \times 10^{-2}$	$3·29 \times 10^{-2}$	$2·93 \times 10^{-2}$
200	$1·77 \times 10^{-2}$	$1·62 \times 10^{-2}$	$1·72 \times 10^{-2}$
225	$10·55 \times 10^{-3}$	$9·37 \times 10^{-3}$	$9·84 \times 10^{-3}$
250	$6·71 \times 10^{-3}$	$5·63 \times 10^{-3}$	$6·28 \times 10^{-3}$
275	$3·90 \times 10^{-3}$	$3·60 \times 10^{-3}$	$3·83 \times 10^{-3}$

The use of this catalyst for ethylene hydration has also been examined by Bliss and Dodge.[176]

Appleby, Glass and Horsley's results when plotted as $\log_{10} K_p$ against the reciprocal of the absolute temperature give a straight line the equation of which is :

$$\log_{10} K_p = 2159/T - 6{\cdot}34$$

This is in fair agreement with the equation

$$\log_{10} K_p = 2100/T - 6{\cdot}17$$

derived by Bliss and Dodge from a combination of their experiments with those of Stanley, Youell and Dymock. The heat of reaction calculated from the slope of the curve obtained by Appleby, Glass and Horsley is 9900 g. cals.

Sanders and Dodge[91] have investigated the hydration of ethylene in the presence of alumina and tungstic oxide catalysts under a pressure of 70 atm. An average value of K_p of 1·07 by 10^{-3} was obtained at 380°C. as a mean of several experiments from both synthesis and decomposition directions. Extrapolation of the data of Stanley *et al.* to the same temperature gives a value of K_p of 1·06 by 10^3 which indicates very good agreement.

Marek and Flege[92] have determined the value of K_p in the hydration of *n*-butylene at 482°C. and 204 atm. and obtained a mean value of 2·9 by 10^{-4}.

The determination by Francis[93] of the equilibrium constant in the hydration of isobutylene at 167°C. gave a value of 2·4 by 10^{-2}, which agrees very well with that obtained by interpolation of the above results of Stanley and his co-workers. Calculation of the equilibrium constant from thermo-dynamic data has been shown to be of little value because of uncertainties in the necessary thermal data.[91]

The vapour-phase hydration of an olefine to the corresponding alcohol by treatment with steam in the vapour phase, involves a decrease in total volume of 50 per cent. thus :—

$$\underset{1\text{ volume}}{C_2H_4} + \underset{1\text{ volume}}{H_2O} = \underset{1\text{ volume}}{C_2H_5OH}$$

and should, therefore, be beneficially affected by the application of super-atmospheric pressure. However, although this is the case, such an increase in working pressure, or, in other words, an increase in the partial pressure of the reacting olefine, may induce certain undesirable side reactions, of which polymerisation of the olefine to higher unsaturated hydrocarbons is the most noticeable at temperatures above about 250°C. In order to avoid such side reactions and limit the reaction to the required direction, it is necessary to increase the partial pressure of the steam and maintain the partial pressure of the olefine at a relatively low figure. By such means, the yields of alcohols may be considerably

improved. Thus, by operating at a temperature of 450°C., and about three atmospheres partial pressure of olefines and 200 atmospheres steam pressure, a conversion of ethylene to ethyl alcohol of about 40 per cent. is obtained at equilibrium.

455. The proper choice of catalysts for the vapour-phase hydration of olefines under pressure is a very important factor, but, unfortunately, catalysts active in promoting the hydration reaction are likewise active towards promotion of the undesirable polymerisation reactions, since this latter reaction often proceeds at a more rapid rate than that of alcohol production. The main advantage of the catalyst is to lower the temperature required for the reaction to proceed at reasonable velocity, for as the temperature is increased to obtain more favourable rates, the equilibrium conversion of alcohol becomes lower and the tendency to polymerise is increased. The catalyst adopted, however, must not promote the dehydrogenation of the alcohol to aldehyde, a reaction which proceeds easily at 450°C., even under a hydrogen pressure of 100 atmospheres.

That ethylene and water react only very slightly in the absence of a catalyst at elevated temperatures and pressures has been shown by Klever and Glaser,[77] who found that in 17 hours at 150°C. and 190 atmospheres, only 0·00011 mole. of ethylene was hydrated per mole. of water, and at 200°C. and 100 atmospheres pressure, 0·0008 mole. was hydrated. The addition of 1·93 per cent. of hydrochloric acid resulted in the hydration of more than 1 mole. of ethylene in the same length of time. Swann, Snow and Keyes[78] have also carried out hydration experiments with ethylene in the presence of dilute hydrochloric acid; they found, however, that alcohol yields were very small. When using propylene at 600 to 800 pounds per square inch (40 to 53 atmospheres), at 135°C., in the presence of 5 per cent. hydrochloric acid solutions and solutions of silver nitrate, yields of alcohol several times that obtained from ethylene were found. The amounts were still very low, however, even with times of reaction as long as one hour.

It should be noted, however, that in both these investigations the yields of alcohol were very small, and since the tests used to determine alcohol were not very specific and might be given by other organic compounds, there appears to be no definite proof that ethyl alcohol was actually synthesised.

456. The catalytic vapour-phase hydration of 2-butene, under pressure, has been considered by Marek and Flege,[79] at temperatures of 427–538°C., and pressures of 3,000–5,000 pounds per square inch (200–333 atmospheres). Very low yields were obtained, however, owing to the use of very inefficient catalysts, as shown in Table 15.

Under comparable conditions the amount of olefine converted to hydrated products relative to that polymerised was greater for phosphoric acid than for any of the other catalysts examined, while at 427°C., an increase in the time of contact of over five-fold had only a slight effect upon the conversion.

TABLE 15. CATALYTIC VAPOUR-PHASE HYDRATION OF 2-BUTENE, UNDER PRESSURE (MAREK AND FLEGE)

EFFECT OF TEMPERATURE AND CATALYSTS

Pressure 211 Kgs./cm.^{2} (204·2 atm.). Mole. ratio, steam/butene = 50/1.

Catalyst	Temp. °C.	Time of Contact, seconds	% of 2-butene converted into		Concentration of Hydrated Product in exit aqueous solution
			Hydrated Products	Polymers	
Cuprous chloride	427	77	6·4	0·0	0·5
Do.	427	78	6·3	<0·05	0·51
Do.	482	70	6·8	0·5	0·58
Do.	482	82	6·8	0·3	0·58
Do.	538	65	—	4·2	0·06
None	427	78	0·46	0·0	0·03
Do.	482	72	2·16	0·0	0·22
Do.	538	68	4·9	2·3	0·38
Copper phosphate	427	74	3·52	<0·05	0·28
Do.	482	69	4·5	<0·05	0·34
Do.	538	64	5·0	5·0	0·44
Thoria	427	71	2·4	<0·05	0·18
Do.	482	67	5·2	0·72	0·53
Do.	538	63	7·7	6·80	0·62

The polymers formed analysed as follows :—

13·5% at 93°C.	Refractive index		1·4111	Sp. gr.	0·727
32·6% at 119°C.	,,	,,	1·4458	,, ,,	0·791
50·3% at 135°C.	,,	,,	1·4560	,, ,,	0·812
57·4% at 152°C.	,,	,,	1·4822	,, ,,	0·863

but varied somewhat according to the experimental conditions. Both increase in pressure and increase of steam / butene ratio increased the yield of alcohol obtained, but increase in pressure also increased the polymer formation.

Sanders and Dodge have described tests on various catalysts in the vapour-phase hydration of ethylene. Preliminary tests were made on ethanol dehydration at 300°C. and atmospheric pressure using

an ethanol flow rate of 5·2 grams per hour per ml. of catalyst and the following conclusions were reached:

1. Addition of a small amount of copper to an aluminium catalyst increases the tendency to cause dehydrogenation at the expense of dehydration.
2. Thoria is inactive and not selective.
3. Tungstic oxide is substantially as active as alumina but not quite as selective. Preliminary treatment with reducing gas at 500°C. greatly enhances its activity.
4. Phosphoric acid is an active catalyst but is either volatile or forms volatile compounds at this temperature and gives rise to phosphates in the products.
5. Aluminium sulphate and phosphate are inactive.
6. Ammonium phosphotungstate yields an active and highly selective catalyst.
7. Aluminium silicate is a good catalyst.
8. Addition of chromium to an alumina catalyst decreases both activity and selectivity.
9. A mixture of tungstic acid and alumina was initially the most active catalyst tested, but the activity decreased somewhat with use.
10. The best methods of preparing an alumina catalyst appeared to be (*a*) solution of aluminium amalgam in water and (*b*) precipitation from sodium aluminate by sulphuric acid.
11. Treatment of an alumina catalyst with air at 500°C. considerably increased its activity. This treatment was particularly effective in restoring activity to a catalyst which had been used in high pressure synthesis.

Sanders and Dodge give some results obtained in the vapour-phase hydration of ethylene to ethyl alcohol, using alumina and tungstic acid catalysts.[94]

457. Numerous patents have been granted for the hydration of olefines under conditions favourable from the thermodynamic standpoint, but some of these appear to make exaggerated claims regarding the conversions obtained when compared with the values of equilibrium conversion given above. [80, 81]

Most of the catalysts proposed are of acidic nature, and the most popular appear to be those containing phosphates, or preferably free phosphoric acid, and are very similar to those found effective in the catalytic polymerisation of olefines (see Chapter VIII). The use, as catalysts, of solutions or suspensions of heavy metal sulphates, has been proposed. Zinc sulphate is preferred at temperatures of at

least 275–325°C. and pressures of 100–200 atm. and it has been claimed[82] that by contacting ethylene at a rate of 1 litre per minute with 300 g. of a 25% zinc sulphate solution at 300°C. and 120 atm. pressure, about 20% of the ethylene is converted into ethyl alcohol.

Elkington[83] has patented catalysts such as the metals silver, gold, copper, iron, nickel, cobalt, chromium, vanadium, etc., or salts or other compounds of these metals which decompose to give free metals under the conditions of the reaction, and states that 15–20 per cent. yields are obtained.

Dreyfus[95] has patented catalysts comprising acid metal chlorides (e.g., zinc chloride) at a temperature of 200°C. and also catalysts consisting of pyrosulphates stable under reaction conditions of 150–350°C. and pressures up to 35 atmospheres[96] and also aqueous solutions of relatively weak acids.[97]

With regard to phosphate catalysts, various patents of the Distillers Co., Ltd., claim the use of such materials containing free, i.e., uncombined, phosphoric acid, but the patents of other concerns claim the use of metaphosphates containing, presumably, no free acid. Under reaction conditions, however, in the presence of an excess of steam even metaphosphates probably hydrolyse to give a mixture containing free acid. It might be expected, nevertheless, that the former catalysts would be more active but more likely to form polymerisation products if the conditions of olefine partial pressure, steam partial pressure and temperature are favourable. The conditions normally employed for olefine hydration are 200–300°C. and either atmospheric pressure or pressures up to 200 atmospheres. The olefine steam ratio is usually in the range 1·0 to 3·0, but at atmospheric pressure may reach a value up to 10·0.

A patent[98] of the I.G. Farbenindustrie claims the use of inorganic or organic acids or their anhydrides in a state of fine division on carriers and also the phosphates of the rare earth metals. Cerium metaphosphate is said to be of good activity. Dreyfus has patented the use of phosphoric acid which is initially in an anhydrous condition[99] and also the use of alkali or alkaline earth metaphosphates.[100] The use of cadmium phosphate as a catalyst in olefine hydration reactions has been patented by G. F. Horsley and I.C.I., Ltd. E.P. 346,288 claims a process for the production of acetaldehyde, etc., by passing a mixture of steam and acetylene at a raised temperature over a catalyst containing in chemical combination cadmium, phosphorus and oxygen, with or without hydrogen. Specific mention is made of cadmium phosphate of the composition represented by the mole. ratio $P_2O_5/CdO = 0{\cdot}4–0{\cdot}6$. The optimum results were obtained with a mole. ratio of 0·47.

Horsley[84] also claims the use of the phosphates of beryllium, zinc, cadmium, etc., as catalysts in the hydration of ethylene and quotes the following results obtained at atmospheric pressure and at 200°C., with a contact time of six seconds and a steam/ethylene ratio of 1 to 1.

Catalyst	% Alcohol by weight in the aqueous condensate	% Conversion of Ethylene
Cadmium phosphate	1·0	0·39
Aluminium phosphate + 25% cadmium phosphate ..	0·61	0·24
Lead phosphate	0·53	0·2
Zinc phosphate	0·26	0·1
Aluminium phosphate ..	0·19	0·07
Tin phosphate	0·44	0·18

In cadmium phosphate, the preferred mole. ratio of CdO to P_2O_5 is between 1 : 0·9 and 1 : 0·725.

In a further patent, Horsley[85] has covered the purification of ethylene from higher olefines by causing the latter to be polymerised at 150°–200°C., and at atmospheric or higher pressure by passing the gaseous mixture over cadmium phosphate, thus indicating that this catalyst, though effective in the hydration of ethylene, has a polymerising effect on higher olefines.

Boron phosphate is also claimed to be an effective hydration catalyst. In E.P. 378,865 (G. F. Horsley and I.C.I., Ltd.) the statement is made that the catalyst is preferably purified before use so that it is substantially free of uncombined phosphoric acid and boric acid, but the Distillers Co., Ltd. claim, in E.P. 396,724, "a catalyst compounded from phosphoric acid and a boron oxide, the amount of phosphoric acid present in the catalyst being at least 10 per cent. in excess of that required to form the orthophosphate, but not in excess of about 95 per cent. of the composition."

Strontium metaphosphate has been mentioned as a hydration catalyst (G. F. Horsley and I.C.I., Ltd., E.P. 407,944), while the Distillers Co., Ltd., have patented catalysts comprising the phosphates of one or more of the elements uranium, ferrous iron or cobaltous cobalt containing free uncombined phosphoric acid (E.P. 392,289) and also the phosphates of copper and/or manganese containing free uncombined phosphoric acid (E.P. 392,685).

In the case of iron phosphates the maximum conversion of ethylene to ethyl alcohol was obtained with a catalyst of the empirical composition FeO, $2{\cdot}5H_3PO_4$, while in the case of manganese phosphates the most active catalyst was of the composition MnO, $2{\cdot}7H_3PO_4$. In E.P. 392,685 mention is also made of the following catalysts: $CuO{\cdot}H_3PO_4$, $MnO{\cdot}CuO{\cdot}4H_3PO_4$ and $1{\cdot}5MnO : 1CuO : 6{\cdot}05H_3PO_4$.

Catalysts comprising the phosphates of one or more of the metals manganese, copper, iron, cobalt or uranium—such catalysts containing free phosphoric acid—have also been patented (E.P. 408,982).

458. Attention is now being given to catalysts containing more than one phosphate, it having been found that mixed catalysts are often more active than those containing one phosphate only. Horsley has patented (E.P. 408,313) catalysts consisting of ferric phosphate associated with a metaphosphate of a divalent metal such as barium, strontium, cadmium, copper or ferrous iron, while the Distillers Co. have covered mixtures of calcium and barium, strontium and magnesium phosphates containing free phosphoric acid (E.P. 415,426 and 415,427).

Other preferred mixed phosphate catalysts are those containing cadmium metaphosphate and small quantities of one or more of the metaphosphates of barium, strontium, titanium, chromium or tellurium (E.P. 423,877) and also catalysts comprising one or two molecular proportions of aluminium metaphosphate associated with about one molecular proportion of a metaphosphate of calcium, cadmium, zinc, divalent copper, nickel, tin or lead (E.P. 435,769).

However, phosphate catalysts cannot be considered as very suitable in hydration reactions because they are not usually mechanically stable under the conditions normally employed. Attempts to improve the mechanical strength have included the incorporation of drying oils such as linseed oil or tung oil (E.P. 404,115), non-drying oils such as castor oil, whale oil, aliphatic alcohols, etc. (E.P. 422,635), and also the incorporation of materials such as molasses, carbohydrates and starch (E.P. 413,043).

As far as is known the production of alcohol by the catalytic vapour-phase hydration of the corresponding olefines has not yet progressed from the experimental scale.

459. The Production of Alcohols by the Controlled Oxidation of Hydrocarbon Gases.—A large amount of research has been carried out on the oxidation of the lower paraffin hydrocarbons to alcohols. It appears, however, that the initial oxidation products are so susceptible to further reaction at the temperatures of operation that they are attacked by the oxidising agent in preference to the original hydrocarbons and, as a result of this, it is difficult to obtain even moderately good yields.

Bones' hydroxylation theory[101] postulates methanol as the primary product when methane is oxidised by air, but very meagre data are available to show that methanol can be produced commercially in this way. In spite of the many attempts made to introduce direct oxidation

of gaseous hydrocarbons at ordinary pressure on a commercial scale, it is questionable whether there are any installations in operation at present. More promising results seem to be obtained by operation at high pressure, and Lewis and Frolich[102] report results on the oxidation of propane with oxygen under pressures of 136 atmospheres and at temperatures of 300–350°C., showing that more than 40 per cent. of the oxygen may be accounted for in the liquid oxidation products. The composition of a typical product is claimed to be

Acetaldehyde and acetone	6·0 per cent.
Methanol	22·0 ,, ,,
Ethyl alcohol (95 per cent.)	37·0 ,, ,,
Propyl alcohol (78 per cent.)	7·0 ,, ,,
Formic acid	1·5 ,, ,,
Water	26·5 ,, ,,
	100·0

According to the explosive limit determinations of Cooper and Wiezevich,[103] it should be safe to operate with methane at a pressure of 204 atmospheres and a temperature of 400°C., in the presence of less than 10 per cent. of oxygen. This figure may be raised somewhat in the case of the higher gaseous paraffins.

460. Production of Higher Alcohols from Ethyl Alcohol.—Ethyl alcohol may be converted into a mixture of higher alcohols by treatment in the vapour phase at elevated temperatures and /or pressures with certain catalysts. Mixtures of magnesia and copper oxide, containing more of the former than of the latter, have been proposed as suitable catalysts,[104] while, in another process,[105] the conversion is effected by passing ethyl alcohol vapour, together with hydrogen, over heated catalysts comprising alkaline earth oxides activated by the presence of less than 10 per cent. of one or more other metallic oxides. The process is characterised by the addition of methanol vapour to the reacting ethyl alcohol. An example is quoted in which ethyl alcohol, methanol and hydrogen, in the molecular ratio of 1·4 : 1 : 3, was passed over a catalyst composed of 97 per cent. magnesium oxide, 8 per cent. alumina and 3 per cent. copper oxide, at 260°C., and at atmospheric pressure. The product obtained had the following composition :— *n*-propyl alcohol, 14 per cent., isobutyl alcohol 18 per cent., *n*-butyl alcohol 29 per cent., amyl alcohol 22 per cent., hexyl alcohol 8 per cent., and higher alcohols 16 per cent.

461. The Dehydration of Aqueous Ethyl Alcohol.—As shown later in this Chapter, the miscibility of ethyl alcohol with normal

petroleum motor spirits and blends containing aromatic hydrocarbons such as benzole, is considerably improved if the ethyl alcohol employed is completely anhydrous. Similarly the water tolerances of alcohol fuels are also improved by the use of anhydrous alcohols. When produced by fermentation or synthetic processes ethyl alcohol is invariably recovered in the form of an aqueous solution, which, when distilled, gives an azeotropic mixture containing 95·57 per cent. ethyl alcohol and 4·43 per cent. water, which boils at 78·15°C. at normal atmospheric pressure. This azeotrope is unsuitable for use in motor fuels and must be dehydrated. Numerous methods of accomplishing this are available and are described in detail in the literature.[106, 107, 108, 109, 110, 111]

A well-known method is fractionation with benzene or benzole, in which two fractions are obtained, the lower boiling fraction being the constant boiling-point mixture of alcohol, benzene and water and the higher boiling fraction absolute alcohol. The first fraction separates into two layers, both of which are recycled to the fractionating unit.

An improvement on this process is the use of tri-chlorethylene in the place of benzole as used by the German State Alcohol Monopoly. This process is known as the Drawinol process.

In the Haig process the dehydrating agent is a mixture of sodium and potassium acetates. An alcoholic solution of these salts flows down a column filled with rings and meets ascending alcohol vapours. The latter are dehydrated and withdrawn after subsequent condensation. The alcohol—aqueous salt solution leaves the base of the column and is freed of alcohol in a small column, while water is removed in a regenerator. The salt passes to a vessel containing dehydrated alcohol and returns to the main column.

A new process has been recently developed by the I.G. Farbenindustrie involving the use of gypsum (calcium sulphate) and is in operation at the Leverkusen works of this company. The plant has an output of 70,000 litres (15,000 gallons) per day of 99·8–99·9% alcohol from the constant boiling-point mixture with water. The dehydrating agent is cheap and is easily regenerated.

During the dehydration the gypsum is only transformed to the semi-hydrate and does not lose its powdery form or apparent dryness. Dehydration takes place in two tapering parallel drums, each 8m. long by 1·2–1·5m. diameter, through which the gypsum is transferred counter-current to the alcohol vapours by a screw. The duration of the reaction is 15–16 seconds. In the first drum alcohol is dehydrated and in the second drum the gypsum is regenerated. The dehydrated alcohol is filtered free of gypsum dust both before and after condensation. Regeneration is effected at 175°C. in a current of heated air. Losses

of gypsum in the process are claimed not to exceed 1·5 kilos per 100 litres of alcohol and the steam consumption is stated to be 50–52 kilos per 100 litres of alcohol produced.

462. The Solubility of Methanol* in Hydrocarbons and Typical Petrols.—Methanol suffers from the great disadvantage that there are very few petrols with which it is miscible in all proportions at ordinary temperatures, even when it is perfectly dry, whereas anhydrous ethyl alcohol is perfectly miscible with all petrols at the same temperatures. This one fact limits the use of methanol as a fuel constituent very seriously and will probably prevent its use in a blended form on a large scale.

The solubility of methanol in any hydrocarbon is a function of (*a*) temperature, (*b*) the molecular configuration and physical properties of the hydrocarbon and (*c*) the presence of water. In general, the lower the temperature, the more narrow are the limits of miscibility between the two, while the presence of even very small amounts of water reduces miscibility to a very marked extent. Of the four main classes of hydrocarbons, namely, paraffins, naphthenes, aromatics and unsaturateds, methanol is soluble to the least extent in the normal paraffins and to the greatest extent in the aromatics and is, in nearly all cases, more soluble in unsaturateds than in naphthenes. This generalisation is only true, however, when comparing hydrocarbons of the same boiling point, for in all classes of hydrocarbons, the solubility of methanol decreases with rise in the hydrocarbon boiling point and molecular weight. Thus, methanol is more soluble, at a given temperature, in normal pentane than in normal heptane: similarly, it is more soluble in cyclohexane than in the substituted cyclohexanes and more soluble in low boiling olefines than in high boiling aromatics. It is also noteworthy that methanol is more soluble in branched chain paraffins than in the normal homologues.

Table 16 gives some figures for the solubility of methanol in hydrocarbons recently published by Howes,[112] which support the above conclusions. The fact that methanol has a lower solubility in pure normal heptane, ex Pinus Sabiniana,[113] than in a technical grade of normal heptane is accounted for by the fact that the latter contains naphthene impurities.

From the figures given in Table 16, it is evident that no definite relationship exists between the aniline point of a hydrocarbon and its solvent power for methanol. It will be noticed, however, as a very

* The methanol referred to in this chapter gave the following figures on analysis:—

Water	0·02% by weight.
Sulphur	<0·001% by weight.
Aldehydes	minute trace only.
Sp. gr. 15/15°C.	0·7964.

approximate guide, that, in general, the lower the aniline point, the higher the methanol solubility.

TABLE 16. SOLUBILITY OF METHANOL IN VARIOUS HYDROCARBONS AT — 20° TO + 20°C.[112]

Hydrocarbon	Aniline Point °C.	Methanol Solubility (per cent. volume)				
		−20°C.	−10°C.	0°C.	+10°C.	+20°C.
n-Pentane*	—	3·2	4·3	7·1	12·8	Completely miscible.
Iso-pentane*	—	3·7	5·6	9·9	Complete	ly miscible.
n-Hexane*	57·0	2·4	3·6	5·6	9·1	24·7
n-Heptane*	68·9	0·9	1·9	3·0	4·5	6·7
n-Heptane (pure) ..	69·7	0·4	1·1	1·9	2·8	4·1
2-2-4-Trimethyl pentane	79·6	—	—	2·1	3·9	5·1
Cyclohexane	31·0	—	Cyc	lohexan	e crystall	ises out.
Methyl cyclohexane ..	41·0	—	1·4	2·1	3·1	4·1
Cyclohexane	— 20·0	7·4	11·8	24·2	Complete	ly miscible.
Di-isobutylene ..	32·2		M	iscible i	n all pro	portions.
Octene-1 and -2 mixture	—	—	20·7	—	—	—
Trimethyl ethylene ..	11·0		M	iscible i	n all pro	portions.
Amylene mixture ..	14·0				Ditto.	
Diethyl methyl ethylene	— 40·0				Ditto.	

* Impure samples.

Data on the solubility of methanol in typical English market petrols, benzole mixtures, aviation spirits, cracked spirits, etc., is given in Table 17, which indicates that :—

(*a*) With the exception of benzole mixtures, methanol is only soluble in normal petrols to a negligible extent at a temperature of −10°C. Therefore the addition of a blending agent, or substance to promote miscibility, is always necessary.

(*b*) In the case of cracked spirits, an olefine content of 20% has a negligible effect upon methanol solubility. (This would appear contrary to the evidence given in Table 17, but it is probable that the unsaturated hydrocarbons present in cracked spirit have a high average boiling point and, consequently, have no effect upon the methanol solubility.)

(*c*) Reduction in average boiling point causes a greater increase in methanol solubility than the presence of olefines normally met in cracked spirits.

(*d*) Methanol is more soluble in benzole mixture K, which contains 53% of total aromatics and 30% of benzole, than in spirit V, which contains 63·2% of aromatics. The reason for this is shown later.

(*e*) Methanol has the same solubility at −10°C., in casing-head gasoline M, of mid-point 59°C. and aromatic content 2·7%, as in spirit

TABLE 17. THE SOLUBILITY OF METHANOL IN VARIOUS PETROLS

	Specific Gravity 15°/15°C.	Aniline Point °C.	Mid-Point. °C.	% Carbon	% Hydrogen	% Unsaturateds	% Aromatics	% Naphthenes	% Paraffins	Methanol Solubility % volume	
										− 10°C.	0°C.
English market spirit A ..	0·7390	48·8	—	85·50	14·5	3·0	15·0	33·0	49·0	0·5	2·4
Do. B ..	0·7377	46·5	120	85·41	13·93	17·0	20·0	13·0	50·0	1·0	3·85
Do. C ..	0·7283	57·1	—	84·41	14·52	9·0	14·0	22·0	55·0	1·0	3·85
Do. D ..	0·7334	48·2	—	84·97	14·62	3·0	12·0	41·0	44·0	0·5	2·9
Do. E ..	0·7307	46·6	—	84·84	14·43	2·0	19·0	25·0	54·0	0·5	2·4
Do. F ..	0·7191	52·1	—	85·19	14·24	9·0	13·0	19·0	59·0	2·4	3·4
Do. G ..	0·7570	47·7	—	85·51	14·41	10·0	10·0	53·0	27·0	0·5	1·0
Do. H ..	0·7559	47·7	—	85·14	14·34	12·0	10·0	49·0	29·0	0·5	1·0
Market benzole mixture K	0·7774	20·6	—	86·92	12·55	1·0	53·0	9·0	37·0	23·7	40·2
Benzole mixture L ..	0·7609	26·7	—	—	—	6·0	36·0	23·0	35·0	15·0	43·0
Casing-head gasoline M ..	0·6711	—	59	84·03	15·93	1·0	3·0	41·0	55·0	2·4	3·3
Aviation spirit N ..	0·7165	50·5	94	84·57	14·92	2·0	12·0	56·0	30·0	2·5	4·0
Cracked spirit O ..	0·7738	—	156	—	—	20·0	34·0	26·0	45·0	1·5	3·5
Cracked spirit P	0·7529	—	138	—	—	13·0	16·0	26·0	45·0	2·0	2·7
Mid-Continent straight-run	0·7388	56·3	122	—	—	4·0	9·0	35·0	52·0	0·5	2·1
California straight-run ..	0·7564	50·2	125	—	—	3·0	8·0	61·0	28·0	0·5	2·6
Spirit R	0·7670	30·3	112·5	85·96	13·81	3·0	26·0	55·0	16·0	2·4	3·3
Do. S	0·7958	18·7	128·5	—	—	3·0	41·0	44·0	12·0	4·3	5·2
Do. T	0·7786	47·0	144	—	—	Nil	9·0	91·0	Nil	1·0	1·0
Do. V	—	−16·0	160	—	—	2·0	63·0	26·0	9·0	19·4	30·0
Do. W	—	39·6	150	—	—	1·0	14·0	52·0	33·0	1·0	2·2

R, which contains 25·8% aromatics. This illustrates the importance of volatility upon methanol solubility and shows that high boiling aromatics do not affect the methanol solubility to any marked extent.

The literature contains information concerning the solubility relationships of methanol with the following: Cyclohexane,[114] hexane,[115] water and benzene,[116] water and hexane,[117] water and heptane,[118] water and gasoline, and water and paraffin. Shepherd[119] has described the results of miscibility tests with gasoline and with benzene. Binary and ternary systems of methanol, water and cyclohexane have been studied by Washburn and Spencer.[120]

463. Blending Agents for Methanol-Petrol Mixtures.—Aromatic Hydrocarbons.—In order to make homogeneous mixtures of methanol and petrol, resort must be made to blending agents, i.e., substances which function in this way because of their mutual solvent power upon both methanol and petrols. Numerous blending agents are known, but none of these can be considered of commercial value because they must be used in comparatively large quantities.

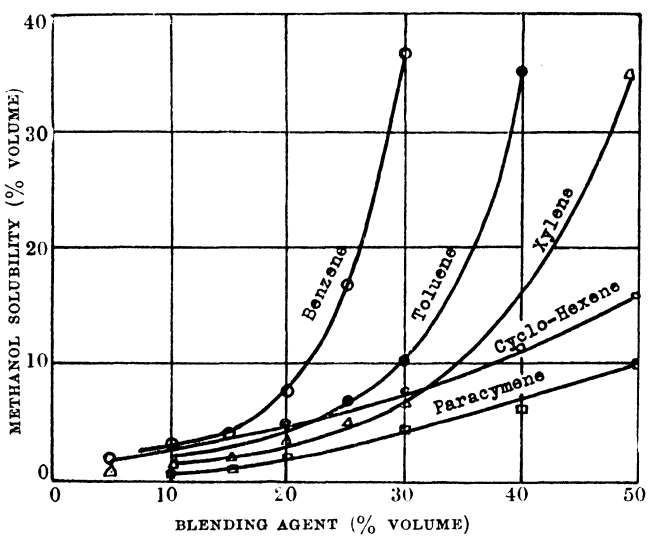


FIG. 3.—CURVES SHOWING THE SOLUBILITY OF METHANOL AT 0°C. IN BLENDS OF PURE HYDROCARBONS AND PETROLEUM ETHER (HOWES)
(Courtesy of Institution of Petroleum Technologists)

As already shown, methanol is completely miscible, at ordinary temperatures, with benzene or benzole; therefore, a petrol to which benzole has been added dissolves a greater amount of methanol than it does by itself. All other aromatic hydrocarbons act in the same way, but to greatly varying extents; their efficiency, in this direction, falling off very rapidly with rise in boiling point and molecular weight. This is illustrated in Fig. 3, which shows the solubility of methanol at

0°C., in blends of benzene, toluene, xylene, para-cymene and cyclohexene, with 100–120°C. aromatic free petroleum ether.

Thus, to dissolve 10% by volume of methanol in this petroleum ether, the following amounts of the hydrocarbons used as blending agents are required :—

	% by Volume
Benzene	21·6
Toluene	30·0
Xylene	34·7
Para-cymene	50·0
Cyclohexene	37·2

Or, expressed in another way, 20% by volume blends of the hydrocarbons in the petroleum ether dissolve the following amounts of methanol (at 0°C.) :—

	Solubility of Methanol (% by Volume)
80% Petroleum Ether + 20% Benzene ..	7·8
80% ,, ,, + 20% Toluene ..	4·7
80% ,, ,, + 20% Xylene ..	3·1
80% ,, ,, + 20% Para-cymene	2·3
80% ,, ,, + 20% Cyclohexene	4·7

Benzene is, therefore, by far the most efficient blending agent of the aromatic hydrocarbons. It will be observed that the cyclic unsaturated hydrocarbon, cyclohexene, is more efficient as a blending agent than para-cymene in all concentrations up to 50%, and more efficient than xylene in all concentrations up to 35%. The relative efficiencies of the aromatic hydrocarbons as blending agents for methanol-petrol mixtures are also evident from Fig. 4.

Such considerations as these adequately explain why there is no definite relationship between the aromatic hydrocarbon contents of petrols and the solubility of methanol therein.

The effect of temperature upon the solubility of methanol, in any given petrol, or upon the amount of blending agent required to produce miscibility, is very marked. Thus, Fig. 5 shows that, in the case of an Iranian spirit, to hold 10% of methanol in solution, there is required :—

9·5% of benzole at ..	+15°C.
18·0% ,, ,, ,, ..	0°C.
23·0% ,, ,, ,, ..	−10°C.
28·0% ,, ,, ,, ..	−20°C.
35·0% ,, ,, ,, ..	−30°C.
38·0% ,, ,, ,, ..	−40°C.

