LIQUID FUELS

LIQUID FUELS

Their Manufacture, Properties
Utilisation, and Analysis

A PRACTICAL TREATISE FOR ENGINEERS
AND CHEMISTS

BY

HAROLD MOORE

M.Sc.Tech., F.C.S., M.I.P.T., A.I.Mech. Eng.

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PREFACE

The author's book, "Liquid Fuels for Internal Combustion Engines," first appeared in 1917, and was followed by a second edition in 1920. At that time it was possible in a small volume to give a reasonably exhaustive survey of the whole subject, but during the last fifteen years the rate of technical development has been so rapid that in order to treat the subject with a corresponding amount of detail it would now be necessary to fill several volumes. The earlier volume had the advantage of being sufficiently short to be useful to the large body of engineers and chemists who are not specialists in this particular branch of technology. As the earlier book is now completely out of date, it has been impossible simply to re-edit and modify the sections, therefore the author has produced an entirely new book and, at the same time, enlarged its scope to cover fuels for external combustion in addition to engine fuels.

In order to keep the work within such dimensions, and so make it available to the great bulk of technical workers who are not actually specialists on this subject, it has been necessary to limit the field very considerably ; no attempt has been made to prepare an exhaustive treatise, and the volume is intended solely as a concise manual for those engaged in the oil trade, for engineers manufacturing or operating internal combustion engines, and for those of the public who may wish to make a survey of the subject.

The author wishes to acknowledge his indebtedness to C. I. Kelly, Esq., M.Sc.Tech., F.I.C., for contributing Part V., "Petroleum Liquid Fuels for External Combustion, etc.," and Section I., Part VI., "Significance of Tests of Liquid Fuels" ; he also wishes to thank W. A. Woodrow, Esq., A.I.C., for assistance in compiling Section II., Part VI., "Methods of Analysis of Liquid Fuels."

The author presents this book to engineers and chemists in the belief that it fulfils the requirements of a handbook dealing with the main aspects of a wide and rapidly developing subject.

Bridge House,
London, E.C.4.

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LIQUID FUELS

PART I

THE CHEMISTRY OF LIQUID FUELS

The majority of liquid fuels consist mainly of hydrocarbons—that is to say, compounds of carbon and hydrogen. Petroleum oils consist almost entirely of hydrocarbons, other bodies containing sulphur and nitrogen being present only in small quantities. Shale oils also consist mainly of hydrocarbons, whilst the coal tars, lignite tars, and their products contain considerable quantities of bodies consisting of carbon, hydrogen, and oxygen, in addition to smaller quantities of compounds containing sulphur and nitrogen. The products of wood and peat contain both hydrocarbons and oxygen-containing compounds, whilst other combustibles, such as the animal and vegetable oils and the alcohols (such as methyl and ethyl alcohol), consist essentially of bodies containing the three elements, carbon, hydrogen, and oxygen.

In order to understand the nature of the compounds present in liquid fuels, it is necessary to have some knowledge of organic chemistry, but those who have not made a study of this subject should be assisted by the following brief description of the types of compounds found in liquid fuels in understanding the properties, both physical and chemical, of the various fuels which are discussed in the later sections.

Hydrocarbons.—Hydrocarbons are compounds of carbon and hydrogen alone. A compound containing any element other than these two is not classed as a hydrocarbon. The element carbon combines with hydrogen to form an immense variety of different compounds ; in addition to its own definite properties, each compound has a definite molecular structure, and a definite proportion of carbon and hydrogen in its composition.

The very large number of the known compounds of carbon and hydrogen can be classified into certain series, the properties and constitution of different members of the same series exhibiting certain similar characteristics. The hydrocarbons encountered in liquid fuels may be classified into three main types :—

Aliphatic hydrocarbons.
Aromatic ,,
Naphthene ,,

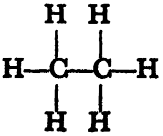
Though it is usual to refer to these series as distinct and separate from each other, it is possible to obtain hydrocarbons the constitution of which is such that they cannot be classified directly in one of these series. Reference will be made later to hybrids containing the features of two series. For rough purposes, however, it is common to assume that fuel hydrocarbons can be classified into one of these three series.

Aliphatic Hydrocarbons.—The aliphatic hydrocarbons may be divided into two series—those which are saturated, or the paraffins, and those which are unsaturated, or the olefines. The term " saturated " is an expression which means that the compounds are incapable of absorbing further hydrogen, thus an unsaturated hydrocarbon is a compound which, under certain conditions, is capable of absorbing further hydrogen when its composition and properties will conform to those of a saturated hydrocarbon.

The saturated aliphatic hydrocarbons form a series for each member of which it is possible to state the number of hydrogen atoms present, provided the number of carbon atoms present is known. This is an outcome of the ability of the carbon atom to attach itself to four atoms of hydrogen ; thus the simplest saturated aliphatic hydrocarbon has the formula CH_4. The mechanism by which atoms of one element attach themselves to other elements is very complicated, and the full explanation, together with proofs of the theories which exist on this subject, can only be treated in advanced textbooks on chemistry and physics. For the present purpose, the simple explanation will suffice that the element carbon has four links, or bonds, which act as arms, and are consequently capable of attaching themselves to other elements. The element hydrogen has only one bond. Therefore, when it forms a compound with carbon, one bond from each of four hydrogen atoms becomes attached to the four bonds from one carbon atom. The result is the formation of the gas, methane, which is the first member of the " saturated aliphatic hydrocarbons," which are also known as paraffins.

The next member of the series is the compound containing two carbon atoms. In this case, one bond of a carbon atom is attached to a bond from the other carbon atom, so that each carbon atom now has only three free bonds, that is to say, a total of six free bonds are available for attachment to hydrogen atoms. The second member of the paraffin series, therefore, has the formula C_2H_6, which is a gas known as ethane.

Ethane (C_2H_6)



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

The structural diagrams of methane, ethane, and propane reveal that each compound above methane differs from the previous member by containing one more carbon atom and two more hydrogen atoms. From this it will be seen that all paraffin hydrocarbons contain twice as many hydrogens as carbons to form the main portion of the chain and two extra hydrogens at the two ends of the chain. Hence one arrives at the general formula for the paraffins, C_nH_{2n+2}, which is a way of stating that for each value of " n " (the number of carbons) the number of hydrogens will be $2n+2$. Such a series may be continued indefinitely. The earlier members of the series are quite well-known bodies, but those members having large and more complex structures are less well known.

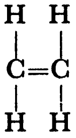
It will be apparent that the chemical constitution of members of the same series is similar, and therefore one finds that the chemical and physical properties resemble each other in many ways. For instance, the paraffin series are incapable of absorbing further hydrogen ; they are comparatively inactive bodies in that they do not readily react with the common chemical reagents such as strong acids and alkalis. They are colourless. The earlier members are gases at normal temperature ; higher up the series (from five to sixteen carbon atoms) the members are liquids, and the members containing over sixteen carbon atoms are solids, the melting points and boiling points of the different members increasing with some degree of regularity as the number of carbon atoms increases.

The following table gives the physical properties of some members of the paraffin series :—

Name.	Formula.	Boiling Point.	Melting Point.	Specific Gravity.
Methane	CH_4	−160° C.	−186° C.	0·415 at −160° C.
Ethane	C_2H_6	−93° C.	−172° C.	0·446 at 0° C.
Propane	C_3H_8	−45° C.	...	0·536 „
Butane	C_4H_{10}	1° C.	...	0·600 „
Pentane	C_5H_{12}	36·4° C.	...	0·627 „
Hexane	C_6H_{14}	68·9° C.	...	0·658 „
Heptane	C_7H_{16}	98·4° C.	...	0·683 „
Octane	C_8H_{18}	125·6	...	0·702 „
Decane	$C_{10}H_{22}$	173° C.	−31° C.	0·730 „
Hexadecane	$C_{16}H_{34}$	287·5° C.	18° C.	0·775 at M.P.
Pentatria-contane	$C_{35}H_{72}$	331 at 15 mm.	75° C.	0·782 „

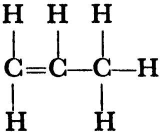
Olefines.—The paraffins have been described as members of the saturated aliphatic series. The olefines are unsaturated aliphatic hydrocarbons. In the paraffin hydrocarbons containing more than one carbon, each carbon atom is attached to one or more other carbon atoms by means of a single linkage or bond, and the remaining linkages which are not attached to carbons are attached to hydrogens. In the olefine series the members contain two carbon atoms which are attached together by means of a double bond, and as a result the number of hydrogen atoms which can be held by the remaining bonds is less than that contained in the corresponding paraffins. As the olefine linkage exists between two carbon atoms, it is impossible to have an olefine containing one carbon atom only, and the series, therefore, starts with a compound which corresponds to the paraffin ethane. Now, in the compound ethane carbons are attached to each other by a single bond. The olefine, which contains two carbon atoms, has these two atoms linked together by a double bond, therefore the carbons, after attachment to each other, have each only two bonds available for attachment of hydrogen atoms. The first member of the olefine series, therefore, has the formula C_2H_4, and is known as ethylene.

The nomenclature in organic chemistry has been so arranged that so far as possible the names should be descriptive of the compound. The names of the paraffins end in "ane." The names of the olefines are the same as those of the paraffins except that the ending "ane" is substituted by the ending "ylene," so that ethane, which has the formula C_2H_6, becomes ethylene, C_2H_4,



$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array}$$

propane, which has the formula C_3H_8, becomes propylene, C_3H_6,



$$\begin{array}{ccccccc} H & & H & & H & & \\ | & & | & & | & & \\ C & = & C & — & C & — & H \\ | & & & & | & & \\ H & & & & H & & \end{array}$$

butane, which has the formula C_4H_{10}, becomes butylene, C_4H_8, and so on.

From the formulæ of these compounds it will be observed that the number of hydrogen atoms in each is exactly twice the number of carbon atoms, therefore the general formula is C_nH_{2n}. The olefine series possess different characteristics from those of the paraffins ; whereas the paraffins are comparatively inert, the olefines are very much more active chemically ; for example, they react readily with sulphuric acid and with chlorine, bromine, and iodine. They are also capable of absorbing hydrogen, whereby they are converted into corresponding paraffins. When these reactions take place, the double linkage in the olefine compound is converted into a single linkage, and the bonds which have been freed by this conversion attach themselves to the substance with which the olefine reacts. For instance, when ethylene reacts with iodine it forms a compound containing two atoms of iodine in addition to the original elements present in the ethylene, according to the formula :—

$$C_2H_4 + I_2 \longrightarrow \underset{\text{ethylene iodide.}}{C_2H_4I_2.}$$

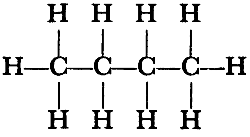
The following list gives the formulæ of a few simple olefines :—

Olefines

(General formula : C_nH_{2n})

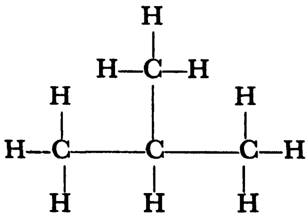
Ethylene	C_2H_4
Propylene	C_3H_6
Butylene	C_4H_8

Isomerism.—In describing both paraffins and olefines, we have referred to the simple straight-chain compounds only, and these may be considered typical examples of the hydrocarbons of each class. It will be observed, however, that it is possible to have more than one compound possessing the same empirical formula ; as an example, it is possible to have two butanes, one being the normal variety in which the carbons are all in a straight chain, possessing the formula :—



$$\begin{array}{ccccccccc} & & H & & H & & H & & H & \\ & & | & & | & & | & & | & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & \\ & & H & & H & & H & & H & \end{array}$$

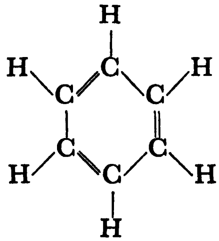
which may be described as normal butane, whilst the other has the formula :—



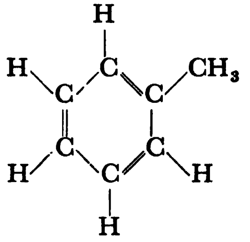
and, whilst being a butane, is chemically described as trimethylmethane. Though both these bodies have the formula C_4H_{10}, the characteristics are not identical. The phenomenon described is known as isomerism, and each form is referred to as an isomer of the other. With methane, ethane, and propane, due to the simplicity of the structure, isomerism is impossible, but as the molecular weight of the compound increases, the number of possibilities of variation in structural formula also increases, so that the number of isomers becomes very large indeed with the more complex bodies found in liquid fuels.

Isomerism may also occur in olefine compounds, as the double linkage may vary in position. For instance, the compound butylene (C_4H_8) may have the double linkage between one of the end carbons and one of the middle carbons, or it may have the double linkage in the middle of the compound. In addition to isomerism due to the position of the double linkage, there is also the possibility of structural isomerism such as that referred to in the paraffin series ; as a result, it will be observed that though the earliest members of both the aliphatic and olefine series can only exist in one form, the more complex bodies which are found in the higher boiling fractions of liquid fuels may exist in an almost infinite variety of forms. Moreover, since the isomers vary in their physical properties, such as the melting point, boiling point, etc., it becomes increasingly difficult to isolate the more complex bodies from mixtures in which they occur. As a result of this, our knowledge of the individual constituents present in liquid fuels, and the proportion of these constituents which are present, is almost entirely confined to the lower boiling fractions.

Aromatic Compounds.—In the paraffins and olefines which we have previously been considering, the carbon atoms are attached to each other in the form of chains, with or without branches attached thereto. The carbon atoms in aromatic compounds are attached to each other in the form of rings ; for example, the simplest aromatic compound is benzene, which has the formula C_6H_6 (the impure commercial quality is referred to as benzole). In this compound the carbon atoms form a hexagon, and to each carbon atom one hydrogen atom is attached. The formula is usually written as follows :—

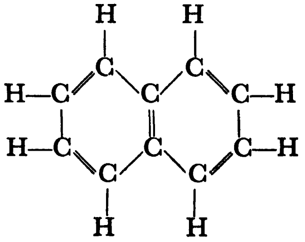


In view of the presence of double linkages in the formula for benzene, one might consider this as a type of olefine, but this would not be correct. As written on paper, the extra bonds are drawn in the same way as the double linkages of an olefine, but actually the nature of the linkage in the aromatic compound is quite different from that of the olefine, since it does not generally exhibit the characteristics of unsaturation. For instance, in the presence of iodine, benzene more readily reacts to form the compound C_6H_5I, by substitution of one of the hydrogens which is liberated in the form of hydriodic acid according to the reaction $C_6H_6+I_2 \longrightarrow C_6H_5I+HI$. If the linkages of the benzene molecule were such as those found in olefines, one would expect iodine to form a simple compound by the addition of two, four, or six iodine atoms without the splitting-off of any hydrogen. Other aromatic compounds exist on which side chains are attached to the benzene rings ; for example, the body methylbenzene, which is better known as toluene, possesses the formula $C_6H_5CH_3$, or



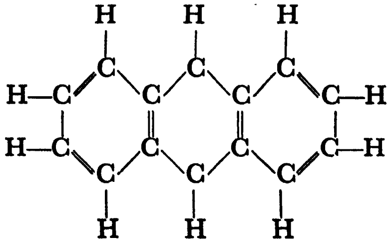
Other isomeric compounds, such as the dimethylbenzenes, known as xylenes, and ethylbenzene, exist in petroleum and coal-tar products. Other compounds of the aromatic series exist in which two or more benzene rings are attached to each other with or without an intermediate chain. For example, naphthalene, which is a white solid at ordinary temperatures, consists of two benzene rings with a side which is common to both rings. It has the structural formula :—

Naphthalene, $C_{10}H_8$,



The well-known substance, anthracene, has the following formula :—

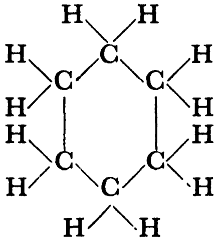
Anthracene, $C_{14}H_{10}$,



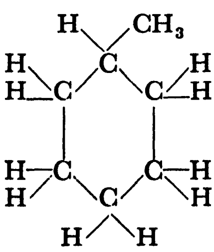
It will be noticed that the aromatic compounds contain a lower proportion of hydrogen than the corresponding aliphatic compounds, and the physical properties are also widely different. For instance, the saturated hydrocarbon hexane boils at 68·9° C. and possesses a specific gravity of 0·658 at 20° C., whereas benzene containing the same number of carbon atoms boils at 80·4° C. and possesses a specific gravity of 0·879 at 20° C. The aromatic hydrocarbons, though they readily enter into chemical combination to form an almost infinite variety of other compounds, are nevertheless very stable and do not decompose under heat as readily as the olefines and the paraffins. They can be formed by the action of heat on paraffin compounds.

In addition to the hydrocarbons mentioned, there are a great variety of oxygen, sulphur, and nitrogen-containing compounds which can be formed from the aromatic hydrocarbons, some of which occur in liquid fuels of aromatic base.

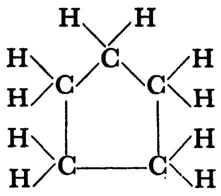
Naphthenes.—Though aromatic compounds, such as benzol, do not absorb hydrogen so readily as do the olefines, it is nevertheless possible to add hydrogen to benzene and form a fully saturated compound of the formula C_6H_{12}. This is a ring compound known as hexahydrobenzene or cyclohexane, and possesses the formula :—



These hydrogenated aromatic compounds are classed as hydro-aromatic compounds or naphthenes. Other naphthenes exist which have the hexahydrobenzene structure, to which side chains are attached ; for example, methylhexahydrobenzene, also known as hexahydrotoluene, possesses the formula :—



Whereas the aromatic compounds are confined to six-sided rings, the naphthenes may vary in the number of carbons present in the actual ring. Many of the naphthenes found in petroleum are derivatives of cyclopentane, which has the formula :—



The naphthenes possess physical properties which are usually intermediate between those of the corresponding paraffins and the corresponding aromatic compounds. They are not so stable at high temperatures as the aromatic compounds, but at the same time are more stable than the paraffins.

As regards the general physical properties of the four types of hydrocarbons, to which reference has been made, it is useful to bear in mind that (1) the paraffins have the lowest specific gravity, the olefines and naphthenes are intermediate in gravity, and those of the aromatics the greatest ; (2) that the hydrogen content of the paraffins is greatest and that they contain more than two hydrogen atoms for each carbon ; (3) that the naphthenes and olefines contain two hydrogen atoms for each carbon ; (4) the aromatic compounds contain considerably less than two hydrogen atoms for each carbon.

Though it is usual to classify hydrocarbons into the categories into which they have been divided, it must be borne in mind that there are many compounds which belong to more than one classification at the same time ; for example, many compounds exist in which a benzene ring is attached to a long side chain. Such a hydrocarbon is usually referred to as an aromatic compound, but the properties of the side chain may be those of a paraffin, and the compound may then behave both as an aromatic and as a paraffin. If the side chain contains a double linkage, the compound will show the properties of an olefine in addition to those of an aromatic compound. That these mixed compounds exist should be borne in mind, as it is a very common practice in the analysis of petroleum spirit to classify the contents of the spirit into various types of hydrocarbons, the total to add up to 100 per cent. The meaning of this analysis can only be understood after studying the method of analysis and by realising that the terms " aromatic," " paraffin," " unsaturated," and " naphthene " are used in a rather loose manner. For technical and commercial purposes it is essential to carry out these analyses, as they are of considerable value in spite of the fact that the terms have a very wide meaning.

CONSTITUENTS OF LIQUID FUELS OTHER THAN HYDROCARBONS.—As previously explained, hydrocarbons are compounds consisting solely of carbon and hydrogen, but in the majority of liquid fuels other compounds are present to a small extent. Of the non-hydrocarbon bodies present in liquid fuels, by far the majority are the compounds of oxygen, sulphur, and nitrogen, and many of these have a structure which is fairly similar to certain of the hydrocarbons, except for the presence of one or two atoms of a third element.

Oxygen Compounds.—Oxygen compounds are found in unrefined petroleum products, but are usually only present to a very small extent in refined products ; resinous and asphaltic oils frequently contain appreciable quantities of oxygen. In coal-tar products quite large amounts of oxygen are found, and the percentage of oxygen-containing compounds is consequently very large ; for example, coal-tar creosote frequently contains as much as 30 per cent. of the oxygen-containing compounds known as tar acids, these being mainly phenol (also known as carbolic acid, C_6H_5OH), the three isomeric cresols which all have the formula $C_6H_4CH_3OH$, and other hydroxy compounds of benzene and naphthalene. These oxygen compounds frequently show acid properties, and can often be removed by washing the oil with alkali.

Sulphur Compounds.—These bodies, generally undesirable constituents of liquid fuels and considered as impurities, are found in petroleum, shale oil, and coal-tar products. Certain petroleum oils are comparatively rich in sulphur compounds, such as mercaptans and thioethers, of which ethyl mercaptan, C_2H_5SH, and diethyl thioether, also known as diethylsulphide, $C_2H_5SC_2H_5$, may be taken as representative examples. These bodies are frequently removed both from petroleum and coal-tar products by washing with sulphuric acid. Very complex sulphur compounds exist in petroleum asphalt, the sulphur content of which frequently exceeds 5 per cent.

Nitrogen Compounds.—Nitrogen compounds are also considered as undesirable constituents of both petroleum and coal-tar fuels. Nitrogen is frequently present in very small amounts in both classes of oil in the form of compounds, such as aniline, $C_6H_5NH_2$, and other more complex bodies, like pyridine (C_5H_5N) and quinoline (C_9H_7N). The nitrogen compounds generally exhibit alkaline properties in that they form compounds with acids. They can, therefore, often be removed by washing the oil with sulphuric acid.

PART II

THE PREPARATION OF LIQUID FUELS

CHAPTER I

THE PREPARATION OF LIQUID FUELS FROM PETROLEUM

CRUDE petroleum occurs in the earth's crust and is occasionally found in the form of pools or seepages on the earth's surface. In order to obtain the oil in quantity, it is necessary to drill a hole down to the strata in which the oil exists, when the oil may be forced up the hole by pressure, or it may have to be extracted by bailing or pumping. The oil is accompanied by natural gas which frequently emerges from the well in very large quantities.

Several methods of drilling are employed, and considerations of space will only allow a brief description. Drilling systems can be divided into two classes, namely, percussion and rotary. Common to both is a superstructure called a derrick, which is used for several purposes ; for suspending the drilling tools, for lowering and raising casing, and for operating the bailer.

In the percussion system a heavy steel tool is suspended by a cable which passes over the crown block on top of the derrick. By this means the tool is raised from the ground to a certain height and then allowed to fall. The impact on falling is sufficient to force a hole into the ground, and the debris formed by the loosening and crushing of the strata is removed by means of a stream of water which is introduced to the bottom of the hole.

The size of the hole at the commencement of drilling is decided by the size of hole which is expected when the well casing penetrates the oil-bearing strata. It may be as large as 20 in. in diameter. In order to increase the impact of the bit on the rock, a heavy steel weight is carried over the bit. Arrangements are made for rotating the bit during operation, so that if desired the end of the bit may be chisel-shaped. A very great variety of different tools are employed, depending upon the depth and the nature of the strata.

When the hole has been drilled a certain depth and it is considered advisable to strengthen the walls, which might otherwise cave in, the drill is removed from the hole and steel casing is dropped into the hole. After a string of casing has been fixed in the hole, a string of tools of smaller diameter is then used and lowered down the centre of the casing, after which drilling is continued. If it is deemed advisable, a second string of casing of a smaller diameter may be inserted, in which case the second string usually runs from the bottom of the hole right to the top, so that at the top there are now two concentric layers of casing. This process may be repeated so that the final well may have four or five different layers of casing at the upper levels, the innermost casing reaching to the lowest level. As the oil strata is approached, arrangements are made for controlling the pressure under which the oil may be found. Special valves are used at the well-head and are coupled direct to pipe lines which run the oil to storage.

If the oil occurs under insufficient pressure to raise it to the surface, it may be bailed or pumped. Bailing consists of lowering a bailer into the oil, then raising the bailer full of oil and dumping the oil at one side of the well, from whence it is run off or pumped to storage. The bailer is a long tube which fits loosely inside the well ; it is suspended from a cable attached to its upper end, whilst at the bottom is an automatic valve which opens when the bailer is immersed in the oil, and closes under the pressure of the contained oil when the bailer is raised. The bailer is operated by a winch, the cable passing over a pulley at the top of the derrick.

When the oil is removed by pumping, the pump is actually situated down the well below the oil level, and is operated by rods from the surface, which operate the piston of the pump. The oil is sucked from underneath the pump and delivered on the upper side of the pump up the casing.

In addition to bailing and pumping, a large quantity of oil is nowadays removed by the gas-lift system. By this process gas is pumped down a narrow tube to the bottom of the well casing, and a mixture of the gas and oil passes up the casing and out of the well at the upper end on account of its specific gravity being lower than that of the surrounding oil. The system is identical with the air-lift system frequently used for raising water.

In the rotary system of drilling, a turntable is situated at the surface. At the centre of this turntable is a chuck which carries the drill stem ; the drill stem, passing through the centre of the turntable and held by the chuck, is rotated and at the same time lowered into the ground, so that the drilling proceeds very much in the same way as with an ordinary metal drill. Debris is removed from the hole by passing water down the stem and through ducts in the bit. Mud is also pumped down the hole in order to assist in the formation of a suitable surface on the sides of the hole. As the drill goes lower into the ground, extra lengths of tube are fastened to the upper end and fed down through the chuck. Speed of rotation and the downward feed can be controlled by the operators.

In addition to the percussion and rotary systems there are combination systems in which use can be made of both methods of drilling, according as the underground strata vary in their general properties. During recent years there has been a continuous increase in the use of the rotary method at the expense of the older percussion system.

Origin of Petroleum.—The many theories which have been propounded to account for the origin of petroleum may be classified in three main groups, namely, theories of Inorganic Origin, the Terrestrial Vegetation theory, and the Marine Animal theory.

The inorganic theories are based upon the action of water on metallic carbides yielding hydrocarbons. Much experimental evidence has been brought forward in support of these theories, but they have not received the support of geologists nor of petroleum experts.

The production of hydrocarbon oils by the action of heat on peat, lignite, and coal has led to the proposition of many theories of the origin of petroleum. The formation of some petroleum may be accounted for in this way. Geologists, however, point out that coal-fields and oil-fields do not generally occur in such positions as to suggest the probability of oil originating from coal.

The formation of petroleum by the action of heat and pressure on the remains of marine animal life appears to be quite possible, and this is the theory most supported by geologists. Engler considers the action to have taken place in stages by fermentation and hydrolysis, then elimination of water and carbon dioxide, followed by cracking.

There has been a considerable amount of controversy on the subject of the origin of petroleum, but the bulk of expert opinion seems to be in support of the theory of either marine animal or marine vegetable life, or some form of marine life which lies on the border line between the two, such as marine algæ. As the chemical properties of petroleum vary considerably in different fields and also in different levels in the same area, it appears probable that the different types of oil may have been formed in different ways which would to some extent account for the amount of controversy on the subject.

Distribution of Petroleum.—The proved oil-fields are distributed widely throughout the world, and there is every probability of oil existing at very many places which have hitherto remained unexplored.

At the present time, by far the greater portion of the world's production is from the United States of America, but it is questionable whether this state of affairs will continue for many years to come, as other parts of the world which have only been explored during the last decade show immense potential oil supplies, and in course of time the production from sources other than the United States of America will probably increase very appreciably. For the time being, the oil production of the world is best indicated by the percentage of production obtained from the various fields, and figures based on the 1931, 1932, and 1933 production of the world's principal fields are given herewith :—

WORLD CRUDE-OIL PRODUCTION

	1931.		1932.	
	Thousands of Barrels.	Per Cent. of Total.	Thousands of Barrels.	Per Cent. of Total.
United States	781,845	59·9	851,081	62·0
Russia (U.S.S.R.)	155,250	11·9	162,842	11·9
Venezuela	116,300	8·9	116,613	8·5
Roumania	54,160	4·1	49,127	3·6
Persia	49,470	3·8	44,376	3·2
Netherland East Indies	39,000	3·0	35,539	2·6
Mexico	32,805	2·5	33,039	2·4
Colombia	16,417	1·3	18,237	1·3
Argentina	13,000	1·0	11,709	0·9
Trinidad	10,100	0·8	9,744	0·7
Peru	9,900	0·8	10,089	0·7
India, British	8,430	0·7	8,200	0·6
Poland	4,115	0·3	4,662	0·3
Sakhalin, Russian	2,800	0·2	2,734	0·2
British Borneo (Sarawak)	2,400	0·2	3,854	0·3
Egypt	1,790	0·1	2,038	0·1
Japan (inc. Taiwan)	1,630	0·1	2,050	0·2
Germany	1,617	0·1	1,606	0·1
Ecuador	1,595	0·1	1,762	0·1
Canada	1,057	0·2	1,543	0·3
Iraq	910		830	
France	528		520	
Italy	210		124	
Czechoslovakia	190		134	
Bolivia	44		25	
Other countries	60		54	
	1,305,563	100·0	1,372,532	100·0

	1933.	
	Barrels.	Per Cent.
United States—		
Mid-Continent	594,360,000	41·35
California	173,085,000	12·04
Gulf Coast	75,388,000	5·24
Appalachian	32,086,000	2·23
Rocky Mountain	14,736,000	1·03
Others	9,219,000	0·64
	898,874,000	62·53
Europe—		
Russia	153,002,000	10·64
Roumania	55,127,000	3·84
Poland	4,030,000	0·28
Others	3,472,000	0·24
	215,631,000	15·00
South America—		
Venezuela	120,442,000	8·38
Argentina	13,686,000	0·95
Peru	13,259,000	0·92
Colombia	13,158,000	0·92
Trinidad	9,369,000	0·65
Ecuador	1,636,000	0·12
Bolivia	112,000	
	171,662,000	11·94
Asia—		
Persia	54,044,000	3·76
India	8,961,000	0·62
Sakhalin	3,198,000	0·39
Japan	1,423,000	
Iraq	313,000	
Others	600,000	
	68,539,000	4·77
Oceania—		
Dutch East Indies	41,870,000	2·91
British Borneo	4,380,000	0·31
	46,250,000	3·22
North America (ex-United States)—		
Mexico	33,880,000	2·36
Canada	976,000	0·07
	34,856,000	2·43
Africa—		
Egypt	1,570,000	0·11
Others	30,000	
	1,600,000	0·11
World Total	1,437,442,000	...

Chemistry of Crude Petroleum from Various Fields.—Petroleum occurs as a liquid, varying in colour from green to brown and black, and it is often accompanied by large volumes of natural gas, a certain amount of water and soft crystals of paraffin wax. The properties of the crude vary greatly and are dependent both on the strata and the locality from which it is obtained. Though the great proportion of petroleum oils are brown or black, occasionally pale green, pale yellow, and even almost water white (in one or two cases) oils are found. The viscosity may vary from liquids thinner than water to semi-solid bituminous bodies, and the proportion of the various products obtained by the working of the crude is therefore subject to wide variation.

Petroleum oils consist almost entirely of hydrocarbons; apart from the little sand which accompanies the oil from the well, only minute quantities of inorganic substances are present. Oils may contain in some cases as much as 3 to 4 per cent. of combined and free sulphur (Mexican, Texas, Californian, and Venezuelan oils), but the larger part of the world's production contains much less than this, usually between 0·4 per cent. and 1 per cent. Combined oxygen is usually present in small amounts, and nitrogenous compounds in extremely small quantities.

An average ultimate analysis of crude petroleum is as follows (according to Neith) :—

Carbon	84·5 per cent.
Hydrogen . . .	12·5 ,,
Oxygen	2·0 ,,

Crude petroleum usually contains a small quantity of ash, the total ash content rarely exceeding 0·3 per cent. The composition of the ash is surprising, in that a large number of comparatively rare elements are often present in quite appreciable percentages in petroleum ash. It is unusual in oil analysis to make a complete examination of the ash itself, as for the majority of purposes it is sufficient to know simply what the total ash content is. Several analyses of ash have been made, however, by various chemists, and the compilation of results on this subject has been prepared by Thomas,[1] from which it will be found that although iron, aluminium, lime, and silica are usually present in the largest proportion, there are still quite detectable quantities of nickel, lead, tin, cobalt, titanium, gold, copper, and silver. Vanadium is present in quite large quantities in many ashes, in some cases the ash consisting of more than 5 per cent. of vanadium.[2] In certain coal, asphalt, and lignite ashes the vanadium content is even greater than this.

The presence of a large number of elements in a comparatively small quantity in the ash of petroleum has been used as an argument in favour of theories of the marine origin of petroleum, as small quantities of a great variety of metallic salts are present in sea water, and marine animal or marine vegetable life might have absorbed these from the surrounding water and concentrated them.

The main portion of all petroleum oils consists of hydrocarbons,

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[1] *I.P.T.J.*, 1924, 10, p. 216.

[2] Gurwitsch-Moore, "Scientific Principles of Petroleum Technology," 1932, p. 289.

and these hydrocarbons belong to various series, but in many cases hydrocarbons of one particular series predominate in crudes of certain origin. This allows the oils to be classified on a chemical basis, *i.e.*, if the paraffin hydrocarbons predominate, then the oil would be classified as a " paraffin-base " crude.

The nature of the hydrocarbons present in various samples of crude petroleum is very difficult to determine, and hitherto our methods of analysis have been mainly limited to the analysis of the lighter distillates from each particular crude. The lighter hydrocarbons which enter into the composition of the motor spirit fractions can in many cases be separated by fractional distillation. The chemistry of these fractions has to some extent been explored, but the separation of individual hydrocarbons from the higher boiling fractions presents great difficulty. Consequently, very little has been known on this subject, but the greater activity in this field of investigation in the U.S.A. is adding rapidly to our limited knowledge of the individual components of typical crudes. It is generally considered as probable that the types of hydrocarbons present in the higher fractions are to some extent similar to those found in the lower boiling fractions. Gurwitsch has compiled a large amount of information on the subject of the chemistry of petroleum oils.

We find, for instance, that petroleum oils of Pennsylvanian origin consist mainly of paraffin hydrocarbons, and that these oils contain the largest proportion of paraffins of any supply of crude oil at the present time. The assumption that the higher boiling fractions possess the same type of hydrocarbon as the lower boiling fractions is strongly supported by the physical properties of the higher boiling fractions of Pennsylvania crude. Paraffin hydrocarbons possess a low specific gravity for bodies of a given boiling point, together with a comparatively low viscosity, and the lubricating oil fractions prepared from Pennsylvanian oils possess lower specific gravities and lower viscosities for a given distillation range than oils from almost any other source.

Based on similar characteristics, it is known that certain oils of the Russian oil-field, particularly those from Balachany and Bibi-Eibat (both in the neighbourhood of Baku) contain a comparatively high percentage of naphthenes, though, according to Gurwitsch, the naphthene content of the oils from those fields is greater in the lighter fractions and decreases with increasing boiling point of the fractions.

The majority of oils from Texas and California are believed to be of comparatively high naphthene and olefine contents, whilst certain of the oils from Roumania and Borneo are rich in aromatic hydrocarbons in their lower fractions. One cannot, however, make a definite rule for each particular field, as in many cases wells in the same field give oils of entirely different characteristics and different chemical composition; for example, both paraffin-free naphthene-containing oils and also paraffin-containing high-aromatic content, and also low-aromatic content oils are found in close proximity in Roumania. The paraffin-base oils are usually accompanied by solid paraffins or paraffin wax, whereas many crudes containing a lower proportion of paraffin hydrocarbons are almost entirely free from solid paraffins.

A frequently used method for classifying crude oils to-day was developed and is being employed by the U.S. Bureau of Mines. It consists of fractionally distilling the crude at atmospheric and finally under reduced pressure. The fractions are then examined chemically and physically. The lubricating oil fractions are subjected to gravity, viscosity, and pour-point tests, the results of which enable the experimenter to classify the crudes under the headings, Paraffin base, Mixed base, Asphalt base, and Hybrid base.