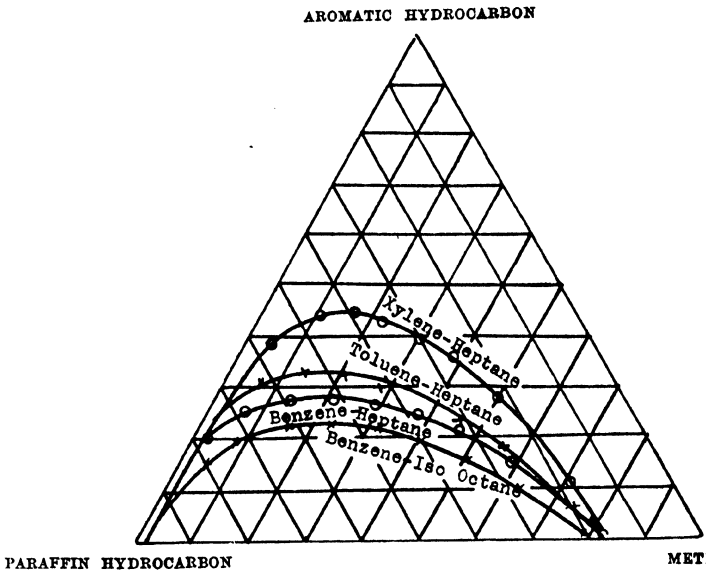


FIG. 4.—CURVES SHOWING THE RELATIVE EFFICIENCIES OF THE AROMATIC HYDROCARBONS AS BLENDING AGENTS FOR METHANOL–PETROL MIXTURES (HOWES)
(Courtesy of Institution of Petroleum Technologists)

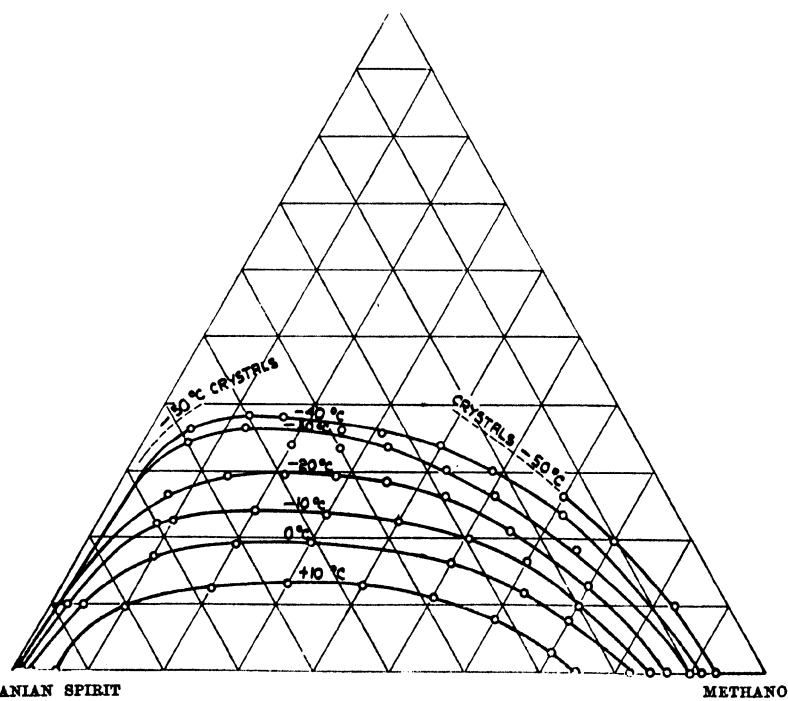


FIG. 5.—CURVES SHOWING THE MISCIBILITY RELATIONSHIPS OF THE SYSTEM, IRANIAN SPIRIT—MOTOR BENZOLE—METHANOL AT TEMPERATURES RANGING FROM + 15°C. TO − 50°C.

464. Other Blending Agents.—As in the case of wet ethyl alcohol–petrol mixtures, there are other substances much more effective than benzole in promoting the miscibility of methanol-petrol mixtures, and substances effective in the first case are also effective in the second case. Moreover, their relative efficiencies are the same in each case.

The compounds most effective in this direction are the higher boiling alcohols and cyclohexanol. Anhydrous ethyl alcohol can also be used as a blending agent for methanol-petrol mixtures, but wet alcohol is of no value in this direction. Miscibility curves for the system methanol–ethyl-alcohol–Iranian spirit are shown in Fig. 6, in which the petrol referred to is typical of those sold on the English market during 1932.

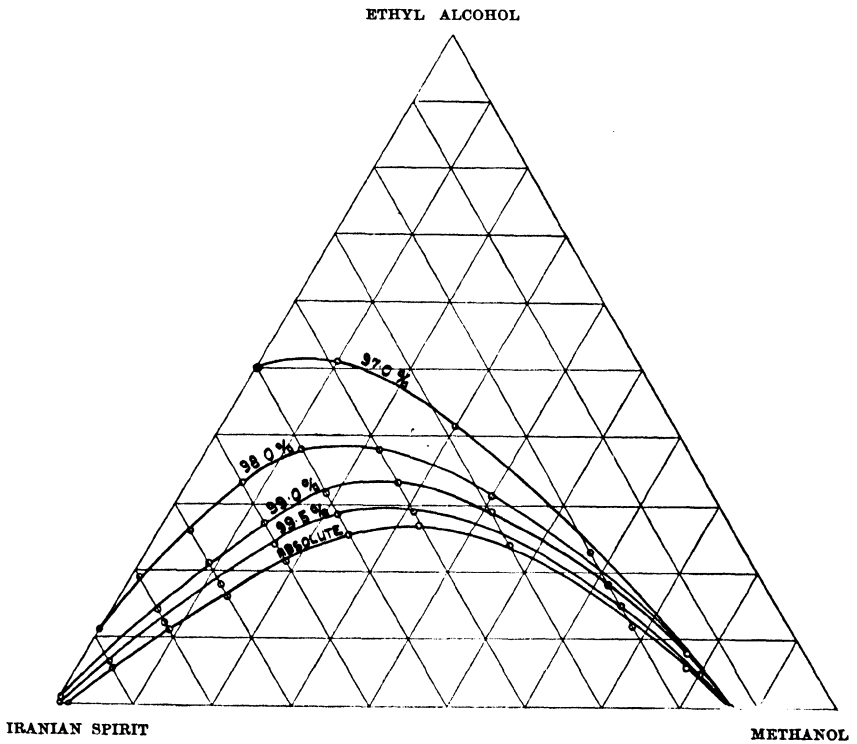


FIG. 6.—CURVES SHOWING THE EFFICIENCIES OF ETHYL ALCOHOL OF VARIOUS STRENGTHS AS BLENDING AGENTS FOR METHANOL–IRANIAN SPIRIT MIXTURES AT — 10°C.

Absolute ethyl alcohol has an advantage over benzole as a blending agent in that smaller quantities of it are required, and it is of interest to note, as shown in Fig. 7, that the maximum requirement of ethyl alcohol is at a methanol concentration of 40 per cent., whereas more benzole is required to give miscibility to a 20 per cent. methanol blend than to a 40 per cent. blend.

The relative efficiencies of the higher aliphatic alcohols and other alcohols as blending agents are shown in Table 18.

TABLE 18. THE HIGHER ALCOHOLS AS BLENDING AGENTS FOR METHANOL-PETROL MIXTURES[121]

(% by volume to hold 10 per cent. of methanol in solution in a standard motor fuel at — 10°C.)

Ethyl alcohol	10·3	Synthetic fusel oil:—	
n-Propyl alcohol	4·0	BP/100–200°C.	5·5
iso-Propyl alcohol	5·0	BP/200–230°C.	5·6
n-Butyl alcohol	3·5	BP/230–280°C.	6·6
iso-Butyl alcohol	4·0	BP/280–320°C.	10·6
tert-Butyl alcohol	6·0	Allyl alcohol	Valueless
sec-Butyl alcohol	5·2	Phenyl-ethyl alcohol	,,
n-Amyl alcohol	3·3	Benzyl alcohol	,,
tert-Amyl alcohol	3·6	Cyclohexanol	3·0
n-Hexyl alcohol	3·2	*p*-Methyl cyclohexanol	3·4
n-Heptyl alcohol	3·2	*m*-Methyl cyclohexanol	3·7
n-Octyl alcohol	3·1	Howard's "Sextol" (methycyclohexanol)	3·2
sec-Octyl alcohol	3·0	α-Terpineol	4·5
		Fenchyl alcohol	5·2

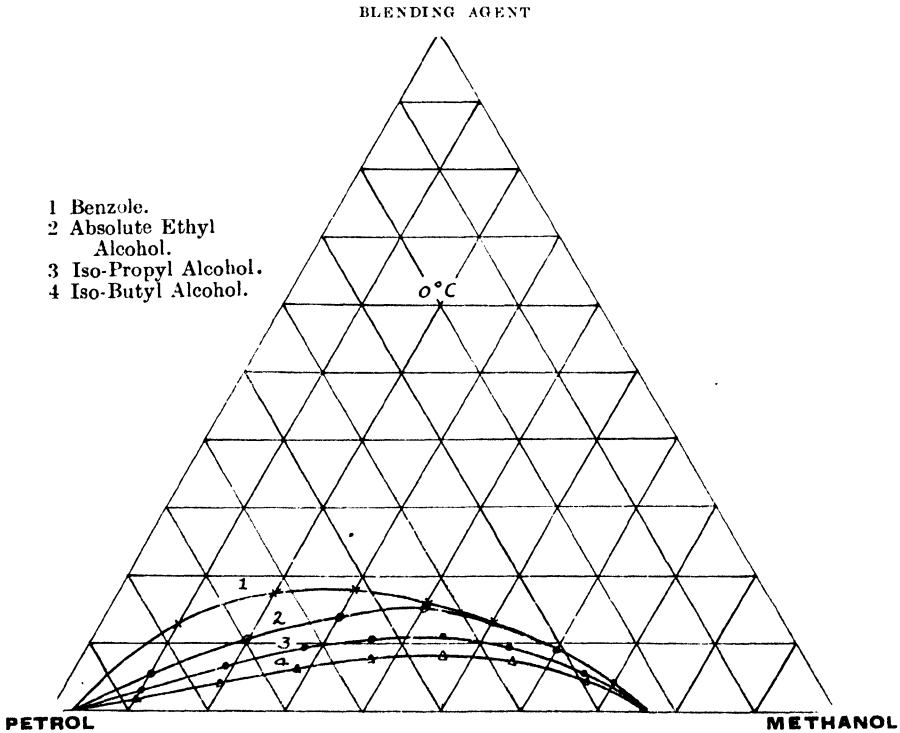


FIG. 7.—CURVES SHOWING THE RELATIVE EFFICIENCIES OF BENZOLE, ABSOLUTE ETHYL ALCOHOL, ISO-PROPYL ALCOHOL AND ISO-BUTYL ALCOHOL AS BLENDING AGENTS FOR PETROL-METHANOL MIXTURES AT 0°C. (HOWES)
(Courtesy of Institution of Petroleum Technologists)

It will be seen that the iso- and tertiary alcohols are less efficient than their normal homologues.

A point of particular interest is that the higher alcohols, such as isobutanol, etc., may be produced synthetically from water gas, simultaneously and in the same plant as methanol itself; consequently, it is possible to produce in one operation a mixture of methanol and higher alcohols which is miscible with petrol.

The results of detailed tests on the miscibility of various hydrocarbons and petroleum spirits with the various aliphatic alcohols have been recently described by Ormandy, Pond and Davies.[122] The water tolerances of blends of gasoline with ethyl alcohol, isopropyl alcohol and benzene have been considered by Bayley and Hopkins.[123]

465. The Solubility of Ethyl Alcohol containing Water in Various Hydrocarbons and Petrols.—Although absolute (i.e., water-free) ethyl alcohol is miscible in all proportions with all but a very few petroleum motor fuels, ethyl alcohol containing water is only soluble to a limited extent, and blending agents are necessary as in the case of methanol-petrol mixtures. Even though absolute ethyl alcohol can be obtained in large quantities, such alcohol is hygroscopic and readily absorbs moisture from the air.

The rules governing the solubility of methanol in hydrocarbons and petrols also apply to the solubility of wet ethyl alcohols. Thus, this substance is more soluble in aromatic hydrocarbons than in naphthenes and paraffins and more soluble in the lower members of a homologous series of hydrocarbons than in the higher members. Similarly, the lower the temperature, the lower the solubility. The effect of water in limiting the solubility of alcohol in petrol is very marked, the addition of even so small a quantity as 1·8 per cent. being sufficient to cause marked separation. In a solution of equal parts of petrol and absolute ethyl alcohol, the amount of the separated layer at 0°C. is as much as 36 per cent. of the volume of petrol present.

Most of the published work on the miscibility relationships of ethyl alcohol–petrol mixtures has been carried out using ethyl alcohol of about 95 volume per cent. strength, the remainder being water. This is because a mixture of ethyl alcohol and water in the proportion of 95·57 to 4·43 by weight is an azeotropic mixture of minimum boiling point and is the mixture normally produced unless special methods of producing absolute ethyl alcohol are employed. King and Manning[124] have carried out experiments in which they determined the miscibility limits of a range of petroleum spirits with 95 volume per cent. alcohol, and concluded that, whilst certain petroleum spirits are fairly readily soluble (40 per cent. at −10°C.) in this alcohol, others are soluble only to the extent

of about 22 per cent. Their results, given in Fig. 8, show that Borneo straight-run benzine and, in a lesser degree, Iranian spirit, differ from the other spirits examined in having higher solubilities. Their solubility curves are, however, steeper, indicating that the effect of temperature is more pronounced in these two cases. Ormandy and Craven[125] have quoted similar figures for five petroleum spirits, as follows :—

TABLE 19

Origin of Spirit	Specific Gravity 15/15°C.	Limiting Petrol Weight per cent. in Mixture with 95 per cent. Alcohol		
		15°C.	0°C.	−10°C.
Borneo or Sumatra (A) ..	0·782	77	47	37
(B) ..	0·723	70	43	36
America .. .. (E) ..	0·719	42	31	26
(F) ..	0·704	38	28	24
Miri (Borneo) .. (H) ..	0·767	32	25	22

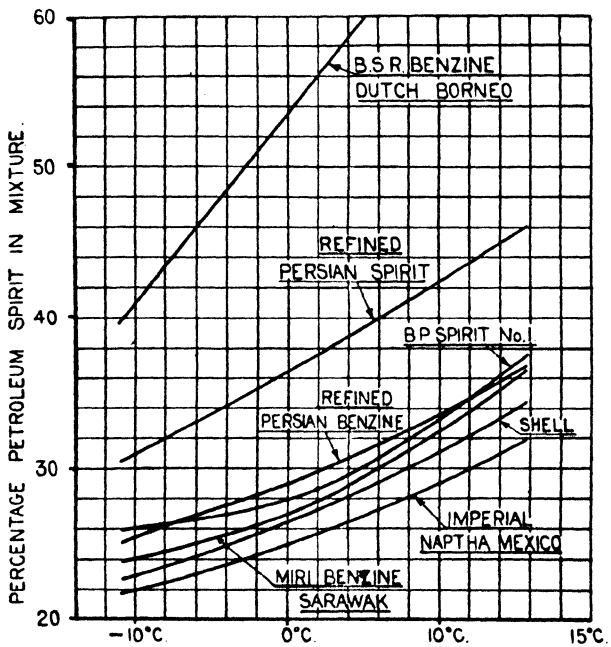


FIG. 8.—CURVES SHOWING THE SOLUBILITY OF PETROLEUM SPIRITS IN 95 PER CENT. ETHYL ALCOHOL (KING AND MANNING)

(Courtesy of Institution of Petroleum Technologists)

The solubilities of certain hydrocarbons in alcohols of various strengths at −10°C., are as follows :—

TABLE 20

	Solubility of Hydrocarbon in		
	95%	92%	90% Ethyl Alcohol
Isopentane[125]	—	37%	—
Pentane[125]	—	35%	—
Hexane[125]	—	29-30%	—
Heptane[125]	—	18-22%	—
Heptane[125]	16%	—	10%
Methyl cyclohexane[126] ..	27%	—	13%

466. An important contribution to our knowledge on the solubility of ethyl alcohol in petroleum spirits has recently been made by Bridgeman and Querfeld[127] who have determined the solubility of alcohols of

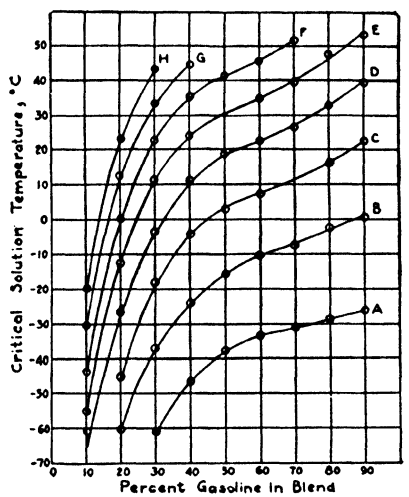


FIG. 9.—CURVES SHOWING THE SOLUBILITY OF ETHYL ALCOHOL OF VARIOUS STRENGTHS IN STRAIGHT-RUN PENNSYLVANIAN GASOLINE (BRIDGEMAN AND QUERFELD)

(Courtesy of Editor, "Industrial and Engineering Chemistry")

various strengths, from 99·13 to 93·21 volume per cent., in gasolines of various types. These workers have found that, for straight-run spirits of the same volatility, the solution temperatures of a given blend composition differ but little from fuel to fuel, and the source of crude from which the fuel is distilled appears to have a comparatively minor effect. Cracked spirits may, however, show much lower solution temperatures than straight-run products of the same volatility. Topping a fuel of about the volatility of U.S. motor gasoline so as to reduce the 90 per cent. temperature approximately 40°C. produces a lowering in solution temperature of from 10 to 16°C. Increase of the volatility at

the lower end of the distillation curve likewise produces a lowering in solution temperature. On the average the addition of 10 per cent. pentane caused a drop of 4°C.

At each constant percentage of gasoline in the blend, it was found that the logarithm of the percentage of water present (S) was a linear function of the reciprocal of the solution temperature in absolute degrees Centigrade (T), so that

$$\log S = a + \frac{b}{T}$$

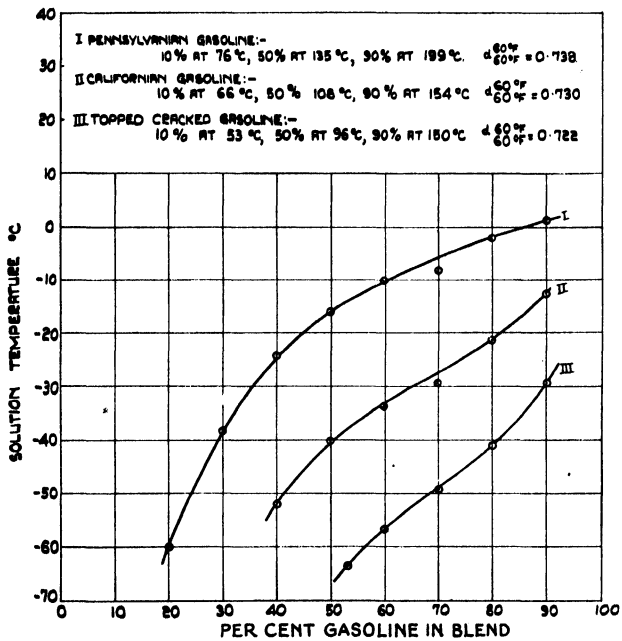


FIG. 10.—CURVES SHOWING SOLUTION TEMPERATURES OF BLENDS OF 98·33 PER CENT. ETHYL ALCOHOL IN PETROLEUM SPIRITS OF DIFFERENT VOLATILITIES (BRIDGEMAN AND QUERFELD)

The results obtained by Bridgeman and Querfeld in the case of a straight-run Pennsylvanian gasoline are shown in Fig. 9, and indicate the pronounced effect of the presence of water upon physical stability. Thus a blend containing 30 per cent. of alcohol of 98·33 per cent. strength has a solution temperature of −29°C., but when the alcohol strength is reduced to 96·67%, the solution temperature is raised to as high as +10°C. This reduction of alcohol strength is equivalent to the addition of only $(98{\cdot}33 - 96{\cdot}67) \times \frac{30}{100} = 0{\cdot}498$ per cent. of water to the blend.

Fig. 10 is also taken from the figures of Bridgeman and Querfeld. This shows the differences in solution temperatures obtained with blends

of 98·33 per cent. alcohol in Pennsylvanian and Californian straight-run spirits and cracked spirits of different volatilities. As already mentioned the differences in solution temperatures are almost wholly accounted for by variations in volatility characteristics. On the other hand, one can regard straight-run Pennsylvanian gasoline having a 50 per cent. evaporated temperature of 135°C. as one of the worst spirits to use for blending with alcohol, and a cracked spirit having a 50 per cent. evaporated temperature of 96°C. as one of the most favourable for this purpose, if such highly aromatic spirits as those from certain Borneo and Sumatra crudes are excepted.

467. The Miscibility Relationships of Ethyl Alcohol and Benzene.—Absolute ethyl alcohol and benzene are miscible in all proportions at temperatures above the melting point of the latter (5·4°C.), but as the initial freezing point of commercial motor benzole is about −11°C., mixtures of alcohol with the latter are susceptible to crystallisation only when pure benzene is used. The freezing points of mixtures of pure benzene and absolute alcohol are such that, at a temperature of −10°C., the maximum amount of benzene permissible in a stable solution is 40 per cent. ; of commercial benzole the proportion is much greater.

468. Ethyl Alcohol–Petrol–Benzole Mixtures.—Interesting data on this ternary system, using 94–98 per cent. ethyl alcohol, have been published by King and Manning.[124] Their results indicate that the particular petrol used (specific gravity 15 /15°C., 0·743 ; 39% distillate at 100°C. ; end point 190°C.), is soluble in alcohols of various strengths to the following extents at 10°C. and 0°C.

	10°C.	0°C.
94% Ethyl alcohol	30·0%	27·0%
95% ,, ,, ...	43·0%	33·0%
96% ,, ,, ...	66·0%	46·0%
98% ,, ,, ...	95·0%	94·0%

The necessity of using absolute ethyl alcohol in blends with petrol is obvious from these figures. Fig. 11, which is reproduced from King and Manning's paper, shows a large area of immiscibility even when 98 per cent. alcohol is used with pure benzene. Alcohol of this strength is not even miscible with pure benzene in all proportions at −10°C., much less can any mixture with benzene be made to mix with petrol in all proportions. The limits of miscibility with motor benzole are even less.

469. With regard to blending agents for aqueous ethyl alcohol–petrol mixtures, it is a general rule that those substances found effective in promoting miscibility in methanol-petrol mixtures are also effective

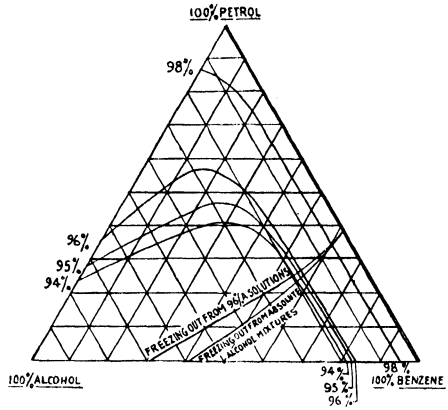


FIG. 11.—THE SYSTEM PETROL–BENZENE–ETHYL ALCOHOL CONTAINING VARYING AMOUNTS OF WATER (KING AND MANNING)
(Courtesy of Institution of Petroleum Technologists)

in the case of ethyl alcohol blends and the relative efficiencies of such compounds are the same in both cases. Ormandy and Craven[128] found in 1923 that when a small proportion of the alcohol was replaced by an equal volume of any one given blending agent the change in separation temperature $\triangle t$ was proportional to the volume of blending agent added, and inversely proportional to the volume of alcohol originally present, within certain limits. Thus, if B = per cent. by volume of blending agent replacing an equal volume of alcohol and A = per cent. by volume of alcohol before replacement, then

$$\triangle t \propto \frac{1}{A}$$

$$\triangle t \propto B$$

$$\text{or} \quad \triangle t = K\frac{B}{A}$$

The constant $K = \frac{\triangle t\, A}{B}$ might be called the " blending power " of the blending agent and when positive indicates that such an agent has a positive action in assisting miscibility. The value of K is not rigorously constant over a range of alcohol concentrations, but is sufficiently so to give an idea as to the relative value of a blending agent. Values for a series of blending agents on this basis are given in Table 21.

Ormandy and Craven state that no substance so far examined is more than one-fifth part as effective in preventing separation as water is in bringing it about, and it is extremely unlikely that any such substance will be found. The truth of such a prediction has been fully demonstrated during the past few years when, in spite of many attempts, no really successful blending agent has yet been found.

TABLE 21. RELATIVE EFFICIENCIES OF VARIOUS BLENDING AGENTS IN PROMOTING MISCIBILITY

in a mixture consisting of 85% hydrocarbons, 10% of 95% alcohol, 5% blending agent

	$K = \frac{\Delta t A}{B}$	
	Heptane	Petrol
Benzene	3	1
Toluene	− 6	—
m-Xylene	−18	—
Turpentine	0 (about)	>0
Heptane	−11	—
Cresol	123	114
Aniline	51	26
Methyl alcohol	−24	−30
Ethyl alcohol 95%	0	0
„ 100%	72	72
Propyl alcohol	90	70
Butyl alcohol	168	144
Amyl alcohol	170	150
Hexyl alcohol	47	—
Ether	small	3
Acetone	41	18
Ethyl acetate	small	27
Cyclohexanol	201	150
Acetaldehyde	−20	—
Water	− 1,000	—

470. Patented Blending Agents for Alcohol-Petrol Mixtures.— The most diverse substances have been patented as blending agents for alcohol-petrol mixtures, some of which are very effective and some, of course, of very little value. Examples are anhydrous fusel oil or amyl alcohol,[129] camphor, pine tars or pine tar products,[130] aromatic hydrocarbons,[131] carbon disulphide,[132] and fatty acids, such as ricinoleic acid or castor oil.[133] Complex ketones[134] have been protected and, despite their bad odour, strongly basic aliphatic amines, such as triethyl amine, benzylamine or piperidine.[135] The I.G. have proposed the use of alkyl formates for a similar purpose.[136]

471. The Stability of Alcohol Fuels to Water Additions.— Because the lower aliphatic alcohols, methanol and ethyl alcohol, are miscible with water, fuels containing these substances are capable of dissolving small amounts of water. When, however, more than a small quantity of water is added to an alcohol-petrol mixture, it causes a separation into two immiscible layers, the lower one of which consists essentially of alcohol and water and the upper layer consists mainly of hydrocarbons. This property is by far the most objectionable

feature of alcohol fuels and, in this respect, methanol mixtures are less satisfactory than ethyl alcohol blends. Under storage conditions, i.e., in tanks, the advantage is obviously all in favour of those fuels, e.g., petrols, that are quite immiscible with water, since if such fuels become contaminated with water, the water can be easily separated off and the composition of the fuel is not affected. On the other hand, if the fuel can be delivered to the tank of an automobile without being contaminated with water, then the advantage lies with the type of fuel which will dissolve small amounts of water. The subsequent addition of quantities of water, less than that required to cause separation, does not affect the running of the engine, whereas, with fuels which do not dissolve water, the same small amounts of water lead to erratic running and even stoppage of the engine. Such water is normally deposited in the carburettor float chambers and fuel line systems of automobiles and frequently causes trouble, but when alcohol fuels are used, this trouble is no longer experienced.

Alcohol fuels intended for use in automobiles must, therefore, have a high " water tolerance," i.e., they must be capable of dissolving large amounts of water without separating into two immiscible layers. Defining " water tolerance " in this way, it follows that the amount of water which can be added to an alcohol blend before separation occurs depends upon the following factors.

(1) The nature of the alcohol or alcohols present.
(2) Temperature.
(3) Alcohol content of the blend.
(4) Excess of blending agent present.

The effects of temperature upon the miscibility relations of alcohols and petrols have already been pointed out and it follows that the lower the temperature the lower the water tolerance of any alcohol blend. The effect of excess blending agent is also obvious, but blending agents which are miscible with water confer to alcohol blends containing them a higher water tolerance than those which are immiscible with water. In other words, of two alcohol-petrol blends, both containing the same amount of alcohol and having the same cloud point or separation temperature, one of which contains a water-soluble blending agent and the other a blending agent that is immiscible with water, the former has the higher water tolerance.

The effect of the alcohol content of a blend upon its water tolerance is evident from Fig. 12, which refers to petrol–benzole–methanol mixtures, and shows that blends rich in methanol will dissolve up to 8 per cent. by volume of water at 0°C., without causing separation (i.e., 360 c.cs. of water per gallon), whereas blends containing small amounts of methanol are capable of dissolving less than 0·1% of water

(i.e., 4·5 c.cs. per gallon). Fig. 12 also shows the effect of excess blending agent upon water tolerance.

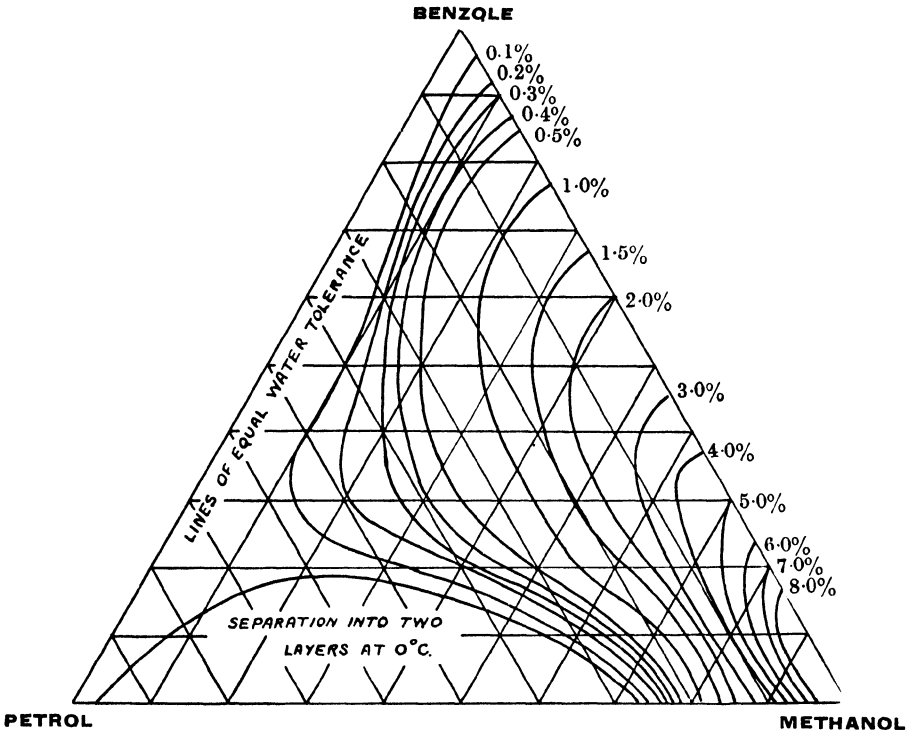


FIG. 12.—WATER TOLERANCES OF PETROL–BENZOLE–METHANOL MIXTURES AT 0°C. (HOWES)
(Courtesy of Institution of Petroleum Technologists)

The effect of temperature upon the water tolerance of a petrol–benzole–methanol blend is pronounced. In the case of a 10/30/60 methanol–benzole–petrol blend at a temperature of +15°C., no less than 6 ml. of water is capable of dissolving in each gallon of fuel mixture without causing separation, whereas, at −10°C., the water tolerance is reduced to 2 c.cs. per gallon (i.e., 0·04 per cent.).

Ethyl alcohol is particularly valuable as a blending agent for methanol–petrol mixtures because blends containing an excess above that necessary to give miscibility have a higher water tolerance than mixtures containing benzole as a blending agent. This is evident from Fig. 13, which shows the water tolerances of mixtures of petrol–methanol–absolute ethyl alcohol at −10°C.

472. A comparison of the water tolerances of ethyl alcohol blends and methanol blends is made possible by the data of Dumanois[137] referring to the former. This is plotted in Fig. 14 together with values for a methanol–benzole–petrol blend containing 30% of benzole.

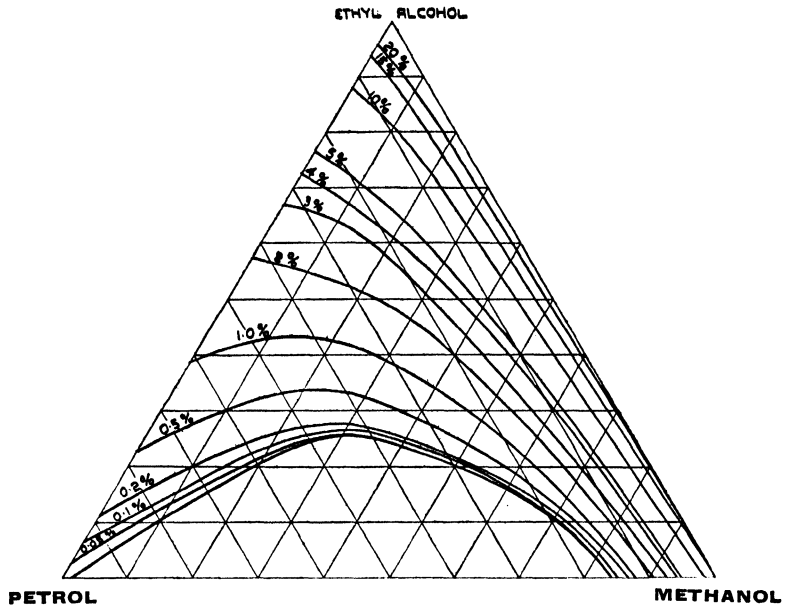


FIG. 13.—WATER TOLERANCES OF PETROL–ETHYL ALCOHOL–METHANOL MIXTURES AT — 10°C. (GORDON)
(Courtesy of Institution of Petroleum Technologists)

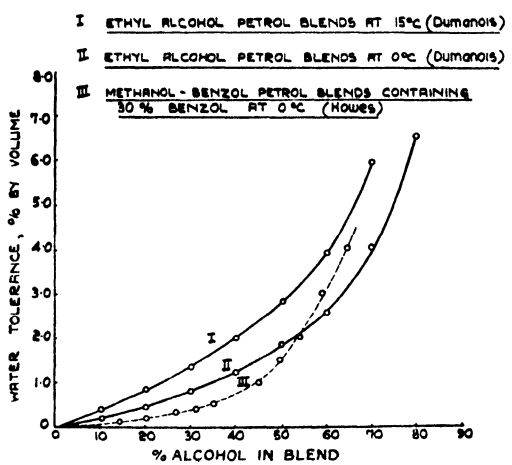


FIG. 14

It is evident that, for the same alcohol concentrations, ethyl alcohol blends have much higher water tolerances than methanol blends for alcohol concentrations of up to 50%. This graph, however, does not give a fair comparison because the methanol blends referred to contain 30% of benzole, which favourably influences their water tolerances. A better comparison is shown in Fig. 15, which refers to mixtures of

methanol and ethyl alcohol with benzene, from which it is evident that a 40 per cent. ethyl alcohol blend in benzene has a water tolerance more than double that of a 40 per cent. methanol blend.

It will be evident from the above considerations that, although an alcohol blend may be quite stable in itself at the temperatures to which it is subjected in use, and even though it may be capable of dissolving small amounts of water without suffering disintegration, it may be separated into two layers by the addition of petrol. This is most prone to occur in the case of alcohol fuels stabilised by the addition of blending agents which are not soluble in water and occurs more readily with methanol blends than ethyl alcohol blends. Thus, referring

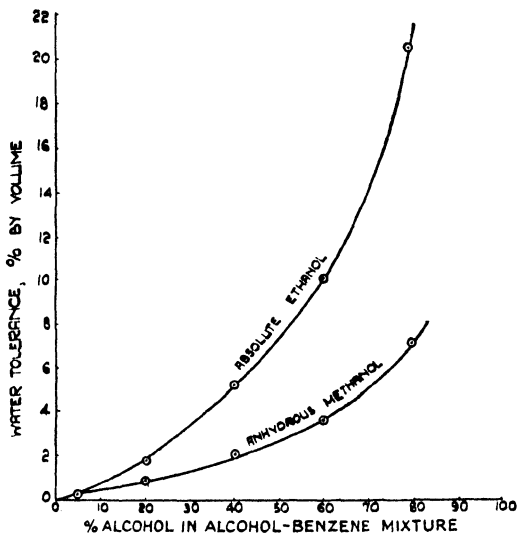


FIG. 15.—WATER TOLERANCES OF BENZENE–ETHYL ALCOHOL AND BENZENE–METHANOL MIXTURES AT 0°C.

to Fig. 12, to hold 10 per cent. of methanol in solution in a blend with petrol at 0°C., 14 per cent. by volume of benzole is necessary, but if this is diluted with an equal volume of petrol, reducing the benzole concentration to 7 per cent., the fuel is separated into two layers. It is, therefore, necessary in practice to employ a considerable excess of blending agent so that dilution with petrol may not bring about separation and so that an adventitious addition of water may not cause the same result. When such precautions are taken, alcohol blends can be used with complete satisfaction and no trouble from separation is experienced. Howes[112] has described the case of a 10 per cent. methanol blend in petrol stabilised by the addition of benzole which was stable at all temperatures down to −28°C., and which had a water tolerance of 3·5 c.cs. per gallon at 0°C. This blend was on sale at the Billingham works of Imperial Chemical Industries, Limited, for over a year and

gave no trouble due to separation, either by water addition or dilution with petrol. This blend was mixed in the usual way at the refinery, transported to the garage in a tank wagon and there transferred to the underground tank connected to one of the garage pumps, from which it was pumped in the normal manner to the tanks of customers' automobiles. The blend was found to be stable even in the coldest weather and did not absorb water. The results of daily cloud-point determinations on the blend, as taken from the garage pump, indicated that no water was absorbed in storage.

A standard practical method for the determination of the water tolerances of alcohol blends has recently been described by Ormandy, Pond and Davies.[138]

473. With regard to the reported hygroscopicity of alcohol fuels and the resulting danger of separation, the experiences reported by Howes (*loc. cit.*) suggest that methanol blends may be used over prolonged periods without any trouble from this cause. It is true that, under laboratory conditions, alcohol–petrol blends absorb water vapour from the air when freely exposed to the latter and eventually separate into two layers, but in actual practice motor fuels are not freely exposed to the atmosphere and, as a result, can often be used with satisfaction. However, it is admitted that the presence of a water-soluble substance in petrols is a potential source of much trouble.

The use of anhydrous, or very nearly anhydrous, alcohols in the production of alcohol fuels is, of course, essential because the lower the water content of the alcohol used, the greater is the general physical stability and water tolerance of the blended fuel, and, moreover, the blending agent requirements are reduced. Fortunately, methanol can be produced in an anhydrous state fairly easily, simple distillation alone being necessary, but with ethyl alcohol this is rather more difficult because of the formation of the azeotropic mixture with water. Nevertheless, ethyl alcohol containing not more than 0·5–0·8 per cent. of water is now produced in quite large quantities in this country and in Europe.

474. Physical Properties of the Lower Aliphatic Alcohols.— The alcohols differ from petroleum motor fuels in that they are chemical entities and single substances, whereas petrols are extremely complex mixtures whose compositions are only partly known. Consequently, the physical properties of the alcohols are known with far greater certainty than those of petroleum products.

The physical properties of methanol and ethyl alcohol which have a bearing upon the behaviour of these substances in internal combustion engines are discussed in Chapter XIV and detailed in Table 22.

TABLE 22. PHYSICAL PROPERTIES OF METHANOL AND ETHYL ALCOHOL

	Methanol	Ethyl Alcohol
1. Ultimate Composition		
Carbon, per cent by weight	37·5	52·1
Hydrogen	12·5	13·1
Oxygen	50·0	34·8
2. Boiling Point at 760 mm. Hg.	64·7°C	78·32°C.
3. Specific Gravity at 15·5°C.	0·7965	0·7937
4. Vapour Pressure, mm. Hg.		
—10°C.	15·6	5·6
0°C.	29·65	12·2
10°C.	53·85	23·6
20°C.	93·95	43·9
30°C.	157·0	78·8
40°C.	255·3	135·3
50°C.	405·5	222·2
60°C.	619·4	352·7
70°C.	929·0	542·5
5. Absolute Viscosity C.G.S. Units $\times 10^3$		
0°C.	8·08	17·90
10°C.	6·90	17·52
20°C.	5·93	17·16
30°C.	5·15	16·81
40°C.	4·49	16·47
50°C.	3·95	16·13
60°C.	3·49	15·81
6. Specific Heat in Liquid State, $Cal._{15}$/gram./°C.		
0°C.	0·5665	0·5355
20°C.	0·600	—
25°C.	—	0·5810
40°C.	0·6165	0·6525
7. Latent Heat of Vaporisation at the Boiling Point		
Joules per Gram	1,100	885
Calories per Gram	263	204·5
B.T.U.s per pound	473	368
8. Calorific Value		
Gross. C.H.U.s per pound	5,535	7,122
C.H.U.s per gallon at 15°C.	42,470	56,540
B.T.U.s per pound	9,605	12,820
Net. C.H.U.s per pound	4,730	6,491
C.H.U.s per gallon at 15°C.	37,650	51,530
B.T.U.s per pound	8,515	11,690
9. Theoretical Air Requirements for Complete Combustion		
Pounds of Air per pound of Fuel	6·53	9·09
Pounds of Air per gallon of Fuel	62·0	72·35
10. Explosive Limits in Air at 760 mm. Pressure (Per cent. by Volume)	7·05–36·5	3·56–18·0
11. Volume of Explosive Mixture per gram Molecule of Fuel	184 litres	346 litres
12. Volume Ratio on Combustion	1·061	1·064
13. Flash Point in Air, °C. (Approximate Values only)	— 1° to 11°C.	11° to 14°C.

475. Alcoholimetry.—It is very necessary, in the examination of alcohols, to be able to estimate their water contents by simple and reliable methods. Specific gravity measurements are usually made use of in this connection and various tables have been drawn up, showing the relation between specific gravity and water content. Such tables are reproduced here for the sake of convenience.

TABLE 23. SPECIFIC GRAVITIES AT 15°C./15°C. OF MIXTURES OF METHYL ALCOHOL AND WATER AND THE CORRESPONDING PERCENTAGES (BY VOLUME) OF METHYL ALCOHOL

(Compiled from the table published in U.S. Bureau of Standards Circular, No. 19, 1911)

% Methanol by Volume	Specific Gravity. 15°/15°C.	% Methanol by Volume	Specific Gravity. 15°/15°C.	% Methanol by Volume	Specific Gravity. 15°/15°C.
0	1·0000	34	0·95708	68	0·89790
1	0·99851	35	0·95576	69	0·89561
2	0·99703	36	0·95443	70	0·89327
3	0·99560	37	0·95308	71	0·89088
4	0·99422	38	0·95170	72	0·88844
5	0·99283	39	0·95029	73	0·88596
6	0·99146	40	0·94886	74	0·88346
7	0·99011	41	0·94741	75	0·88092
8	0·98877	42	0·94593	76	0·87836
9	0·98746	43	0·94443	77	0·87578
10	0·98621	44	0·94291	78	0·87312
11	0·98496	45	0·94136	79	0·87040
12	0·98370	46	0·93979	80	0·86760
13	0·98247	47	0·93820	81	0·86474
14	0·98125	48	0·93657	82	0·86180
15	0·98003	49	0·93493	83	0·85883
16	0·97884	50	0·93326	84	0·85582
17	0·97766	51	0·93155	85	0·85276
18	0·97648	52	0·92982	86	0·84967
19	0·97530	53	0·92806	87	0·84646
20	0·97413	54	0·92626	88	0·84314
21	0·97295	55	0·92443	89	0·83971
22	0·97177	56	0·92256	90	0·83623
23	0·97058	57	0·92067	91	0·83269
24	0·96939	58	0·91877	92	0·82907
25	0·96820	59	0·91682	93	0·82538
26	0·96700	60	0·91483	94	0·82163
27	0·96580	61	0·91282	95	0·81772
28	0·96459	62	0·91079	96	0·81363
29	0·96338	63	0·90873	97	0·80942
30	0·96216	64	0·90663	98	0·80514
31	0·96091	65	0·90450	99	0·80082
32	0·95966	66	0·90234	100	0·79647
33	0·95838	67	0·90014		

TABLE 24. DENSITY AND PERCENTAGE OF ETHYL ALCOHOL BY VOLUME AND PERCENTAGE BY WEIGHT AT 15·56°C. (TRALLES) WATER = 0·9991

Percentage of Alcohol by Volume	Percentage of Alcohol by Weight	Density at 15·56°C.	Percentage of Alcohol by Volume	Percentage of Alcohol by Weight	Density at 15·56°C.	Percentage of Alcohol by Volume	Percentage of Alcohol by Weight	Density at 15·56°C.
0	0	0·9991	34	28·13	0·9596	68	60·38	0·8941
1	0·80	0·9976	35	28·99	0·9583	69	61·42	0·8917
2	1·60	0·9961	36	29·86	0·9570	70	62·50	0·8892
3	2·40	0·9947	37	30·74	0·9556	71	63·58	0·8867
4	3·20	0·9933	38	31·62	0·9541	72	64·66	0·8842
5	4·00	0·9919	39	32·50	0·9526	73	65·74	0·8817
6	4·81	0·9906	40	33·39	0·9510	74	66·83	0·8791
7	5·62	0·9893	41	34·28	0·9494	75	67·93	0·8765
8	6·43	0·9881	42	35·18	0·9478	76	69·05	0·8739
9	7·24	0·9869	43	36·08	0·9461	77	70·18	0·8712
10	8·05	0·9857	44	36·99	0·9444	78	71·31	0·8685
11	8·87	0·9845	45	37·90	0·9427	79	72·45	0·8658
12	9·69	0·9834	46	38·82	0·9409	80	73·59	0·8631
13	10·51	0·9823	47	39·74	0·9391	81	74·74	0·8603
14	11·33	0·9812	48	40·66	0·9373	82	75·91	0·8575
15	12·15	0·9802	49	41·59	0·9354	83	77·09	0·8547
16	12·98	0·9791	50	42·52	0·9335	84	78·29	0·8518
17	13·80	0·9781	51	43·47	0·9315	85	79·50	0·8488
18	14·63	0·9771	52	44·42	0·9295	86	80·71	0·8458
19	15·46	0·9761	53	45·36	0·9275	87	81·94	0·8428
20	16·28	0·9751	54	46·32	0·9254	88	83·19	0·8397
21	17·11	0·9741	55	47·29	0·9234	89	84·46	0·8365
22	17·95	0·9731	56	48·26	0·9213	90	85·75	0·8332
23	18·78	0·9720	57	49·26	0·9192	91	87·09	0·8299
24	19·62	0·9710	58	50·21	0·9170	92	88·37	0·8265
25	20·46	0·9700	59	51·20	0·9148	93	89·71	0·9230
26	21·30	0·9689	60	52·20	0·9126	94	91·07	0·8194
27	22·14	0·9679	61	53·20	0·9104	95	92·46	0·8157
28	22·99	0·9668	62	54·21	0·9082	96	93·89	0·8118
29	23·84	0·9657	63	55·21	0·9059	97	95·34	0·8077
30	24·69	0·9646	64	56·22	0·9036	98	96·84	0·8034
31	25·55	0·9634	65	57·24	0·9013	99	98·39	0·7988
32	26·41	0·9622	66	58·27	0·8989	100	100·00	0·7939
33	27·27	0·9609	67	59·32				

A further table is appended, giving the relation between " degrees proof spirit " and alcohol content, in the case of ethyl alcohol mixtures.

476. The Anti-Knock Values of Methanol and Ethyl Alcohol.— The greatest value of the lower aliphatic alcohols as constituents of motor fuels is their pronounced anti-knocking character, and were it not for this desirable property, alcohol fuels would not possess a single

redeeming feature as compared with petrols, with the possible exception of their high latent heat, which, in certain circumstances, has a beneficial effect upon volumetric efficiency and power output.

TABLE 25. ETHYL ALCOHOL COMMERCIAL STANDARDS. RELATION BETWEEN PROOF SPIRIT DEGREES AND ETHYL ALCOHOL PER CENT. BY WEIGHT

(From Simmond's " Alcohol," page 275)

Proof Spirit Degrees or Per cent	Per cent. Ethyl Alcohol (by weight)
5·0	2·3
10·0	4·6
15·0	6·9
20·0	9·2
25·0	11·6
30·0	13·9
35·0	16·4
40·0	18·7
45·0	21·0
50·0	23·5
55·0	25·9
60·0	28·4
65·0	30·9
70·0	33·4
75·0	35·9
80·0	38·5
85·0	41·1
90·0	43·9
95·0	46·5
100·0	49·3 (Proof Spirit)
105·0	52·1
110·0	55·0
115·0	57·9
120·0	60·8
125·0	63·9
130·0	67·0
135·0	70·2
140·0	73·4
145·0	76·7
150·0	80·1
155·0	83·7
160·0	87·3
165·0	91·1
170·0	95·3

Anti-Knock Value of Methanol.—Considering methanol first, many statements have been made in the literature that this substance is not capable of withstanding high compression ratios and that it possesses strong pre-ignition tendencies. Thus, Ricardo[139] has stated

that methanol pre-ignites in the Ricardo engine at the low compression ratio of 5·2, and a statement has been made that " its incapability of resisting pinking in the engine will prevent its adoption . . . on any large scale." [140] These opinions are not shared by more recent investigators who have successfully applied methanol as a fuel for automobile and aircraft engines of the high duty racing type. Thus, Howes[112] carried out tests on methanol in engines of many different types, from air-cooled motor cycle engines to supercharged eight-cylinder racing car engines, varying in compression ratio from 6·0 to 15·0, and in no case observed any pre-ignition (or knocking) when due care was taken to ensure adequate cooling. When used in an Armstrong Whitworth variable compression engine (see Chapter XVI, Volume II), at a speed of 750 r.p.m., perfectly smooth running was obtained at compression ratios up to 9·4 (the maximum available) and at jacket temperatures up to 150°C. At this jacket temperature, however, and at 9·4 compression ratio, slight running roughness occurred. This may or may not have been due to a slight incipient pre-ignition, but it was scarcely audible and did not promote detonation. An engine of this type was run under these conditions continuously for eight hours, but no more than very slight roughness was evident even after such prolonged running. Howes mentions, however, that in some supercharged engines, operating at high compression ratios and high boosting pressures, the use of methanol may give rise to severe overheating which may be attributed to pre-ignition. As an instance of this, the case of an eight-cylinder supercharged racing engine, operating at a static compression ratio of 6·0 and a supercharger boost of 12 lbs., may be quoted. When run on benzole, the performance was satisfactory, but when run on ethyl alcohol the engine did not, as was expected, run colder but hotter, and when methanol was used the trouble was aggravated to such an extent that the sparking plug points fused after a few minutes' run. The real cause of this overheating was the high latent heat of the methanol, which increased the volumetric efficiency, or, in other words, increased the effective supercharger boost, to such an extent that the amount of heat flow to the cooling system was greater than the latter could cope with, as the cooling water passages in the engine were very small. The latent heat of methanol is 28·6 per cent. greater than that of ethyl alcohol and 179 per cent. greater than that of benzole.

Further experiments by Howes on well-cooled supercharged engines have shown that methanol is a satisfactory fuel to employ in such engines at static compression ratios of up to 8·5, together with supercharger boosting pressures of up to 18 lbs. per sq. in. gauge. In unsupercharged engines, compressions of over 15 to 1 have been used with satisfaction.

It would appear then that methanol is a valuable anti-knock fuel,

and it is claimed that when mixed with petrol, it has an anti-knock value 1·8 to 2·0 times that of benzole, i.e., the addition of 10 per cent. of methanol to a petrol increases the knock rating of the latter to the same extent as the addition of 18–20 per cent. of benzole. The results of tests carried out in an Armstrong Whitworth variable compression engine are shown in Fig. 16, and the results of tests on an Ethyl Gasoline S30 engine, at a jacket temperature of 150°C., are given in Fig. 17.

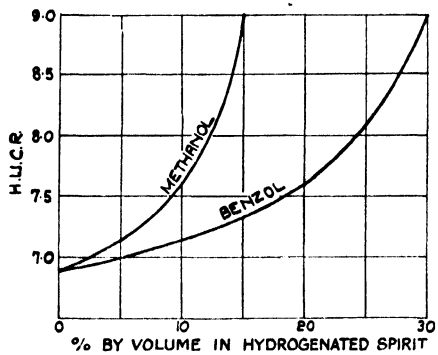


FIG. 16.—CURVES SHOWING THE RELATIVE ANTI-KNOCK VALUES OF BENZOLE AND METHANOL (HOWES)

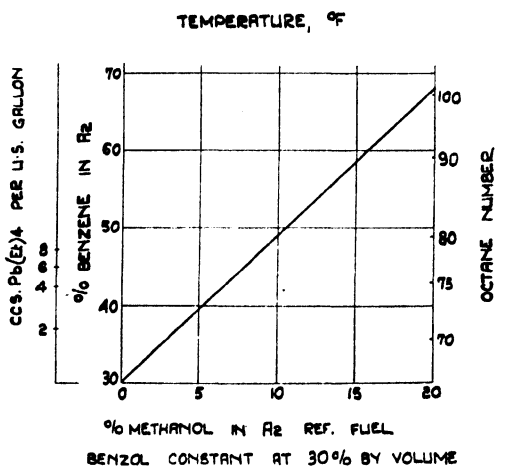


FIG. 17.—CURVE SHOWING THE ANTI-KNOCK VALUES OF METHANOL BLENDS IN TERMS OF OCTANE NUMBERS, BENZOLE AND TETRA-ETHYL LEAD (HOWES)

These results are summarised in Table 26.

477. Anti-Knock Value of Ethyl Alcohol.—The anti-knock value of ethyl alcohol has been recognised for some years and has not been disputed. In 1926, Ross and Ormandy[141] published figures which showed that 10% of ethyl alcohol had approximately the same effect in increasing the knock rating of a petrol to which it was added as 20%

of benzole. In 1924, Ricardo[139] found that ethyl alcohol had an H.U.C.R. above 7·5 to 1, and did not give any pre-ignition except after prolonged runs at engine speeds of 1,675 r.p.m.

TABLE 26. SUMMARISED RESULTS. ANTI-KNOCK VALUE OF METHANOL

A. Armstrong Whitworth Variable Compression Engine. 750 r.p.m. Jacket temperature 50°C. Air inlet temperature 50°C. Spark advance 12°B.T.D.C.

	H.U.C.R.	Benzole equivalent of Blend	Benzole equivalent of Methanol
Hydrogenated Petrol	6·85	—	—
do. + 5% Methanol	7·15	10·0	2·0
do. + 10% Methanol	7·6	20·0	2·0
do. +12·5% Methanol	8·05	25·1	2·0
do. + 15% Methanol	9·0	30·0	2·0

B. Ethyl Gasoline S 30 Engine. Jacket temperature 150°C.

	Octane Number	C.cs. $Pb(Et)_4$ per U.S. gallon	% Benzole	Benzole equivalent of Methanol
Reference Fuel A2—				
+30% Benzole	66·5	—	30	—
+ 5% Methanol	73·0	3·0	40	2·0
+10% Methanol	80·8	over 10·0	49·5	1·95
+15% Methanol	91·0	—	59·6	1·93
+20% Methanol	—	—	68·0	1·9

A direct comparison of ethyl alcohol and benzole as anti-knock agents in an aviation spirit has been made by Dumanois,[137] whose results are given in Table 27, and support the previous findings of Ross and Ormandy.

TABLE 27. KNOCK RATINGS OF ETHYL ALCOHOL AND BENZOLE BLENDS IN AN AVIATION SPIRIT (DUMANOIS)

	Octane Number
Aviation Spirit	65
do. + 5% Ethyl Alcohol	68
do. +10% „ „	72·5
do. +15% „ „	77
do. + 5% Benzole	66·5
do. +10% „	68
do. +15% „	69·5
do. +20% „	71·5
do. +30% „	76
do. +35% „	79

Similar work has been conducted by Peter, Olsevski, Dziewonski and Krasinski,[142] with the results shown in Table 28.

TABLE 28. KNOCK RATINGS OF ETHYL ALCOHOL BLENDS (PETER AND CO-WORKERS)

	H.U.C.R. (Ricardo engine)	Equivalent Benzole Blend	Benzole equivalent of Ethyl Alcohol
Petrol	4·95	—	—
do. + 5% Alcohol	5·15	10·0	2·0
do. +10% „	5·4	21·0	2·1
do. +15% „	5·7	33·5	2·2
do. +20% „	6·0	44·0	2·2

Very little has been published concerning the knock ratings of the higher alcohols.

478. The Use of Alcohol Fuels in Automobiles.—As already shown, the physical properties of the lower aliphatic alcohols prevent their satisfactory adoption as ordinary automobile fuels in an undiluted state. A comparison of their calorific values shows that, at the same compression ratio and overall efficiency, the relative fuel consumptions for a given power output are as follows:

No. 1 petrol	100
Ethyl alcohol	161·4
Methanol	221·6

and it follows that the costs of ethyl alcohol and methanol would have to be less than $\frac{100}{161{\cdot}4}$ × price of petrol and $\frac{100}{221{\cdot}6}$ × price of petrol, respectively, to give any saving in fuel costs.

Apart from calorific value considerations, however, there are other difficulties to be overcome before these alcohols can be satisfactorily used as undiluted motor fuels by the ordinary motorist. These substances have very high latent heats and, in consequence, do not vaporise so readily in a carburettor as ordinary petrols. As a result, general engine flexibility suffers to a very marked extent. Furthermore, their low vapour pressures cause greater difficulty in starting an engine from cold.

For these reasons, methanol and ethyl alcohol are only suitable as motor fuels for ordinary automobiles when diluted with normal hydrocarbon fuels, such as petrols, and in consequence most of the work done in developing alcohol fuels has been carried out with this point in mind. As shown at the end of this Chapter, alcohol-petrol blends are being adopted as standard fuels in most European countries and

are meeting with some approval from the motoring fraternity. The success, or otherwise, of such alcohol fuel mixtures is naturally dependent upon their composition and the amount of alcohol they contain, but it is by no means true in every respect that the greater the alcohol concentration the less satisfactory the fuel, or vice versa.

The point of greatest value in favour of alcohol-containing motor fuels is their high anti-knock value, which enables them to be used in high compression engines without causing knocking. This has already been dealt with and need not be discussed further, but this advantage is completely discounted if the fuels do not embody a proper combination of cost, power output and rate of fuel consumption.

A point of outstanding importance is that concerning the relationship which exists between the alcohol content of a petrol-alcohol blend and the fuel consumption for a given power output. If the latent heats of petrol and alcohol were the same, this relationship would be linear for any given compression ratio, the fuel consumptions of alcohol and petrol being inversely proportional to their calorific values. However, the large difference existing between these two substances in latent heats is almost as important as the large difference in calorific value and it is the cause of very noteworthy, if somewhat unexpected, results.

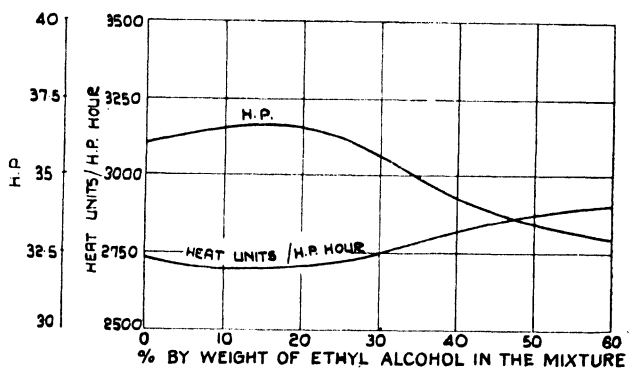


FIG. 18.—CURVES SHOWING THE RESULTS OBTAINED BY HUBENDICK

479. As shown in Chapter XIV, Volume II, the latent heat of a fuel determines, to a large extent, engine volumetric efficiency and, consequently, has an effect upon power output. In the case of alcohol fuels, latent heat is of great importance, and has a noticeable effect upon the fuel consumption for a given power output. Fig. 18 gives results obtained by Hubendick[143] in the examination of a range of petrol-alcohol mixtures and shows that the fuel consumption, in terms of heat units, is not appreciably greater with a 20 per cent. ethyl alcohol blend than with petrol alone, whereas blends containing higher amounts of alcohol give fuel consumption in proportion to the alcohol content.

As, in these tests, no changes in the engine conditions, other than an alteration in carburettor jets, were made, it follows that in blends containing up to 20 per cent. of alcohol, an increase in overall engine efficiency must be compensating for the lower calorific value. This higher overall efficiency is solely caused by the higher latent heat of the alcohol which causes the air consumption per cycle to be increased and so increases the power output. Up to alcohol concentrations of 20 per cent., therefore, the decrease in calorific value of the fuel is compensated for by the increase in latent heat and the fuel consumption is not adversely affected, but, in the case of blends containing more than 20 per cent. of alcohol, the decrease in calorific value is the determining factor and, consequently, the rate of fuel consumption increases.

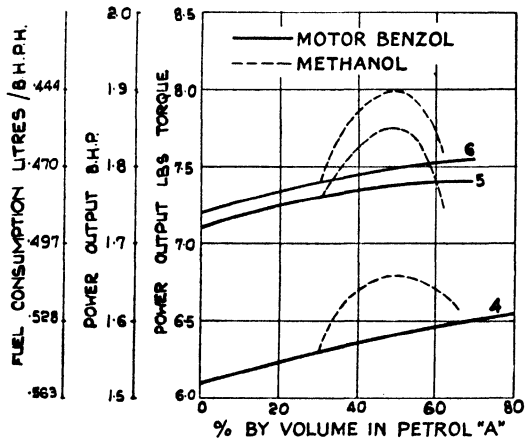


FIG. 19.—CURVES SHOWING POWER OUTPUT OF METHANOL–PETROL–BENZOLE BLENDS, AT COMPRESSION RATIOS OF FROM 4·0 TO 6·0 (HOWES)

Similar results have been obtained by Howes[112] in tests on methanol blends on an Armstrong Whitworth variable compression engine. These results, which are summarised in Figs. 19 and 20, cover a range of compression ratios and methanol concentrations and show that, with the somewhat over-rich fuel-air mixture used, the introduction of methanol in concentrations of up to 15 per cent. in a 30 per cent. benzole-petrol blend actually increases the power output and decreases the fuel consumption. More than 15 per cent. of methanol gives a higher fuel consumption.

Fig. 20 gives the results of tests at high compression ratios at which all the fuels examined, with the exception of those containing more than 10 per cent. of methanol, were knocking heavily. Here the increase in power, resulting from the admixture of methanol, is mainly due to the prevention of knocking, although the effect of latent heat still plays a part, and blends containing more than 15 per cent. methanol are less

economical than those containing smaller amounts. It should be noted, however, that these results were obtained with a fuel-air mixture composition on the rich side, made to approximate as nearly as possible the mixture composition supplied by carburettors on multi-cylinder engines.

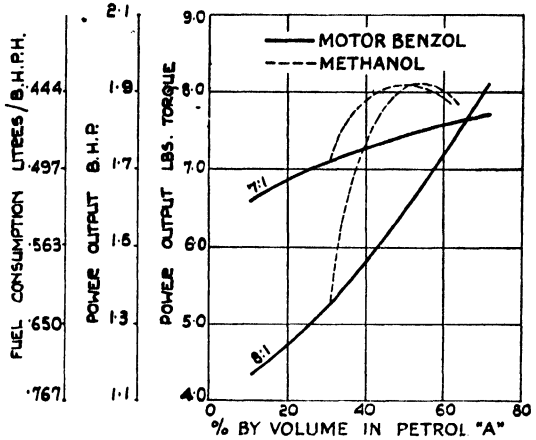


FIG. 20.—CURVES SHOWING POWER OUTPUT OF METHANOL–PETROL–BENZOLE BLENDS AT COMPRESSION RATIOS OF 7·0 AND 8·0 (HOWES)

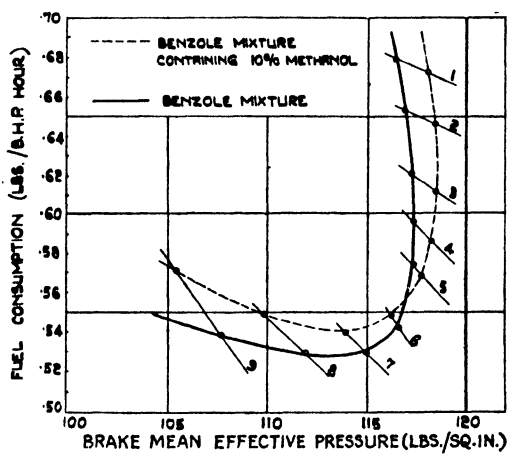


FIG. 21.—FUEL CONSUMPTION CURVES

The results of tests conducted over a range of fuel-air mixture strengths are given in Fig. 21, in the form of the familiar consumption /B.M.E.P. loops, and it is evident from these that the advantage in fuel consumptions, obtained with fuels containing small amounts of alcohols, are only obtained at mixture strengths of richer composition than the theoretical. At weak mixture strengths the fuel consumptions are entirely dependent upon the fuel calorific value and are higher the higher the alcohol content.

Observations obtained on a benzole mixture and on a benzole mixture containing 10 per cent. of methanol at the same carburettor settings are numbered, and these clearly show the effect obtained by changing over from one fuel to the other at any carburettor setting.

480. In the case of multi-cylinder engines, inequalities in fuel-air mixture distribution to the various cylinders noticeably limit the usable range of mixture strengths and, for satisfactory operation, an over-rich mixture must be used, in order to ensure that the cylinder receiving the weakest mixture is being supplied with a mixture that will fire readily and efficiently. On privately owned automobiles, rather rich fuel-air mixtures are almost invariably used because they give engine flexibility over a wide range of speeds and loads, whereas, on commercial vehicles, the carburettor is adjusted to supply the weakest possible mixture, on the grounds of fuel economy and cost.

Because of these facts, it is found that alcohol fuels containing not more than about 20 per cent. of ethyl alcohol or not more than 15 per cent. of methanol give no greater fuel consumption per mile than ordinary petrols when used in privately owned automobiles. Thus, Howes[112] has described a series of tests upon a number of different cars using (*a*) petrol and (*b*) petrol plus 10 per cent. of methanol, as fuels. These cars were selected haphazardly and no adjustments whatever were made to their carburettors or fuel systems. They were driven round a seventeen-mile circular track by their owners and fuel consumptions measured. The results of these tests are given in Table 29, and show that of the ten cars used only three gave higher fuel consumptions on the alcohol blend.