The chemical composition of the crude oil greatly affects the method by which the oil should be treated in the refinery processes, and also affects the value of the products intended for various purposes. Many oils are rich in asphalt, which is a dark product of high molecular weight which cannot be distilled without undergoing a certain amount of decomposition. The chemical nature of asphalt is as yet unknown, but there is every indication that it is a polymerised product formed by partial oxidation, or by the addition of sulphur to the larger hydrocarbon molecules.

Whilst the specific gravity of a crude will be the greater the less the percentage content of the petrol and kerosene fractions, it may be taken as a general rule that the crude oils of the higher specific gravities are richer in asphalts than those of lower specific gravity. It is also common for the asphalt content to bear a relationship to the sulphur content. Sommer gives the following figures for four American crude oils :—

Crude Oil.	Specific Gravity.	Percentage of Sulphur.	Percentage of Hard Asphalt.
Texas . .	0·8955	0·33	0·10
Mexican . .	0·930	3·27	11·08
Californian .	0·9445	3·3	14·98
Venezuelan .	0·980	7·89	17·0

The asphalts prepared from oils are usually richer in oxygen than the oils from which they are prepared.

The asphalt is not a simple substance but consists of a very complex range of products, and for practical purposes investigators have classified them into hard asphalts, soft asphalts, and resinous substances, according to their solubility in various solvents.

Distillation of Petroleum.—Crude petroleum, being a complex mixture, is not directly suitable for use, nor can it be economically used in the crude state. Therefore, in nearly all cases, the crude oil is first subjected to treatment, by which it is split up into various products which are then more suited or more economical for the various purposes for which they are required.

There are many scientific methods of subdividing petroleum into various portions, such as extraction with various solvents, precipitation by special reagents, etc., but the process which is almost universally used for the treatment of crude oil is the process of distillation. By distillation it is possible to divide the crude oil into products of various boiling points, and as the other properties of oil to a large extent are dependent upon boiling points of the fractions, this method is the most convenient for dividing the crude into products of various types. In practically all cases, therefore, the crude oil is first subjected to fractional distillation, other processes being employed subsequently for purification and improvement of the products.

The mode of procedure used in the distillation of crudes may vary considerably, the variety of apparatus used for the purpose being very great. The basic principles are, however, the same, and one or two illustrations will suffice to explain the process and its development.

In the older distillation process intermittent capacity stills were used, the procedure being as follows : a still, usually of the horizontal cylindrical type, holding about 10,000 gals. of crude oil, is gradually ~~heated by means of~~ fire. The fire may either be applied underneath the still or in fire tubes, as in a Lancashire boiler, the flues afterwards being wrapped round the lower outside portions of the still ; the upper portion of the still is lagged to minimise heat losses. The top of the still is provided with a dome, through which the vapours pass before leaving the still. A condenser is connected with the dome by a vapour pipe of wide diameter, the vapours being condensed in a coil immersed in a water tank.

On charging and heating the still the more volatile portions of the oil are first vaporised, then they pass through the vapour line to the condenser, where they condense, and finally they are collected in a tank. This is allowed to continue until the temperature of the still has risen to such an extent that the nature of the condensate has altered sufficiently to warrant collecting it as a separate fraction. Therefore, at certain predetermined temperatures, the condensate is switched over from one receiving tank to another ; in this way the several fractions are isolated one from the other.

The temperatures at which the various fractions, or " cuts," are collected depend upon market requirements. The main fractions collected are :—

1. Gasoline, or petrol.
2. Kerosene (lamp oil).
3. Gas oil.
4. One or more different qualities of lubricating oil, after which residue from the still may be discharged and used for the preparation of asphalt, cylinder oil, or fuel oil as the nature of the crude and the market requirements necessitate.

The number of fractions collected and the final temperature to which the oil is carried is also decided by the nature of residue desired. In some cases only the petrol and kerosene fractions are collected from the first still, and the distillation of the further fractions carried out in a second battery of stills designed to run at higher temperatures. The distillates prepared in this way generally require redistillation in order to separate them more effectively.

This type of still is known as the intermittent capacity still—"intermittent," because it is worked by filling, working, cooling, and then refilling—so as to distinguish it from the various later types of still which work continuously. The term "capacity" is used to denote that it is a still which holds a considerable volume of oil as distinct from the more modern pipe still, in which a comparatively small but rapid stream of oil is being continuously heated.

Intermittent distillation results in very considerable heat loss due to heating and cooling of the still and setting, a comparatively low throughput, and also high labour and maintenance costs. The various fractions obtained from such a still would not be very effectively separated, and due to poor fractionation a certain amount of spirit would remain in the kerosene fraction and kerosene in the spirit fraction. By fitting intermittent capacity stills with dephlegmating columns, fractionation could be improved, but the operating costs still remain high and the presence of a fractionating column or dephlegmator tends to increase the fuel requirements of the still.

The fractionating or dephlegmating column is a tower through which the vapours have to pass in an upward direction on leaving the still. The tower is usually situated above the still, and the vapours on passing upward have to pass through tortuous passages, that is to say, through baffling or scrubbing devices, which cause the more efficient separation of the bodies of various boiling points. The products condensed in the dephlegmating column pass downwards towards the still, whilst the vapours pass out from the upper end of the column, thence to the condenser.

A considerable improvement on the intermittent capacity still was an arrangement by which a series of such stills were coupled together and then operated by continuous flow; for example, instead of removing petrol and kerosene from an intermittent capacity still, it was found more economical to couple two stills together so that the crude oil passed continuously into one still and overflowed from that still continuously into a second still, and thence overflowed as residue out of the plant. By such an arrangement, if the temperature of the first still were correctly controlled, it could be so arranged that petrol alone was distilled in this vessel, whilst the kerosene was removed in the second vessel. By such a device one employs a continuous inflow of crude, a continuous stream of petrol and kerosene distillates, one from each still, and a continuous outflow of fuel oil. Such an arrangement is known as a continuous capacity still, and until the last few years was the main distillation system employed throughout the petroleum industry.

In many cases, instead of two fractions being separated in two stills, five or six different fractions would be collected from separate stills all operating in series. Fractionating towers could be situated on any of the stills as desired, and steam could be applied if necessary to assist with the removal of the higher boiling distillates. The heat efficiency of such stills was greatly superior to that of the intermittent type of still, and very considerable heat economies could be effected by preheating the incoming oil by passing it through heat interchangers, in which it would become heated by the outgoing hot overhead fractions and residue. For example, petrol vapour passing from the first still to its condenser could be passed through a heat interchanger prior to condensing out with water. This heat interchanger would consist of tubes in an enclosed vessel, and the petrol vapour would pass through the inside of the tubes, whilst the incoming crude would be brought into contact with the outside of the vapour tubes. By this means the petrol vapours would be partially cooled, whilst the incoming crude would receive this heat. The incoming crude could be passed through such heat interchangers in series, finally to be heated to a still higher temperature by the heat of the residual oil.

In such a system the crude oil would be first heated by the petrol vapour, then heated by the kerosene vapour to a higher temperature, after which it might receive further heat from the gas-oil vapour, and finally be heated to a further stage by the heat from the fuel-oil residue from the still. After this point it would pass into the first still, when it would contain sufficient heat to drive off the lighter fraction without the application of external heat. In such a way the first, or petrol still, might be a special vessel separated from the main setting and not supplied with external heating arrangements.

The best designs of continuous capacity stills leave very little to be desired as regards fuel economy. They were, however, comparatively expensive installations to construct; they were not always as efficient in fractionation as might be desired, and the presence of very large volumes of oil in close proximity to open fires made them somewhat more dangerous than the modern tube still.

The principle of the tube still is somewhat different. In this appliance the oil is pumped through a series of tubes which are externally heated in the flues from a furnace. The oil passes through a very large number of tubes in series, and becomes heated to a temperature sufficient to vaporise the heaviest fractions which it is desired to vaporise from the oil. The oil, on passing from the still, enters the dephlegmating column, in which are a number of trays containing bubble caps, whereby it is very effectively fractionated as it passes upward through the column. The effect of the bubble caps is that the up-going vapour is brought into very intimate contact with the down-flowing condensate. Each tray operates at a lower temperature than the tray below it, and gives almost the same effect as a series of distillations.

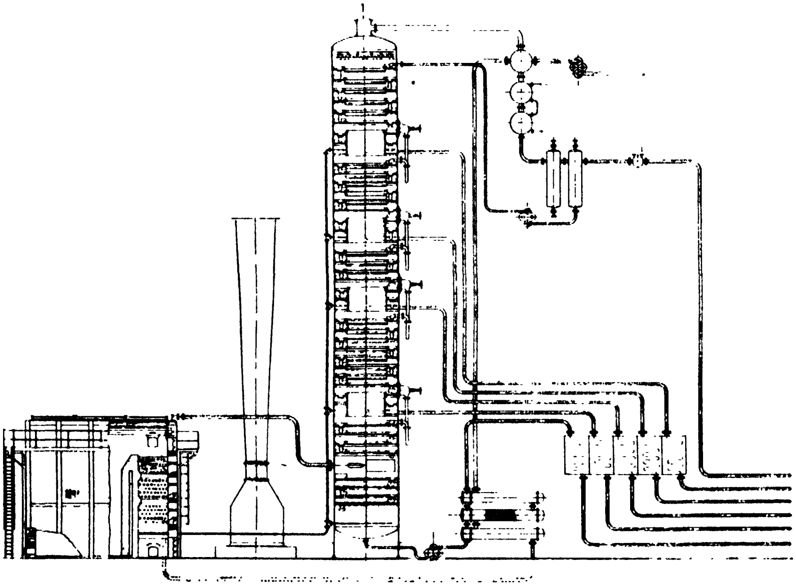

FIG. 1.

The temperature at the top of the column is controlled by means of a water-coil or other cooling means, so that the lightest product can leave the top of the column in a perfectly fractionated state. Intermediate fractions are collected by tappings from the side of the column, whilst the residue is discharged automatically from the base of the column. A modern design of continuous still is shown in Fig. 1.

The tube still described is the type known as the single-flash still, that is to say, the oil is only heated once and then allowed to vaporise. For special work, stills can be so designed that the oil is heated in a tube still, then flashed in a tower where certain fractions are taken off, whilst the residue from the tower is then pumped through a second pipe still, reheated to a higher temperature, and again flashed in a further dephlegmator. Such a system will be known as the two-flash system.

One of the earlier criticisms against the pipe still was on the grounds of heat economy, it being considered that it was undesirable to heat the whole of the oil to the temperature necessary for the vaporisation of the higher fractions, as thereby unnecessary heat was applied to the lower boiling fractions, this, of course, applying to single-flash systems. In practice, however, there is little to be said for this criticism, as the effect of having lighter products present at the time of flashing is to help the removal of the higher boiling products. Thus, in a system in which petrol, kerosene, and gas oil are being removed, the petrol and kerosene vapours, being to some extent superheated on leaving the pipe still, would assist in the volatilisation of the gas-oil fraction, and consequently the maximum temperature necessary for vaporising the gas oil is lower than would be necessary were no petrol or kerosene present.

In a modern tube still the superheating of the lower boiling fractions does not necessitate any considerable loss of heat, as very efficient heat-interchanging systems are employed, and a large proportion of this heat is recovered.

A further criticism which was levelled against tube stills was that the heating of oil in comparatively narrow tubes might result in local overheating, with consequent cracking or charring of the oil, thereby spoiling the products. There is no doubt that in some of the earlier designs of tube stills cracking and carbonising of the oil did take place. This was due to incorrect design of the furnaces, which, instead of being designed to give an even temperate heat for all the tubes, often resulted in excessively high-temperature gases being applied to certain of the tubes, whilst other portions of the tube furnace did comparatively little heating work. This, nowadays, has been overcome by improved design of furnaces, and it is on this account mainly that more modern furnaces are of the up-and-down type, that is to say the main portion of the tubes are heated simply by convection by down-coming gases which have been burnt in a separate combustion chamber. These tubes are known as the convection banks. Other tubes are situated at the upper portion of the combustion space, or in some cases round the walls of the combustion space. These are known as radiation banks, and are heated almost entirely by radiation but not simultaneously by radiation and convection, as was the case in some of the earlier designs where all the tubes were situated over the combustion space.

In the modern tube furnace the oil is passed through the tubes at a comparatively high velocity so as to create a sufficiently turbulent flow to prevent local overheating. Another precaution is sometimes taken in that the temperatures of the combustion gases are considerably reduced by admixture of flue gas, which has the effect of reducing the gas temperature without bringing about any loss in efficiency. This system, which is known as gas recirculation, consists of drawing gases by means of a fan or injector from the base of the chimney and passing them into the combustion space. A large quantity of gas, from one to three times the total quantity of combustion gas, is thereby recirculated, which brings about a reduction of the maximum flame temperature, but at the same time an increase of the total quantity of gas passing the tubes. The increase in the rate of gas flow results in a somewhat higher temperature at the base of the chimney, therefore the total effect is that instead of having a very high temperature gradient between the combustion zone and the base of the chimney, one obtains a comparatively small temperature range and a rapid flow of gas. When furnaces are not fitted with means for recirculation, it is sometimes necessary to burn a considerable quantity of excess air in order to prevent the flame temperature becoming excessively high; this large quantity of excess air means a larger quantity of heat loss through the chimney.

Where recirculation is used, the fuel can be burnt with a smaller quantity of air, and, consequently, the total volume of gas leaving the chimney is reduced, so that in spite of the stack temperature being somewhat higher, the total heat loss is not so great as would be the case if no recirculation were employed.

Other devices besides that of recirculation have been used to prevent violent local overheating in the neighbourhood of the combustion zone. Special furnaces with carborundum arches have been used for this purpose, such a furnace employing a special high temperature zone which is shaded from the main part of the combustion chamber by an arch made of carborundum, a substance which is capable of withstanding very high temperatures.

The tendency at the time of writing is to employ single-flash systems when operating stills at atmospheric pressure, but when lubricating distillates are required it is common practice to make a combined distillation unit containing both an atmospheric and a vacuum section, in which case the preheated oil is flashed in a tower, when petrol can be removed simply by the temperature obtained by preheating. The depetrolised residue is then passed, firstly through a tube still, thence to the main atmospheric column where white spirit, kerosene, and gas oil are withdrawn, and afterwards the bottoms from this tower, whilst still hot, are drawn off, reheated through a smaller pipe still, and raised to a temperature sufficient to distil off the lubricating fractions, when the reheated residue is passed into a dephlegmator operating under reduced pressure. Side streams may be taken from the vacuum tower in a similar manner to the side streams collected from atmospheric towers, but they will have to discharge into vacuum receivers from whence they have to be pumped against the atmospheric pressure outside the system.

The actual construction of fractionating towers is similar on atmospheric stills and on cracking plants, and only slightly different on the majority of vacuum towers. The simplest forms of fractionating tower are usually found on cracking plants where there are no intermediate cuts, and the operation of such a tower is described briefly in the section on "Cracking."

When towers are required to give intermediate products in addition to the residue collected at the bottom of the overhead distillate, these "side streams" are drawn off from suitable positions inside the tower. It is not sufficient simply to draw off the condensate from one particular tray, as it must be borne in mind that condensate in a fractionating tower is continuously in contact with lighter products passing up the tower, although it may be free from heavier products which may have condensed before reaching that particular tray.

The condensate further consists of a range of products of approximately the correct boiling point, saturated with a small quantity of lighter products, and in order to remove the latter it is necessary to blow steam through the condensate whilst it is in the hot state. This latter procedure is known as "stripping," and stripping may be carried out either inside the tower in a "stripper section" or outside the tower in an "external stripper." With internal strippers the condensate falls into a trough where it is maintained at a constant level whilst steam is blown through it, and at the same time the stripped condensate is withdrawn from the tower through a control valve which is adjusted to draw off the requisite quantity. The exact quantity drawn off must be controlled with great care. In the external stripper the condensate from one of the trays is run to a small tower situated outside the column. The oil entering this small stripping tower descends through three or four plates provided with bubble caps, where it is subjected to contact with a rising current of steam. The distillate passes from this stripper, and after being fractionated through three or four more trays, is passed back to the column at a level one or two trays higher than the level from which it was withdrawn, whilst the stripped distillate is withdrawn from the base of the external stripping tower.

THE THEORY OF DISTILLATION.—The process of distillation consists of separating the various products contained in the oil by taking advantage of their different boiling points. When a mixed body, such as petroleum, is heated, those substances which are of lower boiling point are vaporised first at a comparatively low temperature and can therefore be removed from the remainder of the oil and collected separately. By increasing the temperature, various products of various boiling points can be removed in a similar manner. Volatile bodies exert a pressure at temperatures much below their boiling points. This pressure increases with rise of temperature, and what we know as the boiling point is the temperature at which the pressure exerted by the vapours of the liquid is equal to the atmospheric pressure. At this temperature, conversion of the liquid to the vapour form becomes rapid and the phenomena is known as "boiling."

A pure chemical substance has a definite boiling point and is entirely distilled at this boiling point, but complex mixtures such as occur in the petroleum industry do not allow many of the individual substances being separated at their different boiling points ; it is possible, nevertheless, to separate the original complex mixture present in the crude into various "fractions," each of which contains bodies of roughly similar characteristics, and the mixtures are consequently less complex than the original body. As a result, the fraction, though not of a definite boiling point, possesses a comparatively narrow distillation range, that is to say, it commences to boil and is completely distilled over a narrower temperature range than was the case with the original crude. Mixtures usually distil at a temperature below the mean value of the boiling points of the various individual bodies present.

Vacuum Distillation.—As the boiling point is the temperature at which the vapour pressure is equal to one atmosphere in a still operating at atmospheric pressure, we find that if the pressure is decreased or increased over atmospheric pressure, the boiling point is reduced or increased to the temperature at which the vapour pressure of the liquid corresponds with the conditions in the distillation apparatus. For example, a liquid boiling at 80° C. at normal pressure would require this temperature in order to commence distillation in a still operating at atmospheric pressure. If, however, the still is worked under partial pressure, for example at a total pressure of 250 mm. of mercury, instead of the atmospheric pressure of 760 mm. of mercury the temperature of distillation would be reduced from 81° to the temperature of 45° C. at which this liquid possesses a vapour pressure of 250 mm. The same liquid possesses a vapour pressure of 100 mm. at a temperature of 23° C., therefore, if the distillation is carried out at a total pressure of 100 mm. instead of atmospheric pressure, the distillation temperature will be 23° C.