TABLE 29. RESULTS OF ROAD TRIALS (17 MILES COURSE)

Type of Car	Fuel Consumption (M.P.G.)	
	Petrol	Petrol + 10% Methanol
12 H.P. Saloon	22·8	23·8
12 H.P. 2-Seater	24·6	25·0
16 H.P. Saloon	18·8	20·6
8 H.P. Saloon	46·0	41·4
12 H.P. 2-Seater	32·0	32·4
9 H.P. Saloon	29·3	29·2
7 H.P. Saloon	43·1	45·2
15 H.P. 4-Seater	23·6	24·8
7 H.P. 4-Seater	44·7	44·2
14 H.P. Saloon	19·1	19·8

Similar results on other multi-cylinder engines have been obtained by other workers in this field, but most of the work has been concerned with ethyl alcohol blends. Dumanois[137] has described results obtained

on various types of aero-engines using aviation fuel and aviation fuel plus 10 per cent. by volume of ethyl alcohol. His results are reproduced in Table 30, and show that the alcohol blend gives almost the same power output and fuel consumption as the aviation petrol.

TABLE 30. RESULTS OF EXPERIMENTS BY DUMANOIS IN AERO-ENGINES

Engine	Fuel	Atmospheric Pressure mm. Hg.	Atmospheric Temperature °C.	R.P.M.	Horse Power	Specific Consumption
Hispano 180 H.P.	Aviation petrol d=0·70	761	15	1770 1785	187·5 190·5	230 236
	90/10 Petrol-alcohol d=0·71	761	15	1800 1810	194·5 197·0	235 233
Renault 300 H.P.	Aviation petrol d=0·70	741	11	1526 1530	284 289	282 282
	90/10 Petrol-alcohol d=0·71	741	11	1530	289	282
Hispano 180 H.P.	Aviation petrol d=0·70	744	11	1750	182	284
	90/10 Petrol-alcohol d=0·71	744	11	1755	183·3	288

It is of interest, in this connection, to note the result of the yearly "5-litre" car competition held in France in September, 1932. Two fuels were used, (*a*) petrol and (*b*) 70 per cent. petrol, 15 per cent. benzole and 15 per cent. alcohol. All the competitors covered a distance of 1 to 4 kilometres greater on the latter blend than on petrol.[144]

As a result of extensive bench tests on omnibus engines, Ross and Ormandy[141] arrived at the following conclusions with respect to the relative merits of a petrol and petrol mixed with 10 per cent. of ethyl alcohol :—

(1) When burnt . . . in an engine under favourable conditions and with variable ignition, the average consumption of the alcohol-petrol mixture is 2·3 per cent. (by volume) worse than . . . petrol. Running with a fixed ignition setting, the difference becomes nil, in spite of the lower calorific value. Maximum power, regardless of economy, is somewhat greater.

(2) More ignition advance is generally required for good results as well as higher induction temperatures.

(3) The fuel (alcohol blend) appears to be quite satisfactory as regards starting and general running qualities.

(4) There is little doubt that, with petrol of a poor grade, the addition of alcohol would considerably improve its performance. In addition to

improving performance at full loads, the economy at fractional loads would be increased.

With regard to the behaviour of alcohol fuels in ordinary automobiles, therefore, if the alcohol content is kept below 20–25 per cent. by volume (15 per cent. in the case of methanol fuels), such mixtures may be used with satisfaction without any alteration in carburettor setting and without any alteration to the engine. Such blends will give approximately the same fuel consumption as ordinary petrol and will give about the same power output. Neither starting properties nor engine flexibility will be impaired to any marked degree. If, on the other hand, the alcohol concentration is increased above these limits, power output will be decreased and fuel consumption correspondingly increased, with the result that the blend will not give satisfaction, as instanced by the marked unpopularity of " Carburant National," in France, which contains 50 per cent. ethyl alcohol, and the success of " Lattbentyl," containing only 25 per cent. ethyl alcohol, in Sweden.

481. The Use of Alcohol Fuels in High Duty Engines.—The alcohols methanol and ethanol find ready application as fuels for high duty engines in racing events and so on. In such applications, where fuel economy is not a major consideration and where maximum power is essential, these alcohols offer many advantages over straight hydrocarbon fuels or hydrocarbon fuels doped with anti-knock agents.

As shown in Chapter XIV (Volume II), there is no relationship between the calorific value of a fuel and the power output which may be obtained by its use, calorific value only determining the quantity of fuel required to do this work. Therefore, if fuel economy is not the prime requirement, the two factors which control power output, as far as the fuel is concerned, are (*a*) latent heat of vaporisation, which determines the volumetric efficiency obtainable and (*b*) knock rating, which determines the highest engine compression ratio which may advantageously be employed.

The lower alcohols are, therefore, capable of giving very high power outputs in high compression engines because their anti-knock properties are very good, and because their latent heats of vaporisation are much higher than those of hydrocarbons. High rates of fuel consumption must, however, be employed in order to obtain this advantage, and this consideration limits the use of undiluted alcohols as fuels in racing and record-breaking events to short distance runs. For long distance races, the high fuel consumption, which determines the amount of fuel carried by the machine consuming it, more than counterbalances the increased power output obtained, and such fuels cannot compete in general suitability with high anti-knock hydrocarbon fuels.

Little information is available concerning this special use of alcohol fuels, although Howes has described results obtained in various single-cylinder motor cycle engines and multi-cylinder automobile engines, both supercharged and un-supercharged.[112]

Experiments in Single-Cylinder Motor Cycle Engines.—Motor cycle engines are, except for a few isolated cases, air-cooled, and are expected to run for long periods at high operating temperatures. Compression ratios are high, and, due to the high temperatures developed, the pistons, cylinders and valves must be designed so as to give satisfactory service under most exacting conditions. It will be readily understood, therefore, that any fuel which can be satisfactorily used at the high compression ratios and high temperatures employed, and also give a cooler engine under load, is of real value. This is especially true in the case of racing engines, particularly those used in dirt- or grass-track racing, where the engine is kept running at high speeds in low gear, when air cooling is inefficient and insufficient for the amount of power being developed. The cooling effect of alcohol fuels is, in such cases, as important as the higher power output obtainable by their use, because it gives a higher degree of engine reliability.

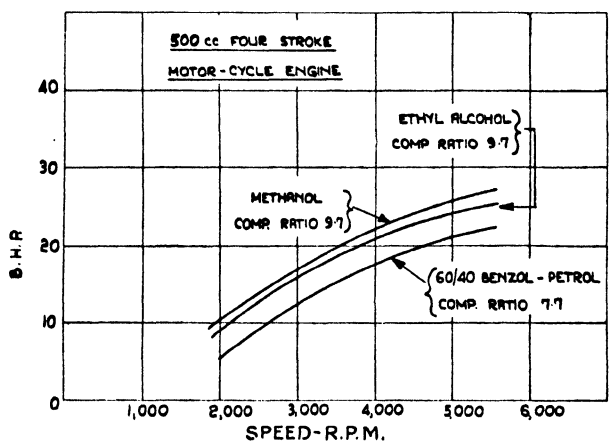


FIG. 22.—POWER OUTPUT CURVES FOR 500 C.C. MOTOR CYCLE ENGINE (HOWES)

The results shown in Fig. 22 refer to tests carried out by Howes in a motor cycle engine of a well known English make. This engine was of 500 c.c. capacity, single-cylindered and un-supercharged. It was a four-stroke engine, fitted with two overhead valves, one inlet and one exhaust. By increasing the compression ratio from 7·7 to 9·75 and substituting ethyl alcohol for a 60/40 benzole-petrol mixture, an increase in power of 18·7% was obtained at a speed of 5,500 r.p.m. At the latter compression ratio, methanol gave 23·3% greater power, but at a higher

rate of fuel consumption, 1·02 pints/brake-horse-power/hour as against 0·92 pints/brake-horse-power/hour for ethyl alcohol.

The results of experiments in a motor cycle engine of higher efficiency are shown in Fig. 23. These experiments were carried out at compression ratios of 9·6 and 10·6, and the results show that the use of methanol in place of ethyl alcohol gives about the same increase in power output as an increase in compression ratio of 1 unit. This result is in keeping with the higher latent heat of methanol compared with ethyl alcohol.

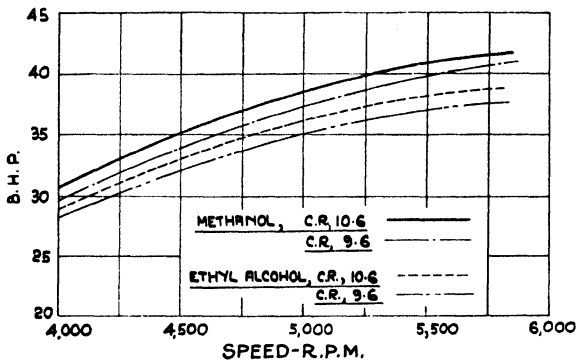


FIG. 23.—COMPARISON OF POWER OUTPUTS OF METHANOL AND ETHYL ALCOHOL AT COMPRESSION RATIOS OF 9·6 AND 10·6 TO 1 (HOWES)

482. Experiments in Multi-cylinder Engines.—Tests by Howes, in a wide range of multi-cylinder engines, confirm those obtained in single-cylinder engines but exhibit other phenomena, such as the effects of distribution and pre-heating of fuel charge, etc. Howes points out that the efficient carburation of methanol is more difficult to obtain than that of ethyl alcohol, due to the high latent heat, high surface tension and low vapour pressure at the temperatures existing in the inlet manifold. The effect of the high surface tension is to facilitate the coalescence of small liquid droplets into large drops, and, as a result, precipitation of the fuel out of the fuel-air stream occurs readily. Consequently, the optimum air speed through the carburettor choke tube and inlet manifold is greater than in the case of either petrols, benzoles or ethyl alcohol, due to the fact that a high air stream velocity helps to maintain the fuel droplets in suspension.

Tests on a supercharged four-cylinder engine of low cylinder capacity and static compression ratio 5·0 have been described,[112] the results of which are shown in Fig. 24, and summarised in Table 31.

As a concluding remark on the use of alcohols in high duty engines, it is of interest to note that the air speed record until recently held by Great Britain was obtained using a special fuel of which methanol was the major constituent.

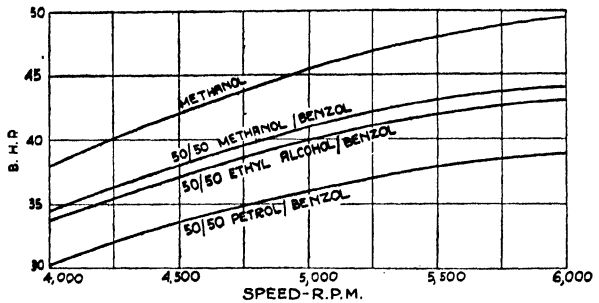


FIG. 24.—POWER OUTPUT CURVES OF FOUR-CYLINDER SUPERCHARGED ENGINE (HOWES)

TABLE 31. TESTS AT 6,000 R.P.M. COMPRESSION RATIO 5·0. SUPERCHARGER PRESSURE 12 LBS. GAUGE

Fuel	B.H.P.	Relative Power Outputs
Methanol	49·3	127·4
50/50 Methanol/Benzole	44·7	115·5
50/50 Ethyl alcohol/Benzole ..	44·0	113·6
50/50 Petrol/Benzole	38·7	100

483. Distillation Characteristics of Alcohol-Petrol Blends.—When an ethyl-alcohol- or methanol-containing fuel is distilled, a considerable quantity of material is found to boil at low temperatures. The material which vaporises at these temperatures consists mainly of constant boiling-point mixtures of the alcohol and the lower hydrocarbons present in the petrol. These constant boiling-point mixtures have vapour pressures usually greater than either of their two constituents and hence boil at a lower temperature than either. Typical A.S.T.M. distillation curves of a petrol containing 0, 10, 15 and 20% by volume of ethyl alcohol are given in Fig. 25, from which it will be seen that the addition of 10 per cent. by volume of alcohol increases the proportion of material boiling over at 60°C. from 6 per cent. to 10 per cent., although ethyl alcohol itself only boils at 78°C.

All alcohol-containing fuels give the so-called "alcohol flat" in their distillation curves. Data concerning some of the chief constant boiling mixtures of methanol and ethyl alcohol with hydrocarbons are shown in Tables 32 and 33.

484. Vapour-Lock Properties of Alcohol Blends.—The following conclusions of Bridgeman[93] are of interest:

1. When used in the same engine, a 10 per cent. alcohol blend is more likely to give trouble than the gasoline with which the alcohol is blended. Little difference would be expected with a 20 per cent. blend and the situation would be reversed with a 40 per cent. blend.

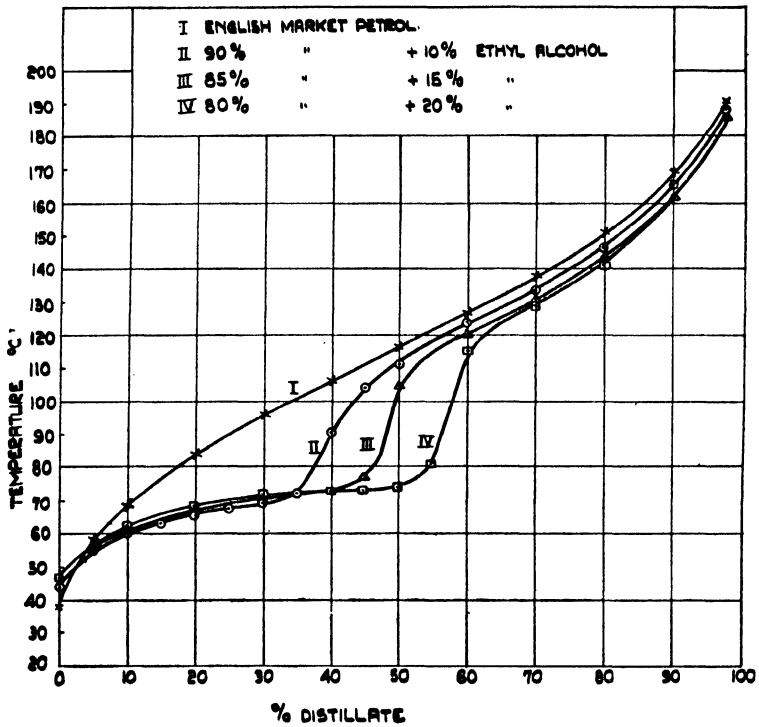


FIG. 25.—A.S.T.M. DISTILLATION CURVES FOR PETROL–ETHYL ALCOHOL BLENDS

TABLE 32.—CONSTANT BOILING-POINT MIXTURES OF METHANOL AND HYDROCARBONS

Substances in the Mixture		Boiling Points °C.			% by Weight of Methanol in the mixture
A	B	A	B	Constant Boiling-Point Mixture	
Methanol	Isopentane	64·7	27·95	24·5	4·0
Methanol	Trimethyl-ethylene	64·7	37·15	31·75	7·0
Methanol	Diallyl	64·7	60·2	47·05	22·5
Methanol	*n*-Hexane	64·7	68·95	50·0	26·4
Methanol	Benzene	64·7	80·2	58·34	39·55
Methanol	Cyclohexane ..	64·7	80·75	54·2	37·2
Methanol	1-3-Cyclohexadiene	64·7	80·6	56·38	38·8
Methanol	Cyclohexene ..	64·7	82·75	55·9	40·0
Methanol	*n*-Heptane	64·7	98·45	60·5	62·0
Methanol	Methyl cyclohexane	64·7	101·8	60·0	70·0

2. The same freedom from vapour lock may be obtained for a 10 per cent. alcohol blend and gasoline if the vapour pressure of the gasoline used for blending is lower than that of the gasoline with which the blend is compared. In this case there is

some loss of octane number due to the use of less butane and there is increased difficulty in engine starting. On the other hand, with a 40 per cent. blend a gasoline of increased vapour pressure may be employed with enhancement of the octane number.

TABLE 33.—CONSTANT BOILING-POINT MIXTURES OF ETHYL ALCOHOL WITH HYDROCARBONS

Substances in the Mixtures		Boiling Points °C.			% by Weight of Ethyl Alcohol in the constant boiling-point mixture
A	B	A	B	Constant Boiling-Point Mixture	
Ethyl alcohol	Cyclohexane		80·75	64·9	30·5
Ethyl alcohol	Cyclohexene		82·75	66·7	35·0
Ethyl alcohol	1·3-Cyclohexadiene		80·8	66·7	34·0
Ethyl alcohol	Methyl cyclohexane		101·8	73·0	53·0
Ethyl alcohol	Toluene		110·6	76·7	68·0
Ethyl alcohol	Benzene		80·2	68·25	32·41

485. General Remarks on the Use of Alcohols as Fuels.—When alcohol fuels are used for the first time in an automobile that has been run on petrol for a considerable period, trouble in the form of choked petrol filters and carburettor jets is almost invariably caused. This is due to the fact that alcohols and alcohol-petrol mixtures are extremely good solvents for resins deposited from petrols and for solder fluxes, etc., left in the fuel system. They are also particularly effective in loosening rust deposits from the inside surfaces of tanks and fuel lines. Such materials quickly block up carburettor jets and choke filters inserted in the fuel lines. It is therefore necessary when changing over from a petrol to an alcohol blend, thoroughly to clean out the fuel system with the latter before putting the automobile on the road, otherwise inconvenience may be caused. Once the fuel system has been thoroughly cleaned out no further trouble results, although it recurs immediately after petrol has been used again.[143]

Alcohol fuels have also an extensive solvent action upon lacquers and shellacs and if allowed to come in contact with the paint work of certain cars have a disastrous effect upon it.[144] However, Hubendick[145] contends that this does not happen in practice, although he has mentioned the case of a petrol tank varnished on the inside with a spirit varnish. When an alcohol fuel was placed in the tank, the varnish was completely dissolved and subsequently deposited in the induction pipe of the engine.

486. Ease of Starting and Acceleration.—Blended fuels containing up to about 30 per cent. of alcohol exhibit very good engine

starting characteristics, due to their high volatility and high vapour pressure, as shown above, and the high latent heat of the alcohol does not appear to have any detrimental effect. On the other hand, after the engine has started, resort has to be made to the choke control much more often in order to keep the engine running and to enable it to warm up. This effect is mainly due to the higher latent heats and is more noticeable with methanol blends than with ethyl alcohol blends.

With regard to engine acceleration, this may be superior when using alcohol blends when the engine is thoroughly warm, but with a cold engine alcohol blends do not give the same measure of flexibility and ease of acceleration as straight hydrocarbon fuels. Hubendick,[143] a well-known protagonist of alcohol fuels, has made the following statement with regard to these properties :

> " A chauffeur who does not know that the fuel tank has been filled with such a fuel (alcohol blend) instead of benzine, will not notice any change in starting or in operation. At most, he expresses surprise at the good acceleration of the vehicle and observes that hills are easily taken."

On the other hand, Egloff[146] states that the greatest difficulty when using alcohol fuels is the lack of engine flexibility at low speeds. Between 20 and 25 m.p.h. on the road no difference is noticed but when, after running slowly, an attempt is made to accelerate quickly the engine gives trouble and does not respond to the throttle.

487. Effect of Alcohol Fuels on Engine Temperatures.—When running on alcohol fuels, engine temperatures are usually lower than when running on petrols and the greater the alcohol content of the blend, the lower the temperature. This is due mainly to the higher latent heats of the alcohols which give a lower induction stroke temperature and, consequently, a slightly lower average temperature over the whole cycle, but the lower flame temperatures of alcohol fuels also play a part.

In the case of 95 per cent. ethyl alcohol, Ricardo[147] has shown that the temperature at the end of compression is about 70°C. lower than in the case of petrol, while the maximum flame temperature attained will be approximately 170°C. lower. The loss of heat to the cooling water and that due to change of specific heat, etc., will be substantially reduced.

Fig. 26 has been plotted from Ricardo's data and shows the heat distribution observed when running on petrol and on 95 per cent. ethyl alcohol, at a compression ratio of 5·45, at mixture strengths giving the maximum efficiency. The horizontal scale denotes the number of B.T.U.s per hour supplied to the engine in the form of fuel and the vertical scale the percentage accounted for in I.H.P. and

cooling water. The upper curves, i.e., those referring to the heat lost in the exhaust and by radiation, are plotted by difference.

The reduction in cooling water temperature experienced when running on alcohol blends containing up to 40 per cent. of alcohol amounts up to 15°C., and may be an advantage or a disadvantage, depending upon circumstances. Thus, in hot summer weather, a lower radiator temperature is to be desired, especially in hilly country, but in wintry weather it may cause excessive deposition of liquid fuel upon the engine cylinder walls, and may lead to crank case dilution, excessive lubricating oil consumption and poor cylinder lubrication. Because of the lower radiator temperatures obtained when running on alcohol blends, these fuels require a longer time for the engine to become thoroughly warmed up, this causing a lack in general flexibility on starting the engine from cold.

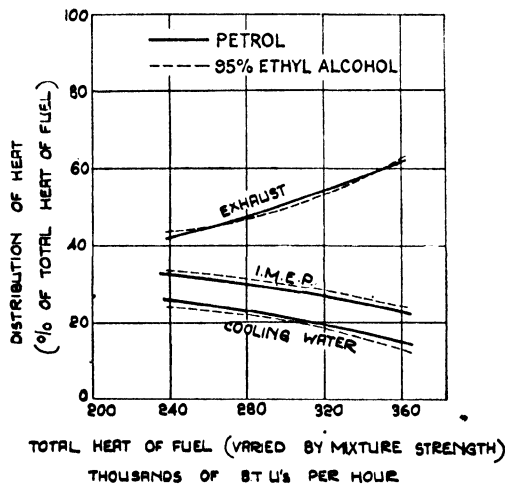


FIG. 26.—GRAPH SHOWING HEAT DISTRIBUTION IN AN ENGINE (COMPRESSION RATIO 5·45 TO 1 RUNNING ON (*a*) PETROL AND (*b*) 95 PER CENT. ETHYL ALCOHOL (RICARDO)

488. Crank Case Dilution and Cylinder Wear.—Little precise information is available regarding the extent of crank case dilution experienced with alcohol fuels, but it would appear that this phenomenon would occur to about the same extent as with petrols. With high alcohol blends, however, in which cases a large amount of liquid fuel enters the engine cylinder, crank case dilution may be somewhat higher than normal. Harsh running, ascribed to the washing action of the fuel on the cylinder walls, has been said[148] to be a peculiarity of alcohol fuels, but this does not find general support,[145] although Egloff says that harshness of running is so marked when starting from cold that the engine will not deliver anything approaching its full power for some

time. Examination shows that the moving parts are much drier and free from lubricant than when ordinary petrol was used.[146]

489. Carbon Formation.—Alcohol fuels are generally stated to deposit less carbon in the combustion chambers of engines in which they are used than petrols, but definite evidence on this point has not been published.

490. The Corrosive Properties of Alcohol Fuels and their Combustion Products.—Methanol, ethyl alcohol and the higher alcohols are much more corrosive to the metals commonly employed in automobile construction than ordinary petrols or benzoles, though whether, in actual use, serious corrosion is encountered with these fuels is a matter of some doubt since Hubendick has stated that no corrosion has been found with the Swedish alcohol fuel "Lattbentyl," containing 25 per cent. of alcohol. On the other hand, tests on three vehicles of the London General Omnibus Company, over 2,000 miles, showed "a slight corrosion of the brass and copper parts of the carburettor."[141]

Corrosion of engine parts by alcohol fuels may be caused by

(*a*) the fuels themselves in the liquid state,
(*b*) carburetted fuel-air mixtures,
or (*c*) the exhaust products.

Corrosion by the Fuels themselves in the Liquid State.—Methanol has a vigorous action upon metallic magnesium, forming magnesium methylate and hydrogen, according to the equation:[149]

$$2\,CH_3OH + Mg \rightarrow Mg(OCH_3)_2 + H_2$$

but the extent and speed of the attack depends upon the condition of the magnesium. The attack appears to start at the intercrystalline spaces of the metal and then it spreads rapidly,[150] and it would appear that perfectly pure magnesium is not attacked by methanol. Louis[150] has reported that a sample of powdered magnesium, placed in methanol at ordinary temperatures, only gave a few bubbles of gas, whereas, if the powder were previously heated above 360°C., for several minutes, a very vigorous attack with an abundant evolution of hydrogen was obtained. According to Terentieff,[151] anhydrous methanol reacts with magnesium powder only at 235°C., but Tessier and Grignard[152] have stated that methanol containing less than 1 per cent. of water rapidly attacks magnesium in the cold.

Ethyl alcohol reacts with magnesium much less rapidly than methanol, as shown by the following figures of Louis.[150]

Pure Magnesium		Commercial Magnesium	
Time	Loss in Weight %	Time	Loss in Weight %
10 days	0·3	7 days	0·17
25 ,,	1·0	31 ,,	0·6
40 ,,	1·5	59 ,,	0·7
55 ,,	2·1		
70 ,,	2·4		
90 ,,	3·2		

Mixtures of methanol and ethyl alcohol are less active in their attack on magnesium than methanol alone, but only when the ethyl alcohol concentration is above 10 per cent.

The action of water is very noticeable and the addition of 5 per cent. of water to methanol slows down the corrosive action to a very marked extent. According to Louis, methanol also attacks lead, forming a white voluminous crystalline deposit, the nature of which has not yet been determined. Ethyl alcohol reacts with lead in the cold to form lead ethylate, this reaction being accelerated by the presence of water, thus :

	Time	Loss in Weight %
Ethyl alcohol ..	8 days	Slight attack
do. ..	29 ,,	0·05%
do. + 10% water	8 ,,	0·2%
do. do.	29 ,,	0·3%

Methanol has also a slight action upon tin. The effect upon other metals is shown in the following table by Louis.[153]

Metal	Loss in Weight % after 334 days	
	Methanol	Ethyl alcohol
Industrial aluminium	0·61%	0·4%
Duralumin	1·28%	0·3%
Copper	Very slight attack. Slight pale blue deposit. Samples became brown in places	—
Cast iron, steel, brass and bronze	No attack	No attack

Magnesium alloy (94% *Mg*, 2% *Al*, 4% *Cu*) is said to be completely dissolved by methanol fuels containing more than 41 per cent. methanol.

In the case of metallic couples, the metal playing the part of the

anode is the one most commonly attacked by alcohol fuels, and it has been stated that, even by passage through taps, carburettors, etc., composed of two dissimilar metals, methanol can bring about appreciable corrosion. Ethyl alcohol is much less corrosive. According to Egloff[146] ethyl alcohol blends are markedly corrosive to galvanised metals.

According to Bauer and Schikorr, ethyl alcohol blends containing 20 per cent. ethyl alcohol have no action on certain aluminium alloys and pure aluminium except when they contain 0·15 per cent. water; in this case a uniform attack results.[154]

Corrosion by Carburetted Alcohol-Air Mixtures.—The corrosive action of carburetted alcohol-air mixtures has also been investigated by Louis,[150] who has subjected such mixtures to the action of heat and determined the quantities of the various oxidation products obtained. In the case of both methanol and ethyl alcohol, the formation of aldehydes below 300°C. is insignificant, and the production of acetic acid increases from 1·5% at 150°C., to 8·9% at 440°C. Methanol gives lower yields of aldehydes and acid than ethyl alcohol and would appear to be the more stable to heat. Tests on the corrosive action of such hot mixtures upon the metals generally used in automobile construction show that the alcohols do not exhibit any specific corrosion of the metals at high temperatures and that acetic acid and formic acid and aldehydes in the amounts formed (up to 1 per cent.) cause no appreciable corrosion.

Tests conducted by the Institution of Automobile Engineers Research Committee (England)[155] have shown that cylinder wear increased by 80 per cent. and top piston-ring wear increased by 100% by the use of a blend of alcohol and petroleum spirit containing 17% alcohol at a jacket temperature of 50°C. The acidity of the condensate from the exhaust gases was trebled by the use of the same alcohol blend. At higher jacket temperatures the corrosive effects of the blend were not so pronounced.

Corrosive Action of Exhaust Products.—Acetic and formic acids may be formed during the partial combustion of ethyl alcohol and methanol, and if these products are allowed to remain in the engine cylinder, particularly in the presence of condensed water, corrosion may be caused. In the same way, exhaust valves and exhaust pipes may be corroded. However, no direct evidence of such action has been presented and it may therefore be assumed that the acidity of the exhaust gases formed by the combustion of alcohol fuels is not much greater than that obtained with petrols.

491. The Possible Poisonous Properties of Alcohol Fuels and their Combustion Products.—Of the poisonous nature of the aliphatic alcohols, little need be said about ethyl alcohol as huge quantities of

this material are consumed every year in the form of beverages. With regard to the higher alcohols, these are definitely poisonous, but, up to the present, they have not been used as motor fuel to anything but a negligible extent.

Methanol, however, is very poisonous, whether it be crude or refined, made by the wood distillation process or made synthetically. This fact needs emphasis, because the erroneous opinion is sometimes held that the poisonous action of methanol is due mainly to impurities and that the purified material is relatively less toxic. The quantity of methanol required to produce poisoning when the product is taken into the stomach is fairly well known. Small amounts have been taken without apparent harm, but, on the average, 1 to 2 ounces will cause serious poisoning with probable blindness and death, while twice this amount will frequently cause death.

The effects of inhaling air containing various amounts of methanol vapour are not so well known, although there are conditions of exposure which will produce serious poisoning. Records of cases of severe poisoning by inhaling methanol vapour show, however, that the majority of such cases have occurred in the use of methanol as a solvent, in relatively small, confined and unventilated places.

Data regarding the dangers to health from absorption of methanol through the skin are contradictory.

It would therefore appear that a further disadvantage of the use of methanol as a motor fuel is its extremely poisonous properties.

Referring to the toxicity of alcohol fuels and their combustion products, all investigators on this subject agree that the type of fuel used, whether gasoline, benzole or alcohol, has no influence on the toxicity of the normal exhaust products.

The general toxic nature of methanol has been commented on by Leisegang, who has pointed out that, because of this property, methanol is one of the most dangerous of fuels.[156]

492. The Use of Alcohol Fuels in Various Parts of the World.— For many years past, but particularly since the Great War, considerable interest in alcohol fuels has been shown in many countries not endowed by nature with a supply of petroleum. These countries have, naturally, been rather anxious regarding their fuel supplies in times of national stress, when external sources of supply are cut off completely or else considerably curtailed, and they have directed their attention to the production of liquid fuels from their home resources. Moreover, during years of general economic depression, agricultural industries have suffered as much, or even worse than most other enterprises and, at the same time, extreme nationalistic tendencies have been the cause of the erection of extensive tariff barriers. Such circumstances as these,

all occurring together, have given a big impetus to the development of alcohol fuels as a means of helping agricultural industries, of reducing adverse trade balances and of reducing imports of foreign materials. That such a development has come about during a period of unprecedented petroleum surplus is to be regretted in every way, but the fact remains that, by the imposition of taxes upon imported oil and legislature demanding admixture of home-produced alcohol with imported motor fuels, most European countries have reduced their fuel imports considerably.

Whether the use of alcohol fuels, on any large scale, will ever be developed in the United Kingdom is a matter of some considerable doubt. It would not be necessary for the cost of such alcohols to be brought down to the level of imported petrol because of the import tax of eightpence per gallon levied on such material, and it would appear that, when such alcohols can be produced at any price below about tenpence per gallon, they can be used as motor fuel selling at its present price, i.e., nineteen pence per gallon, and give a satisfactory profit.

The following is a brief summary of the present position of alcohol fuels in various parts of the world. The economic aspects of alcohol fuels in Europe are summarised in Table 34.

TABLE 34. USE OF ALCOHOL FUELS IN EUROPEAN COUNTRIES, 1935[8]

Country	Metric Tons Consumed	Price of Alcohol Cents/Gallon	Number of Motor Vehicles	Cost per Motor Vehicle U.S. Dollars	Total Cost of Alcohol Fuel to Country* U.S. Dollars
Austria ..	4,400	57	45,000	17·50	793,000
Czechoslovakia	42,477	76	90,000	61·66	5,549,800
France ..	293,600	27	2,182,000	35·50	77,529,000
Germany ..	180,000	76	1,104,000	55·87	61,688,000
Hungary ..	8,731	79	15,200	136·30	2,072,000
Italy	5,000	88	392,000	4·00	1,577,000
Jugoslavia ..	6,592	40	10,400	21·83	227,000
Latvia ..	5,457	59	3,950	356·00	1,408,000
Poland ..	5,941	19	25,200	33·73	851,000
Spain ..	12,000	52	179,500	1·13	204,000
Sweden ..	12,250	31	154,800	6·37	986,000
Total	576,448		4,202,050	36·38	152,884,800

EUROPE

493. Italy.—A government decree of December 9th, 1931, published in the Gasetta Ufficiale of January 13th, 1932, provided

* Including direct loss to government on sale of alcohol below cost, loss of customs revenue on replaced gasoline, and addition to cost of gasoline owing to inclusion of alcohol.

that sufficient 99·6 per cent. ethyl alcohol should be mixed with imported gasoline in the ratio of 1 volume of alcohol to 4 volumes of gasoline, to consume one-quarter of the annual domestic production. Producers of domestic gasolines were not exempt from this law.

Although synthetic methanol is produced in Italy to the extent of 600 tons per year, it is not used in Italian motor fuels.

494. Latvia.—In order to help the agricultural industry, a law has been passed that requires all gasoline, kerosene, benzole, etc., used for engine operation, to be mixed with 25 per cent. by volume of alcohol, purchased from the State Alcohol Monopoly.

495. Hungary.—Hungary produced 226,000 barrels of alcohol in 1930, of which approximately 75,000 barrels were used as motor fuel. Alcohol is sold by the National Alcohol Trading Company, i.e., the alcohol monopoly, and mixed with gasoline in accordance with the 1929 decree, which makes it compulsory for all gasoline of specific gravity 0·735 or over to be mixed with 20 per cent. by volume of alcohol; gasoline of lower specific gravity than 0·735 and all gasoline used by agriculture is exempt. The alcohol-gasoline mixture is marketed in Hungary under the name " Motalko."

496. Austria.—Following the passage of a law in February, 1931, which became effective in May, 1931, and which called for the mixture of alcohol with motor fuel, alcohol became a factor in the Austrian motor fuel market. This law authorised the Minister of Finance to compel the mixture of alcohol with gasoline so long as the price of alcohol was lower than the wholesale price of gasoline. The amount of alcohol to be blended was left to the discretion of the Minister, with the stipulation that it must not exceed 25 per cent. by volume. The alcohol used for this purpose must be of Austrian origin and have a purity of at least 99·5 per cent.

A later government decree, which became effective July 7th, 1934, prescribes the compulsory purchase of alcohol from the Austrian Alcohol Monopoly by importers or refiners of gasoline. The Austrian alcohol to be purchased is 2 per cent. by weight for imported gasoline and 3·75 per cent. for domestically refined gasoline. The alcohol is to be used in motor fuels containing 20–40 per cent. by weight of alcohol.[159]

A motor fuel known as " Coreth " has recently been introduced on the Austrian market. This is described as a " 100 per cent. domestic fuel " and consists of a benzole-alcohol mixture containing various distillates from coal and wood distillation.[160]

The output of industrial alcohol in Austria during 1931–2 amounted to 6,786 hectolitres (149,000 gallons).

497. Czecho-Slovakia.—During 1930, 433,765 barrels of alcohol were produced, of which 34,000 barrels were used as a motor fuel in "Dynalkol," which consists of 30 per cent. gasoline, 50 per cent. absolute ethyl alcohol and 20 per cent. benzole. This alcohol fuel has been produced since 1923 and is distributed by the Czecho-Slovak alcohol sales office to the extent of about 60,000 barrels, or 2,100,000 Imperial gallons per year. According to a recent Bill, which became effective on September 1st, 1932, all imported motor fuels of specific gravity at 15°C. below 0·79 must be mixed with 20–30 per cent. by volume of alcohol, consisting of 95 per cent. anhydrous ethyl alcohol and 5 per cent. of wood spirit methanol. This law is strictly enforced and unblended motor fuels are only available for pharmacies, hospitals, scientific institutions and the like. The use of this fuel is anticipated to produce a 60 per cent. increase in employment in the alcohol industry and a 5 million quintals higher potato production: it is also expected that 15,000–18,000 hectolitres of wood spirit will be consumed per year. Experiments show that the above fuel gives a 6–8 per cent. higher consumption for a given mileage as compared with petrol. The seven Czecho-Slovak wood distillation plants produce, on an average, about 35,000 hectolitres of methanol per year, but in 1932, two of these plants were shut down and the others were operating on a substantially reduced schedule.

The quantity of alcohol sold in Czecho-Slovakia during the year ending August 31st, 1933, was 955,000 hectolitres (21 million gallons), and in the previous year 527,000 hectolitres (11·6 million gallons). The quantities of alcohol used in motor fuels during these periods were 544,940 hectolitres (12 million gallons), and 15,850 hectolitres (350,000 gallons) respectively.[161]

498. Sweden.—Sweden possesses no domestic crude oil production, but produced 79,260 barrels of alcohol from waste sulphate pulp liquor in 1931, of which 48,000 barrels were used as motor fuel. This alcohol was mixed with gasoline and sold under the name of "Lattbentyl" through the filling stations of the large oil companies, at a slightly higher price than the regular gasolines. The total consumption of this mixture, during 1931, was 170,000 barrels. In August, 1931, all Swedish government departments using gasoline were ordered to buy "Lattbentyl," provided that the price quoted did not exceed the price of foreign gasoline by more than 10 per cent.

A new Swedish law compelling gasoline importers and producers to purchase power alcohol became effective on October 1st, 1934, when the amount of alcohol to be purchased was fixed at 3·6 per cent. on all gasoline imported or made. One result of this compulsion was an immediate increase in gasoline price.[162] "Lattbentyl" consists

of 75 per cent. gasoline—25 per cent. ethyl alcohol. No methanol fuels are used in Sweden.

499. Denmark.—A report recently issued by the Danish Agricultural Society emphasises that the production of alcohol from grain and potatoes offers special difficulties because of high costs, and concludes that agriculture itself would have to bear a considerable part of the increased cost of transportation and the balance of benefit to the agricultural industry over the disadvantages to the national economy would be of no great order. It is believed that a mixture of 25 per cent. alcohol with gasoline would result in an increase of 9·5% in the price of motor fuel.

500. France (One of the chief protagonists of alcohol fuels).—There is in use in France a gasoline-alcohol mixture known as "Carburant National," consisting of 50 per cent. by volume of ethyl alcohol and 50 per cent. by volume of gasoline, which accounted for the consumption of 168,000 barrels of alcohol during 1930. Government departments and the Paris bus services are the chief consumers of this fuel, but private car owners use it to some extent. The French Government compels the oil companies to buy the alcohol, who have to do the marketing and suffer any loss sustained. In October, 1931, a decree was passed compelling importers of gasoline and any other products used as motor fuel to add to such products 25–35 per cent. by volume of anhydrous alcohol. This decree, however, only affected motor fuels used for commercial purposes, e.g., in lorries and trucks, and the alcohol mixture is designated "heavy carburant national." This decree was followed by a further one on November 14th, 1931, compelling the addition of 10 per cent. by volume of alcohol to *all* imported gasoline. Production of alcohol in France during the season October 1st–September 30th, 1931/32, amounted to 3,314,991 hectolitres, compared with 3,092,892 hectolitres in 1930/31. Imports increased to 533,995 hectolitres, as against 330,743 hectolitres, while exports decreased to 141,520 hectolitres from 179,155 in 1930/31.

Methanol is also produced in France, but the quantity of it used in motor fuels is negligible.

501. Spain.—The Spanish Petroleum Monopoly is to purchase annually, commencing August 1st, 1935, alcohol from grape residue up to 175,000 hectolitres (3·84 million gallons). This will be blended in the motor fuels sold in Spain.[157]

502. Bulgaria.—By virtue of a law, dated December 1st, 1934, a Bulgarian State Monopoly for alcohol and light mineral oils has been set up. The monopoly has the right to control alcohol production and admixture with gasoline.[158]

503. Finland.—The Finnish Government has appointed a special committee to investigate all the technical and economic aspects of domestic motor fuels.[164]

504. Yugo-Slavia.—Under regulations issued by the Minister of Finance and published in the Sluzbene Novine, Belgrade, September 29th, 1932, all motor fuels having a density of less than 0·795 at 15°C. must, after October 1st, 1932, be mixed with 25% by weight of alcohol. By a further decree, becoming effective on December 1st, 1932, motorists in Yugo-Slavia are forbidden to drive motor vehicles upon any fuel other than this alcohol blend.

505. Lithuania.—A law passed on July 6th, 1935, to come into force not before March, 1936, provides that the Minister of Finance shall prescribe the conditions under which compulsory addition of alcohol to gasoline is to be enforced, the proportion and grade of alcohol to be used, and also the minimum prices of the blended fuel. Importers of gasoline will be required to purchase the prescribed quantities of alcohol.[165]

506. Germany.—During recent years the production of domestic motor fuels in Germany has been as follows :

METRIC TONS

	1934	1933	1932	1931
Motor Spirit.				
Domestic	250,000	174,000	150,000–170,000	130,000–135,000
Imported	1,250,000	905,000	—	—
Total	1,500,000	1,079,000		
Benzole.				
Domestic	280,000	233,700	200,000	250,000
Imported	40,000	33,600	—	—
Total	320,000	267,300		
Alcohol.				
Domestic	171,000	138,000	80,000	50,000
Total—All Motor Fuels ..	1,991,000	1,484,300		
Total Domestic Production	701,000	545,700	430,000–450,000	430,000–435,000
% Domestic Production	39	37	33	29

In August, 1930, a decree was introduced enforcing the addition

of 2½ per cent. by weight of alcohol to all imported and home produced gasoline. Later this amount was increased to 10 per cent.

A significant feature with regard to Germany's domestic fuel supplies is the recent introduction of synthetic methanol which may be construed as presaging the steady decline of ethyl alcohol as a motor fuel constituent. Whereas prior to the beginning of 1936, ethyl alcohol comprised 10 per cent. of all the motor fuel consumed, at present the amount is less than 8 per cent. and further reductions are expected to occur in the future, probably resulting in the complete elimination of ethyl alcohol of agricultural origin as a compulsory motor fuel ingredient. Measures instituted by the Reich government relative to synthetic fuels are likely to create entirely new outlets for methanol.

507. Other European Countries.—The only motor fuel used in Greece, Holland, Portugal, Norway or Rumania is gasoline, except for a certain quantity of benzole. Alcohol fuels have not yet been adopted. In Poland, legislation is in force to compel the admixture of 6–12 per cent. of alcohol with gasoline.

508. Great Britain.—At the present time only two alcohol fuels are on general sale in Great Britain. Various fuels containing ethyl alcohol and methanol as major constituents are sold in small quantities for use in racing events. Details regarding the properties of these various fuels are given in Chapter XVII (Volume II).

Very marked increases in the amount of ethyl alcohol used in motor fuels in the United Kingdom are evident from the following figures :—

PROOF GALLONS OF ETHYL ALCOHOL

	England and Northern Ireland	Scotland	United Kingdom
1931	17,369	5,781	23,420
1932	96,098	9,382	105,480
1933	374,960	16,054	391,014
1934	1,670,890	24,318	1,695,208
1935	—	—	1,475,275
1936 (Jan.-March) ..	—	—	420,973

The loss in Inland Revenue during the financial year ended March 31st, 1935, due to exemption of alcohol from tax, was about £30,000. By far the larger amount of the alcohol used in the alcohol motor fuels sold in the United Kingdom is produced from imported molasses.

509. Ireland.—At the time of writing there are five plants in course of erection in the Irish Free State for the production of ethyl

alcohol from potatoes, having an aggregate capacity of 660,000 gallons of industrial alcohol per year. This will entail the cultivation of 20,000 acres of potatoes. The ultimate aim of the Free State government is to enforce the admixture of 10 per cent. of domestic alcohol with imported gasoline. The cost of the alcohol has been estimated at 21·22 pence per gallon.[166]

510. The Union of South Africa.—At the end of 1927 the manufacture of "Natalite," consisting of 60 per cent. ethyl alcohol and 40 per cent. ethyl ether, was begun by Natal Cane By-Products Ltd., but due to the use of alcohol for munition purposes during the War, sales were not considerable until 1919, when the shortage of gasoline gave an impetus. When supplies of gasoline became more plentiful again the sales of Natalite fell off considerably due to its low calorific value, and the same company then introduced a mixture of equal parts of Natalite and gasoline, to which the usual denaturants were added, and known as Union Motor Spirit. The fuel attained a fair measure of success but owing to the 3–4 per cent. of water contained in the alcohol much trouble was experienced with die-cast zinc carburettors and the metal tops of auto-vac tanks. As soon as the azeotropic process for the manufacture of absolute ethyl alcohol on a commercial scale was proved to be a success, a plant was commissioned operating under the patents of the Usine de Melle, and a new fuel consisting of 50 per cent. absolute alcohol and 50 per cent. gasoline was introduced, the government of the Union of South Africa at that time allowing a rebate of the whole of the duty payable on the gasoline, i.e., sixpence per gallon. This rebate was reduced after a few months to threepence per gallon. The sales of this motor fuel still continue in Natal and other parts of the Union.*

511. British India.—A sugar committee appointed by the government of India has decided to carry out an experiment on the marketing and distribution of power alcohol for admixture with gasoline. The government is to meet the cost of equipping two existing commercial distilleries with the special plant required for the production of absolute alcohol. The government is also to enter into an agreement with various distributing companies for sale to the public of a mixture of 20 per cent. alcohol and 80 per cent. gasoline at reduced prices. The experiment will at first be confined to a limited area and there is the proviso that the use of such fuels shall not, directly or indirectly, increase the motorist's taxes.[167]

India is, however, rapidly becoming self-supporting in motor spirit without the help of alcohol. Motor fuel imports, which amounted to 12·7 million gallons in 1932, were only 5·1 million gallons in 1933.[168]

* The authors are indebted to Natal Cane By-Products Ltd., for the above information.

512. Australasia.—Many attempts have been, and are being made in Australia to commercialise ethyl alcohol as a motor fuel. The manufacture of power alcohol by the fermentation of molasses and cassava was first started by the Australian National Power Alcohol Company, in 1927, in Northern Queensland. More recently, arrangements have been made between the Distillers Company and Australian interests, together with the Shell Oil Company, to produce and market an alcohol-gasoline mixture.

South America

513. Argentina.—The large domestic petroleum industry has, so far, been successful in forestalling any legislation to compel the use of motor fuel substitutes, but there has, however, been considerable agitation by the agricultural interests and the sugar refining industry for government action to compel the mixture of motor fuels with alcohol made from such products as corn, grapes and molasses. During 1930, the National Chemical Office of Argentina conducted an investigation which resulted in a statement that alcohol could be used for mixing with gasoline as a fuel. Another study was made by a Commission, appointed in February, 1931, by the Federal Inventor of the Province of Tucuman, to determine methods of using locally produced alcohol. In July, 1931, a government decree designated a committee to investigate the possibility of utilising domestic alcohol as a constituent of a domestic fuel, with a view to aiding agriculture and reducing petroleum imports. As a result of this investigation, the committee suggested a national fuel, containing 30 per cent. alcohol, with corn as its chief raw material, but, as yet, no definite action is known to have been taken to make its recommendations effective and there are, at present, no alcohol fuels used in Argentina.

514. Brazil.—Brazil has no crude petroleum of its own and is entirely dependent upon imports. It is, however, a large sugar producing country and much of its waste molasses and sugar surplus is converted into alcohol, of which the annual production is estimated to be 16,000,000 gallons, and most of which is consumed in the manufacture of beverages. During the past few years, owing to the low price of sugar, considerable influence has been exerted by the producing interests to have the Federal Government effect legislation requiring the admixture of alcohol with imported gasoline. Small amounts of ethyl alcohol have been used as fuel, for the past few years, in the cities of Pernambuco, Rio de Janeiro and Nictheroy, but sales have been strictly confined to these cities and the alcohol consumption in this way has been small compared with the gasoline consumption. Two alcohol mixtures are sold in Pernambuco, one consisting of 70 per cent. alcohol and 30

per cent. ether, and the other, 90 per cent. alcohol and 10 per cent. ether. In Rio de Janeiro and Nictheroy an alcohol fuel, known as "Gasalco," is sold, consisting of 82 per cent. ethyl alcohol and 18 per cent. gasoline. Consumption amounts to about 100 barrels per day, or just over one and a quarter million gallons per year.

The disposal of alcohol in these three fuels has been of such slight help to the sugar industry that the Government demanded, in February, 1931, that gasoline importers should purchase alcohol to the extent of 10 per cent. of their imports. However, alcohol for this purpose was not available in sufficient quantity, and in November, 1931, a new decree was issued, whereby importers were compelled to deposit, at the Bank of Brazil, in a special account, and at the disposition of the Government, an amount of money corresponding to the sum necessary to purchase the alcohol. Due to insufficiency of alcohol supplies and many complex problems in putting the law into operation, the law requiring the mixture of 10 per cent. ethyl alcohol with gasoline has not yet become fully effective and ordinary gasoline has been sold over long periods.

No methanol is produced in Brazil.

515. Chile.—Chile possesses no crude oil production of its own. In May, 1932, a law was passed providing for the importation and distribution of petroleum and its products by a Chilean State monopoly, in which a participation of foreign capital, to the extent of 25 per cent., and foreign labour, to the extent of 10 per cent., was allowed. It also provided for the expropriation of existing private installations.

In 1930, Chile produced 3,700,000 litres of alcohol and stocks were rapidly accumulating. To relieve the situation, in August, 1931, a law was passed demanding the mixture of alcohol with all imported gasoline, with the exception of that used for aviation. The effective date of the law was fixed by the President at not later than one year from its date of publication and the same official was empowered to fix the proportion of alcohol to be used, although this must not be less than 10 per cent., or greater than 25 per cent.

516. Uruguay.—In 1931, the Uruguay Government announced a policy of attempting to reduce gasoline imports and imposed a tax of 7·8 cents per U.S. gallon, which has recently been increased to 11·7 cents. The Uruguay Government has also passed a Bill providing for a complete government monopoly in petroleum refining and distribution as well as the distilling of alcohol. The date on which this Bill becomes effective is not yet known.

517. Cuba.—Under a proposed Carburant Decree-Law of the Cuban government increases will be imposed on the import duties

on gasoline and also on internal combustion engines of the automotive type " not specially constructed to use an alcohol gasoline mixture." The tax on motor fuel is to be graded inversely to the proportion of alcohol incorporated. Two years following the passing of this measure it will be compulsory for all motor fuel sold in Cuba to contain 40 per cent. of domestic alcohol.[170]

518. The Philippines.—A Bill providing an increase in the tax on gasoline from 4 to 10 centavos per litre, exempting aviation gasoline, has been introduced into the Philippine House of Representatives. The measure is intended to increase the production of alcohol and provides for tax reductions on gasoline mixed with alcohol.[171]

519. Panama.—A statement has been made that the National Assembly of Panama has a Bill under consideration, providing for the establishment of a government monopoly in gasoline.

In order to provide a market for domestic alcohol, a decree has been passed providing for the mixture of domestic alcohol with gasoline and also providing for an increase of the import duty on gasoline and a decrease of the duty payable on the mixture.[169]

520. Salvador.—The Government of Salvador have recently[76] passed a decree authorising a certain company to erect and work an alcohol distillery of 6 million litres (1·33 million gallons), half of which shall be used as a motor fuel mixed with gasoline. The whole of the output will be sold to the government for twenty-five years, at the end of which time the plant will become the property of the Government, without cost.

521. Other South American Countries.—No alcohol fuels are produced or marketed in Peru, Venezuela or Colombia.

522. North America.—United States of America.—Even in the U.S.A., the largest producer of crude petroleum in the world, a movement to compel the use of ethyl alcohol is spreading throughout the west territory of the country. The economic situation of the farmer has here long been a serious problem. A number of solutions have been offered, among them curtailment of production, crop substitution, manufacture of industrial products from farm crops and government subsidy. One important proposal is the production of alcohol from corn and other farm crops and its use as a partial substitute for gasoline. Plants for the production of alcohol have been erected—one being at Atchisson, Kansas—and the Chemical Foundation have taken an active interest in the project. Plans have been completed for the disposal of the alcohol produced—amounting to 10,000 gallons of anhydrous material per day.

It is significant that ethyl alcohol could be produced in America

from waste petroleum gases at a cost less than it can be obtained from grown products.

Arguments against the adoption of alcohol fuels in America have been ably presented by Egloff and Morrell.[172]

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Chapter X

SYNTHETIC FUELS AND AUXILIARY SUPPLIES OF MOTOR SPIRITS

529. Introduction.—The essential need of an internal source of liquid fuel to a nation in time of stress was demonstrated beyond question during the Great War, and the motive which is now urging most nations of the world to seek some cheap substitute for petrol or other liquid fuel from their own resources is, undoubtedly, a desire to be independent of foreign supplies due to political pressure.

Much has been said regarding the possible limited reserves of crude petroleum and various estimates have been made concerning the period of time for which these reserves will suffice, after which alternative supplies will be required; but although no mineral deposit can last indefinitely if it is constantly being used up, no evidence has been brought forward to show that crude petroleum supplies will not be sufficient to meet the demands of the next five hundred years at least. Vast areas of the earth's surface have not yet been prospected for oil and, undoubtedly, enormous stores of petroleum are still untapped.

The various methods proposed for the production of synthetic fuels have, during the past few years, received severe setbacks through the prevailing low prices of the natural supplies, but more recently they have received substantial encouragement by the growth of tariff protection and nationalistic tendencies.

In England, the utilisation of coal has naturally received the greatest attention in this field and various low temperature carbonisation schemes have been launched; hydrogenation has also received considerable attention. In Europe, the position is rather different, and here the depressed state of the agricultural industries has caused attention to be particularly focussed upon the utilisation of ethyl alcohol, produced from potatoes, as a fuel for internal combustion engines. Numerous European countries have passed the requisite legislature whereby the addition of home-produced alcohol to imported petroleum motor fuel is insisted upon by law. This affords a considerable subsidy for agriculture.

In this Chapter, the production of liquid fuels from materials

other than petroleum by various processes is discussed under several headings. Alcohol fuels are considered separately in Chapter IX, and the hydrogenation of coal and coal tars is dealt with in Chapter VII.

Oil Shales, Torbanites and Bituminous Sands

530. The Occurrence of Oil Shales.—Oil shales are very widely distributed throughout the world and although they have only been worked in a few cases, notably in Scotland, France, Manchuria, Estonia and Australia, they constitute an important world reserve of oil.

Scotland.—As early as the seventeenth century it was known that oil could be obtained by distilling coals and shales, but it was not until the middle of the nineteenth century that the process was put on to a regular commercial footing. By that time the need of oils for lubrication and lighting and improvements on the materials then available for candle-making were being keenly felt, and the possibility of supplying these needs by refining natural mineral oil was investigated by James Young, a Glasgow chemist at that time employed in Manchester. He succeeded in obtaining the desired products from oil occurring in the Derbyshire Coal Measures. The supply was too limited for a permanent industry, and assuming that the natural oil had been produced from some kind of coal by underground heat, he commenced a study of means to produce such oil artificially. This finally led to the establishing of plant at Bathgate in 1851 to produce oil from the Boghead Coal or Torbanehill Mineral, a very rich cannel coal which had been discovered in that district a few years earlier. The supply of this coal was limited, and the demand for it for oil works in Scotland, on the Continent and in the United States practically exhausted the field by the early 'sixties. In 1858, however, oil shale yielding similar products and differing mainly in the percentage of ash, was discovered near Broxburn and shortly afterwards in the West Calder district. The oil shale gave only a fraction of the yield got from Boghead Coal, but its great abundance and cheapness permitted the oil industry in Scotland to expand to an extent impossible with Boghead Coal, and by 1865 it is recorded that no less than 120 works were in operation using the oil shales of the Lothians or cannel shales of the Coal Measures. In 1859 the commercial development of petroleum in the U.S.A. began, and its products reached European markets a few years later, causing a rapid fall in prices and the abandonment of many of the Scottish oil works. Those that survived did so by reason of the closest attention to technical and commercial matters, and notwithstanding the very unequal competition with the

imported product, the output in Scotland continued to expand through extension of well-managed undertakings. With the fall in value of the primary product, burning oil, greater attention was given to lubricating oils, paraffin wax and latterly sulphate of ammonia, resulting in remarkable advances in the efficiency of plant and methods in both the retorting and refining departments. Retorting was at first carried out in horizontal iron retorts. These were displaced by vertical iron retorts with saving in labour and improvement in yields. Arrangements were then introduced by which the fixed carbon of the spent shale was utilised as fuel (Henderson, 1878) and in the Young and Beilby retort of 1882 a great advance was made in ammonia recovery by the use of steam. In 1894 the Pumpherston retort was patented by Bryson, Jones and Fraser, in which the Young and Beilby principle was embodied in greatly improved mechanical design with a marked gain in economy and control of operation.

The output of shale reached a maximum of $3\frac{1}{4}$ million tons in 1913, when further development was checked by the late War. During the War a scheme for the joint marketing of certain products was brought into operation, and on the conclusion of the War this was extended to deal with all products. At the same time the six surviving companies were brought under one management, their ordinary shares being acquired by a new company—Scottish Oils Limited—whose ordinary capital in turn was subscribed by the Anglo-Iranian Oil Company (then the Anglo Persian Oil Co.). The economic difficulties of the subsequent period have brought about successive reductions in the scale of operation until to-day the output of shale is a little short of $1\frac{1}{2}$ million tons. This output is drawn from various shale mines, retorted in several crude oil works, and the crude products are refined in a central refinery at Pumpherston. In addition there are two sulphuric acid works, one candle factory and a coal mine. Mining and manufacturing operations are carried on in the districts of West Calder, Livingston, Pumpherston, Broxburn and Winchburgh.

In order to provide supplies of shale to replace the output of mines which are now approaching exhaustion, Scottish Oils Limited have recently begun the sinking of further pits. The existence of a considerable area of the Dunnett deposits to the south-west has recently been proved.

Scottish oil shale is dark brown to black in colour with a laminated structure which is more obvious after retorting than in its natural state. It shows a brown streak, and rich specimens can be cut with a sharp knife giving a thin curly shaving like leather or rubber. It contains about 80 per cent. of ash, which consists mainly of silica and alumina. The oil shales of the Lothians occur in the calciferous sandstone series near the base of the Carboniferous system, constituting

a local development peculiar to West and Midlothian and adjacent portions of Fife and Lanark.

A full description of the geology of the oil shales, the methods employed in mining, the chemistry and methods of manufacture, is contained in the Memoir of the Scottish Geological Survey on " The Oil Shales of the Lothians " (Third Edition 1927).

The Scottish Geological Survey has estimated the reserves of shale as follows :

Midlothian	163,500,000 tons
Linlithgowshire	416,540,000 ,,
Lanarkshire	16,730,000 ,,
	596,770,000 tons

These figures are subject to a deduction of, say, 25 per cent. for loss in working.

In 1924, the quantity of shale mined amounted to 2,854,600 tons, the average yield of oil being 25 gallons per ton.

During later years the production of oil shale has been as follows :

1932	1,368,596 tons
1933	1,397,000 ,,
1934	1,401,000 ,,

The larger part is produced in the Linlithgow district. In 1934 the yield of crude oil and crude naphtha amounted to 30·3 million gallons, an increase of 331,000 gallons over 1933.

531. English Deposits.—Large deposits of oil shale are found in Norfolk and Dorsetshire, but one of the major difficulties to be encountered in the use of these resources is the high sulphur contents of the resulting oils. The occurrence of bands of inflammable shale, known as " Blackstone " or " Kimmeridge coal," in the Kimmeridge clay in Dorsetshire has been known for centuries. In 1848, works were erected at Weymouth for the distillation of the shale and it was stated that 1 ton of shale yielded 7·5 gallons of naphtha, 10 gallons of lubricating oil, 1 hundredweight of pitch and 11·5 hundredweights of residue, together with paraffin wax and gas. In 1851, an occurrence of bituminous shale near Portlesham was noted by W. Manfield, and in 1883–4, large scale tests were carried out on the shale. It was found that the mineral yielded about 40 gallons of oil per ton and it was estimated that 1½ million tons of shale were available. The workable shale at Kimmeridge covers an area of 2,900 acres and that at Corton (about midway between Upway and Portlesham) 1,500 acres, the estimated amount of shale and oil obtainable being as shown in Table 1.[1]

With regard to the Norfolk deposits, the occurrence of shale was recorded at Southrey in 1835 and at Downham Market in 1895. It is only within recent years, however, that any attempt has been made to exploit the shales, but although much interest has been shown in those in the neighbourhood of King's Lynn, no serious attempt at commercial development has been made.

The following analyses of three samples may be taken as representative of the general composition of the shales found in this district.[1]

	(*a*)	(*b*)	(*c*)
Moisture	9·8	8·0	4·1
Volatile organic matter ..	35·1	31·7	37·1*
Fixed carbon	15·3	16·3	12·0
Ash	39·8	44·0	46·8

* Includes combined water and organic sulphur.

TABLE 1. SHALE DEPOSITS AT KIMMERIDGE AND CORTON (DORSETSHIRE, ENGLAND)

	Thickness ft. ins.	Tons per acre	Total Tons of Shale	Dry Oil per ton. (Imperial Gals.)	Total Quantity of Oil. (Imperial Gallons)
Kimmeridge.					
Shale	1 11	3,913	11,000,000	8·1	92,000,000
Blackstone ..	2 6	4,375	12,000,000	37·6	363,000,000
Total ..	4 5		23,000,000	—	455,000,000
Corton.					
Main bed with inferior shale	10 0	21,000	32,000,000	14·0	442,000,000
Grand Total			55,000,000		897,000,000

A test carried out on the shales of analyses (*b*) and (*c*) gave 40 gallons of oil (specific gravity 0·942–0·960) per ton and a distillation on this oil gave the following figures:

0–100°C.	3·8 per cent.
100–170°C.	5·7 ,, ,,
170–245°C.	19·2 ,, ,,
245–310°C.	39·2 ,, ,,
Water	0·8 ,, ,,
Pitch and loss	31·5 ,, ,,
Sulphur content	Up to 6·4 per cent.

Shale oil deposits also occur in Yorkshire at Specton and in Somersetshire near Watchet.

532. In Canada, oil shales occur in New Brunswick, Nova Scotia, Quebec and Newfoundland, some of which give quite good yields of oil. In Australia, shales occur in New South Wales and Queensland and a rather peculiar deposit, known as " Tasmanite," of high oil yield, is found in Tasmania. Two grades of shales have been mined and retorted in New South Wales, of which one is termed " kerosene shale," a torbanite which has been used locally and exported for gas making; and another, a lower grade, which has also been utilised locally.

Africa has shales in Southern Rhodesia, Transvaal, and Natal, some of which, e.g., those at Ermelo in the Transvaal, give oil yields as high as 60 gallons per ton, and are now being commercially exploited. Shale deposits have also been reported in Morocco, Angola and the Belgian Congo. In Australia, considerable quantities of shale oil have been produced at Newnes, New South Wales.

Extensive shale deposits occur in Europe. In France, the most important oil-shale deposits are at Buxière and St. Hilaire (Allier) and at Autun (Saône-et-Loire). The oil-shale industry of France dates from 1830.

The products obtained from the crude Autun shale oil to the extent of 12–25 gallons per ton of shale are :—

Lamp oil	35–40 per cent.
Heavy oil	4 ,, ,,
Green oil	25 ,, ,,
Pitch	20 ,, ,,
Loss in refining	14 ,, ,,

With the exception of the United States of America, Russia has the most extensive shale deposits in the world. These have hitherto been used for heating purposes but shale utilisation in gas, gasoline and asphalt production has now begun on a large scale.

533. The Estonian oil shales are very well known, chiefly because of the vast amount of work carried out by Kogerman, who has described the raw shale and its oil products in detail.[3] The deposits of oil shale (called " Kukkersite " in Estonia) cover an area of about 2,400 square kilometres and are present in seven seams interspersed with limestone bands and located in the Ordovician system. These were discovered in 1790 but were not exploited until 1916, when there was a severe fuel shortage. The largest mine and plant in Estonia at Kohtla has been operated by the government since 1919, other concessions being made later to private companies at Vanomoisa, Pussi and Sillamagi.[4] The State oil-shale works mined 365,700 tons of shale in 1929 and this quantity yielded 5,450 tons of oil on retorting.[5] The total crude shale oil production in Estonia was 10,000 tons in 1930 and 17,000 tons in

1931. The raw shale, as well as the shale fuel oil, is used in factories and railways as fuel. The crude shale is soft, light to dark brown in colour and burns easily. The freshly mined shale has a calorific value of 3,000–3,500 cals./kg., this figure rising to 4,200–4,250 cals./kg. after air drying.

The following properties have also been reported.[6]

Water content	5·18 per cent.
Ash	30·7 ,, ,,
Ash content of dry shale	32·4 ,, ,,
Sulphur content of dry shale	2·3 ,, ,,

The organic matter content is usually about 55 per cent.

Oil shales also occur in Sicily near Ragusa and Vizzire. An agreement has been signed between the Italian Government and an Italian Company subsidising the utilisation of these shales for the production of oil, the subsidy amounting to about 140 lire per ton of oil of specified grade. It is estimated that 50,000 tons of oil will be produced per year, the oil yield being 12 per cent. by weight.[7] Other European countries known to possess oil shales are Yugo-Slavia, Spain, Sweden, Bulgaria, Germany and Switzerland.

In other parts of the world, shales are found in the United States (in Colorado, Nevada, Utah, Wyoming, Kentucky, etc.), in Brazil, Argentina, Chile, Manchuria, Mongolia and Syria.

534. In Australia, oil shales occur in New South Wales and particularly in the Newnes-Capertu district and in Queensland. A rather peculiar deposit, known as " Tasmanite," which gives a high oil yield, is found in Tasmania. A comprehensive report[2] concerning the economics of the commercial development of the New South Wales deposits has recently been issued by the Newnes Investigation Committee appointed by the government of the Commonwealth of Australia and New South Wales in February, 1933. When this committee was originally formed, the success of the industry seemed assured, but, due to decreases in the retail prices of motor fuel in Australia and to other economic considerations, the establishment of operations can only now be contemplated if substantial government help, with respect to both capital investment and relief from excise, is forthcoming. The report was issued in May, 1934.

Estimates indicate that up to 20,000,000 tons of shale oil are available in the Newnes-Capertu deposits, but much of this may be in seams not thick enough for economic exploitation.

The oil shale is of high grade, yielding over 100 gallons of oil per ton.

535. The Production of Shale Oil.—Oil shales and torbanites do not contain oil in the free state. They contain a complex organic material

often referred to as " Kerogen " or pyrobitumen, which on heat treatment is decomposed and oil is liberated. This crude oil is very similar to crude petroleum as far as its constituent oil fractions are concerned.

In the decomposition of shales by heat treatment, several stages can be distinguished. It is believed that first of all the kerogen decomposes to give a bituminous material insoluble in organic solvents, then a soluble bituminous substance is formed and, finally, this is decomposed into oils of wide boiling range and permanent gases such as methane and hydrogen. Carbon dioxide is evolved in quantity in the early stages of the decomposition, probably in the reaction producing soluble bitumen from the kerogen, and also at a later stage, due to the decomposition of inorganic carbonates. The reaction producing the intermediate bitumen is also attended by an evolution of sulphuretted hydrogen and ammonia. The production of hydrogen and permanent gases, together with unsaturated gases, occurs during the thermal decomposition (i.e., cracking) of the intermediate bitumen.