As certain petroleum fractions, particularly those of high boiling point such as the lubricating fractions, are liable to undergo decomposition at higher temperatures, it is common practice to distil them under a reduced pressure to overcome the necessity to use the high temperatures which might bring about decomposition and consequent deterioration of the marketing qualities of the products.

Steam Distillation.—When a distillation is carried out in the presence of vapour of another substance, the distillation takes place at a temperature lower than the boiling point of the higher boiling product. In this way, by using a product of comparatively low boiling point to provide the carrying vapour, the distillation can be effected at a lower temperature than would be necessary by direct distillation without a " carry " vapour. The vapour almost invariably used in practice is steam. Steam is particularly suited for this purpose in that it is cheap, always available at refineries, and also because the low molecular weight of water gives a low density vapour, that is to say, a large volume of vapour for a given weight of water. It is also particularly suited because the water is insoluble in the oil, and consequently can be easily separated after condensation.

Suppose we have a liquid which gives a vapour pressure of one-tenth of one atmosphere at a temperature of 200° C., we find that by distilling in a current of steam in which a very intimate contact is maintained between the steam and the oil, the mixed steam-oil vapour would consist of nine-tenths by volume of steam and one-tenth by volume of oil. These volumes apply to the vapour phase, but as the density of oil vapour is very much higher than that of water vapour, and the specific gravity of the condensed oil is lower than that of the condensed water, on calculation we find that when this vapour is condensed the proportion of oil to the water is very much higher than when they are in the vapour state.

Suppose the oil has a mean molecular weight of 180, then the density of its vapour will be $\frac{180}{18}$ times that of water, as the molecular weight of water is 18, that is to say, the vapour will be ten times as dense as the steam. There are, however, nine parts of steam vapour to every one part of oil vapour. Therefore, on condensation, the weight of the various products present in the condensate will be $\frac{180}{18} \times \frac{10}{90} = \frac{1{\cdot}1}{1}$, therefore the mixture will contain slightly more oil by weight than water. As the density of the oil is somewhat lighter than that of water, the proportion by volume of liquid oil will be still higher. Such distillation will have been effected at the temperature which corresponded to a vapour pressure of 76 mm., that is to say, one-tenth of one atmosphere, and consequently a much lower temperature than would have been necessary on a distillation carried out without the use of steam. In practice the quantity of steam used is somewhat more than the theoretical calculation, but nevertheless the use of steam for the distillation of the higher boiling petroleum products effects great economy in working and improvement in the quality of the products.

Vacuum Steam Distillation.—It is possible to effect a still greater reduction in temperature of distillation by the combined use of vacuum and steam. There are, however, certain practical difficulties encountered in the operation of stills under combined vacuum and steam distillation. The present tendency in the distillation of such products, which are particularly liable to decomposition, is to employ vacuum only and to maintain a very high vacuum on the still. The employment of a very high vacuum effects a very great reduction in the boiling point of the products, as can be observed from an examination of vapour-pressure curves.

Distillates of Petroleum.—We have considered the methods by which separation of the various products of petroleum are effected. The actual nature of the separate fractions collected depends very largely on the type of crude undergoing distillation. Crudes vary to such a great extent that it is impossible to make any regular rule ; some crudes contain no petrol, others contain large proportions. Some may contain as much as 60 or 70 per cent. of bitumen, a product which is not capable of undergoing distillation, whilst others are practically free from bitumen. The quality of intermediate cuts is also affected by the nature of the crude. Crudes of extremely high sulphur content cannot be economically worked for kerosene, as kerosene of high sulphur content cannot be marketed as an illuminant.

The main fractions collected from light and medium gravity crudes are, however, as follows :—

Extremely low boiling fractions are specially collected in certain cases for use as a blending agent for mixing with spirit and for one or two industrial purposes. These products commence to distil from the crude at a temperature only slightly over that of the atmosphere.

The collection of fractions of motor spirit commence from a temperature slightly over atmospheric and may continue up to a temperature as high as 220° C., according to the quality of spirit it is desired to prepare. Spirit for aviation purposes requires to be very volatile in order to evaporate rapidly at extremely low temperatures ; therefore, where aviation spirit is being made, special portions of the main petrol fractions are collected, usually with an end point in the neighbourhood of 150° C.

Motor spirit used for commercial purposes and for private cars usually covers a distillation range of between 30° and 200° C., the heaviest product having an end point of about 220° C. Special qualities such as No. 1 spirits used in England have end points in the neighbourhood of 180° to 190° C. In the earlier days of the petroleum refining industry, the motor spirit fraction was collected at lower temperatures than is the practice to-day, as carburetters at that date were incapable of dealing with high boiling-point fractions. For many years the petrol cut was effected at 150° C., and the next large fraction was kerosene which covered the range of 150° to 300° C. Increased demand and modification of carburetter design has brought the end point of the petrol fraction up to 220° C., and, as the kerosene market demands a much smaller proportion of the crude now produced, it has become the practice to cut down this fraction very considerably by increasing the commencement of the cut from 150° to 200° C., and in many cases decreasing the end of the cut from 300° to 275° C.

There is a certain demand for fractions intermediate between the petrol and the kerosene fractions, mainly for white spirit, a substance which is used as a turpentine substitute in the paint industry. The distillation range of white spirit varies according to industrial requirements, and a large number of special narrow boiling fractions are collected for industrial solvents. These may be selected from any portion of the distillate that falls within the petrol distillation range.

With heavy crudes the distillation is often stopped at the end of the kerosene fraction and the residue used for fuel oil, the fraction which follows the kerosene, namely, the gas-oil fraction, being left in the residue in order to keep the residue fluid. With medium and light crudes the gas-oil fraction is usually extracted.

The gas-oil fraction has a very variable distillation range. In crudes which are comparatively free from sulphur the kerosene is generally cut at temperatures between 275° and 300° C., and the collection of the gas oil commences at the latter point and is carried on to a temperature in the region of 350° C. Frequently the finishing temperature of the gas-oil cut is decided by the considerations of the flash point required on the following fractions.

Where crudes are high in sulphur content, it is frequently uneconomical to attempt to make kerosene on account of the poor properties of the sulphur-containing distillate, and in such cases it is common practice to run the whole of the kerosene fraction into the gas oil. This gives a much more mobile gas oil, and one particularly suited for internal-combustion engine use. The gas-oil fraction is generally sold as a crude distillate, although in a few cases it is washed for the removal of naphthenic acids. Special narrow cuts are occasionally made within the gas-oil fraction, and these are generally sold as special burning oils, mineral colza, etc.

As these are required for use in lamps, they require acid washing before they are suitable for the market.

Gas oils containing a small percentage of lubricating oil are often preferred by Diesel engine users, as the lubricating oil serves a purpose in keeping the fuel pump lubricated and prevents the tendency to bind or score, which is encountered when light gas oils or kerosenes are used as fuel.

After the removal of the gas-oil fraction the residue may be an asphalt, if the original crude is of high asphalt content such as Mexican or Venezuelan crude. The residue from lighter crudes may be sold as fuel, or if the crude is of exceptionally good quality this may be worked further for the manufacture of lubricating oils. It is not usual to work up lubricating oils in the same still as the preliminary distillation, although it is common practice to remove the hot residue from the first still, which works at atmospheric pressure, and pass through a further heating unit and into a vacuum tower. There are a variety of methods available for working up such residues into lubricating oils. In some cases the residue is subjected to vacuum distillation, when a range of distillate lubricating oils may be prepared. These oils will consist of thin oils of the spindle-oil class, engine oils, and perhaps distillate bright stocks, leaving a hard pitch or asphalt as residue. In other cases the residue is subjected to solvent treatment, whereby the asphaltic material is dissolved out, leaving a high grade master lubricant, which may undergo viscosity adjustment by a further distillation process. In such cases, light distillate lubricating oils would be taken from the master lubricant, and a residue of long residuum (about motor oil viscosity) or of bright stock (high-viscosity lubricant) would remain. A fairly common procedure has been to treat the residuum, after the removal of gas oil, with sulphuric acid, whereby the asphalt is precipitated, and then make a master lubricant by contact clay treatment. In this case the master lubricant may be subjected to further distillation *in vacuo* in order to split it up into viscosities suitable for the market.

When crudes contain paraffin wax, the major portion of this body usually occurs either at the end of the gas-oil fraction and in the light lubricants, or throughout the whole of the residue. Such residue after distillation or acid treatment may be dewaxed either by cold settling or centrifugal processes. The gas-oil fractions are used mainly for gas-making and as fuel for heavy-oil engines ; about half of the lubricating oil is employed for automobile lubricants, the remainder for a very large variety of industrial purposes, whilst the asphalt is used mainly for road-making. Smaller quantities of asphalt are used for insulation, manufacture of roofing felts, varnish-making, and a great variety of other industrial purposes.

CRACKING.—Many years ago it was observed by petroleum refiners, when oil was distilled in intermittent capacity stills, the upper surface of which was exposed to the cold air, that a larger proportion of lighter products, *i.e.*, petrol and kerosene, was obtained from a given amount of crude than was obtainable when properly insulated stills were employed. It was found that this phenomenon was produced by the condensation of the distillate vapours on the upper portion of the still. The condensate dropped back into the hot residue when some form of decomposition took place with a formation of products of lower boiling point.

Thompson and Young made classic researches in 1871 into the action of combined heat and pressure on shale oils, and the cracking of petroleum may be said to be based on the results of their investigations. In 1889 Redwood and Dewar patented an apparatus for distilling and condensing oil under pressure, thus preventing the escape of gases which were soluble in the cracked distillate. At the time of this patent there was little incentive to employ a process for converting high boiling products into low boiling products as there was no demand for volatile spirits, and the only object in employing the cracking process was to increase the yield of kerosene at the expense of lubricants or fuel oil.

With the advent of the automobile, the increasing demand for the lighter petroleum fractions was met by increased production of crude, and during times of partial shortage the increase in the yield of motor spirit was obtained by the widening of the distillation limits. With the rapid increase in the demand for fuel for automobiles, a comparative scarcity of petrol occurred, and the price of petrol rose above that of kerosene and considerably exceeded that of gas oil and fuel oils. This gave an incentive to the development of the cracking process.

The earlier cracking processes were mainly of the Burton type (Fig. 2), which was practically the same system as that advocated by Redwood and Dewar, the oil being heated under pressure in capacity stills. The technique of cracking has gone through very considerable changes during the last twenty years ; whereas the old cracking plant was practically a modified still, the cracking plant of to-day is a highly specialised installation and gives a very efficient conversion.

The disadvantages of cracking in capacity vessels such as horizontal cylindrical stills is that the oil is brought into contact with heated still walls, where the movement of the oil film is not very rapid. This brings about a superheated layer on the wall of the still, which may considerably exceed the optimum cracking temperature, and may result in the formation of coke. Such conditions also result in the oil being subjected to a high temperature for a period which is longer than that which gives maximum efficiency in the cracking process. There is no necessity to go through the history of the various improvements and modifications which have been made during recent years in cracking-plant design, but a description of a modern plant will give a fairly good idea of the process at present employed.

In a modern liquid-phase plant the oil is heated in a pipe still; the temperature of the pipe and the throughput of the still is such that a high rate of flow is maintained throughout the pipe. This prevents local overheating, which is liable to produce coke deposits in the tubes. The still is maintained at a high pressure in order to keep both the raw material and the products of cracking as far as possible in the liquid state. In actual practice there is no doubt that a certain amount of gas is formed in the still, so that although we refer to the process as liquid-phase cracking, actually the conditions which exist are such that the mixture at the outlet of the still is partially liquid and partially gaseous.

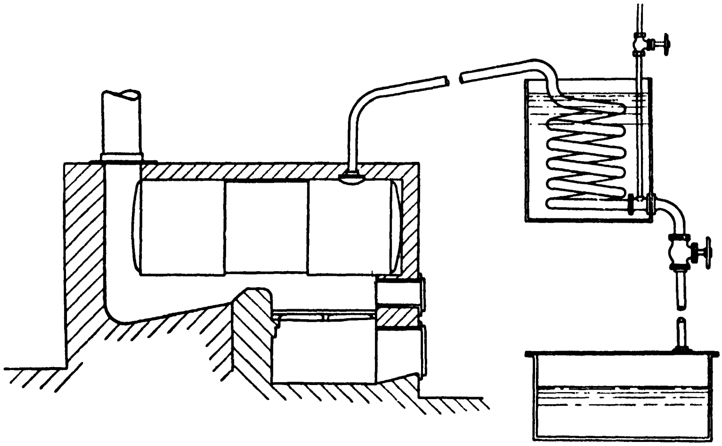

DIAGRAM OF THE BURTON APPARATUS FOR CRACKING HEAVY OILS.

FIG. 2.

In some processes after leaving the still the oil passes through a reaction chamber, where it is allowed to stand at practically the same temperature as the still outlet temperature for a certain period of time, so as to allow the reaction to take place. The presence or absence of the reaction chamber affects the design of the still itself, as when a reaction chamber is omitted it is usual so to design the still that the products approach cracking temperature some time before leaving the still, and a portion of the still tubes serve the purpose of maintaining the oil at the reaction temperature for a desired period so as to allow the reaction to take place.

In a tube still fitted with reaction chamber, the oil attains maximum temperature immediately prior to its leaving the still and passing along the transfer line to the reaction chamber. The pressure within the tube still may vary between a minimum of about 200 lbs. per sq. in. up to a maximum of about 900 lbs. per sq. in. There is usually a considerable drop in pressure due to friction throughout the length of the still, so that the pump pressure may be 50 lbs. or more over the transfer line pressure.

The furnaces used are very much the same as those used for tube-still distillation (in which the combustion chamber is separated from the main part of the heating tubes). A certain number of radiation tubes are fixed on the upper portion of the sides of the combustion chamber, a large portion of the heating being done in the convection banks where the gases are passing in a downward direction. The path of the oil through the heater varies according to the design of furnace. In some cases it is counter-current to the gas, that is to say, the hottest oil comes into contact with the hottest gases. In many cracking plants it is found preferable to avoid the hottest oil coming into contact with the hottest gases, as this might produce undesirable overheating. In such cases the cooler oil is used to reduce the temperature of the hot flue gases, after which the partially heated oil is passed counter-currentwise against the partially cooled gas.

The advisability of employing a reaction chamber is a matter of opinion. Dubbs and Cross processes employ reaction chambers, whereas the Winkler-Koch process dispenses with a reaction chamber. the transfer line being coupled directly to the evaporator. The high-pressure reaction chamber used in the Cross process is a large steel forging which is heavily lagged to prevent loss of heat. The result is that only a small temperature difference exists between the inlet and outlet of the reaction chamber. The pressure in the reaction chamber in the Cross process is in the neighbourhood of 800 lbs. per sq. in. The Dubbs process utilises a lower pressure and employs a larger reaction chamber made of riveted or welded heavy section plates. With the large reaction chamber employed by Dubbs it is possible to vary the process so as to produce either a residue of fuel oil or a residue of coke as may be considered most desirable for market requirements. The Cross process makes comparatively little coke, the main portion of uncrackable material leaving the evaporator in the form of fuel oil. In the Winkler-Koch process very small amounts of coke are formed, and coke-free oil is delivered from the evaporator.

After the reaction chamber, the oil passes through a control valve where its pressure is reduced to approximately that required for the dephlegmating system. For example, in the Cross process the pressure will be dropped from about 800 lbs. down to about 45 lbs. per sq. in. In the evaporator the bulk of the oil is vaporised, whilst the portion which is not vaporised at the prevailing temperature condenses out and is withdrawn by an automatic dumping valve operated in such a way as to maintain a constant level. The temperature of the evaporator can be controlled by pumping in cold oil to reduce it as desired. The product separating out in the evaporator is usually employed as a furnace oil, that is to say, for external combustion, and is not allowed to re-enter the circuit to undergo further cracking.

In the upper portions of the evaporator are a series of baffles, or trays, which effect a partial fractionation and removal of suspended oil particles from the issuing vapours. The vapour from the evaporator enters the dephlegmating column at a point about one-third of the way up the column. The dephlegmating column is considerably larger than the evaporator and varies with different types of unit, being generally from 50 to 70 ft. high and from 6 to 10 ft. in diameter. The bottom of the dephlegmator contains condensate which is maintained at a constant level by an automatic dumping valve. Above the liquid level are a few dephlegmator trays fitted with bubble caps which have the effect of ensuring more complete removal of the lower boiling products from the condensate. Above the vapour inlet are bubble-cap trays, from 12 to 30 in. apart, filling up the rest of the column except for those parts of the column taken up by heat interchanging or cooling devices. The bubble-cap trays are cast-iron or pressed steel plates which cross the entire diameter of the column. The up-going vapours pass through holes in the trays, and above these holes are situated inverted cups or bells partially submerged in the condensate. The result is that the up-going vapour has to emerge past the edge of the cups and thereby comes into contact with the condensate. The trays are fitted with pipes which allow the condensate to pass down from one tray to the one beneath. The upper edge of this pipe is somewhat above the tray level and thereby controls the amount of condensate held by the tray. The lower end of the pipe is submerged in the condensate of the tray beneath.

The effect of such trays carrying a large number of bubble caps is to produce a sharp fractionation of the products which leave the top and bottom of the column. At the top of the dephlegmator are situated coils by which the outgoing vapour is cooled so as to bring it nearer to the actual temperature required for the control of the quality of spirit emerging from the column. These coils contain incoming charging stock passing to the plant, and are therefore heat interchangers. A final and more delicate control of the top temperature of the dephlegmator may be obtained by a smaller water-coil or by pumping cold gasoline into the top of the tower. In some dephlegmators a heat interchanging coil is used in the middle of the column ; this removes some of the heat from the benzine at this point and also helps to heat up the ingoing charging stock on its way to the furnace. The temperature maintained at the top of the dephlegmator is such that the spirit made has the desired end point. This is controlled automatically.

The vapour passing from the dephlegmator is then condensed and passes through a gas separator, wherein permanent gas generated by the cracking process is separated from the cracked spirit. As the gas leaving the separator is saturated with the lighter products of the spirit, it is usual to strip this gas by bringing it into contact with an absorbing oil. In cracking plants it is common practice to use the charging stock as an absorption material for stripping the gas. The motor spirit so recovered, therefore, goes back into the plant and is recovered on the next cycle.