Regardless of the exact mechanism of the conversion of kerogen into oil and gas, the process is fundamentally the decomposition or cracking of heavy and complex molecules to simpler ones. It is possible to control the process in various ways so that, for example, the relative proportion of oil and gaseous product can be varied. It has not yet been possible to suppress the formation of the considerable quantities of gas generated in this process.

Of the factors influencing the yield and composition of the oils obtained, undoubtedly the most important are the retorting conditions and the maximum temperature.

536. In the Scottish shale oil industry the shale is retorted in vertical retorts of the Pumpherston type (see Fig. 1). These are 43 ft. 6 ins. high, circular in section, 2 ft. diameter at the top and tapering outwards to 2 ft. 9 ins. diameter at the bottom. From top to bottom the retort consists of four sections :—

1. Charging hopper, which holds approximately four tons of shale.
2. Cast iron portion, 11 ft. 6 ins. high, 2 ft. diameter at the top and 2 ft. 4 ins. diameter at the bottom. This carries the vapour off-take pipe leading to the gas main and condensers.
3. Firebrick portion, 20 ft. 9 ins. high, 2 ft. 4 ins. diameter at the top and 2 ft. 9 ins. at the bottom.
4. Spent shale hopper.

Four such retorts are included in one set, 13 sets in a bench, and at the Deans works of Scottish Oils Limited, there are six benches installed, i.e., a total of 312 retorts. The charge of shale rests on a

cast iron table at the bottom of the firebrick portion, and on this table rotates an arm which pushes the spent shale over the edge of the table into the hopper below. The retort itself holds about four tons

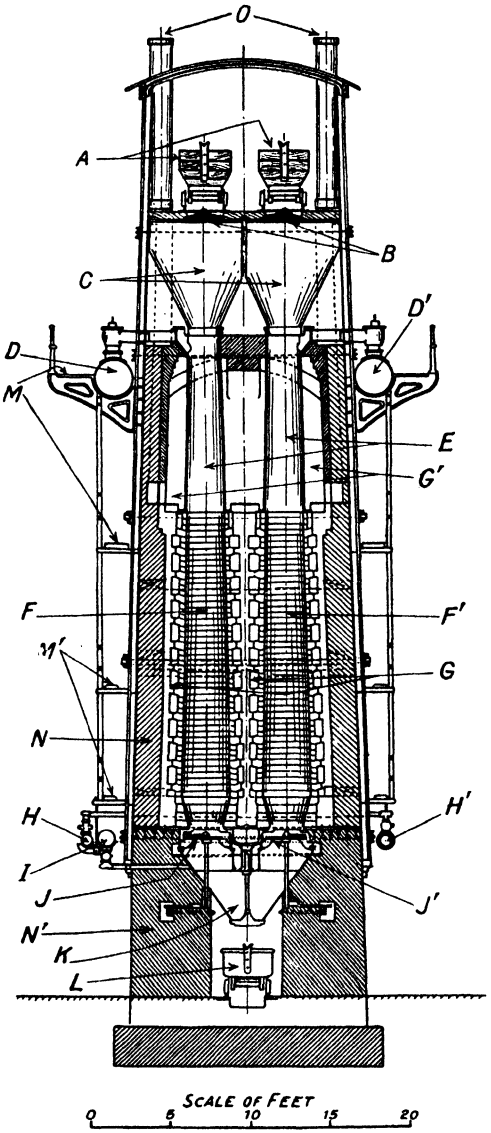


FIG. 1.—SECTION OF A SCOTTISH SHALE RETORT (PUMPHERSTON TYPE)

of shale and any given portion takes about twenty-four hours to pass through the retort. The shale is heated by permanent gas obtained in the process augmented when necessary by producer gas, each set

of four retorts being heated separately. The heating gas and primary air enter each set near the bottom and by means of baffle walls are directed upward and around each retort evenly: the temperature in each section is controlled by regulating the secondary air supply, and therefore the combustion, at various points.

In its passage through the retort, the shale is gradually heated to a maximum temperature of 1,300°F., the temperature in the combustion space around the retort at this stage being approximately 1,800°F. Oil vapour is given off from the shale at comparatively low temperatures, 650–900°F., and as the shale reaches its maximum temperature the steam passing up the retort converts into ammonia 90 per cent. of the nitrogen content of the shale. Steam is introduced into the retorts at a rate of 900–1,000 lbs. per ton of shale, at the spent shale hopper, its main functions being:—

1. To cool the spent shale.
2. To convert the nitrogen of the shale into ammonia and the fixed carbon into water gas.
3. To remove rapidly the oil vapours when formed, thereby preventing overheating and cracking of the oil.
4. To distribute heat evenly through the retort.
5. To seal the retort against inward leakage of air through the discharge hopper.

The mixture of oil vapour, ammonia, steam and permanent gas is drawn by exhaustion from the top of each retort to a bank of atmospheric condensers, where oil and water condense, the latter dissolving ammonia; the mixture of oil and ammonia liquor then passes through separators to the respective storage tanks and the uncondensed gas passes on for further treatment.

537. In Estonia, the State-owned plant at Kohtla operates six Pintsch producer retorts. Other plants in the same country use Eesti-Patendi retorts and Davidson rotary retorts. At Kohtla, the Pintsch retorts consist of vertical cast iron shafts lined with firebrick, of external diameter 2 metres and 5 metres high. Raw shale is graded to pass a 4-inch mesh, but retained by a 2-inch mesh, this grade being found most suitable. The shale is charged through a bell hopper and descends by gravity through the retort. The gases generated in the combustion chamber at the base of the producer enter annular flues at the top of the combustion zone and pass into the charge undergoing retorting along with cold gas, which reduces the temperature of the combustion gases to about 550°C., the shale distillation temperature. Part of the permanent gas is used for firing Babcock and Wilcox boilers.

The Eesti-Patendi A/S system at Pussi consists of a tunnel oven, rectangular in cross section, capable of a throughput of 70 tons per day, and so dimensioned as to allow the free passage of trucks holding 680 kg. of shale. The tunnel accommodates 20 trucks, 5 in the preheating section, 12 in the carbonising section and 3 in the cooling section where the shale is quenched with water. Each section is sealed by hydraulically operated doors. The steel tubs or trucks are rectangular and provided at the bottom with a short flanged pipe; the shale rests on a false bottom perforated to allow the passage of volatile matter. During distillation the volatile matters are circulated over and over again through the charge in each tub, and to achieve this, flanged pipes of the same diameter as those in the tubs, are provided at regular intervals along the tunnel. At each position in the retort the tub rests immediately above the circulating pipe and below an electrically driven fan. The vapours are drawn by the fan and forced through a horizontal duct leading to a distributing channel above vertical reheater tubes which are heated in a combustion chamber running alongside the retort. Passing through the tubes the gases are led into the flanged pipe below the tub. The tubs are moved forward one stage every 12 to 14 minutes. From the retort the vapours pass to vertical atmospheric condensers where heavy and medium oils are separated. Medium and light oils are condensed in water coolers.

The Davidson rotary retort consists of a rotary steel tube 50 ft. long and 4 ft. diameter. The tube is externally heated, the temperature of the heating flues being maintained at 590°C. The interior is fitted with scrapers to keep the inner surface of the tube clean. Shale is fed continuously and automatically and in its passage through the tube is raised to 480°C. As the retort revolves the shale is turned over 200 to 300 times and travels a few thousand feet over the retort shell. The vapours are removed and pass a dust eliminator situated near the discharge end of the tube. The hot residue is discharged into the heating furnace.[8]

538. In the Salermo process, which is installed at Ermelo, in the Transvaal, for the South African Torbanite Mining and Refining Company, the retorts are arranged as shown in Fig. 2. A series of semi-circular troughs are joined together, edge to edge, the number and size of the troughs being determined by the purpose for which the retort is designed. A steel shaft lies along the axis of each trough and carries a number of T-headed paddles placed in such relative position one to another that on the turning of the shaft the whole of the surface of the trough is swept successively by the heads.

The shafts are turned at uniform speeds so that when the material to be carbonised is being fed into the first trough uniformly over its

length the turning of the paddles results in the uniform overflow into the adjacent trough, with the consequence that the amount of material in the first never exceeds a certain amount. Similarly, the turning of the paddles in the second causes an overflow into a third and the

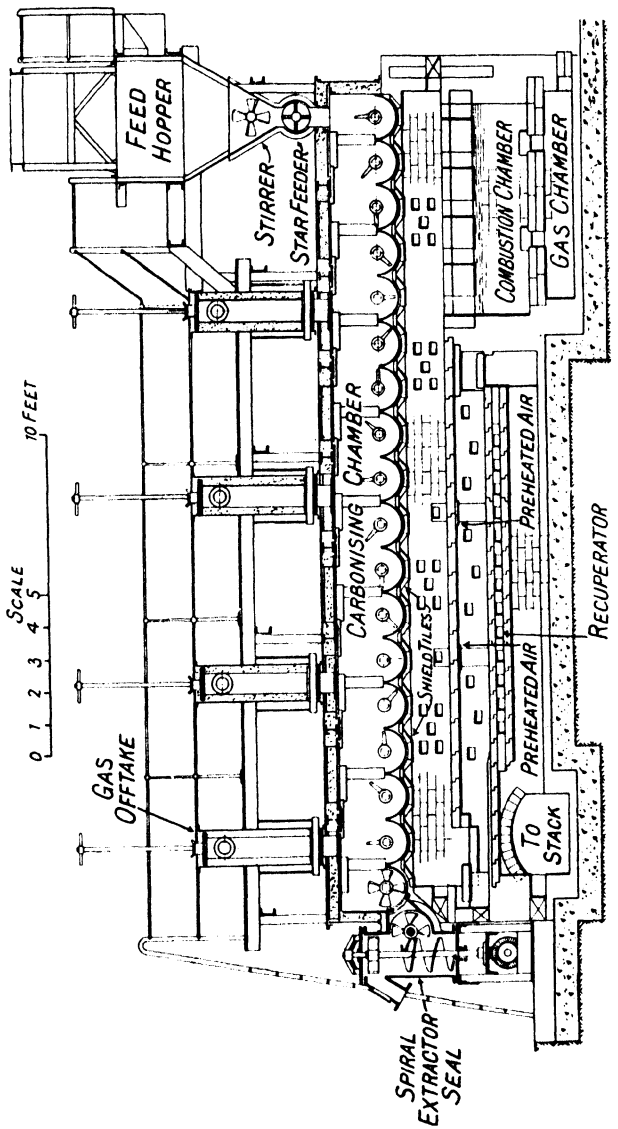


FIG. 2.—SALERMO RETORT

amount of material in the second is the same. This goes on until the whole of the troughs of the retort are full and the material is discharging over the edge of the last trough of the series. When all the troughs are full and the feed is uniform, the discharge is also uniform.

The material has two major motions, (*a*) a disturbing circular motion within the troughs, (*b*) a flowing one from trough to trough towards the discharge end.

539. Experiments have been described in which Estonian shales have been heated under pressure with water vapour, nitrogen and hydrogen.[9] The results obtained by heating under a pressure of water vapour are reproduced in Table 2.

TABLE 2. THE DECOMPOSITION OF OIL SHALE UNDER A PRESSURE OF WATER VAPOUR

No. of Expt.	Pressure kg. per sq. cm.		Temperature °C.	Duration Hours	Catalyst	Oil Yield. B.P. up to 170°C. % of Shale Charged
	Maximum	Final				
1	259	34	390-400	$1\frac{3}{4}$	Fe_2O_3	7·7
2	242	30	370-380	1	,,	7·7
3	210	27	380 390	1	,,	7·7
4	165	22	380 390	$\frac{1}{2}$	,,	6·7
5	187	22	380-390	$\frac{1}{2}$	,,	6·3
6	192	18	375 385	2	,,	8·0
7	240	28	400-405	2	,,	10·5
8	232	27	400-406	2	None	11·5
9	287	34	390-402	2	,,	10·7

Under these various experimental conditions the products formed a yellowish brown oil and a brown asphalt-like sticky substance. The mixture was distilled, the fraction boiling up to 170°C. being termed the gasoline fraction. This was almost water-white in colour but darkened on standing. After treatment with 10 per cent. caustic soda solution and dilute sulphuric acid, followed by redistillation, the product remained water-white on standing. Fractionation gave the following fractions.

(*a*)	B.P. 60–120°C.	Sp. gr. at 20°C.	0·7137	N_D^{20} 1·4018
(*b*)	,, 120–150°C.	,, ,, ,, ,,	0·7848	,, 1·4357
(*c*)	,, 150–190°C.	,, ,, ,, ,,	0·8073	,, 1·4499

By heating under nitrogen pressure, similar results were obtained.

In the hydrogenation experiments it was found that the amount of kerogen of the shale converted into oils did not exceed, to any noticeable extent, that obtained by simple heat treatment. The absorption of hydrogen was about 1·8 per cent. by weight, but below the decomposition point of the kerogen no hydrogenation took place. On the other hand, hydrogenation did suppress coke formation.

540. Properties of Shale Oils.—The properties of Scottish shale oil, as determined by distillation according to the U.S. Bureau of Mines Hempel method, are as follows[1] :—

TABLE 3. PROPERTIES OF SCOTTISH SHALE OIL
Specific Gravity 0·864. Setting Point 32°C. (90°F.).
Viscosity at 140°F. 41 secs. (Saybolt)

Temperature °C.	Per cent. of Cut	Total per cent.	Specific Gravity of Cut	Viscosity at 140°F.
0-50	0·169	0·169	—	—
50-75	0·236	0·405	0·740	—
75-100	1·18	1·42	—	—
100-125	2·77	4·19	—	—
125-150	4·06	8·25	0·770	—
150-175	3·82	12·07	0·798	—
175-200	4·56	16·63	0·810	—
200-225	5·57	22·20	0·825	—
225-250	7·33	29·53	0·840	—
250-275	7·57	37·10	0·855	—
Vacuum distillation at 40 mm.				
Up to 200	2·10	2·10	0·868	38
200-225	4·38	6·48	0·872	41
225-250	5·88	12·36	0·874	43
250-275	7·30	19·66	0·894	50
275-300	9·45	29·11	0·898	60
Residuum.	Specific Gravity 0·968.		Setting Point 45°C.	

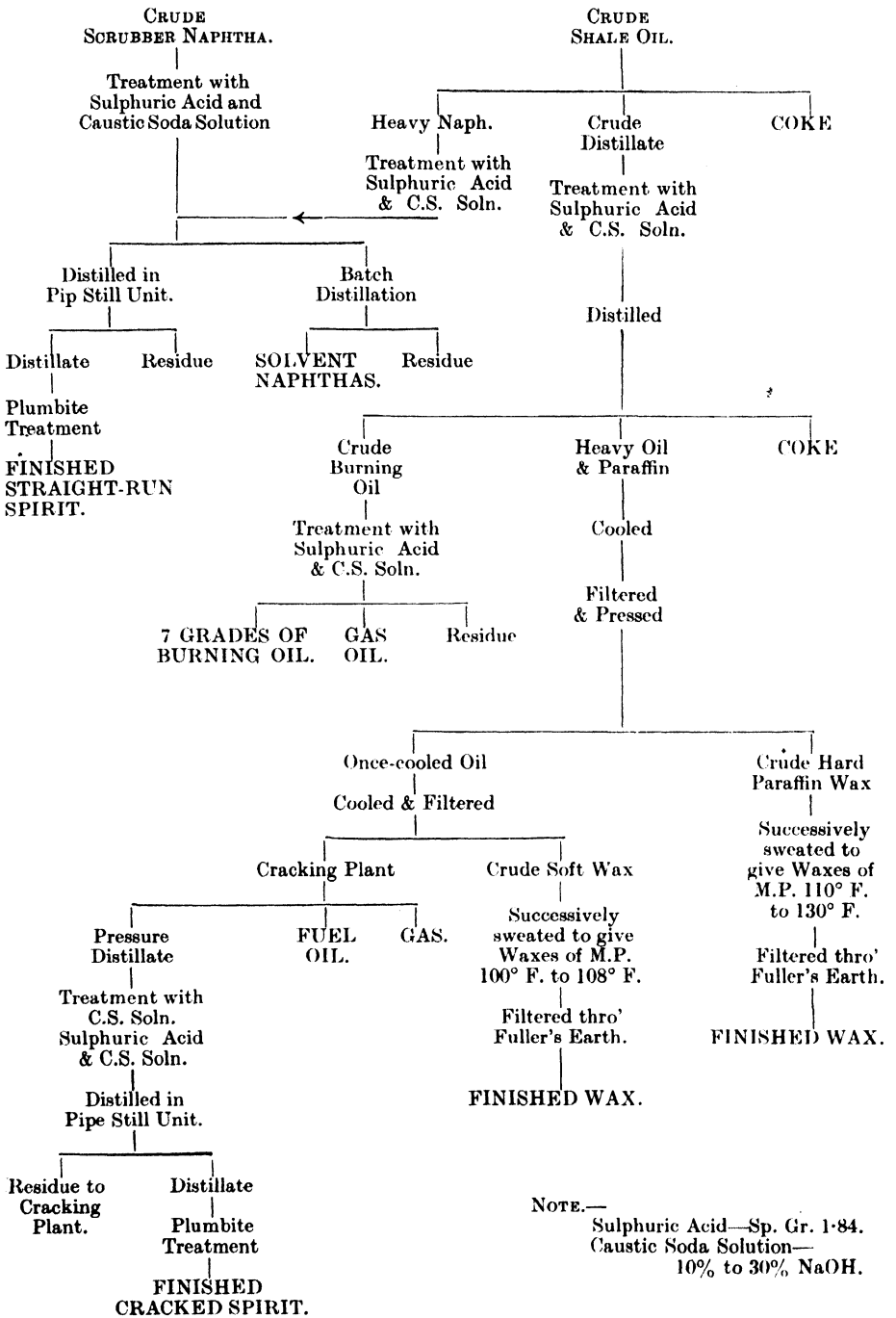
The refining losses encountered in working up Scottish shale oil are high. This is because of the unsaturated nature of the oil. The gas yields in the retorting of Scotch oil shale are approximately 9,800 cu. ft. per ton of shale, a typical analysis being as follows (Nash[10]) :—

H_2S	.. ..	Trace.
CO_2	.. ..	20·0 per cent.
CO	.. ..	4·3 ,, ,,
H_2	.. ..	34·2 ,, ,,
C_nH_{2n}	.. ..	3·1 ,, ,,
CH_4	.. ..	10·8 ,, ,,
O_2	.. ..	5·1 ,, ,,
N_2	.. ..	22·5 ,, ,,

Calorific value 302·5 B.T.U. per cubic foot (gross) or 271·4 B.T.U. per cubic foot (net).

A typical refining scheme for the work-up of shale oil is shown in Table 4.

TABLE 4. TYPICAL REFINING SCHEME FOR SHALE OIL



541. The products obtained from African torbanites have been described by Niemann[11] and by Bleloch,[12] of whom the former examined Transvaal torbanite with the following results :—

The torbanite was a dark brown hard solid and gave, on retorting, a tar that was poor in paraffin wax and which, on distillation, yielded a residue containing 27·6 per cent. of fixed carbon. The distillation water reacted alkaline and had an ammonium content of 0·15 per cent., equivalent to 8·15 kgs. ammonium sulphate per ton of torbanite, an amount 20 per cent. greater than that obtained from Scottish shales. The following yields were obtained by distillation of the tar and subsequent refining.

	Kgs. per ton of torbanite containing 1% moisture
Spirit up to 150°C.	34·08
Heavy benzine (150–200°C.)	28·40
Motor oil	57·12
Paraffin oil	117·68
Machine oil	39·05
Paraffin wax	11·54
Coke	44·73
Gas and loss	28·40
	355·00 kgs.
Ammonium sulphate	8·15 kgs.

Bleloch examined a shale from the Ermelo district of the Transvaal which gave an oil of dark brown colour and a specific gravity higher than many crude petroleum oils and shale oils, although it was far more mobile than shale oils obtained in Scotland and Australia. Its specific gravity was 0·921 at 18°C., and its viscosity (Redwood No. 2) was 72 seconds at 20°C. The yield of oil was approximately 80 gallons per ton of torbanite. Fractionation of the crude oil gave the following fractions :

1. Up to 200°C.	17 gallons per ton.	Specific gravity 0·77	
2. 200–250°C.	3 ,, ,, ,,	,, ,,	—
3. 250–300°C.	10 ,, ,, ,,	,, ,,	0·85
4. 300–320°C.	13 ,, ,, ,,	,, ,,	—
5. 320–360°C.	14 ,, ,, ,,	,, ,,	0·87
6. Above 360°C.	6 ,, ,, ,,	,, ,,	—
7. Pitch	14 ,, ,, ,,	,, ,,	1·05

Loss 4 per cent. by volume.

Calculated on the basis of 100 lbs. of torbanite, the sulphur distribution in the various cuts was as follows :—

	Specific Gravity	Weight (lbs.)	Sulphur %	Weight of Sulphur, lbs.
Torbanite	—	100	0·62	0·62
Crude oil	0·912	32·6	0·43	0·148
1st fraction 0–250°C. ..	0·77	6·9	0·13	0·008
2nd ,, 250–300°C. ..	0·85	3·8	0·53	0·020
3rd ,, 300–320°C. ..	0·86	5·0	0·48	0·024
4th ,, 320–360°C. ..	0·87	5·4	0·39	0·021
5th ,, Above 360°C. ..	0·87	2·3	0·45	0·012
Pitch	1·05	6·6	0·56	0·037

542. The Cracking and Hydrogenation of Shale Oils.—In attempts to increase the motor spirit yields from shale oils, cracking and hydrogenation of the higher fractions have been employed.

Cracking.—Egloff and Nelson[4] have described in detail the results obtained by the cracking of Estonian shale oils and their results may be summarised as follows :—

Typical Crude Oil from Kohtla Plant

Specific gravity 1·0.	Insolubles in benzole 0·3 per cent.
Flash point 181°F.	Engler viscosity at 122°F. = 5.
Water content 1%.	Sulphur content 1%.
Reaction neutral.	Cal. value 9,600 cals. per kg.

This oil contains little motor spirit. The chief marketable products are Diesel oil, lubricating oil and Esto-bitumen.

The *Diesel oil* has the following properties :—

Flash Point (Pensky-Martens)—above 140°F.
Engler viscosity at 122°F. (50°C.) = 1·0–1·3.
Specific gravity 0·93–0·95.
Cal. value 9,700–10,000 cals. per kg.
Up to 392°F. (200°C.) 5–8 per cent.
392°F.–482°F. (250°C.) 15–20 per cent.
482°F.–572°F. (300°C.) 20–30 per cent.
572°F.–680°F. (360°C.) 30–40 per cent.

Typical oils from the Eesti-Patendi retorts

These oils, the average properties of which are given in Table 5, contain motor spirit fractions as well as light, medium and heavy oils, the properties of which are appended.

Cracking tests on the crude and topped shale oils were carried out, the former giving 42·7 per cent. of spirit of 73 octane number and the latter 27·4 per cent. of spirit of 74 octane number.

TABLE 5. TYPICAL ANALYSIS OF ESTONIAN SHALE OILS FROM EESTI-PATENDI RETORTS (EGLOFF AND NELSON)

	Crude Shale Oil	Straight-run Gasoline (Crude)		Light Oil
Specific gravity	0·95	0·767–0·77		0·83
A.P.I. gravity	18·2	52·1		38·7
Unsaturateds	—	28%		30%
Tar acids ..	—	—		6·5%
Tar bases ..	3·5%	—		—
Distillation—				
I.B.P.°F.	164°F.	118		147
5% at ..	239°F.	At 212°F.	21·5–25·2%	2–3%
10% at ..	293°F.	212–257°F.	21·7–23·8%	8–10%
20% at ..	366°F.	257–302°F.	18·8–19·4%	13–15%
50% at ..	598°F.	302–365°F.	15–16%	17–23%
70% at ..	690°F.	365–392°F.	4·3–4·6%	7·6–8·8%
90% at ..	746°F.	392–428°F.	5·4–5·6%	10·4–12%
95% at ..	751°F.	Above 428°F.	—	33%
F.B.P. ..	754°F.			
Cold test ..	Below 0°F.			
Viscosity at 77°F. (Saybolt Furol)	15 secs.			

Details of these tests are as follows :

TOPPING.

	1	2
E.P. of gasoline removed °F.	392	437
Topped shale oil per cent.	76·1	69·8
Per cent. gasoline	22·0	28·3
Water	0·9	0·9
Loss	1·0	1·0
ANALYSIS OF GASOLINE.		
Gravity °A.P.I.	50·5	47·2
Colour	Brown	Brown
Gum, mgs./100 mls. (Copper dish)	430	570
Sulphur	0·28	0·32
Tar acids	3·0	4·5
Tar bases	0·5	0·8
Octane number	72	69
I.B.P.°F.	139	144
5 per cent.	184	186
10 per cent.	202	208
20 per cent.	226	238
50 per cent.	274	294
90 per cent.	349	394
F.B.P.	391	437

CRACKING TESTS.

	Crude Shale Oil	Topped Shale Oil
Pressure, lb./sq. in.	350	200
Temperature, °F.	915	900
Gasoline, per cent. of charge	42·7	27·4
A.P.I. gravity	53·1	52·7
Specific gravity	0·767	0·768
Octane number	73	74
Residue, per cent. of charge	51·7	69·6
A.P.I. gravity	2·8	2·7
Specific gravity	1·18	1·17
Viscosity at 122°F. (Saybolt Furol)	172	103
Gas and loss, per cent. of charge	5·6	3·0
Gas, cu. ft./bbl. charge	281	—
DISTILLATION OF GASOLINE.		
I.B.P.°F.	116	106
5 per cent.	149	156
10 per cent.	170	176
20 per cent.	200	217
50 per cent.	268	296
90 per cent.	353	372
95 per cent.	375	—
End point	390	396

The cracking of Manchurian shale oil has been described in detail by Egloff and Nelson.[13] This oil, when cracked by a flashing process at 930–950°F. and at 350 lbs. per square inch pressure, gave 52–56 per cent. gasoline of 67–71 octane number and 388°–390°F. end point. The residuum was found suitable for use as bunker fuel (C grade). By a non-residuum method of operation at 935°F. and 300 lb. pressure, the yield of gasoline was 67·5 per cent. (68–70 octane number), the yield of coke 54·8 pounds per barrel and the gas formation 726 cu. ft. per barrel.

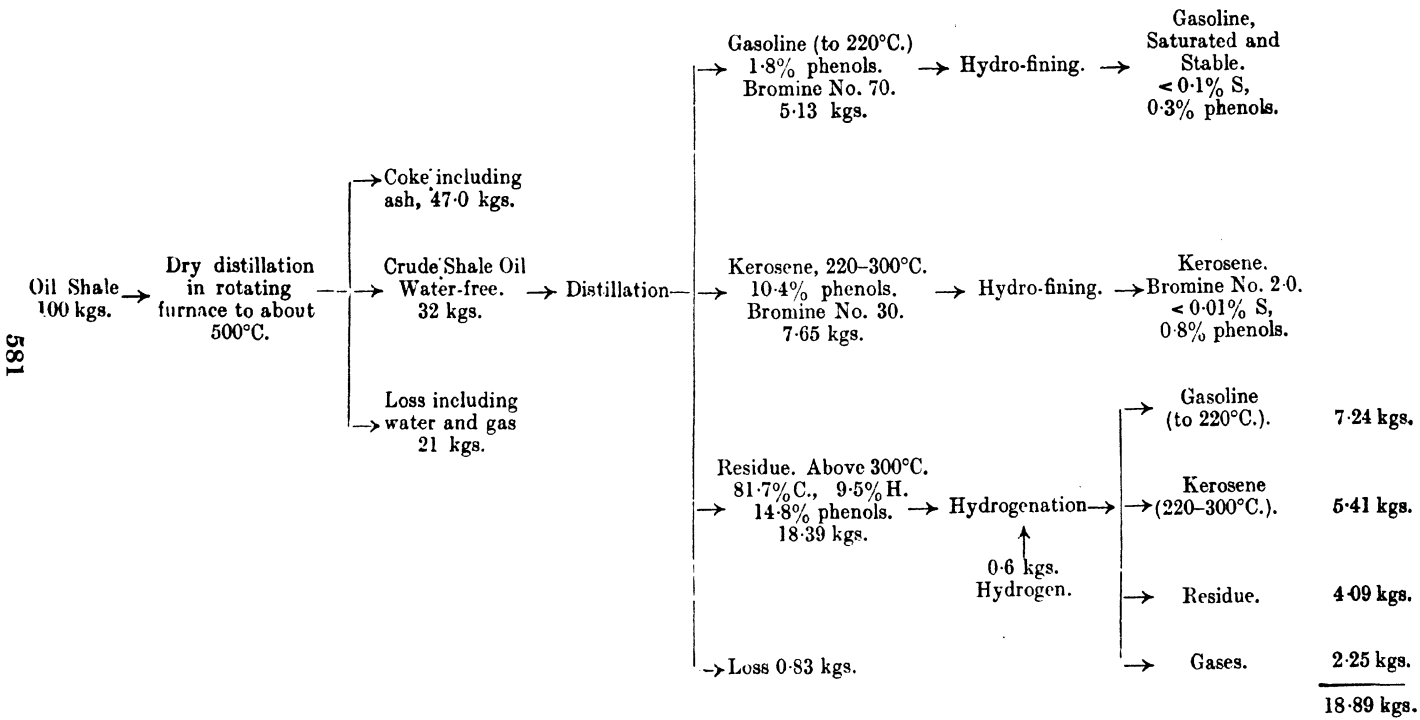
The cracking of Australian (New South Wales) shale oils by both Dubbs and Kellogg processes is considered in detail in the report of the Newnes Investigation Committee, 1934.

543. Hydrogenation.—A scheme of treatment of Estonian shale oil in which special attention has been given to the catalytic high pressure hydrogenation of the distillation residue has been described by Waterman, de Jong and Tulleners.[6] The results of this treatment are detailed in Table 6. Molybdenum–active charcoal catalyst was used in the hydro-treatments.

Similar experiments have been reported by Kogerman and Kopwillem.

544. Bituminous Sands.—A reserve of oil which must not be

TABLE 6. TREATMENT OF ESTONIAN OIL SHALE AND SHALE OIL (WATERMAN, DE JONG AND TULLENERS)



overlooked is the huge quantity which remains in an oil-sand after gas and other pressures have caused the wells to cease to flow. If these sands are near the surface, mining operations could be resorted to, to drain the sands further, and such operations have been suggested for the Pechelbronn deposits.[15] Methods of freeing oil from oil sands by flooding the fields with dilute alkaline solutions have been attempted.

There also occur, in certain localities, sands which are impregnated with heavy bituminous material, which may be the remains of petroleum deposits. Such deposits are known as Bituminous or Tar Sands and those in Northern Alberta, Canada, are the best known. These sands contain from 7 to 20 per cent. by weight of a heavy asphaltic oil. Several methods have been suggested for the separation of the sand and bitumen, namely :

1. Distillation in retorts by external heating or partial combustion of the bitumen itself.
2. Treatment with combustion gases, steam or hot water.
3. Treatment with solvents, such as petroleum distillates.
4. Treatment with acids, such as dilute sulphuric acid.
5. Treatment with solutions of sodium silicate, alkalies or alkali salts.

The method described by K. A. Clark and S. M. Blair[16] involves the intimate mixture of the bituminous sand with dilute sodium silicate solution, the whole mass being raised in temperature near to that of boiling water, and passed quickly into reservoirs of hot water. Separation of the crude bitumen containing 28% of water and 7% of sand takes place.

Dry distillation of the bituminous sand gives light oils, for example, 18·8% distilling up to 230°C., formed by decomposition of some of the heavy bitumen. The bitumen from Alberta tar sands is amenable to the cracking process and has been shown by G. Egloff and J. C. Morrell[17] to be capable of cracking at 399°C. and 90 lb. per square inch pressure to give, approximately, 35% of high anti-knock spirit, coke and gas being formed simultaneously. Egloff and Morrell calculate that there are 100,000,000,000 barrels of bitumen available in the Alberta deposits.

545. Hydrogenation has been suggested as a method for treating Alberta bitumen and the following experimental figures[18] show comparative yields from cracking and hydrogenation experiments.

Cracking of Alberta bitumen for 1 hour at 450°C. (Maximum pressure 78·4 atmospheres.)

Yields :

Oil	41·3 per cent.
Coke	29·0 ,, ,,
Gas and loss	29·7 ,, ,,

Hydrogenation of Alberta bitumen for 1 hour at 450°C. (Maximum pressure 131·5 atmospheres.)

Yields :

Oil	50·5 per cent.
Coke	21·6 „ „
Gas and loss	27·9 „ „

The oil from the hydrogenation experiment was more stable and saturated than that from the cracking experiment. The non-catalytic hydrogenation of bitumen from tar sands has been patented by Rule, Watts and I.C.I. Ltd., in E.P. 317,346. Some recent experimental figures on the hydrogenation of Alberta bitumen have been given by T. E. Warren,[19] who has concluded that the bitumen may be hydrogenated to yield 90·5 wt. per cent. of crude oil and 18·2 wt. per cent. of unrefined gasoline.