The condensate formed in the dephlegmator is purely a distillate, as it has passed from the evaporator in the form of vapour. It is therefore a comparatively clean product, and can be recycled through the plant. As it is hot when it emerges from the dephlegmator, it is common practice to recycle this by means of a hot oil pump directly through the tube still. In some plants used for cracking crude or residual oils, the raw material introduced into the plant is not passed through the cracking still when first entering, but is passed through another preliminary still, whereby it is raised to a temperature less than that required for actual cracking. From there it is discharged into the evaporator, when any bituminous or exceedingly heavy material separates out into the fuel oil, whilst distillates pass to the dephlegmator, where any straight-run benzine present in the original material emerges together with the cracked spirit in the form of a blend and the heavier distillates are condensed and join the recycle stock. This circuit has a distinct advantage, in that the heavy asphaltic materials which are liable to produce coke in the cracking furnace are removed within the circuit of the plant and only pure distillates enter the cracking still itself.

The yields obtainable from cracking plants vary considerably, dependent on the raw material used as charging stock. When a distillate oil such as gas oil is employed, the yield by volume is usually from 60 to 70 per cent. upon the raw material charged. The weight yield of gas is from 4 to 5 per cent. ; the coke yield is extremely small, and the remainder is fuel oil. These figures are based on the assumption that the recycle stock is recycled to infinity. This high crack ratio is not employed in a single operation, but is obtained by the continuous recycling of the condensate from the dephlegmator. The actual crack obtained on a single cycle is usually from 15 to 40 per cent. When residual oils are used and cracked to form fuel oil and gasoline, the yield is of course smaller, dependent on the amount of heavy bituminous material present in the fuel oil. Highly sulphurous raw materials have generally been found to give difficulty in cracking on account of their corroding the plant, and also because the quality of the gasoline produced is not satisfactory.

VAPOUR-PHASE CRACKING.—Some of the earliest attempts to crack petroleum were carried out in the vapour phase. The obvious advantage of using vapour phase is that the plant can be designed to operate at low pressures, thus overcoming many of the engineering difficulties which have to be dealt with in liquid-phase cracking.

Vapour-phase cracking differs from liquid-phase cracking in that in the former only the vapours of the oil are subjected to the cracking process. They are heated to cracking temperature whilst in the vapour state, whereas in liquid-phase cracking the whole body of the oil is treated at cracking temperature, as the pressure employed is such as to maintain an even temperature throughout the oil as it passes through the tubes when it is in the liquid state. Liquids conduct heat better than vapours, and the possibility of local overheating on the tubes is much less when liquid is being heated than when the material within the tubes is in a gaseous state. As a result of this it is generally found that the decomposition on cracking which takes place in liquid-phase plants is not so violent as that produced in vapour-phase units ; consequently liquid-phase cracked spirit contains a lower proportion of unsaturated hydrocarbons than is the case with the vapour-phase cracked product, and also the amount of gas generated by the cracking reaction is lower when operating in the liquid phase.

At the time of writing the bulk of cracking plants operate on liquid phase, but a considerable number of vapour-phase plants have been erected, and it is generally considered that although the liquid-phase plants are more economical for the production of petrol and usually yield a larger quantity of cracked spirit from a given quantity of raw material, there are special conditions under which the vapour-phase process has an advantage. The advantages possessed by the vapour-phase process are, firstly, that the product has a very high anti-knock property and, consequently, can often be sold at a premium as a blending stock for raising the anti-knock properties of inferior grade spirit. Secondly, although the generation of gas in most circumstances may be considered as a loss to the process, in some circumstances this gas may be of considerable use for local supply or it may be used as raw material for chemical synthesis, such as the preparation of alcohol, glycol, organic chlorides, and other organic compounds.

During recent years there has also been a new development, in that the gas produced from cracking plants can now be polymerised to form volatile liquid hydrocarbons by the use of special polymerising plant. The product so obtained is of an extraordinarily high anti-knock value, and therefore has a ready outlet as a blending agent for the manufacture of premium anti-knock spirit. This has to a large extent overcome the earlier objection to vapour-phase cracking, namely, that the gas losses were so high.

Reforming Processes.—As motor spirit obtained by cracking has a higher anti-knock value than the straight-run product, it has recently become the practice to subject straight-run spirit to heat treatment whereby its constitution is changed so as to produce a product of higher octane number. This process is in the nature of a cracking process, and the plants are usually referred to as "reforming" plants.

REFINING OF PETROLEUM PRODUCTS

Distillation separates out the constituents of petroleum according to their boiling points. Even after the most careful fractionation there are small quantities of undesirable impurities present in the fractions. Some of these bodies are soluble in acid, some are soluble in caustic soda, and a very large proportion of them are affected by the sulphonating and dehydrating action of strong sulphuric acid. Some of these bodies are of higher molecular weight than the remainder of the fraction in which they are present and have different surface-tension characteristics, which allows them to be removed by absorption agents such as fuller's earth. The impurities present consist mainly of sulphur derivatives such as mercaptans and thioethers, of unsaturated bodies which are not desired in the final product such as diolefines, of nitrogen-containing bodies, and of certain hydroxy compounds.

By far the most frequently used refining agent is sulphuric acid. Sulphuric acid may be used either in the very dilute state or at a strength of over 95 per cent. In the dilute state, it acts as an acid and absorbs basic materials such as pyridine or organic amines. The action of dilute acid is not very important, and it is comparatively rarely used for refining.

(The action of strong sulphuric acid on petroleum fractions is very complex.) It undoubtedly acts as a sulphonating agent, thus removing aromatic compounds and olefines by creating sulphonic acids which are extracted from the oil in the form of a tar. It also produces polymerisation of certain unstable bodies, precipitating them also in the form of a tar. In addition to these reactions, it also acts as an acid in removing basic bodies.

The usual procedure in sulphuric acid treatment of a distillate is to agitate the distillate with from 1 to 5 per cent. of strong sulphuric acid. The temperature is usually about normal, but with certain viscous oils the temperature of agitation may be raised with advantage. After agitation the mixture is allowed to settle, when the sulphuric acid together with tarry bodies separate into a lower layer whilst the refined oil forms the upper layer. These two layers are run off separately, the acid tar generally being considered a waste product, whilst the refined oil is passed on to another plant where it is washed with a dilute caustic soda solution, which has the effect of removing the sulphuric acid and of removing acidic bodies still remaining in the oil. After being washed with dilute caustic soda, the product may be washed with water and in many cases redistilled.

This procedure may be taken as standard refinery practice of lighter bodies. Although the writer has described this operation as a batch process, it is often carried out in continuous plants in which a small stream of acid is mixed with a larger stream of the crude distillate, then agitated, the agitated mixture passing over to settling vessels from which the upper and lower layers are continuously removed. Agitation may be effected mechanically, or the necessary intimacy of contact may be brought about by passing the acid-oil mixture through a tube filled with pebbles or other material which breaks up the stream. Modern continuous acid-treating plants frequently employ centrifuges as a means of separating the acid tar from the oil. In such systems continuous mechanical agitators are used to mix the oil and the acid, after which a small tank is employed to give the mixture a certain period during which the reaction can take place. The capacity of this vessel is usually variable by altering the overflow level. The mixture is then passed to a centrifuge which gives a particularly effective separation between the tar and the oil. Such processes are claimed to be very advantageous when employed on pressure distillate (crude cracked petrol) as by controlling the period of reaction with accuracy the polymerisation is reduced. These processes are also claimed to be advantageous in lubricating oil treatments, where the separation of tar from oil presents difficulties on account of the viscosity.

Continuous operation may be applied to the caustic soda and water washers, as well as the acid washers. It is common practice to give four washes, namely, strong acid, water, caustic soda, and water. One effect of acid treatment on the lighter distillates, such as the petrol fraction, is to leave in the petrol certain hydrocarbons which possess a higher boiling point than those originally present in the crude product, that is to say, the acid not only removes certain bodies but it also generates high boiling products by polymerisation. Consequently, if a crude spirit fraction of a given end point is refined with acid and soda, the end point of the product after refining is considerably higher than it was before refining. These high boiling bodies would be undesirable constituents of the finished product, and are therefore usually removed by redistillation.

THE ACTION OF SULPHURIC ACID ON RESIDUAL OILS.—Sulphuric acid may be used as a reagent for the treatment of crude oil or residual oil. In this case the method of application is similar to that employed in the treating of distillates, although there is every reason to believe that the chemistry of the reaction is somewhat different.

Acid treatment of residual oils is only employed for the manufacture of residual lubricants. Crude oil contains certain lubricating oils which have extremely high boiling points, and which are liable to decomposition if it is attempted to distil them as overhead products. Even when distilled under high vacuum, they still undergo a certain amount of change, which results in loss of viscosity and deterioration in some of their other physical characteristics. These detrimental products can, however, be recovered by treating the residual oil with sulphuric acid. By this means bituminous bodies present in the original crude and concentrated in the residue may be sulphonated or polymerised by the action of acid, when they will be precipitated as a tar, leaving behind a solution of lubricating oil, gas oil, or other such bodies as have been left in the residue from the distillation. This residue, if it can then be further distilled so as to remove gas oil and other comparatively low boiling point products which are unsuitable for lubrication, leaves behind a residue which will be known as a long residuum or a cylinder stock. In this process it is necessary to remove the remains of the acid tar and any free sulphuric acid after the acid treatment, therefore it is possible to use caustic soda in the same way as in distillate treatment.

Contact Clay Process.—During recent years it has been found that the contact clay process is more effective and economical than an alkali wash. When a heavy oil after acid treatment is washed with water or dilute soda solution, a certain amount of the acid tar which has remained in the oil in the form of fine particles (known in the industry as a " pepper ") is decomposed by the action of water and goes into a tar which is insoluble in the water but soluble in the oil. This black tarry body, therefore, redissolves in the oil, with the result that there is a distinct darkening of the colour of the product when the acid-washed oil is mixed with an aqueous solution. This fall in colour is known to refiners as the " throw-back," and causes a serious deterioration in the product. The " throw-back " can be minimised by very complete settling of the tar from the oil by which the amount of pepper is reduced to a minimum. Under no condition, however, is the finished colour obtainable by alkali washes so good as that obtainable by the contact clay process.

In the contact clay process the oil, after acid treatment, is mixed with a comparatively small quantity, usually from 2 to 8 per cent., of very finely divided absorption clay. The mixture is agitated and heated to a temperature of from 60° to 150° C., depending on the nature of the oil. The result is that the acid tar is absorbed by the clay and completely removed. Further, sulphuric acid is also completely removed, and in addition to this the clay removes certain organic colouring matters which still remain in the oil. As this process completely dispenses with water washing, no throw-back can possibly take place, and the finished product is much superior to that obtainable by the older process. After the heating treatment, the mixed oil and clay are passed through a filter press, where the clay is removed. The oil is a finished product without any further refining treatment being necessary.

The clays used are very often acid in character, but in spite of this, due to their strong absorbent action, they are capable of removing sulphuric acid and leaving a perfectly neutral oil entirely free from sulphuric acid. A modification of the contact clay process is the one known as Prutzman's Process, in which, instead of using the clay in the form of powder it is used in the form of a slurry of water and clay. This substance is emulsified with residual oil after acid treatment and heated to a temperature over that required to drive off the moisture. It is considered that by this process the clay, being burst open by the generation of steam within the clay particles, becomes extremely absorbent and reacts more effectively than when it is used in the powdered state. These processes are mainly used for the preparation of lubricating oils.

Another method of refining is to treat oils, either residues or distillates, directly in the liquid state with fuller's earth or floridin. This process is too expensive to apply to fuel oils, and its use is mainly confined to lubricants. The absorbent earth is packed into cylindrical vessels and the oil allowed to percolate slowly through the earth. The earth absorbs colouring matter and other impurities from the oil, and when the earth is completely saturated with the colouring matter and tarry bodies, it is regenerated by calcining in a furnace.

VAPOUR-PHASE REFINING.—Some of the lighter spirits, particularly those prepared from cracking plants, are now refined with absorbent material in the vapour phase. The vapour-phase refining process consists of passing the hot vapours from the dephlegmators through fuller's earth or floridin, whereby certain diolefines and other impurities are removed. The product, after this treatment, may either be washed with caustic soda solution or else marketed without further treatment. This process particularly applies to cracked spirit, where it is very difficult to employ sulphuric acid, as the acid will react to some extent with the olefines, resulting in very large losses of spirit.

When dealing with straight-run products, olefines are only present in very small quantities, and their loss is not a very serious matter, but in cracked spirit the olefine content varies from 20 to over 50 per cent., consequently, it is very undesirable to remove the olefines which have high anti-knock values and are desirable constituents of the finished spirit. Any loss of olefines brought about by acid treatment is therefore not only a loss of spirit but also reduces the quality of the finished spirit. As fuller's earth treatment in the vapour phase does not affect simple olefines, this method of refining has considerable advantages when applied to cracking plants.

REMOVAL OF PARAFFIN.—A large proportion of the crude oil produced contains solid paraffins. In certain cases this substance is an objectionable constituent of lubricating oils in that it causes the oil to solidify on cooling. It is also an undesirable constituent of fuel oils for the same reason. Residual oils containing a high proportion of paraffin may be quite solid at temperatures of from 60° to 80° F. This makes them very difficult to handle, necessitating their being warmed before they can be pumped. It also completely debars lubricants from use for many purposes, as the oils would be liable to solidify and cause failure of the lubricating oil supply.

Paraffin is usually found in the lighter lubricating oil distillates and in the residues. It can be removed from the lighter lubricating oil distillates by chilling and filter pressing, when the crude wax is obtained from the presses in the form of a cake. For this process the lubricating oil distillate, usually distilled so as to contain a certain proportion of gas oil, is passed through a cooling plant where it is cooled by means of a refrigerator. The mixture of comparatively thin oil and wax crystals is then passed through a filter press, where the wax is extracted. The filtrate can afterwards be redistilled to remove the gas oil and collect the necessary lubricating fractions. Lubricating residues can be treated for wax removal by diluting them with light distillate such as petrol or naphtha, then freezing and allowing the wax to settle by gravity. After distilling off the naphtha from the upper layers of the oil, a partially dewaxed lubricating residue is obtained. This process is known as the cold-settling process.

A newer process which gives a much more effective removal of the wax is the Sharples process, which can be applied either to residual oils or to heavy lubricating oil fractions which have been distilled *in vacuo*. For this process it is necessary that the crystals of wax should be very fine, so that distillates which have undergone an appreciable amount of cracking are generally found unsuitable. In the Sharples process the lubricating oil is diluted with naphtha, then cooled slowly by means of a refrigerator, and the mixture then passes through centrifuges which operate at a speed of about 17,000 revs. per min. The wax passes to the walls of the centrifuge bowl and the solution of oil goes to the centre of the centrifuge.

The Sharples centrifuges used for this purpose are so designed as to allow continuous discharge of both wax and the lubricating oil solution. The wax leaves the centrifuge in the form of a jelly. The lubricating oil solution, almost entirely freed from paraffin wax, is then subjected to distillation to remove the naphtha, and in some cases to adjust the viscosities of the lubricants. The Sharples process results in a much more effective removal of the solid paraffins, and consequently the lubricants have a much lower cold test than the products obtained by the cold-settling process, while the mineral jellies or petrolatums have higher melting points and flash points.

A similar process developed by the Alfa Laval Company makes use of a solvent heavier than paraffin wax, in which case the oil-solvent mixture is removed from the outside of the centrifuge bowl. The solvent employed is trichlorethylene.

Paraffin Wax.—The crystalline wax which is removed from the lubricating oil fractions by filter pressing is afterwards subjected to a sweating process which removes the lower melting-point wax and free oil. It is then further subjected to an acid and clay refining treatment, grades of various melting-point waxes being made.

The wax present in fuel oil cannot be economically removed by any of these processes, and it is either left in the oil or else decomposed by means of the cracking process.

Where fuel oil is generally considered unsuitable for cracking, and at the same time contains sufficient wax to give it a high cold test, and thereby interfere with its use as fuel oil, it is frequently subjected to a process known as " viscosity-breaking." Viscosity-breaking is really a mild cracking treatment ; paraffin wax present in residual oils cracks more readily and at a lower temperature than the bulk of the oil, and therefore a thick paraffinous residue treated in a cracking plant at such a temperature that only a small proportion of the oil is actually cracked will yield a residue of comparatively low viscosity and low cold test. In this process a small amount of spirit is generated. The plant used for this purpose need not be built for such high temperatures or pressures as the standard liquid-phase cracking plants, and are usually known as " viscosity-breakers."

USES OF PETROLEUM PRODUCTS.—The lower boiling-point products of petroleum are mainly used as motor spirit, but a great variety of special products of low boiling point are prepared for industrial purposes. Low boiling-point petroleum fractions find a considerable industrial application as solvents. A certain amount of very volatile naphthas are used for illuminants, mainly as petrol gas.

The kerosene fractions consist of products mainly boiling between 150° and 300° C., and at one time these were used almost exclusively for illumination. At the present time a very large proportion is used for illumination in lamps, but large quantities of kerosene are also used as fuels for engines fitted with vaporisers. Considerable amounts are used as raw material for cracking processes.

As a general rule, it is found that kerosene which originates from paraffin-base crude finds the readiest application on the illuminating market, whilst that of aromatic or naphthene base is not so suited for illumination, as it tends to give a smoky flame when burnt in a lamp. Aromatic and naphthene base kerosenes, however, are more suitable as engine fuels, but as the market is not sufficient to consume a large proportion of it for this purpose, a considerable quantity of kerosene is cracked in cracking plants either in the form of distillate, or it may be left in fuel residues which are to be subjected to cracking.

The gas-oil fractions from sulphur-free crude are largely used for the enrichment of coal gas. Those of higher sulphur content give difficulty in the oil-gas process, and are used to a large extent as fuel for Diesel engines. In very many cases, however, the gas-oil fraction is not extracted from the crude but left in and sold along with the heavier fractions as fuel oil. Gas oil of medium quality is used to a very great extent as raw material for cracking plants, for which purpose it is a very satisfactory charging stock.

The viscous distillates are only extracted from crudes which have been found to give reasonable qualities of lubricants ; when the crude is not of good quality they are usually left in the fuel residue. Cylinder stocks are only manufactured from the higher-grade crudes. Distillate lubricating oils are used for lubrication throughout industry. Cylinder stocks, although used to a considerable extent for general industrial lubricating purposes, are mainly used either for steam cylinder lubrication in the form of dark cylinder oils, or are worked up into filtered cylinder oils, which are used as thickening agents for blending distillates to manufacture lubricating oils for general uses.

Residues of lower-grade crude which are not suitable for the manufacture of cylinder stock are usually marketed as fuel oil, or run down to bitumen for road-making, etc. Those of low asphalt content find use as Diesel fuels and fuels for central-heating units, in some cases the quality being improved by the addition of gas oil. Heavier asphaltic residua of high viscosity or high asphalt content are used for external combustion, either for steam generation or furnace heating, and sell at a lower value than Diesel fuel oil.

YIELD OF PETROLEUM PRODUCTS FROM CRUDE.—The nature of crude varies so greatly that it is impossible to give even the roughest estimate of the yield of the various products without a knowledge of the particular crude. Some crudes contain no spirit, very little kerosene, and yield over 60 per cent. of solid bitumen on distillation. A typical crude of this type is that of the Panuco field in Mexico.

The heavy Venezuelan crudes give yields up to 50 per cent. of asphalt with practically no spirit content. The light crudes from northern Venezuela may yield up to 60 per cent. of gasoline and practically no asphalt. Crudes yielding even more than 60 per cent. of motor spirit are met occasionally, such as that from Kettleman Hills, California. Practically all intermediate grades of crude can be encountered in the various oil-fields of the world.

Straight distillation enables one to obtain from the crude the lighter products which are there in the first place. The heavier crudes are liable to undergo a certain amount of cracking under direct distillation at atmospheric pressure, but by the use of high vacuum stills the heaviest distillates can be removed almost entirely without cracking.

The majority of cracking processes enable one to obtain a yield of from 50 to 60 per cent. of spirit from all the distillate oils obtainable from a crude over a temperature of about 200° C. Thus the crude would be distilled (the normal spirit fraction being kept aside), and then the remainder of the crude is distilled until the maximum amount of distillate is obtained. The whole " overhead " fraction from the end point of the motor spirit fraction up to the temperature at which a solid residue is left in the still can be subjected to the cracking process, to yield from 50 to 60 per cent. by volume of cracked spirit. In cracking processes where residual oil is cracked, the yield is about the same because the asphaltic bodies which would normally constitute the bitumen at the end of the distillation process only yield small quantities of spirit.

CHAPTER II

SHALE OIL AND ITS PRODUCTS

The oil shale industry was founded in France about the year 1840, and in 1850 the distillation of bituminous coals with a view to obtaining paraffin wax and oils was the subject of a patent by Dr James Young, of Glasgow. After working for some time on a highly bituminous mineral known as Boghead coal, or Torbanehill mineral, Young turned his attention to bituminous shales. This resulted in the founding of the Scottish shale industry. Shale is very widely distributed throughout the world, and exists in enormous quantities in Colorado, U.S.A., Esthonia, and Scotland. The difficulty which stands in the way of its industrial application at the present time is that the mining and destructive distillation of shale involves a much greater amount of effort than is required to obtain the corresponding amount of oil from an oil-field. As a result it is generally found impracticable to develop shale-fields in view of the comparatively low ruling price of petroleum products. The only shale-field which has been developed on a fairly large scale is the Scottish field, the production of oil shale from which was as follows for the years 1921 to 1931 :—

1921	1,850,649 tons.
1922	2,586,656 „
1923	2,860,563 „
1924	2,857,103 „
1925	2,464,829 „
1926	1,959,795 „
1927	2,047,263 „
1928	2,038,114 „
1929	2,023,609 „
1930	2,020,510 „
1931	1,732,746 „

Statistics show that the production of oil from shale during recent years is about 21 gals. per ton. Shale oil production during 1931, 1932, and 1933 was as follows :—

1931	36·5 million gallons.
1932	29·7 „ „
1933	30·0 „ „

In recent times the shale industry in Esthonia has assumed comparatively large dimensions.

The proportion of oil contained in the shale varies very greatly with different deposits. Scottish shales yield about 20 gals. of oil per ton of shale, but the oil obtainable from some of the richer shales, such as those of Esthonia, is very much higher. The best Esthonian shales yield 58 gals. per ton.

There is still some doubt as to the geological formation of shale. Shale is not usually mined at great depths except in such positions where the mining costs can be kept low. The most favourable conditions exist when the "overburden" is very small. It is usually obtained by quarrying, or by the methods used in coal mining. It is then broken up by machinery and placed in retorts, where it undergoes destructive distillation. Retorts of various types have been employed, such as the horizontal, inclined, and vertical designs, which work both on the intermittent and continuous systems. The retorts work at a dull red heat (about 485° C.), and it is common to employ the retorted shale as fuel, since it contains a considerable quantity of carbon.

In the Scottish shale industry about 3,000 cub. ft. of gaseous products are generated from each ton of shale. These are passed through a series of vertical pipes, the lower ends of which are provided with outlets for the condensed products. Ammoniacal liquor and crude oil are condensed together, and are separated by allowing them to settle, when the oil rises to the top, and each product can be removed by pumping. The gas produced is stripped of condensable products by scrubbing or by cooling under pressure. After separation from the ammoniacal liquor the oil is known as crude shale oil. The production of synthetic ammonia has reduced the price of the former commodity and, accordingly, the shale industry has suffered.

The crude oil is refined by repeated distillation, the treatment resembling that of petroleum refining. Washing with sulphuric acid and caustic soda is employed as a further means of removing certain constituents.

The first distillation yields green naphtha, green oil, and still coke. After further treatment, the naphtha mainly goes to form motor spirit.

From the green oil are obtained solid paraffin, burning oils for lamps, fuel oils, gas oil (for carburetted water-gas plants), and lubricants. The still coke finds use as a smokeless fuel.

The lighter products obtained in the distillation of shale find use as motor spirits, and their high olefine content gives them a good anti-knock value. Other fractions available for internal combustion engines are lamp oils, and gas oils which may be used in Diesel and semi-Diesel oil engines. Crude shale oils vary in composition, but they do not form good fuels, as the proportion of light products is sufficiently large to make them dangerous to handle (as shown by their low flash points). This light material also makes them somewhat too rapid in combustion when employed in such heavy-oil engines as are capable of burning them. The oils are rich in unsaturated hydrocarbons (olefines), but this does not interfere with their use in internal-combustion engines. As fuels they very closely resemble petroleum products. They are easily distinguished from petroleum products by a characteristic and peculiar odour.

CHAPTER III

COAL TARS AND THEIR PRODUCTS

RAW TARS.—When coal is heated to redness in an enclosed vessel it yields volatile products and a residue of coke. When the volatile products are cooled, tar and water condense and are deposited, whilst the gas can be passed on to purifiers and finally to gasholders.

The nature and quantity of tars produced by the carbonisation of coal are influenced by four main factors :—

1. The type of coal employed.
2. The maximum temperature attained in the carbonising chambers.
3. The speed at which this temperature is attained.
4. The speed of removal of volatile products.

1. Coal varies considerably in composition, and certain kinds (*e.g.*, anthracite) are entirely unsuitable for carbonisation. The " gas coals " yield moderate quantities of tar. Cannel coals and highly fatty coals yield comparatively large quantities of low-gravity tar.

2. High-maximum temperatures form large quantities of gas and high-gravity viscous tars, rich in aromatic hydrocarbons and " free carbon " when suitable coals are processed.

3. Rapid heating decomposes the aliphatic compounds, thereby yielding small quantities of high-gravity viscous tars, mainly consisting of aromatic compounds.

4. If the speed of removal of volatile products be slow, further decomposition takes place on the heated retort walls. This decreases the proportion of aliphatic products, and gives heavy viscous tars, rich in free carbon and aromatic bodies.

Low-maximum temperatures, slow heating of the retort or chamber, and rapid removal of volatile products, all tend towards the production of less gas and large yields of thin tar, containing little free carbon, and consisting largely of aliphatic bodies. The tars produced under such conditions resemble petroleum more closely than tars produced at high temperatures with rapid heating and slow removal of the volatile products. Such " low-temperature " tars, however, are not very similar to petroleum, the percentages of phenolic compounds being very large.

The methods by which coal is carbonised may be divided into three groups :—

1. Processes for gas manufacture.
2. Processes for coke manufacture.
3. Miscellaneous processes.

Raw coal tars and the heavier products obtained from distillation are suitable for external combustion. Certain of the raw coal tars, and more particularly the creosote fractions obtained by distillation of the tar, have been used as fuel for internal-combustion engines. In Germany, considerable quantities of coal-tar distillates have been used as Diesel engine fuel, but in petroleum-producing countries the price of petroleum oil has generally discouraged the use of coal-tar products as fuel for Diesel engines. The use of coal-tar products which has been extended in Germany has been due to the tariffs on the importation of petroleum. In this country a more extensive adoption of creosote as a fuel has taken place within the last few years. This tendency has been particularly marked since the introduction of the tax on imported heavy oils.

Tars Produced by Gas Manufacture.—It has been shown how the composition of coal tars varies according to the conditions prevailing in the carbonising chamber. These conditions are generally inherent in the type of plant, and it is therefore found that the nature and yield of tar is dependent upon the type of retort. Retorts may be horizontal, inclined, or vertical, the horizontal being the oldest type. Modern installations are most frequently of the vertical type.

According to Kraemer the average values of the more important constituents of German gas-works tars are as follows :—

	Approximate Composition.		
Benzene and its homologues .	C_nH_{2n-6}	2·50	per cent.
Phenol	$C_nH_{2n-7}OH$	2·00	,,
Pyridine bases . . .	$C_nH_{2n-7}N$	0·25	,,
Naphthalene and acenaphthene .	C_nH_{2n-12}	6·00	,,
Heavy oils . . .	C_nH_n	20·00	,,
Anthracene and phenanthrene .	C_nH_{2n-18}	2·00	,,
Asphalt (soluble portion of pitch) .	$C_{2n}H_n$	38·00	,,
Carbon (insoluble portion of pitch)	$C_{3n}H_n$	24·00	,,
Water	...	4·00	,,
Gases and loss . . .	...	1·25	,,

Horizontal Retort Tar.—Horizontal retort tar is a viscous black liquid containing from 20 to 30 per cent. of free carbon. It is rich in aromatic bodies, being at present the main source of benzene, toluene, naphthalene, and anthracene. The ultimate composition of the dry tar averages about 91 per cent. carbon and 5 per cent. hydrogen, the remaining 4 per cent. being oxygen, nitrogen, sulphur, and inorganic matter. This tar is the richest in carbon, and it possesses a specific gravity in the neighbourhood of 1·20. On account of the high ash and free carbon content it is unsuitable for engine use in the raw state and is rarely used for external combustion. These properties are due to the high temperatures employed in horizontal retorts, and the very rapid heating to which the charge is subjected.

INCLINED RETORT TAR.—As might be anticipated, the properties of this product are intermediate between those of horizontal and vertical retort tars.

VERTICAL RETORT TARS.—Both continuous and intermittent vertical retorts yield low specific gravity tars which are mobile and dark brown in colour. These tars contain some 7 per cent. of hydrogen, denoting the presence of chain compounds, and are comparatively free from inorganic matter and free carbon. The older gas works installations employ horizontal retorts, but the majority of the newer installations are either the inclined or vertical type. In many cases vertical retorts and horizontal retorts are installed in the same works and the tar is mixed, a practice which decreases the amount of vertical retort tar which might be available for direct use as fuel.

TARS PRODUCED IN COKE MANUFACTURE.—Coke-oven tars vary greatly, and may resemble in composition either the products of horizontal retorts or of vertical retorts. The nature of the tar is determined by the design of the oven. Tars from chamber ovens are very similar to vertical-retort tars, and experiments in Germany have demonstrated their suitability for Diesel engines.

TARS PRODUCED FROM LOW-TEMPERATURE CARBONISATION.—Very many patent processes have been advocated for the low-temperature carbonisation of coal. Several of these processes have been carried through to the experimental stage and a few have been installed as commercial units. At the time of writing, the total production of low-temperature tar is small.

The object of these processes is to distil the bituminous coal at comparatively low temperatures and thereby obtain coke suitable for domestic fuel. Coke obtained from coke ovens and having had nearly all the volatile matter driven out is hard, difficult to ignite, and extremely slow burning. These properties make it admirably suitable for blast-furnace work or for the manufacture of water-gas, a friable coke being troublesome in either of these plants. Because coke obtained from low-temperature distillation has a certain amount of bituminous matter remaining in it, it is more easily ignited and will burn with a normal draught on the fire. It gives a high-quality domestic fuel, as a large proportion of the heat is radiated from open fires, which are smokeless when burning this fuel.

The oils produced by the various processes differ considerably, but on the whole the retorting processes employed in low-temperature carbonisation are such that the coal is heated slowly to a comparatively low maximum temperature. These conditions prevent decomposition of the tar, which is consequently richer in aliphatic compounds, *e.g.*, paraffins and olefines. The tar also contains a lower ratio of aromatic compounds together with a comparatively small free carbon content and a lower average boiling point than tars obtained by other methods of carbonisation.

The percentage of motor spirit obtained by this type of carbonisation process is higher than that obtained in gas works or coke-oven practice. The motor spirit fractions of low-temperature tar are rich in olefines ; they do not contain large quantities of benzene, but nevertheless they have excellent anti-knock properties. In their general properties the products of low-temperature tar are intermediate in characteristics between the products of high-temperature tar and petroleum products.

BLAST-FURNACE TARS.—Coke is generally used as a heating and reducing agent in blast furnaces. In certain localities, however, coal is used instead of coke. When coal is used for this purpose a tar is generated which possesses some of the characteristics of low-temperature tar. The tar, however, is usually very rich in ash (admixed dust) and is of little value in the raw state. On distillation it yields a small quantity of light products and a large quantity of low-gravity oil, which in some cases has been used as fuel for heavy-oil engines.

PRODUCER TARS.—When coal, other than anthracite, is used in gas producers, a certain amount of tar is generated. This product is usually full of dust, ash, and water ; where large quantities are available it can be distilled, but in the majority of installations the quantities available are insufficient to warrant the working up of the product.

OIL-GAS TAR.—The residue known as carburetted water-gas tar or oil-gas tar is not a product of coal, but it may be most conveniently dealt with here. It is common practice to use oil gas to enrich coal gas for illuminating purposes. Oil gas is produced by violent cracking of gas oil (a high-boiling distillate of petroleum or shale oil). By this process a residue is obtained which consists of unchanged oil mixed with a large proportion of aromatic hydrocarbons produced by the cracking of the oil. Some products from the water-gas plant which runs in conjunction with the oil-gas generator also become mixed with this residue. The result is a light, mobile, reddish-brown liquid possessing a specific gravity of about 1·05, which is an excellent fuel if it be dehydrated, and provided that the ash content is not excessive. It resembles a highly cracked petroleum product, and is said to consist largely of aromatic compounds.

In many cases the tar appears as an emulsion of water and oil, and sometimes it is practically impossible to obtain the tar free from water by settling. The amount of water present in these tars depends on the conditions of working which are maintained in the plant, and if these conditions were scientifically investigated there is little doubt that the tar could be obtained practically free from water, either by simple settling or by centrifugal methods.

During recent years the use of high-speed centrifuges has made it possible to make an almost complete removal of water from low-temperature tar, and the Sharples centrifuge has been used to a considerable extent for this purpose. This treatment also has the effect of reducing the ash content of the oil.

Distillation of Coal Tar.—Of the tars previously described, only the gas works and coke-oven tars are at present prepared in large quantities.

The tars are usually sold by the gas works, and conveyed by tank wagon, pipe line, or barges to a tar distillery.

Though many complex and more economical stills have been designed, it is usual in this country to distil tar in cylindrical upright stills (see Figs. 3, 4, 5), which are provided with concave bases. The bases are almost hemispherical in order to allow for expansion of the plates, and to allow the heat more easily to reach the body of the charge.

The stills are usually of 10 to 30 tons capacity, and are made of $\frac{3}{8}$-in. or $\frac{1}{2}$-in. steel plates riveted together.

A dome, or " crown," is situated on the upper portion of the still, and from this a pipe leads the vapours to a water-cooled worm condenser.

The still is heated by a fire under the base, the flues being so arranged as to cause the hot gases to encircle the walls of the still. It is usual to cover the curved upper portion of the still with brickwork in order to minimise the loss of heat.

For many years comparatively little change has taken place in the design of tar stills, and tar distilling plant of to-day appears very obsolete when compared with the automatically controlled atmospheric and vacuum tube still units used for distillation in the petroleum industry. The reason for this is largely because of the comparatively small quantities of tar which have to be handled, also that the tar distiller frequently has to make small quantities of special products to meet different industrial requirements. These fractions are only wanted intermittently, and the changes are so frequent that it would be very inconvenient to use large units.

Another reason why the tube still has not hitherto met with success in tar distilling is on account of the very large amount of free carbon present in the majority of coal tars, which prevents the clean working of the tubes.

Many of the installations have been modified to effect a greater heat economy than the simple type of still which has been described ; it is fairly common, for instance, to use a preheater of approximately the same capacity as the still so that the raw charge can be preheated by the heat of the distillates before being passed into the main still. Such preheaters have the advantage of driving off the water, thereby giving the main still a dry charge which may be heated up more rapidly than the original raw tar. Various other forms of heat exchanger have been used by which small amounts of heat recovery have been obtained.