Coal Carbonisation

546. On heating any coal in retorts, three main products are given off : inflammable gas, tar and aqueous liquor. Coke is left behind as a residue. The proportions of each of these products and their precise nature depends, very considerably, upon the nature of the original coal and upon the method of carbonisation. It is the tar fraction which is the interesting material from the point of view of motor fuel production, especially as large amounts of motor fuels are already being produced in Germany by the hydrogenation of brown coal tar.

Cannel coal must be considered separately from bituminous coals as this yields a different type of oil on carbonisation. Whereas coal is derived largely from plant remains, cannel coals are considered to be derived from plankton ; in many respects, the cannel coals resemble oil shales. Many coalfields in this country contain beds of cannel or canneloid coals, the carbonisation products of which are as follows.[20]

Crude Oil.—

31 gallons per ton, plus 3 gallons recovered from the gases.
Specific gravity 0·941.
Setting point—above normal temperature.

	%
To 170°C.	5·0
170°–240°C.	21·0
240°–320°C.	33·5
Heavy Oil	4·0
Wax	22·0
Residue	Soft pitch

Finished Products Total:

Motor spirit	2·32 gals.	per ton
Naphtha	0·80 ,,	,,
Burning oil	6·80 ,,	,,
Diesel oil	9·60 ,,	,,
Heavy oil	3·00 ,,	,,
Wax	4·80 ,,	,,
Sulphate of ammonia	95 lb.	,,

547. High Temperature Carbonisation of Coal.—High temperature carbonisation of coal is carried out at temperatures of 1,095°C. to 1,205°C. in the coke oven and town's gas industries. The former aim at providing a suitable coke for blast furnaces, and the other, gas for domestic and industrial consumption. Coke and gas are, in these cases, the primary products of the processes; some 10 to 12 gallons of tar per ton of coal are formed as a by-product. This tar and the spirits scrubbed from the gases constitute a source of benzole, an important motor fuel which is dealt with in Chapter VI.

548. The Use of Tar Oils and Creosote as Fuels for Internal Combustion Engines.—Experiments have been carried out in several quarters on the use of coal tar oils and particularly creosotes as fuels for internal combustion engines. There has been great diversity in the nature of the fuels employed, the methods adopted to enable them to be used, the results obtained, and the degree of satisfaction expressed by individual users. The use of such fuels has received considerable encouragement in Great Britain by the imposition of 8d. per gallon import duty on both gasolines and Diesel fuels, home-produced fuels being free of any tax.

Fuels Employed.—Details are available regarding the specifications decided upon by certain British users of coal tar oils for spark ignition engines and these are summarised in Table 7, further details being available in the literature.[14]

Such fuels are usually prepared by washing light creosote to reduce the tar acid content to 15 per cent. and then redistilled. Ten per cent. of 90/190 water-white solvent naphtha or a certain quantity of benzole is then added to the washed tar oil to keep the naphthalene in solution at low temperatures. The reason for a retention of a portion of the tar acids is partly their solvent power for naphthalene. A fuel of very low tar acid content is possible if larger amounts of benzole or naphtha are present or if the creosote is derived from certain types of vertical retort tar, and in some cases the tar acid content has been reduced to as little as 1–2 per cent. More refined methods of production have been used by some suppliers. In some cases naphthalene

TABLE 7. SPECIFICATIONS FOR TAR OIL FUELS FOR SPARK IGNITION ENGINES

Specification	Belfast Corporation Gas Department	London General Omnibus Company	Gas Light and Coke Company	Newcastle-on-Tyne and Gateshead Gas Company
Composition and Description.	90% light creosote oil (washed and redistilled) 10% 90/190 water white solvent naphtha.	Redistilled creosote with sufficient benzole to prevent separation of naphthalene at any low temperature likely to be experienced. The mixture to be free of water and adventitious matter.	Redistilled creosote mixed with sufficient benzole to prevent separation at any temp. likely to be experienced. The mixture to be free of water and adventitious matter.	—
Specific gravity.	0·951	Not below 0·935 at 15·5°C.	0·935–0·953 at 60°F.	0·922 at 15·5°C.
Tar acids.	15%	Not to exceed 12% (approx.).	4·5–8·5%	4%
Carbon residue.	0·34%*	Not to exceed 0·1%	Not to exceed 0·1%	—
Ash.	0·04%	—	—	—
Flash point.	129° F.	—	70°F. max.	Below 73°F.
Water.	Nil.	Not above 0·1%	Not above 0·2%	—
Distillation test.	I.B.P. 148°C.† 10% at 180°C. 20% at 189°C. 30% at 198°C. 40% at 206°C. 50% at 213°C. 60% at 221°C. 70% at 230°C. 80% at 244°C. 90% at 273°C.	—	5% at 135–160°C. 10% at 150–170°C. 50% at 200–210°C. 90% at 230–250°C. F.B.P. 255–265°C.	10% at 150°C. 20% at 165°C. 50% at 190°C. 90% at 225°C. F.B.P. 270°C.
Cold test.	Pour point not above 10°F.—no appreciable formation of crystals at 0°F.	—	No deposit at 40°F. (summer) or 25°F. (winter) Viscosity 27–28 secs. Redwood at 100°F.	—

* Later reduced to 0·03%. † Average figures only.

has been removed by systematic redistillation several times, and in others careful filtration and settling has been employed to ensure cleanliness. In another case, namely one in which a product containing only 0·5 per cent. of tar acids was made, naphthalene was removed from the washed creosote by crystallisation and sulphuric acid and soda treatment applied prior to final redistillation.

The yield of coal tar oils to specification quality is limited and the cost is much greater than if a straight tar distillate could be employed, rising to as high as 7d. to 8d. per gallon in England. Even so, some consumers have obtained much reduced running costs as against petrol.

The quantity of such fuel available in England without encroaching upon other markets has been estimated at 7 per cent. of the whole country's petrol consumption, but due to the present demand for creosote for hydrogenation, this figure has recently decreased considerably.

549. Types of Vehicles on which Tar Oil Fuels have been Employed and the Engine Alterations Required.—In view of the lack of volatility of tar oil fuels, carburation is much more difficult than in the case of petrols. It is therefore necessary to heat the induction system quite considerably and this is effected by use of heat derived from the exhaust gases. Sufficient heat must be applied to give fuel vaporisation and to ensure that condensation of fuel cannot occur in the induction pipe and so adversely affect throttle response and fuel distribution. Such heating of the fuel charge necessarily causes a considerable loss in volumetric efficiency and power output. Due to the fact that tar oil fuels have high final boiling points, considerable crank case dilution and contamination occurs, and to prevent this as much as possible, cooling water temperatures should be maintained as high as is convenient—namely above 80°C.

Various carburation arrangements have been developed for the use of such non-volatile fuels, among which the *Solex Bi-Fuel System* is one of the most important, and by far the most widely used. This was developed in connection with the pioneering work carried out in Belfast in 1929 and comprises a large carburettor for use on the tar oil fuel and a small carburettor for use on petrol. The small size of the latter prevents the use of petrol for purposes other than starting up, idling and running at low speed. The petrol carburettor is controlled by hand, the tar oil control being linked to the accelerator pedal, depression of which cuts off the petrol carburettor. A special manifold, cast integrally with the exhaust pipe and heated by the exhaust gases, is substituted for the ordinary manifold. It provides highly heated impact surfaces for the oil leaving the main carburettor, a moderately heated length of pipe to induce further vaporisation by warmth and turbulence, and port leads arranged to take off from the coolest parts and so disposed to give good distribution. The choke area of the oil carburettor is the same as for petrol, but the main jet is much larger than for petrol because of the much higher viscosity of the tar oil. A mechanical device ensures that, when the throttle is opened, the petrol throttle is entirely shut and that, when the oil is shut off, the small carburettor continues to supply slow running facilities on petrol, a flat spot thus being avoided.

In the A.E.C.-Solex system, the Solex principle is modified by the incorporation of thermostatic control which automatically changes

over from one fuel to the other according to the temperature of the engine.

The Daimler system also comprises two carburettors as in the above arrangements, and also a thermostatic change-over device. The Gas Light and Coke Company employed the Solex system on 30 cwt. Dennis commercial vehicle engines and found that for efficient operation the metal of the manifold should be thick enough to act as a heat accumulator and maintain the induction pipes at an even temperature. The latter should be totally immersed in the exhaust gases to give even heating of the fuel and should be as long as possible and of approximately equal lengths for each cylinder. The flow of the gas in the induction pipes should be extremely smooth and all sharp bends avoided. Manifolds made on these lines are claimed never to have given any trouble due to carbon deposits. The most satisfactory induction pipe temperature was found to be about 230°C. although engine performance over a range from 230–350°C. was satisfactory.

Subsequently the Gas Light and Coke Company decided that twin carburettors were not essential and developed a system embodying one carburettor, the change-over from one fuel to another being effected by a thermostatic control.

Of the remaining methods of carburation employed the Claudel Heavy Oil Atomiser need only be mentioned here. This is cheaper than the Solex equipment and may possibly be regarded as superior to it in performance, although further experience is necessary to confirm this. It is claimed that the temperature of the atomised fuel is not raised to too high a value and that the loss in volumetric efficiency is not as great as would otherwise be the case.

The Claudel atomiser embodies, in a single appliance, separate float chambers for petrol and oil and also filters. The petrol chamber feeds a slow running jet, the mixture from which is supplied into the induction pipe immediately above the throttle and a change-over jet. Between these two and entirely separated from the petrol passages is the main oil jet. The vaporising feature takes the form of a hot box included in the exhaust system. This supplies warm air to the carburettor intake and contains an additional superheater from which superheated air is led up inside the control tube of a diffuser. The upper end of the diffuser is somewhat restricted and is drilled with holes communicating with an annular space surrounding it.

Oil fuel from the main jet is drawn up this annular space and is heated by the hot tube. In being drawn through the holes at the top of this tube it meets the stream of superheated air so that vaporisation is completed.

There is an annular space between the outer diffuser tube and

an inner sleeve and a further annular space between the inner sleeve and an outer sleeve. During the change-over from petrol to oil, petrol from the change-over jet enters and fills a well formed by the two annular spaces up to a level just above a series of holes drilled through the bottom of an inner sleeve. This supply is drawn up the inner annular space to the engine and is quickly exhausted. Immediately the level descends and uncovers the holes in the inner sleeve, air is admitted through the latter and mixes with the fuel. When the well is emptied, the engine runs solely on oil.

With regard to other engine modifications necessary for operation on tar oil fuels, in many cases the compression ratio has been increased to take advantage of the increased anti-knock value of the fuel. This often entails heavy initial costs in stiffening up the crankshaft and increasing the bearing diameters in order to accommodate the increased stresses involved.

550. Behaviour of Tar Oil Fuels.—Tar oil fuels possess a number of disadvantages which have caused a number of users to decide that the use of such fuels is definitely impracticable.

Exhaust Gases.—These have usually a pronounced odour of creosote, but are clear under normal running conditions. There is generally evidence of smoke during the change-over from petrol to tar oil, during acceleration and also during gear changing. These objections have led to the discontinuance of the use of such fuels in London by London Transport and in Manchester by the Corporation Transport Department. One good feature is shown by the exhaust gases from engines running on tar oil fuel, namely, the comparative absence of carbon monoxide.

Lubrication.—Much sludge formation occurs in engines running on tar oil fuels and using normal lubricating oils, although with castor oil lubricants this trouble is reduced.

Mechanical Troubles.—These take the form of abnormal wear, overheating, gumming of valves and spark plugs. With regard to the first item, the following individual instances of abnormal wear have been mentioned :—

(*a*) Inlet valve stems.
(*b*) Crankshaft main bearings, bottom end and cylinder walls.
(*c*) Cylinder.
(*d*) Big end bearings.
(*e*) Valves and valve seatings.

Figures given by the Belfast Omnibus Company are as follows :—

	Approximate increased wear relative to petrol %
Cylinder	50
Timing chain	50
Timing gear	50
Gudgeon pin	50
Big end bearing	10
Journals	10

Furthermore tar oil fuels have a very bad corrosive effect on all brass and copper fittings.

The general concensus of opinion appears to be that the use of tar oil fuels causes increased engine maintenance costs.

551. General Conclusions on the Use of Tar Oil Fuels in Spark Ignition Engines.—The attempts made in Great Britain to popularise the use of the coal tar oil fuels described has, in large measure, failed. The Belfast Omnibus Company, after using 72,000 gallons of the fuel in 28 omnibuses over a period of nearly two years, have reached the conclusion that their experience is unfavourable and have discontinued the use of the fuel. The London General Omnibus Company (now known as London Transport), quite early in their work formed the opinion that the use of tar oil in their fleet is impracticable. In the long run nearly all users find that the disadvantages outweigh the advantages.

552. Low Temperature Carbonisation of Coal.—Low temperature carbonisation of coal, as its name implies, consists in carbonising coal in retorts at temperatures well below those used in town's gas manufacture. On distilling coal, the tar yield attains a maximum at about 550°C., and the usual temperatures for low temperature carbonisation are about this figure or somewhat higher, to about 625°C. Under these conditions of carbonisation, the nature of the tar is very different from that produced under high temperature conditions.

The plants suggested for the low temperature carbonisation of coal are of many types: some 200 processes have been put forward in various stages of evolution, in this country ; of these, from ten to fifteen have reached the technical stage, but only three or four methods have developed to large scale working. Reviews of some of these processes have been made recently by F. S. Sinnatt[21] and J. G. King.[22]

The production of motor spirit and tar by the low temperature carbonisation of British coal is slowly increasing, but still forms only a small fraction of that produced by gas works and coke ovens. As the main product of the industry is a solid free-burning smokeless

fuel, the expansion of low temperature carbonisation will depend on the increasing demand for this kind of coke.

In 1935 twelve such plants were in large scale operation, and more than 90 per cent. of the smokeless fuel produced during 1934 was made by the "Coalite" process of Low Temperature Carbonisation Ltd., which used no less than 270,000 tons of the total of 284,242 tons of coal carbonised at low temperatures. The crude coal oil returns show that the Coalite process produced 98 per cent. of the total during this period. A part of the heavy oil produced in this process is now being converted to motor spirit at Billingham by the new I.C.I. hydrogenation plant.

The products obtained from coal by low temperature carbonisation differ with the type of coal and nature of the process used, as shown in Table 8. The usual yields are 14 to 20 gallons of water-free tar, some aqueous liquor, and 3,000–5,000 cu. ft. of gas per ton of coal carbonised. The semi-coke remaining amounts to about 14 cwt. The tar yields about one and a half gallons of spirit, while about two gallons of light spirit can be extracted from the gas by scrubbing.

The tar is not entirely composed of hydrocarbons, but contains appreciable amounts of phenolic (acidic) and nitrogenous (basic) substances. The bituminous coals can yield primary tars with large contents of phenolic substances, whereas brown coals give tars more paraffinic in nature.

Table 9 gives some data upon oils, obtained from ten processes, coal being used except in the case of the Midland Coal Products figures where pitch briquettes were carbonised and except in the case of the Fusion Rotary Retort where a cannel coal was being treated.

From this table it will be seen that the yield of motor spirit from low temperature tar is not very high. The spirit, nevertheless, has quite good value from the point of view of engine performance, due to its olefinic and aromatic content.

553. Cracking of Low Temperature Tar.—The amount of motor spirit obtainable from low temperature tar can be increased by either cracking or hydrogenating the middle and heavier tar fractions. Some information upon the cracking aspect of this subject has been given by A. E. Dunstan[25] and also by G. Egloff and J. C. Morrell.[26] About 25 per cent. of the tar is converted into motor spirit and 45 per cent. into coke by this process.

It has been stated that an estimate of the world's coal reserve is 3,154,000,000,000 tons, which would produce, by low temperature carbonisation, 336×10^{11} gallons of tar. Again, if the latter were cracked, approximately 84×10^{11} gallons of motor fuel of high anti-knock quality would be obtained. Egloff and Morrell have described

TABLE 8. YIELDS OF PRODUCTS FROM L.T. CARBONISATION PLANTS TESTED BY THE DIRECTOR OF FUEL RESEARCH
(Calc. to Dry Coal)

	External Heating, 550–650°C.					Internal Heating					Steam Distillation
Name of Retort	Parker	Crozier	Fusion	Freeman Multiple		MacLaurin	Babcock	Midland Coal Products	Bussey	L. and N.	Turner
Name of Coal	Dalton Main	Hawkhill Seam, Tullygarth Colliery	Welbeck Cannel	Kirkby Top Hard, Washed Slack	"Brynna" Gas	Virgin Seam, Clydeside Colliery	Low Main, Yard and High Main Seams	Briquettes from Top Hard Seam Kirkby and Coal Tar Pitch	Bothwell Washed Treble Nuts	Slack from Middle Nether Lount and Roaster Seams	Auchlochan Trebles
Ash content, %	4·7	11·8	15·0	6·3	7·3	2·9	8·4	5·4	5·4	10·4	8·5
Coke, cwt. ..	14·68	15·4	11·9	15·46	15·58	12·12	15·04	8·6	11·36	7·4	15·3
Breeze, % ..	4·7	15·4	100·0	—	—	9·6	52·3	13·9	19·5	75·0	18·9
Vol. matter, %	4·3	14·6	9·7	16·9	14·5	3·9	16·0	—	13·0	18·6	13·5
Gas, cu. ft. ..	5,930	7,390	2,790	1,850	1,830	33,160	38,700	68,000	45,300	—	2,470
,, B.Th.U./cu.ft.	705	323	1,070	914	978	233	70	193	189	—	862
,, therms. ..	41·81	23·9	29·85	16·91	17·90	77·26	27·09	131·1	85·6	—	21·30
Spirit, gal. ..	1·88	0·8	3·75	0·9	1·0	1·5	2·6	—	3·6	—	0·7
Tar, gal. ..	19·6	16·4	47·3	21·1	19·8	17·8	16·8	24·5	19·8	14·1	23·6
Sp. gr. at 15°C. ..	1·063	1·028	0·947	1·057	1·042	1·035	1·051	1·076	1·041	1·113	1·019

TABLE 9. YIELD AND COMPOSITION OF LOW TEMPERATURE TARS (SINNATT)

Name of Retort	Parker	Midland Coal Products (Pitch Briquettes)	Fusion Rotary (Cannel)	Freeman Multiple	Crozier Retort	MacLaurin Plant	Leigh Smokeless Fuels	Coal Extraction Ltd. K.S.G.	Salermo Process	Fuel Research
Yield of tar, gals. per ton ..	18·6	21·0	50·2	21·1	16·4 2·4	20·4 (wet)	20·0	—	20·3	17·3
Specific gravity	1·063	1·076	—	1·057	1·028	1·032	1·027	1·053	1·023	1·050
Spirit from gas. Gals. per ton	1·78	—	3·7	0·85	0·80	—	—	—	—	1·4
Water	—	—	—	—	—	1·70	1·5	—	—	—
Oil distilling to 120°C. ..	—	—	—	—	—	0·64	—	—	—	—
Oil distilling to—										
170°C.	4·7	1·1	—	6·9	4·1	—	9·5	6·1	7·0	3·4
120°–230°	—	—	—	—	—	5·47	—	—	—	—
170°–230°	14·9	3·9	—	9·5	11·7	—	1·0	17·2	19·9	14·7
230°–270°	12·9	4·1	—	13·9	11·9	14·14	7·0	12·9	12·4	11·1
270°–300°	—	—	—	—	—	—	—	—	—	—
270°–310°	18·1	—	—	—	—	—	13·0	—	11·2	—
270°–330°	—	—	—	—	15·7	—	—	—	—	—
270°–345°	—	—	—	—	—	26·04	—	—	—	23·4
270°–360°	—	26·9	—	29·8	—	—	—	23·0	—	—
300°–350°	—	—	—	—	—	—	45·0	—	—	—
Pitch	48·4	63·2	—	39·3	55·9	48·50	23·0	40·7	48·7	45·8
Loss	1·0	0·8	—	0·6	0·7	3·51	—	—	0·8	1·6
Tar acids	17·0	13·4	—	24·5	14·3	—	—	25·5	—	—

cracking experiments on a West Virginian bituminous coal low temperature tar of specific gravity 1·074, which gave only 10 per cent. of distillate when heated up to 196°C. On cracking this tar under pressures of 100 lb. at an average temperature of 452°C., 80 per cent. of crude motor fuel, containing 25 per cent. tar acids, was obtained. On a tar acid-free basis, a yield of 22·5 per cent. of refined motor fuel was obtained.

From other experiments with an Ohio-Indiana bituminous coal, containing 27·5 per cent. tar acids, cracked at 800°F. and 100 lb. per square inch pressure, they estimate the ultimate yield of products per 85,000 gallons of low temperature tar cracked to be :

Motor fuel	7,700 gallons.
Tar acids	4,200 ,,
Coke	107 tons.
Gas	571,200 cu. ft.

554. The Hydrogenation of Coal Tars.—Because of their highly aromatic character, coal tars and coal oils are not particularly amenable to cracking and much larger yields of spirit may be obtained by hydrogenation because, in this process, if it is properly carried out, the polymerisation reactions leading to the formation of coke are prevented. Thus, in a continuous method of operation involving two separate stages, King and Matthews[27] obtained by the hydrogenation of low temperature tar, using ammonium molybdate–charcoal catalyst, the following yields :—

	Kgs.		Kgs.
Tar (dry)	100	Light product (sp. gr. 0·85) ..	75
Hydrogen	9	Heavy product (sp. gr. 0·92) ..	8
	—	Water	6
	109	Gaseous hydrocarbons ..	15
	—	Loss	5
			109

Motor Spirit (up to 200°C.) = 45% by weight of original tar.

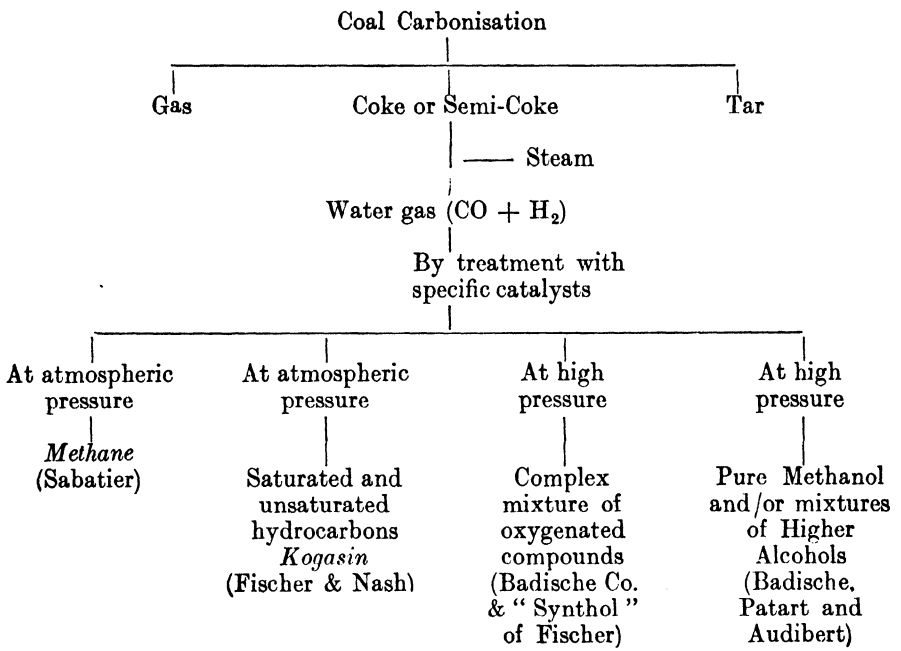
The petrol produced contained 40 per cent. aromatic hydrocarbons, 4 per cent. unsaturateds and 56 per cent. saturated hydrocarbons. Motor spirit yields of over 75 per cent. by weight were obtained when the heavier oils were recycled.

High temperature tars and creosote give similar results.

555. Hydrocarbon Fuels produced by the Catalytic Treatment of Water Gas.—The production of liquid fuels from coal has been investigated for a considerable period and syntheses *via* coke

and water gas have assumed commercial importance, particularly the high pressure methanol and higher alcohol synthetic processes. These, and other developments, are shown diagrammatically in the following chart.

TABLE 10. SYNTHESES FROM COAL VIA COKE AND WATER GAS



Sabatier[23] pointed out in 1905 that, as two of the valency directions of carbon monoxide (one of the two constituents of water gas, hydrogen being the other) are unsatisfied, the molecule will combine with oxygen, sulphur and chlorine, and it should combine therefore with hydrogen to give formaldehyde and then methyl alcohol. The use of a nickel catalyst gave methane only.

It appears that up to the year 1913 the formation of methane, carbon dioxide and water were the only established reactions when carbon monoxide and hydrogen were passed over a catalyst. In 1913 appeared a patent of the Badische Co. (Ger.P. 293,787 (8/3/13) with additions 295,202 (31/5/14) and 295,203 (23/6/14) and corresponding E.P. 20,488 of 1915) describing the formation of liquid hydrocarbon and oxygenated compounds by passing carbon monoxide together with an excess of hydrogen over a catalyst. Pressure was employed and temperatures higher than 250°C. The catalyst mentioned was alkali and zinc carbonate on pumice. Attempts to verify the claims of these patents were made by Fischer and Tropsch with no success.

However the use of a modified catalyst led to the desired results, and the iron-alkali catalyst developed by these investigators gave from water gas at about 400°C. and several atmospheres pressure a product, called "Synthol," which comprised a mixture of aliphatic alcohols, aldehydes, ketones, acids, esters and hydrocarbons.[24]

Subsequent to 1913 numerous patents were taken out by the Badische Co. relating to the synthesis of liquids—particularly methanol —from water gas, and a great variety of oxides and metals have been specified as suitable catalysts.

In France similar investigations were carried out by Patart[28] and Audibert.[29] Patart was mainly interested in methanol production and demonstrated that at 400–420°C. and 150–250 atm. pressure methanol was produced from water gas using zinc oxide as catalyst. Audibert investigated the catalytic activity of various sub-oxides such as CrO, U_2O_3, etc. and found that methanol was produced in a pure condition at 225–300°C. At temperatures higher than 300°C. other organic compounds, water and methane appeared in the products. The addition of a strong base to one of the active sub-oxides induced the formation of a mixture of compounds which formed an aqueous and an oily layer similar to the mixture obtained by Fischer and Tropsch. Comparatively small yields were obtained by the use of the oxides alone.

556. In 1926 Fischer and Tropsch described[30] the production of petroleum-like hydrocarbon materials from water gas by atmospheric pressure operation. The catalysts employed were the metals, or partly reduced oxides, of Group 8 of the Periodic Classification, and it was considered expedient to make additions to prevent sintering and to accelerate carbide formation (carbides being considered by Fischer and Tropsch to be the intermediate compounds formed in this reaction). Iron and cobalt appeared to be satisfactory catalyst materials. The passage of hydrogen and carbon monoxide over iron–zinc oxide gave a mixture of methane and homologues but the use of cobalt and chromium oxides at 270°C. led to the formation of liquid and solid, as well as gaseous, hydrocarbons. These observations were confirmed by Elvins and Nash,[31] who obtained in addition to hydrocarbons also oxygenated substances soluble in water when using catalysts comprising reduced copper, cobalt and manganese oxides. The production of olefine hydrocarbons in the liquid products was also observed.

Tests on various catalysts comprising cobalt metal used in conjunction with copper and other metal oxides were described by Erdely and Nash in 1928,[32] who reached the following conclusions :—

1. At a temperature of 285°C. and atmospheric pressure, using

a gas containing equal volumes of carbon monoxide and hydrogen, a cobalt–copper–zinc oxide catalyst was the most suitable. Nearly as satisfactory was a cobalt-copper-alumina catalyst, but this formed less oil and more water. The oil yield was highest with a non-promoted cobalt-copper catalyst but the activity of this catalyst rapidly deteriorated.

2. The best temperature for the formation of liquid hydrocarbons was found in the case of a cobalt-copper-alumina catalyst to lie between 280° and 290°C. Above this chiefly carbon dioxide and methane were formed. Below 230°C. no reaction could be observed.
3. An excess of hydrogen in the original gas mixture increased the formation of water while an excess of carbon monoxide rapidly lowered the activity of the catalyst.
4. The optimum space velocity in the case of a cobalt–copper–zinc oxide catalyst was about 120 volumes of gas per hour per unit volume of catalyst (measured at N.T.P.).

557. The work of Fischer has continued to the present time, and the process for the production of liquid hydrocarbon fuels from water gas is now almost universally known as the *Fischer Process*—the liquid products obtained being known as *Kogasin.* The gas mixture usually employed is $CO : H_2 = 1 : 2$ and this must be free of H_2S and not contain organic sulphur compounds to an extent greater than 0·2 grams per 100 cubic metres. Of the catalytic materials available (normally used on a Kieselguhr support), cobalt base catalysts appear to be favoured, giving a yield of 130 grams of liquid hydrocarbons per cubic metre of gas treated. Modified nickel base catalysts have been investigated in the production of which an aluminium or silicon alloy is treated with sodium hydroxide solution to give a skeleton of the insoluble constituents of the alloy.[33]

The reaction is strongly exothermic as shown by the following equation given by Fischer :—

$$CO + 2H_2 = (CH_2)_x + H_2O + 48 \text{ K. cals.}$$

The products from the reaction comprise hydrocarbon oil and water in proportions varying from 1 : 1 to 1 : 2 together with small quantities of gaseous hydrocarbons and a hard wax which becomes deposited on the catalyst. Small quantities, i.e., traces, of oxygenated compounds are present in the liquid products and recently a number of fatty acids have been isolated.[34]

The composition of the hydrocarbon products obtained are illustrated by the following figures referring to an initial gas mixture containing 29% CO and 58% H_2 and a cobalt base catalyst.[35]

Component	Boiling Range °C.	Per cent. by weight	Olefine Content % vol.
Low boiling fraction ..	Below 30°C.	4	50
Benzine	30–200°C.	62	30
Heavy oil	Above 200°C.	23	10
Solid paraffin from the oil ..	M.P. 50°C.	7	—
Hard paraffin from catalyst..	M.P. 70–80°C.	4	—

Usually the olefine content of the liquid products is lower when a nickel catalyst is used, or when an initial gas containing a greater concentration of hydrogen is employed—as shown in the following figures given by Fischer.

Basic Metal in Catalyst	Volume % of Olefines in Benzine from gas mixtures of composition		
	$CO : H_2 = 1 : 1$	$CO : H_2 = 1 : 2$	$CO : H_2 = 1 : 3$
Cobalt	55	35	12
Nickel	35	16	5

With regard to the distribution of olefines in the product, in general the olefine content falls with rise in boiling point. Thus, in the case of a product obtained from a gas of the composition $CO : H_2 = 1 : 2$, the following figures have been quoted.

	Volume per cent.	Olefine Content vol. %
Original	100	26
50–100°C.	22·5	39
100–150°C.	20	27
150–200°C.	19·5	18
200–250°C.	13	11

Owing to the pronounced aliphatic nature of the benzine fraction, its octane number is very low. Fischer has quoted 47 octane number for a benzine boiling between 50 and 150°C. which could be raised to 67 and 71·5 by the addition of 2·25 and 4·5 c.cs. per Imp. gallon respectively of tetra-ethyl lead. Myddleton and Walker[36] have shown, however, that the octane numbers of the benzines produced increase with the olefine content—thus :

10% Olefines .. .. .. Octane number = 25
20% ,, ... ,, ,, = 40
30% ,, ... ,, ,, = 52
60% ,, ... ,, ,, = 65

Fischer has also stated that a benzine of 47 octane number drops to 12 octane number on hydrogenation—a statement which agrees with the above figures.

Because of the low octane number benzines obtained, much attention has been given to the cracking of the heavier fractions, which, being paraffinic, crack easily and give cracked distillates of improved knock-rating characteristics.[37]

The only refining treatment required by the benzine present in the initial product is a light soda wash, after which it is of merchantable colour, odour and gum stability. The sulphur content is negligible because the gases treated are desulphurised.

The higher fractions of the crude product form a suitable Diesel fuel on account of their pronounced paraffinic character, but the high wax content necessitates dewaxing to secure a reasonably low pour-point product. The minimum yields of marketable Diesel oils of cloud points 10°C., 20°C. and 28°C. respectively are 78%, 62·5% and 45% of the original crude Diesel oil fractions.[38]

The crude Kogasin products contain no fractions suitable as lubricating oils, but considerable work has been carried out by Fischer and his co-workers in Germany and by Nash in England on various methods by which merchantable lubricating oils may be prepared synthetically from Kogasin products. The methods employed are as follows :—

1. The Kogasin gas oil is chlorinated and condensed with aromatic hydrocarbons in the presence of aluminium, aluminium chloride or its addition products ;
2. Chlorinated Kogasin gas oil is condensed with unchlorinated gas oil;
3. Dechlorination of chlorinated hydrocarbons ;
4. Polymerisation of the olefines present in Kogasin products ;
5. Polymerisation of cracked Kogasin waxes ;

and for further details a recent comprehensive paper by Nash and his co-workers[39] should be consulted.

With regard to the commercial application of the Kogasin process, one of the chief technical difficulties is the absorption of the products of the reaction (chiefly the paraffin wax) on the catalyst. This has a serious effect in reducing the activity of the catalyst and causes a decrease in the space velocity allowable. It also causes a reaction chamber to be put out of action periodically for the removal of waxes of high melting point by circulation of a suitable solvent. At the present time numerous Kogasin plants are in course of erection in Germany.