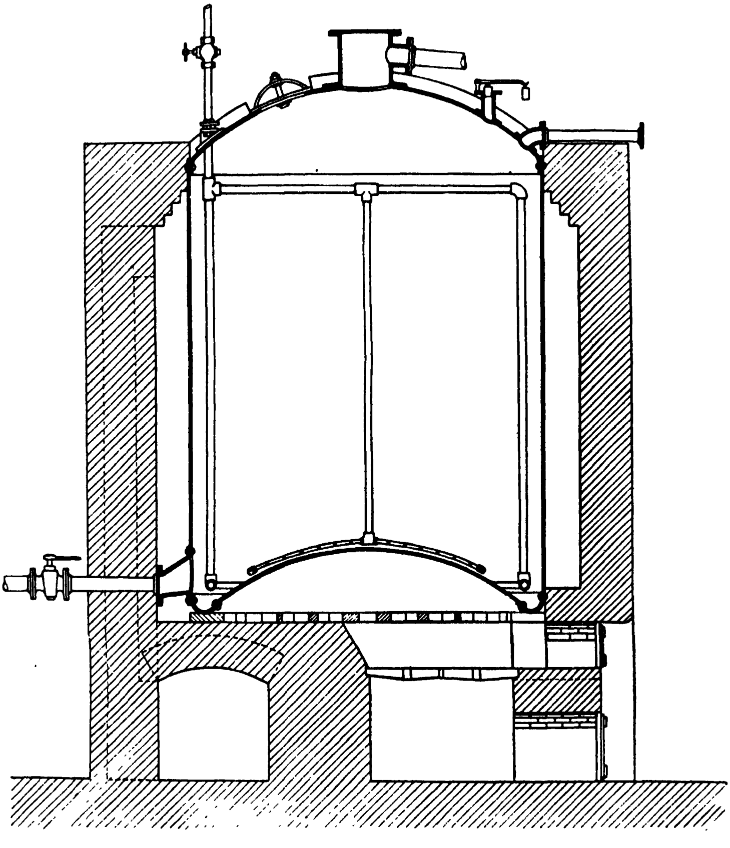

FIG. 3.—Sectional Elevation of English Tar Still.

The still is charged and heated gently until the water (which is accompanied by the lighter products) has passed off, as rapid heating during the earlier period of the distillation causes frothing over. When all the water has been driven off, the distillation proceeds quickly until the latter stages, when superheated steam is admitted to the still through perforated steam pipes (shown in Figs. 3 and 4) to assist in driving over the heavier oils (mainly anthracene oil).

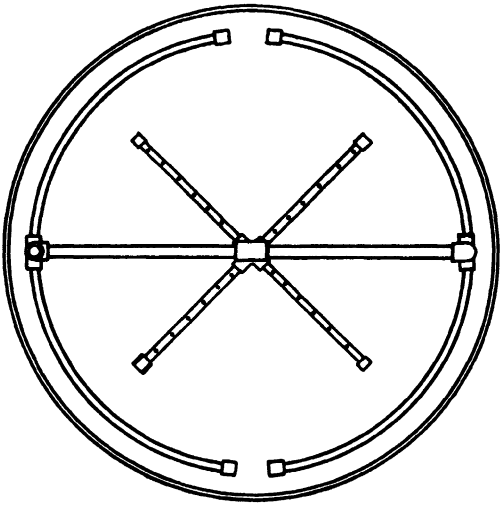

FIG. 4.—Sectional Plan of English Tar Still.

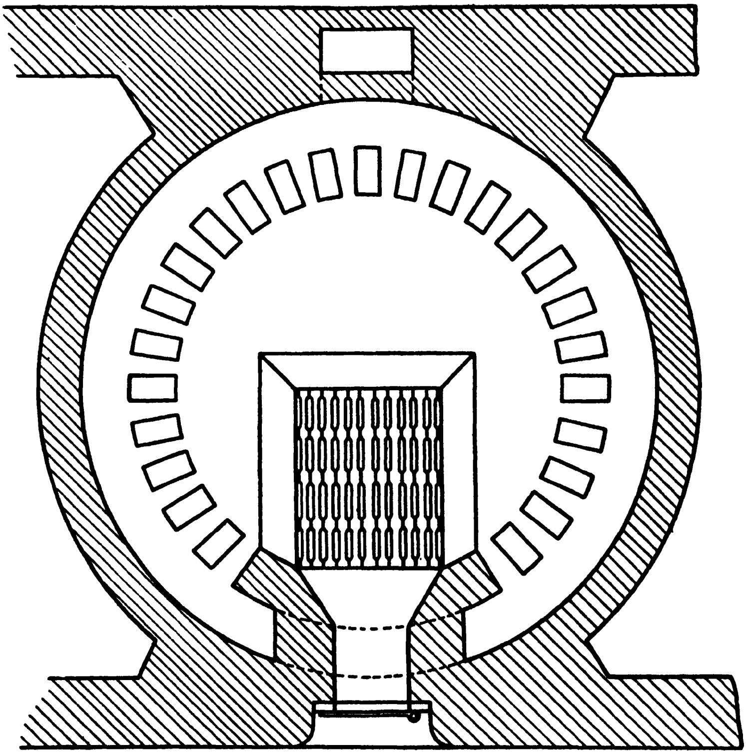

FIG. 5.—Sectional Plan of English Tar Still, showing Fire Grate.

It is standard English practice to separate the following fractions :—

	Temperature of Distillation.	Sp. Gr. (approximate).	Percentage Yield (approximate).
First-runnings or crude naphtha	Up to 110° C.	0·920	3·1 per cent.
Light oil	110° to 200° C.	0·995	1·7 „
Crude carbolic oil	200° to 240° C.	1·015	3·5 „
Creosote oil	240° to 270° C.	1·050	12·0 „
Anthracene or heavy oil	Above 270° C.	1·095	9·7 „

A residue of pitch is left in the still.

The "first-runnings" or crude naphtha is accompanied by water (containing ammonia) which settles out, and can be separated by decantation. Benzene and toluene are extracted from the first-runnings and from the light oil by distillation, followed by caustic soda and sulphuric acid washes, and redistillation.

Benzene is marketed in various grades of purity, the pure hydrocarbon being generally sold as benzene, whilst commercial mixtures containing other hydrocarbons are known as benzole. A common product used for blending with petrol is the commercial grade known as 90 per cent. benzene, but this is a product which, on distillation, yields 90 per cent. of distillate at 100° C. (benzene boils at 81° C., toluene at 111° C.), 90 per cent. benzole, or 90's benzole, contains about 75 per cent. of benzene and 25 per cent. of toluene, traces of other hydrocarbons being also present.

Pure benzene possesses the following properties :—

Benzene

Boiling point	80·4° C.
Latent heat of vaporisation	93·7 cals.
Vapour tension	45·4 mm. mercury at 0° C., 74·66 mm. at 20° C.
Explosive range	2·7 to 6·3 per cent.
Temperature of spontaneous ignition in oxygen	566° C.[1]
Gross calorific power[1]	About 10,050 cals. = 18,090 B.Th.U.
Specific gravity at 15° C.	0·8846
Theoretical air required for combustion	13·46 lbs. per lb.
Elementary composition	7·7 hydrogen, 92·3 per cent. carbon.

[1] 100 per cent. commercial benzole.

Pure benzene is used for the dyestuff industry and for other chemical purposes. The remainder of the production of benzole is usually employed mixed with motor spirit for the manufacture of benzole mixtures, and the National Benzole Association have from time to time prepared specifications controlling the quality of benzole required for this purpose. Benzole answering these specifications is usually referred to as "motor benzole." The

National Benzole Association's Specification, No. III., 1932, is as follows :—

1. *Colour.*—The Benzole shall not be darker than a freshly prepared solution of 0·5 ml. of N/10 iodine solution in 1,000 ml. of distilled water.
2. *Specific Gravity.*—The specific gravity of the Benzole at 15·5° C./15·5° C. shall not be lower than 0·8700 nor higher than 0·8850.
3. *Water.*—The Benzole shall be free from water and other visible impurities at 15·5° C.
4. *Distillation.*—When 100 ml. of the Benzole are tested by the standard method, the volume of distillate collected when the temperature has reached 100° C. (running-point) shall not be less than 60 ml., and when the temperature has reached 120° C. (running-point) at least 85 ml. shall have distilled. When the temperature has reached 145° C. (stop point) the volume of distillate shall be at least 95 ml. The residue in the flask at the end of the distillation shall remain liquid when cooled to 0° C. for thirty minutes.
5. *Rectification Test.*—The Benzole shall pass *either* the standard acid-washing test *or* the standard oxidation test.
    (*a*) *Acid-washing Test.*—When the Benzole is tested by the standard method, the acid layer which separates shall be clear, and shall not be darker than a solution of 5 gm. of pure potassium dichromate in 1,000 m., of a mixture of equal volumes of pure sulphuric acid (containing 98 per cent. by weight H_2SO_4) and distilled water.
    (*b*) *Oxidation Test.*—When the Benzole is tested by the standard method, the weight of residue which is obtained shall not exceed 8 mg. per 100 ml. of the Benzole.
6. *Total Sulphur.*—The Benzole shall not contain more than 0·4 per cent. by weight of (total) sulphur.
7. *Free Sulphur.*—The Benzole shall not give a steel grey or black discoloration when tested by the standard method.
8. *Freedom from Acids, Alkalis, and Sulphuretted Hydrogen.*—The Benzole shall not give a positive reaction for acids, alkalis, or sulphuretted hydrogen.
9. *Odour.*—The Benzole shall have a pronounced odour of the aromatic hydrocarbons.
10. *Crystallising Point.*—The crystallising point shall not be above −5° C.

(This specification, which supersedes No. III., 1929, applies only when the standard methods of testing of the Standardisation of Tar Products Tests Committee are used, except that for 5 (*b*) the standard method of the National Benzole Association shall be used.)

The presence of toluene in motor benzole is not objectionable, and is even desirable, as, though it slightly decreases the volatility of the mixture, it lowers the freezing point. Pure benzene solidifies at 6° C., so that benzole mixtures tend to have high freezing points, a property which is very undesirable in a motor spirit. A mixture containing about 20 per cent. of toluene will not freeze at ordinary cold-weather temperatures.

At one time benzole was used on motor cars as a cheap substitute for petrol, and it was some time before people discovered that it had many properties definitely superior to petroleum spirit. Nowadays it is almost entirely used in the form of mixtures of which petroleum spirit constitutes the larger proportion. Used as a blending agent in this way, benzole is able to command a considerably higher price than petrol, apart from the question of its being immune from taxation. The presence of benzole in a mixture has the advantage of giving a high anti-knock number, and it is for this reason that it can command a premium.

During the process of carbonisation obtaining in gas works and coke-oven plants, the major portion of the benzole and toluol remains in the gas, only a small proportion being condensed with the tar. It is possible to remove these bodies from the gas by the stripping process. This process is usually carried out by bringing the gas into contact with a heavy oil, which absorbs the benzole and toluol. The oil is afterwards heated in continuous stills, where the volatile products are driven off and the residue used again for absorption. It is standard practice to remove benzole and toluol from coke-oven gas by this method.

In so far as illuminating gas is concerned, the benzole and toluol increase its calorific value. In spite of this, it generally pays to extract them from the gas, as the prices which they command for motor spirit are greater than the cost of replacing the heat value by other means. At the time of writing, this condition is really brought about by taxation ; the extracted benzole from gas has a tax advantage due to its exemption from the imported motor spirit tax, and if it is removed from gas it is possible to make gas from imported petroleum by means of an oil-gas plant without paying the motor spirit tax on the gas so produced, so that by removing the benzole and replacing with oil gas, the gas works obtain the advantage of the motor spirit taxation.

During the war, when there was a shortage of toluol for explosive purposes, all gas works were compelled to strip the gas, but after the war, when there was no particular demand for toluol, many works ceased to employ the stripping process for the removal of the aromatic hydrocarbons. The oil used for absorption may be either ordinary creosote, blast-furnace creosote, or a petroleum distillate such as gas oil. Coke-oven gas contains from 0·8 to 1·6 per cent. by volume of benzole, and yields from 4 to 6 gals. per ton of coal carbonised.

The xylenes (of which the three isomeric forms—ortho, meta, and para xylene are all found in tar) are occasionally separated from the crude naphtha and light oil fractions, though they are generally sold for solvent purposes without complete separation from some of the other hydrocarbons.

Light oil contains by far the larger portion of the xylene. It also yields pyridines which are recovered by treating the fraction with dilute sulphuric acid. Carbolic acid, on the other hand, is extracted from light oil by means of dilute caustic soda.

The carbolic oil consists largely of naphthalene and carbolic acid (phenol), together with cresols and pyridine bases. After the removal of naphthalene, a liquid hydrocarbon is left which is sold for disinfectant manufacture. Alternatively the carbolic acid is removed, and the residue is added to the creosote oil fraction. Creosote oil made from gas works or coke-oven tar contains considerable quantities of naphthalene and cresols, either of which may be extracted as the markets demand. Naphthalene solidifies in the creosote and carbolic oil fractions, and falls to the bottom of the storage tanks in the form of crystals. This behaviour on the part of naphthalene makes it necessary to heat many tar oils in order to prevent obstruction of the pipe lines.

Naphthalene may be extracted from the crude carbolic oil and the creosote oil by allowing these fractions to cool in storage tanks, and running or pumping off the oil. The resulting deposits of naphthalene are known as "drained salts," and after treatment in a centrifuge machine, a purer product known as "whizzed salts" is obtained.

The yield of naphthalene from coal is about 0·3 per cent., and the refined product possesses the following properties :—

Specific gravity (solid) . .	1·15 at 15° C.
,, ,, (liquid) . .	0·977 at 80° C.
Melting point . . .	80° C.
Latent heat of fusion . .	36 calories.
Flash point . . .	176° F.
Gross calorific value, 9,668 calories	=17,402 B.Th.U.
Net ,, ,, 9,260 ,,	=16,668 ,,

Naphthalene, being a hydrocarbon, is completely combustible. Its spontaneous ignition temperature in oxygen as determined in the author's apparatus is 402° C.

Anthracene oil is the highest boiling distillate of coal tar, and is rich in the hydrocarbon anthracene. As a fuel it is very similar to naphthalene and is subject to the same objections. A frequent practice is to mix the creosote and anthracene oil fractions, which are sometimes sold as fuel. They are generally known to engineers as " tar oil," and have been utilised in Diesel engines.

The pitch or residue from the tar is of little interest to internal-combustion engineers, but it has been used in solution in creosote for external combustion. These mixtures, known as pitch-creosote mixtures, have been used in considerable quantities by the Admiralty for steam-raising on warships. In some cases, instead of actually dissolving pitch in creosote, a very similar liquid fuel for external combustion has been prepared by distilling off the lighter products from the tar and using the residue with or without the addition of creosote. Residues from which the lighter products have been removed by distillation are known as " treated tars," and are used for road-making.

It is quite possible that at some future time it may be found more expedient and profitable to collect tars at the gas works or coke ovens by a process of fractional condensation, thus obtaining direct from the carbonising plant a series of products which might resemble closely the products of tar distillation. If this were done, it is certain that by such means a large yield of a product suitable for Diesel and semi-Diesel engines could be prepared directly.

Reviewing the coal-tar distillates, the lightest products, benzole and toluol, find considerable use in the preparation of benzole mixtures for use in petrol engines. The employment as fuel of the heavier distillates, such as creosote and anthracene oil, is entirely an economic question. In the past the prices have been from time to time below those of corresponding petroleum products, and when such is the case they are used to a considerable extent as petroleum substitutes.

Recent taxation, which is applied to imported heavy oils but not to the home manufactured oils, has had the effect of stimulating the use of coal-tar products for both internal and external combustion, particularly the latter.

The use of coal-tar products for external combustion presents practically no difficulties ; there is a slight alteration in the air-fuel mixture ratio and adjustments of burners may be necessary, but in other respects they can be burnt readily. For use in heavy-oil engines, however, creosote and anthracene oils present many technical difficulties, and unless their prices are distinctly below those of the corresponding petroleum products, they have little chance of competing. With heavy-oil engines which have been designed primarily to burn petroleum products, it is a comparatively costly undertaking to equip them for burning coal-tar oils, and therefore, without a pronounced price advantage, users are not inclined to make the change.

CHAPTER IV

LIGNITE TARS AND THEIR PRODUCTS

Lignite, or brown coal, is a natural product formed by the action of heat and pressure upon vegetable matter. In this respect it is closely related to coal, but probably the conditions under which the lignite were formed were not so drastic as those required to form coal. Consequently the composition of lignite is intermediate between that of wood and coal. The most noticeable chemical difference is that lignite contains a much higher oxygen content than coal, and is therefore more closely related to the cellulosic material from which both originated. The composition of lignite varies very considerably and sometimes approaches the softer types of coal.

Lignite occurs in very large quantities, and is commonly found much closer to the surface than coal, and can consequently be won at a much lower cost. As obtained from the ground, lignites sometimes contain as much as 50 per cent. of water and may also be high in ash content.

Lignites are widely distributed throughout the British Empire, important deposits occurring in India, Australia, Canada, New Zealand, and Europe. In Saxony a large and highly developed lignite industry has existed for many years.

Lignite is often burned under boilers, where it is found to be much inferior to coal. It is sometimes subjected to destructive distillation, tar being the most important product.

The yield of tar varies from 1 per cent. to as high as 12 per cent., but is usually about 5 per cent. The tar has a specific gravity of 0·88 to 1·08, and is semi-solid at normal temperatures, owing to the presence of paraffin wax. It is rich in unsaturated compounds and absorbs oxygen from the air. On distillation, lignite tar yields not only light products suitable for motor spirits, but also burning oils, lubricating oils, and paraffin wax.

The products of this first distillation may be redistilled and refined by treatment with caustic soda and acid washes, much in the same manner as for coal-tar products. The liquid products are a mixture of aromatic and aliphatic hydrocarbons. Benzene and naphthalene are also present in considerable quantities, though the specific gravities of the fractions indicate a large proportion of aliphatic bodies. The lightest fractions possess specific gravities of about 0·75.

The lighter products make good fuels for engines fitted with carburetters, whilst the intermediate and heavy products are suitable for vaporising and atomising engines respectively. The lignite-tar distillates, as fuels, are very similar to the corresponding distillates obtained from shale and from petroleum. Crude lignite tar has been used with complete success as fuel for Diesel engines ; the proportion of aliphatic compounds present is sufficiently high to allow ignition to be effected in a normal manner, consequently it is unnecessary to modify the design of the engine or to supply extra fitments.

The liquid products obtained from lignite are used in Germany as a base from which motor spirit may be manufactured by the hydrogenation process.