558. A recent development of some importance concerning the Kogasin process is the catalytic reduction of carbon dioxide to higher

hydrocarbons at atmospheric pressure. Hitherto it has not been found possible to reduce carbon dioxide to hydrocarbons higher than methane, but Fischer and his co-workers[40] have found that this can be accomplished with a ruthenium catalyst to which has been added small amounts of alkali. At temperatures as low as 100°C. ruthenium catalyses the reduction of carbon dioxide to methane, but when 2% of potassium carbonate is added to the catalyst the temperature of incipient reduction is raised to 150°C., and beginning at 170–180°C. there are formed not only methane but also higher gaseous and liquid hydrocarbons. The gaseous products formed at 180–225°C. contain 1·32–1·45 carbon atoms per molecule and the most favourable temperature for oil production appears to be 220–225°C. although higher hydrocarbons are formed up to 300°C., above which temperature only methane is produced. The activity of the ruthenium catalyst decreases rapidly, but may be regenerated by heating in a current of air at 300–400°C.

559. A comparison has recently been made of the technological characteristics of gasoline production by the Fischer Kogasin process and by the I.G. high pressure hydrogenation process.[41] The main feature of Fischer's process is that it uses a large number of smaller units, while hydrogenation is carried out with few large reaction units.

TABLE 11. BASIS OF COMPARISON. MANUFACTURING CAPACITY 100,000 TONS OF PETROL PER ANNUM

	Fischer	H.P. Hydrogenation	Ratio $\frac{\text{Fischer}}{\text{Hydrogenation}}$
Number of reaction units ..	21,000	10	2,100
Reaction volume (cu. m.) ..	1,510	110	14
Weight of reaction vessels (tons) ..	10,000	1,000	10
Heat of reaction to be carried away (cals. kg.)	5,700	1,400	4·1
Cooling surface per cu. m. of reaction volume (sq. m.) ..	166	27	6·1
Cooling surface per Kg. of product (sq. m.)	20	0·1	200
Temperature zone, °C.	± 5	± 25	0·20

560. Cracking of Kogasin Oils.—Interesting details concerning tests made on cracking Kogasin oil for maximum gasoline production have been given recently by Egloff, Nelson and Morrell.[42] The scheme adopted involved a primary distillation to give light gasoline, naphtha and bottoms. The naphtha was then reformed and the bottoms cracked and the gases produced in both these operations subjected to catalytic polymerisation.

The crude Kogasin oil had a boiling range of about 113°F. to 702°F. (45–372°C.) and contained 68·4 per cent. of gasoline having an octane number (C.F.R.M.M.) of 40 and an end point of 396°F. (202·2°C.) Fractionation of this crude oil to give gasolines of lower end points gave the following relationship between end point and octane number.

Yield of Volume	End Point		Octane Number (C.F.R.M.M.)
	°C.	°F.	
20	98·3	209	73
33·8	121·1	250	66
43·5	148·3	299	58
56·3	176·7	350	49
68·4	202·2	396	40

The 396°F. end-point gasoline was then refractionated to give 68 octane number gasoline and a residual naphtha. This naphtha was then reformed at a temperature of 1,020°F. (549°C.) and 750 lb. per sq. in. pressure. The bottoms fraction obtained in the first distillation was subjected to Dubbs selective cracking in two-coil operation, the conditions adopted being 935°F. (501·7°C.) and 500 lb. per sq. in. in the light oil coil and 969°F. (520·6°C.) and 300 lb. per sq. in. in the heavy oil coil.

The scheme adopted is given in Table 12 and the yields of gasoline obtained were as follows :—

	% Vol. on Crude Oil	Octane Number
Light gasoline	29·1	68
Reformed naphtha	26·8	57–62
Cracked spirit from bottoms	22·6	60
Polymer gasoline	5·8	81
	84·3	

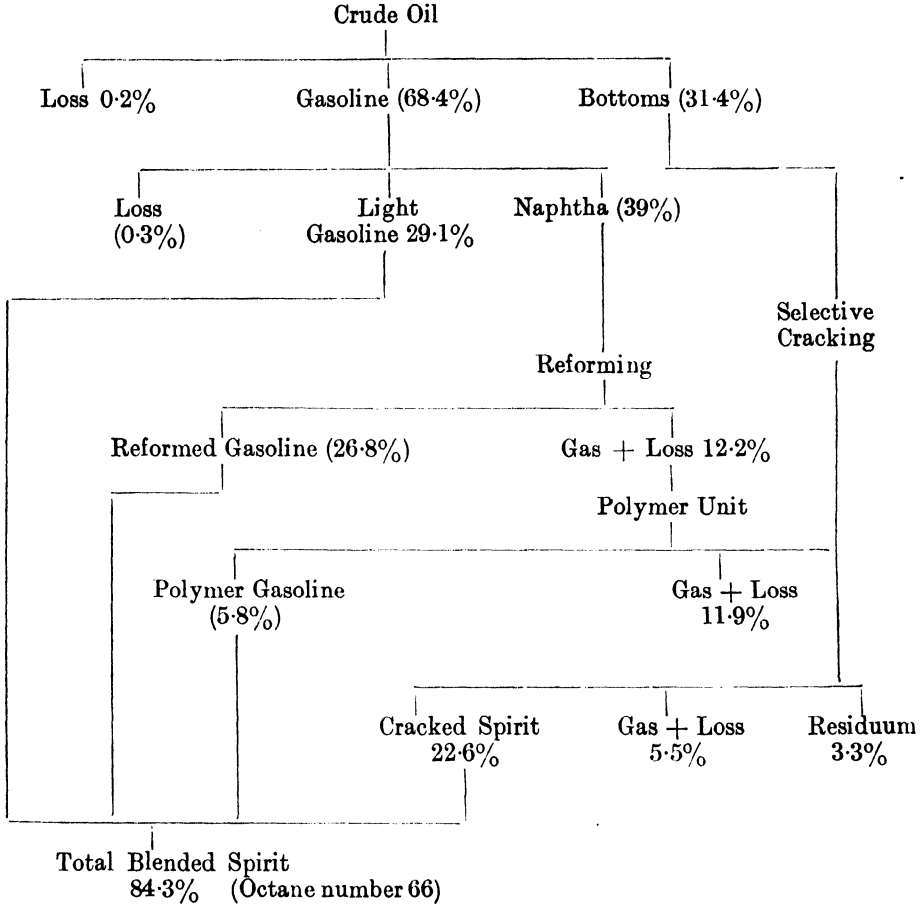
Octane number of final blend = 66

561. Gaseous Fuels.—The following gaseous fuels have been considered in some detail as possible fuels for spark ignition internal combustion engines :—

1. Town's gas.
2. Hydrogen.
3. Paraffin and olefine gases derived from petroleum.
4. Producer gases.

These may conveniently be considered in this order.

TABLE 12. FLOW DIAGRAM. CRACKING OF KOGASIN OIL[42]



Town's Gas.—The use of town's gas as a fuel for high speed internal combustion engines dates back to pre-War days, when, as at present, large quantities of town's gas were used for the "running in" of high-speed engines primarily designed for running on petrol.

In those days, the compression pressures used in engines of this type were comparatively low, with the result that when running on town's gas, the maximum power developed did not reach that obtained with petrol.

During the period of the War, many types of vehicles were run on gas, owing to the shortage of petrol, the gas being stored in the majority of cases in large flexible bags, usually housed on the roof of the vehicle, and where the compression ratios of the engines were reasonably high, the thermal efficiencies realised were of a high order.

The main difficulty which presented itself, however, was the some-

what limited capacity of fuel storage, which resulted in the radius of action of the vehicle being restricted.

At that time, the possibility of storing gas in the compressed form in steel cylinders was given serious consideration, but it was found that this scheme was impracticable owing to the weight of the containers being too great in comparison with the amount of gas stored.

During the last ten years a considerable amount of research work has been carried out in England and also in Europe in connection with the manufacture and use of high tensile alloy steel cylinders, made from nickel-, nickel-chrome- and nickel-chrome-molybdenum steels and of sufficiently low weight to enable a vehicle to carry a reasonable supply of high pressure gas. In England, the City of Birmingham Gas Department have been very active in encouraging the use of compressed town's gas in automobiles, while in France the Société du Gaz in Paris have also carried out much original work on the same lines. In Germany the Stuttgart Gas Works has been supplying consumers with compressed town's gas for some time.

The investigations carried out by the City of Birmingham Gas Department have been very complete and the results obtained may be described in some detail as being representative of general experience. In a paper published by C. M. Walter[43] in 1932, the following conclusions were arrived at as a result of work done to that date.

1. The thermal efficiency of high speed internal combustion engines when supercharged is greater when using town's gas than when petrol is used, and is further increased by carburetting the gas with benzole.
2. The thermal efficiency with petrol as a fuel is decreased by the application of supercharging.
3. The maximum power developed w th gas alone is lower than that obtained with petrol.
4. The carbon monoxide content of the exhaust gases is considerably less with town's gas as a fuel than in the case of petrol.
5. Gas is more responsive to supercharging than petrol, the power output being increased to a greater extent. This is corroborated by the fact that with supercharging the thermal efficiency is only decreased by 0·25% on town's gas compared with 6·45% on petrol.
6. The thermal efficiency obtained with town's gas is further increased by increasing the compression ratio. (Note: this applies to petrol also.)
7. The performance of the engine is very much improved by saturating the gas with gasoline or benzole, the amount of gasoline required being about 0·75 gallons per 1,000 cu. ft. of gas.

From these results it may be assumed that with a standard type of engine having a compression ratio of 5 to 1, one gallon of petrol would give about the same performance under average conditions of running as 265 cu. ft. of gas of 475 B.T.U. per cu. ft. calorific value —this figure being reduced as the compression ratio is increased. It would also appear that in the case of gas carburetted with benzole, this figure would be reduced to about 200 cu. ft., the carburetted gas having a calorific value of 575 B.T.U. per cu. ft.

In 1933, Walter[44] described further work, a short summary of which is as follows :—Experimental work was carried out on the compression of town's gas and the use of light-weight storage cylinders suitable for mounting on vehicles for storing the gas at working pressures up to 3,000 lb. per sq. in.

The dimensions of these cylinders approximate to 8 inches outside diameter and 73 inches long, with a wall thickness of 0·22 inch. The internal volume is 1·76 cubic feet, and thus at a working pressure of 200 atmospheres the volume of free gas contained is about 352 cubic feet, and the approximate weight of each bottle empty is 119 lb. The number of bottles carried depends on the size and type of vehicle.

Alloy steel bottles of this type are being manufactured by Vickers-Armstrong, Limited, Newcastle-on-Tyne, and the Chesterfield Tube Company. In the case of a test specimen from a bottle made by the former firm, the following results were obtained :

Ultimate strength	67·9 tons per sq. inch.
Yield	59·5 „ „ „ „
Impact	53·0 ft. lb.
Elongation	22·8%
Reduction of area	59%

Bending Test : Bent through an angle of 180° without cracking. Limit of proportionality, i.e., maximum stress at which strain is proportional to load, 47 tons per sq. inch.

In the case of vehicle bottles with a working pressure of 3,000 lb. per sq. in., the wall thickness is such that the maximum working stress is 25 tons per sq. in., whilst in the case of the stationary storage cylinders where a working pressure of 5,000 lb. per sq. in. is employed, it is proposed that a working stress of not more than 16·7 tons per sq. in. should be employed, this giving a factor of safety of three in the case of cylinders heat-treated to give an ultimate strength of 50 tons per square inch.

562. Vehicle Equipment.—The complete equipment necessary to operate a vehicle on town's gas includes :—

A battery of storage cylinders of the type already described, suit-

ably attached to the chassis frame and interconnected by means of solid-drawn steel pipes fitted with suitable valves of forged steel.

The number of storage cylinders employed will, of course, depend on the type and weight of vehicle, and the mileage required from a single charge.

Further, a suitable reducing valve to reduce the pressure from the working pressure in the storage cylinders to any desired pressure at the engine inlet, is required, in addition to an air-gas mixer which takes the place of the ordinary carburettor.

The usual form of reducing valve employed consists of a two-stage diaphragm type, so designed as to reduce the pressure from, say, 3,000 lb. per sq. in. to 5 lb. per sq. in. in the first stage, and from 5 lb. per sq. in. to any pressure that may be required at the air-gas mixer, in the second stage.

The valve areas are such that at all loads the requisite flow of gas into the induction system is maintained.

With the system at present employed, the pressure of the gas is reduced to sub-atmospheric in the second stage of the reducing valve, in order to ensure that when the engine is stationary, the supply of fuel is automatically cut off, as the second stage valve will only operate when under the influence of the depression caused in the induction system by the engine suction. It might however, be desirable with certain designs of engines to arrange for the gas to be supplied at a slight positive pressure, in order to maintain a high volumetric efficiency over a wide range of loads. In the latter case, the gas and air required would be admitted to the cylinders through independent valves, and not as an admixture.

With regard to air-gas mixers, the results of experimental work carried out with engines on bench tests and also on vehicles running under service conditions indicate that when the gas and air are admitted to the induction system by means of a choke, the most satisfactory way of obtaining the best admixture of air and gas is to reduce the gas pressure to atmospheric pressure or slightly below and to depend on the suction of the engine to cause both air and gas to be induced into a choke tube of suitable dimensions, where intimate mixing takes place. In the case of certain designs of engines, it has also been found advantageous to introduce velocity tubes in the induction manifold further to assist admixture of gas and air by bringing them more into intimate contact.

The type of mixer at present employed consists of a Venturi choke tube through which the air is drawn, the gas entering through ports, in the form of slots, arranged at right angles to the air stream, these ports being suitably placed circumferentially around the contracted section of the choke tube itself.

The advantage of being able to ensure a constant air-gas ratio over a wide range of speeds with this simple type of mixer will be apparent, as the volume of gas and air induced into the induction system will follow closely the square root law, the proportion of air to gas thus remaining constant over a wide range of throttle openings.

563. An economic study of the possible use of compressed town's gas as a substitute for petrol has recently been presented by Cook,[45] who points out, quite rightly, that the fundamental objection to the use of compressed gaseous fuels is the difficulty of carrying sufficient gas for economic mileage range, as the radius of action of a gas-propelled vehicle is restricted by the size and weight of storage cylinders to some 60–70 miles on a single charge. Cook concludes that gaseous fuels cannot compete economically with Diesel oil at its present price, and would only show to advantage if the price of Diesel fuel rose considerably. Moreover it is concluded that, taking all relevant charges into account, compressed gas can only compete with petrol fuel in the case of vehicles of less than two tons capacity. The truth in such conclusions is borne out by the fact that at the present time there are only about 24 gas-driven vehicles on the roads of the United Kingdom —although gas-filling stations are available at both Birmingham and Chesterfield. The reason for the lack of development is the advance of the Diesel engine—especially for buses and heavy long distance lorries.

564. Hydrogen as a Fuel for Internal Combustion Engines.— A very early attempt at producing an internal combustion engine proposed the use of hydrogen as a fuel. In 1820 the Rev. A. Cecil read a paper before the Cambridge Philosophical Society on "The Application of Hydrogen Gas to produce a Moving Power in Machinery." This engine followed current practice and depended on atmospheric pressure and the partial vacuum produced by the explosion of hydrogen in air. The engine is said to have run satisfactorily. Very little more attention was given to the use of hydrogen as a fuel until quite modern times. A new impetus was given by the possibility of using hydrogen as an additional fuel in the petrol or Diesel engine used in lighter-than-air aircraft, rather than releasing the hydrogen to waste as progressive fuel consumption lightens the airship.

In Aeronautical Research Committee Reports and Memoranda No. 1029 experiments are described on the use of hydrogen in this way. Hydrogen was not considered by the experimenters as likely to increase the thermal efficiency of the petrol engine. On the other hand Ricardo (*loc. cit.*) has called attention to the very wide range of weak mixtures of air and hydrogen that can be used, enabling power output to be controlled by the quality of the charge. With a rich mixture, even

at a compression ratio as low as 3·8 to 1, violent pre-ignition was observed accompanied by firing back into the carburettor. Very good results were obtained at a compression ratio of 7 to 1 provided the I.M.E.P. was maintained below 74 lb. per sq. in.; at this point detonation occurred.

Most of the experimental work reported on the use of hydrogen as a fuel has been conducted by the Erren Motoren G.m.b.H., an account of which has been given by Erren and Campbell.[46]

565. Paraffinic and Olefinic Gases derived from Petroleum, etc. —Experiments were carried out in Germany some years ago to obtain a gas fuel suitable for use in airship engines. As the production of a gas consisting of one chemical entity presented difficulties, "Blau-gas" was considered the most suitable and was ultimately used satisfactorily. The first stage of its manufacture consists in the production of "Pintsch Gas" by cracking a mineral oil such as "mineral seal oil," Scotch shale oil or Russian Solar oil at 600–700°C. The resultant gas, freed from carbon dioxide and sulphur compounds by lime treatment, is compressed to about 10 atmospheres when a small amount of liquid hydrocarbons separates. The gas is then compressed to 100 atmospheres and cooled and yields a liquid consisting of ethane, propane, butane, propylene and butylenes with ethylene and methane in solution. This liquid is "Blau-gas" and contains about 40 per cent. paraffins; it can be used at compression ratios up to 9 to 1. In America, suitable fuel of a similar composition has been prepared from natural gas, by similar methods. Under the name "Pyro-fax" liquefied propane containing about 2 per cent. butane has been marketed in U.S.A. The Graf Zeppelin has used this fuel in some of its flights, sometimes mixed with hydrogen and sometimes with natural gas.

Detailed experiments on the use of oil gas as a fuel have been described by Helmore.[47] Using a gas containing 49 per cent. methane, 36 per cent. ethylene and 6 per cent. hydrogen, very promising results were obtained. In a Ricardo E.35 engine, it was found impossible to cause backfiring into the fuel intake with this gas either by varying mixture strength or engine speed, the engine being capable of being brought to a standstill by this means at either end of the mixture range. No signs of detonation or pre-ignition were observed at 7 : 1 compression ratio. Engine tests carried out with this fuel on a Rolls-Royce 350 h.p. aero-engine confirmed the single-cylinder results, the absence of detonation and tendency to misfire being maintained. Very smooth running and improved distribution were obtained whilst easy starting and flexible control over the whole mixture range was found to result. Satisfactory results on oil-gas kerosene mixtures were also obtained.

Vogt[48] has described engine tests on butane fuel. Using a single-cylinder variable compression engine, he found that it was possible to increase the compression ratio appreciably over that allowable when operating with gasoline, but the fuel consumptions were higher with butane than with gasoline under comparable conditions. This agrees with general road experience. The maximum power output was greater with butane.

The liquefied gas industry in America is undergoing great expansion, the products being used mainly in domestic heating appliances, oven-heating and metal cutting. Liquefied gases—both propane and butane—are sold in large quantities at 5–10 cents per gallon. Distribution is effected in tank cars, and truck units.

In the United Kingdom liquefied butane has recently appeared on the market, while in Germany liquid propane has been marketed by the I.G. for some time. In steel cylinders of similar capacity, propane gives 10 times the quantity of heat available from town's gas compressed to 150 atmospheres.

With regard to the utilisation of such fuels for internal combustion engines, the octane numbers are of considerable importance. The following values have been reported.[49]

BLENDING OCTANE NUMBERS

	212°F. Jacket Temp.	300°F. Jacket Temp.
Ethylene	85·5	82·5
Propylene	102·0	94·5
1-Butene	111·5	95·0

n-Butane has an octane number of 91 and iso-butane an octane number of 99.[50]

566. Producer Gases as Engine Fuels.—With regard to this development, numerous difficulties are encountered, due to the slowness of operation of the gas generator and to impurities in the resulting gas. The weight of the generator and the weight of the solid fuel carried is also a disadvantage.

The equipment consists essentially of a small gas producer and a gas scrubber. The former comprises a fuel hopper and a small refractory-lined insulated combustion chamber, which is fitted with a grate which must be designed to avoid difficulty from clinkering. Webster[51] has described such an arrangement for burning low temperature coke, in which the producer can be operated on up-, down-, or combined draught. Water flows into a vaporiser above the refractory or into the annular space around the base, according as the

draught is up or down. The gas cleaner and scrubber consist of an oblong box fitted with shutters through which the gas passes, after which it is filtered through wood wool before it passes to the engine. The generator is operated by the engine suction. A fire of wood sticks is started in the combustion chamber, the hand blower is used for a few minutes and the hopper is filled with coke. The engine is started on spirit and after running a few moments is switched over on to gas.

The coke requirements of such small producers are stringent. Suitable cokes are those high in volatile content, low in moisture and of low ash content. Gas coke is not suitable. According to Webster, with low temperature coke at 30 /– per ton, the fuel cost per b.h.p.h. is 0·176 pence, whereas, with motor fuel at 1 /– ger gallon, the fuel cost is 1·024 pence per b.h.p.h.

Details concerning the sizes of the producers used on automobiles in this way have been given by Charles-Roux.[52]

Raw wood and wood charcoal have been used as gas-producing materials. The former, however, gives rise to troublesome tarry substances carried away in the gas. Charcoal is the cleanest fuel to employ.

To obtain satisfactory results with such gaseous fuels, the engines must be modified to run at a higher compression ratio and a greater degree of turbulence in the cylinder head. The power output from a normal petrol engine is reduced when running on gaseous fuels. Figures have been quoted regarding a test in a four-cylinder Chevrolet vehicle, 94 mm. bore and 102 mm. stroke, which, when operated on gas from birch wood containing 20–30 per cent. moisture, gave 40 per cent. less power than with petrol at a compression ratio of 4·64. When the latter was raised to 6·1, the decrease in power was still about 20 per cent. One kilogram of wood was found to be equivalent to 210 g. of motor spirit.[53]

Apart from a slight saving in fuel cost, such producer plant equipment has nothing to commend it. It is heavy, cumbersome and unsightly and it materially reduces the overall reliability of the motor vehicle. On the other hand the use of portable producer-gas plants of this type has been advocated by Russel.[54]

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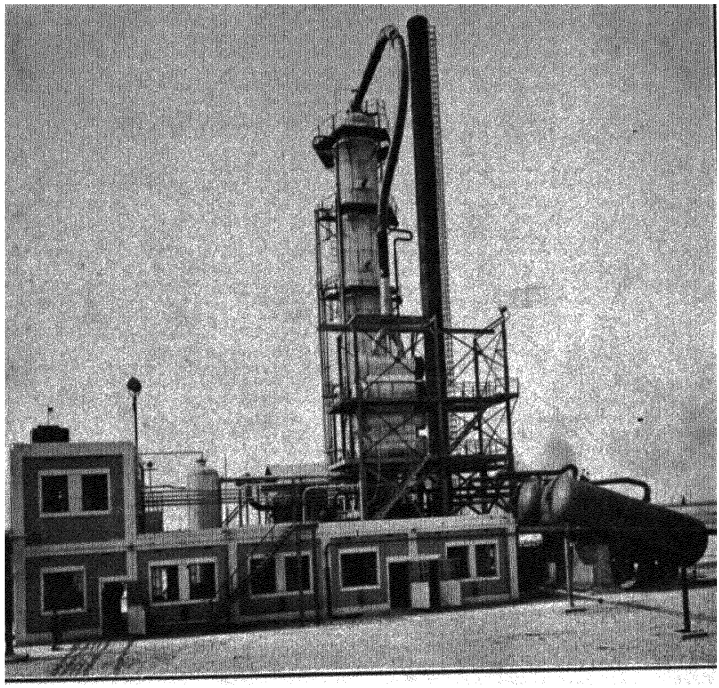
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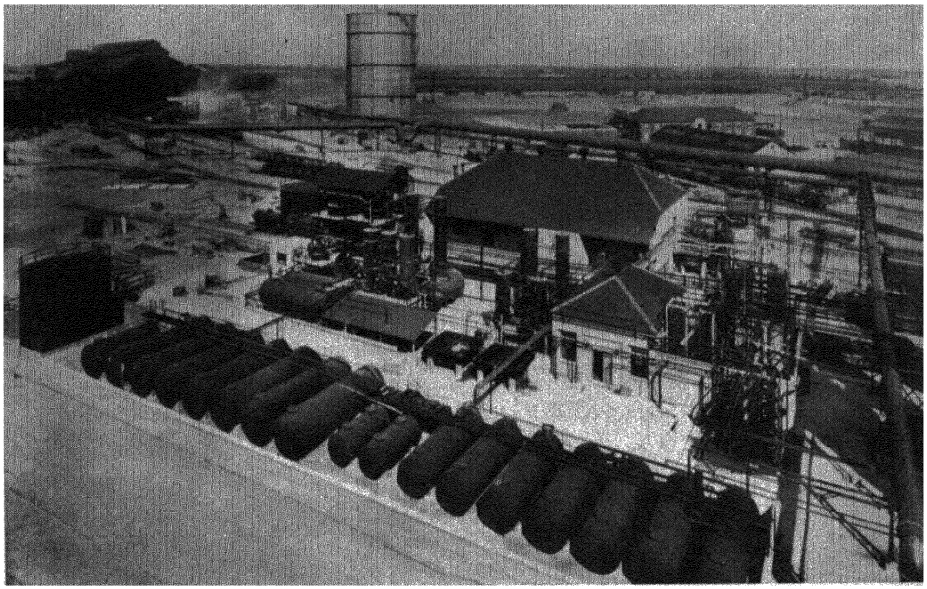
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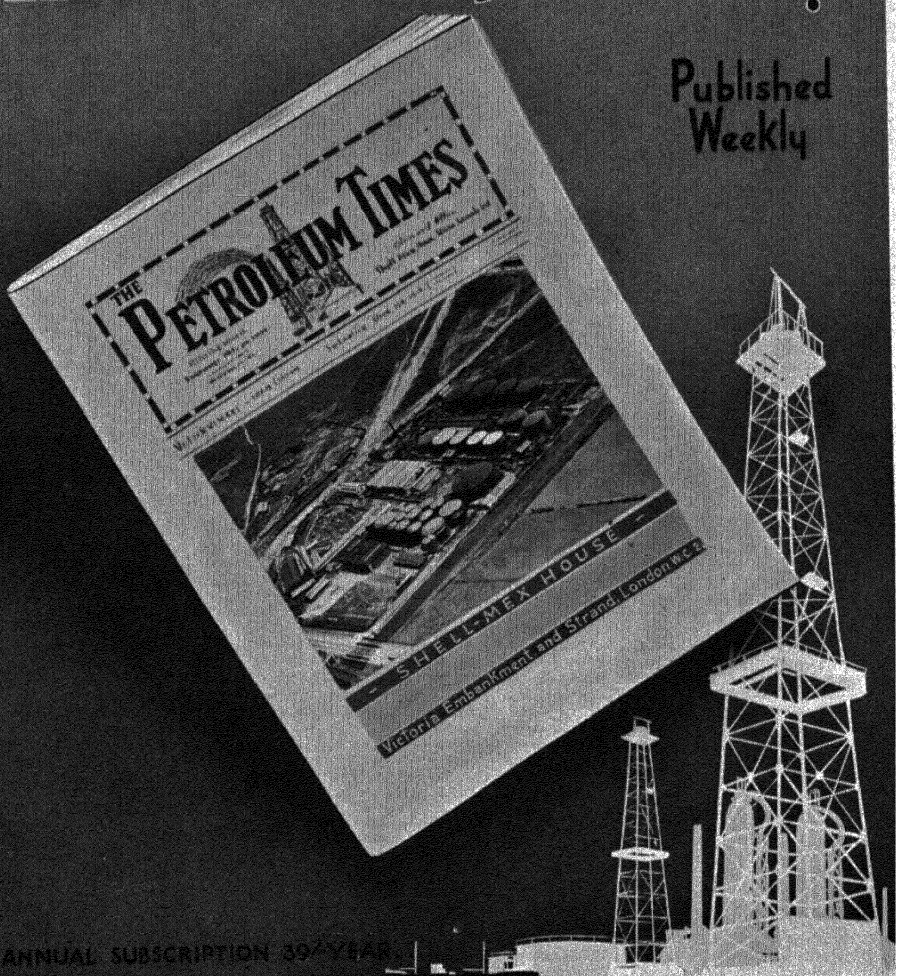
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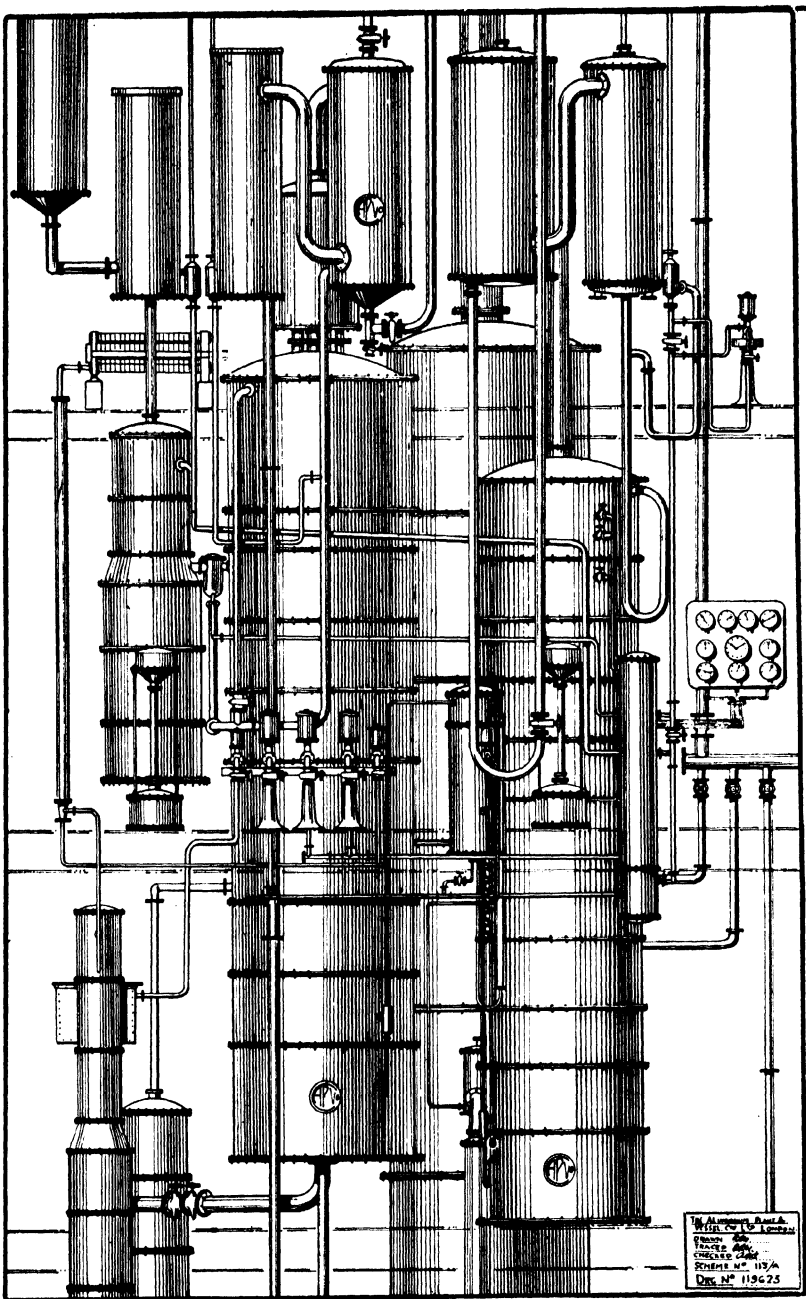


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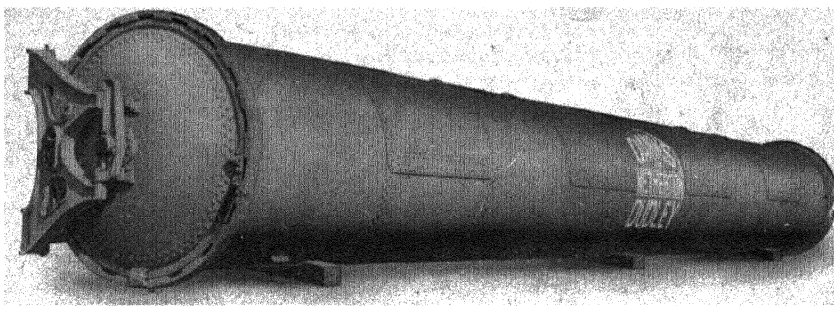
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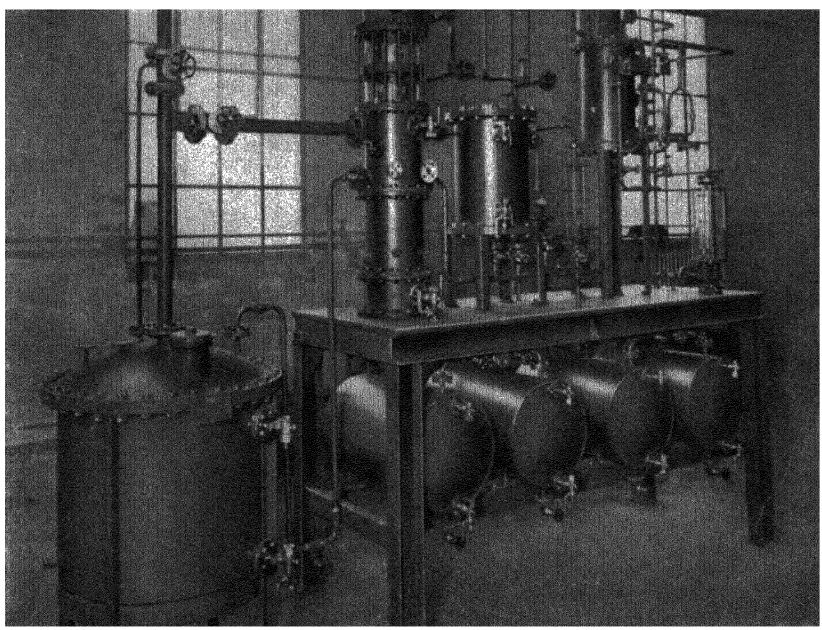
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