CHAPTER V

PRODUCTS OF THE CARBONISATION OF WOOD AND PEAT

WOOD.—When wood undergoes destructive distillation in a by-product recovery plant, charcoal is produced in the oven and liquid products condense from the volatile portion. A large amount of permanent gas is also produced. According to Pritchard,[1] one cord (4,000 lbs.) of wood yields :—

Best turpentine	40 gals.
Light oils	16 ,,
Heavy oils	128 ,,
Charcoal	950 lbs.

The products are dependent upon the type of wood burned. Methyl alcohol and acetic acid are obtained as by-products when hard woods are carbonised.

The comparative scarcity and high cost of wood prevents the liquid products attaining much importance as fuels, though several are quite suitable. Methyl alcohol can be used in the form of mixtures on carburetter engines, whilst turpentine and the heavier oils are suitable for vaporising and atomising engines.

PEAT.—Peat is formed by the decay of vegetable matter in the presence of moisture. It is very widely distributed throughout the world, and enormous quantities are available. Large beds of peat occur in the British Isles. Little has been done towards the utilisation of these deposits on account of the difficulty of drying peat, and the low density and calorific power of the finished product. A great amount of experimental work, both in the laboratory and on a commercial scale, has been carried out with a view to the exploitation of these deposits, but at present there is little chance of peat products competing with the more easily won petroleum products.

The combustible portion of peat contains 55 to 60 per cent. of carbon, and about 6 per cent. of hydrogen and 2 per cent. of nitrogen, the remainder being mainly oxygen.

Peat may be carbonised to a peat charcoal, or it may be treated by a process yielding a semi-carbonised residue which is suitable for the manufacture of fuel briquettes. Certain of the other

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[1] *Journ. Soc. Chem. Ind.*, 1912, p. 418.

products of carbonisation serve as a binding material in the briquetting process.

From the results of tests by the Power Gas Corporation the gasification (in a producer) of one metric ton of peat has been found to yield :—

Cubic feet of gas at 0° C. and 760 mm. . .	99,000
(Calorific value per cubic foot . . .	157 B.Th.U.)
Tar	110 lbs.
Calcium acetate	9 ,,
Ammonium sulphate	165 ,,

In the case of a Yorkshire peat, F. M. Perkin states that 38 gals. (about 16 per cent.) of tar are obtainable per ton of dried peat. This tar on fractionation yielded :—

1·35	per cent. oil, specific gravity	0·867.	B.P. below	150 C.
29·90	,, ,, ,, ,,	0·953.	,, ,,	250′ C.
50·00	,, ,, ,, ,,	0·941.	,, above	250 C.

The oils obtained are mostly of the paraffin type.

E. and F. Bornstein found a sample of peat tar to yield 18 per cent. of phenols, 1 per cent. of bases, 34 per cent. of oils, and 47 per cent. of pitch, while Morgan and Scharff[1] found a sample of crude tar to contain 29·3 per cent. moisture, 52·6 per cent. volatile oils and waxes, 5·8 per cent. pitch, and 11·7 per cent. solid matter. The latter authorities state that peat tars are highly unsaturated, and readily absorb atmospheric oxygen.

Oils from peat are not available on the market at present, but there appears to be no doubt that the distillates of peat tar would prove suitable as fuels for internal-combustion engines. The use of the raw tar would probably present many difficulties.

[1] G. T. Morgan and G. E. Scharff, *Economic Proc. Roy. Dublin Soc.*, 1915, pp. 2, 161.

CHAPTER VI

ANIMAL AND VEGETABLE OILS

THE cost of production of animal and vegetable oils is such that they can only find use as fuels in special cases where other fuels are practically unobtainable. They are more liable to chemical change than the hydrocarbon oils, and on account of their oxygen content are lower in calorific power.

They consist mainly of the glycerides of unsaturated organic acids, and have been used on heavy-oil engines, but only to a limited extent. Dr Diesel advocated the use of arachis or ground-nut oil as a fuel for the Diesel engine. The oil that he used had the following analysis :—

Specific gravity	0·915 at 15° C.
Flash point	233° C. (451° F.)
Hydrogen	11·41 per cent.
Carbon	74·73 „
Oxygen and nitrogen	13·86 „
Net calorific value	8,823 cals. (15,880 B.Th.U.)

The author had occasion to test whale oil on a Mirrlees-Diesel engine, and found no difficulty in obtaining excellent running, no modification of engine settings being required. This oil showed the following characteristics on analysis :—

Specific gravity	0·921 at 20° C.
Flash point	Over 320° F.=160° C.
Sulphur	0·13 per cent.
Coke	1·27 „
Water	Trace
Ash	„
Net calorific value	8,707 cals. (15,673 B.Th.U.)

Further analyses were made on arachis and palm oils with a view to their use on Diesel oil engines, by Constam and Schläpfer. Their results are given below :

	Arachis or Ground-nut Oil.	Palm Oil.
Specific gravity	0·916	0·915
Flash point	310° C.	244° C.
Temperature of spontaneous ignition	400° C.	400° C.
Sulphur	0·1 per cent.	...
Coke	0·45 „	0·13 per cent.
Water	trace	0·14 „
Ash	„	0·01 „
Hydrogen	11·8 per cent.	11·8 „
Carbon	77·3 „	76·2 „
Oxygen and nitrogen	10·8 „	12·0 „
Net calorific value	8,866 cals. (15,958 B.Th.U.)	8,790 cals. (15,822 B.Th.U.)

The demand for animal and vegetable oils for various industrial purposes is large, so that there is little chance of them assuming much importance in the fuel market, where low prices are essential. Animal and vegetable oils only lend themselves for use in heavy-oil engines, and no animal or vegetable oils are produced suitable for vaporising engines. Experiments have shown that by the application of heat in the presence of a catalyst, such oils can be decomposed by a process very similar to cracking, and thereby carbon dioxide and monoxide, together with saturated and unsaturated hydrocarbons, are generated. If desired, the products can be subjected to hydrogenation. During the last few years, Egloff has subjected various animal and vegetable oils to the Dubbs cracking process, and has been able in this way to produce internal-combustion fuels having excellent properties.

There is no doubt that should the economic position warrant it, such processes could be developed on a commercial scale. At the present time, however, when volatile products from petroleum are very much cheaper than animal or vegetable products, the process is only of scientific interest.

CHAPTER VII

ETHYL ALCOHOL

Ethyl alcohol is of particular interest as a liquid fuel, as its production is not dependent upon existing natural resources. Petroleum products can only be obtained by exploiting underground reserves, and consequently these reserves are being continually depleted, and as the conditions under which petroleum was formed are believed to exist no longer, there must at some time come a day when it will be impracticable to obtain large supplies of petroleum from the earth.

Ethyl alcohol is generated by the fermentation of vegetable matter which can be grown for this purpose. Consequently, the amount of ethyl alcohol made can be adjusted to meet the demand. Ethyl alcohol, together with traces of other bodies, is formed by the alcoholic fermentation of sugars through the action of yeast. The sugars may already be present in the raw material as in molasses, grape juice, etc., or the starch present in cereals, potatoes, etc., may be converted into sugar which may afterwards be fermented to alcohol. By fermentation, there results a dilute alcohol solution which is afterwards concentrated by fractional distillation using dephlegmating columns.

Mixtures of alcohol and water cannot be completely separated by distillation because the mixture, 95·57 per cent. alcohol to 4·43 per cent. water, distils at a lower temperature than any other mixture of these two components. Such a liquid is called an " azeo-tropic " mixture. It is, therefore, impossible by simple distillation to obtain alcohol of a greater concentration than 95 per cent. by volume, the remainder being water. Distilling over lime will give alcohol of higher concentration, but this increases the cost.

The equilibrium of such an azeo-tropic mixture can be disturbed by the introduction of a third component in which only one of the constituents is completely miscible. Hence we find that very concentrated alcohol is now being manufactured by the addition of benzene to the contents of the still, and suitably continuing the distillation.

Pure ethyl-alcohol, C_2H_5OH, is a colourless, mobile liquid of sweet smell and a burning taste. It possesses the following properties :—

ALCOHOL

Boiling point	78·4° C.
Latent heat of vaporisation	203 cals.
Vapour tension	41·3 mm. at 18·7°; 766·5 mm. at 78·5° C.
Explosive range	4 to 13·6 per cent.
Temperature of spontaneous ignition in oxygen	395° C.[1]
Gross calorific power[1]	7,054 cals.=12,697 B.Th.U.
Specific gravity	0·794.
Theoretical air required for combustion	9·08 lbs. per lb. fuel.
Elementary composition	Carbon, 52·17 per cent.; hydrogen, 13·04 per cent.; oxygen, 34·78 per cent.

[1] Mineralised spirit, specific gravity, 0·819.

The properties of alcohol-water solutions of various concentrations are shown in the following table:—

PROPERTIES OF ALCOHOL-WATER SOLUTIONS

Specific Gravity at 15° C.	Percentage Alcohol by Weight.	Percentage Alcohol by Volume.	Net Calorific Power.	
			Calories.	B.Th.U.
0·794	100·00	100·00	6,362	11,452
0·809	95·08	96·85	6,019	10,834
0·823	90·02	93·28	5,666	10,199
0·836	85·01	89·48	5,318	9,572
0·848	80·21	85·64	4,984	8,971

Although until recently alcohol has not been used as a fuel to any large extent in this country, it has found use in France, Germany, South Africa, and Australia, usually in the form of mixtures with benzole or petroleum products. It has been used in all countries for racing, as mixtures containing alcohol are capable of giving a higher power output in specially designed engines than can be obtained with hydrocarbon fuels. During the war, alcohol was used by the German army in the form of mixtures with benzole and naphthalene for motor transport.

On account of its comparatively low heat value, the consumption of alcohol is very high when this fuel is used in an engine designed to operate on petrol. As alcohol can withstand much higher compression ratios than petrol, the deficiency in heat value can be largely overcome by using a high compression-ratio on alcohol engines. For motor transport purposes it is generally necessary to employ engines which are capable of running on petrol, so that one cannot take full advantage of this property of alcohol.

As alcohol has the property of imparting its anti-knock properties to mixtures, the most useful method of using it is in the form of mixtures containing a large percentage of petroleum spirit. There has been, however, a certain amount of difficulty in making mixtures containing small percentages of alcohol and large percentages of petrol on account of the difficulty in obtaining complete miscibility when commercial grades of alcohol have been employed. Pure alcohol is soluble in petroleum spirit in all percentages, but alcohol containing a little water is much less soluble, and though it is possible to obtain solutions containing a large proportion of commercial alcohol and a small proportion of spirit, it is necessary to dehydrate the alcohol in order to bring about a solution containing a small percentage of alcohol.

Ormandy and Craven[1] have investigated the solubility of alcohol of various strengths in motor spirit and in certain pure hydrocarbons. Solubility tests on various spirits and ethyl-alcohol mixtures, together with the reports of experimental engine trials on such mixtures, have been the subject of experiments by King and Manning.[2] They determined the limiting volumes of petrol which could be added to 100 volumes of alcohol, the alcohol consisting of 95 per cent. by volume pure alcohol and 5 per cent. of water. This concentration corresponds to 92·4 per cent. alcohol by weight.

MISCIBILITY LIMITS OF CERTAIN PETROLEUM SPIRITS WITH 95 PER CENT. ALCOHOL

(*Volumes per* 100 *Vols. of Alcohol*)

Petroleum Spirit.	Source.	Limiting Volumes of Petrol per 100 Volumes Alcohol.		
		15° C.	0° C.	−10° C.
1. B.P. No. 1	U.S.A.	59	39	35
2. Imperial naphtha . .	Mexico	46	33	28
3. Refined spirit	Persia	83	58	45
4. Refined benzine . . .	Persia	57	41	34
5. B.S.R. benzine . . .	Dutch Borneo	263	114	70
6. Miri benzine . . .	Sarawak	56	38	32
7. Shell	...	52	36	30

As a result of their engine experiments they concluded that petrol-alcohol-benzole mixtures were quite suitable for use in petrol engines without any alteration being made beyond enlarging the carburetter jets.

The solubility of alcohol-water and petrol mixtures is further complicated by the fact that the solubility is greatly affected by the temperature. As an example of the solubilities of various hydrocarbons and alcohol mixtures, it may be noted that it is necessary to have a minimum alcohol strength of 88·4 per cent. by weight in order to render stable a mixture of eighty parts alcohol and twenty parts benzine at 15° C. A mixture of 90 per cent. alcohol and 10 per cent. benzine requires alcohol of 92·3 per cent. con-

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[1] *J.I.P.T.*, 1922, vol. viii., p. 181.

[2] *J.I.P.T.*, 1929, vol. xv., p. 350.

centration by weight to become stable at the same temperature. Corresponding figures for toluene are at 15° C.; 80 per cent. alcohol plus 20 per cent. toluene requires alcohol of a minimum concentration of 90·5 per cent. by weight; 90 per cent. alcohol and 10 per cent. toluene requires alcohol of a minimum concentration of 93·5 per cent. by weight.

Hydrocarbons of the paraffin series are much less readily soluble than the aromatic, and the solubility rapidly decreases with increase in molecular weight, normal pentane being soluble in all proportions at temperatures below 15° C. Isopentane is much less soluble. The addition of alcohol appreciably increases the highest useful compression ratio on petrols, being in this respect about twice as effective as commercial benzole. For practical purposes, therefore, the question of greatest interest is the condition under which small quantities of alcohol can be dissolved in petrol.

Mixing Agents.—Ormandy and Craven have investigated the value of various bodies as agents for bringing about the solubility of alcohol-petrol mixtures.[1] Of the various bodies they examined, they found that none were as much as one-fifth part as effective in stopping separation as water is in bringing about separation. The best agents are hydroxy compounds, amyl alcohol being the most effective. The minimum concentration of alcohol required to bring about a 10 per cent. solution of alcohol in Pratt's No. 1 spirit was found to be 95·8 per cent. by weight. After adding 5 per cent. of amyl alcohol the concentration of 93·2 per cent. was sufficient, the temperature being in both cases 15° C. This shows comparatively little effect, considering that the amount of amyl alcohol used is half the quantity of the actual ethyl alcohol employed in the mixture.

The result of research of stabilising agents indicates that it is not probable that they will meet with success in industrial use, and the incentive to make investigations along this line has ceased since the installation of large-scale plant in this country for the manufacture of anhydrous alcohol.

Alcohol used in Great Britain for fuel purposes has to be denatured in order to conform with the Excise laws; denaturing consists of adding impurities in order to make the spirit undrinkable. The bodies used as denaturants are usually pyridine, wood spirit, and certain petroleum fractions. The cost of this treatment is considerable, but at the present time an allowance or rebate is made by the Government to cover this. In addition, the Excise laws necessitate intermittent working of the distillation plants which produce the alcohol, thus preventing the use of more modern types of alcohol distillation equipment.

For some time after the war, alcohol-petrol mixtures were

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[1] Ormandy and Craven, *J.I.P.T.*, 1923, vol. ix., p. 129.

marketed in this country and used as motor spirit ; the mixture then consisted of approximately 50 per cent. of alcohol. Due to conditions, such mixtures could not be prepared at an economic price, and for a number of years there were no alcohol mixtures marketed. Since anhydrous alcohol became available in quantity the position has been greatly changed, in that it is now possible to prepare mixtures of low alcohol content in which a small quantity of alcohol, usually between 15 and 20 per cent., serves as an anti-knock agent when mixed with a large proportion of petrol. Such mixtures have all the anti-knock property that is desired for engines constructed at the present time, and the advantage obtained by possessing a high anti-knock value is sufficient to overcome the disadvantage of the mixture possessing a somewhat lower heat value than normal petrol.

Investigations into the properties of such mixtures indicate that if the nature and proportions of the petroleum bodies present and the quantity of alcohol present are suitably adjusted, a blend may be prepared which is suitable for existing engines without any modification in either carburetter adjustment or any other manner. Such mixtures sometimes contain benzole, but the presence of this body is not essential. The performance of such mixtures will be dealt with in a later section of the book.

Ethyl alcohol can be made from ethylene by absorption in sulphuric acid and hydrolysis of the ethyl hydrogen sulphate formed. This method was employed for some time at the Skinningrove Iron and Steel Works. Both ethyl and other alcohols are being made on a considerable scale in the U.S.A. from ethylene and other unsaturated hydrocarbons obtained as by-products from the cracking process in the American petroleum industry. Olefines are also obtained by cracking the lower hydrocarbons found in both natural gas and in the uncondensible vapours from petroleum distillation units.

CHAPTER VIII

SYNTHETIC FUELS

THE most important methods of preparing synthetic fuels are :—

1. The hydrogenation process by which either coal, coal tars, lignite tars, or other kindred substances are hydrogenated.
2. Processes for the reduction of carbon monoxide.
3. Processes for the condensation of gaseous hydrocarbons into motor fuels.

HYDROGENATION PROCESSES.—The earlier work on hydrogenation was carried out by Bergius, who found that by treating coal with hydrogen at extremely high pressures it was possible to produce liquid hydrocarbons. Since the earlier work of Bergius, a large number of experimenters have entered into this field and, although hydrogenation is only a partially investigated subject, commercial units have recently been installed, the whole subject being covered by a very large number of recent patents.

In Bergius' earlier work the reaction was obtained by employing extremely high pressure and comparatively high temperatures. The tendency in recent years, however, has been to reduce the pressure and use catalysts. Both these methods effect hydrogenation. By employing temperatures below the temperature required for the cracking of the material under treatment, simple hydrogenation can be obtained, but, when desired, the temperature can be raised whereby simultaneous cracking and hydrogenation can be made to take place. The former process is used for the manufacture of hydrogenated lubricating oils, the latter process being employed when high yields of saturated motor spirit are desired. It is very questionable whether the preparation of spirit by any of the existing hydrogenation processes would be possible were it not for the influence of import tariffs, which both in Germany and in this country give a very substantial subsidy in favour of hydrogenating plant when the latter operate on raw material of domestic origin.

A large proportion of the work in this country and in Germany has been carried out by the two chemical combines, the I.G. in Germany and the Imperial Chemical Industries in this country. The larger oil groups have working arrangements with the chemical companies. Hydrogenation is not likely to be employed for the manufacture of fuels other than those in the motor spirit range unless there should be a considerable change in the position with regard to petroleum supplies. As motor fuels, there is no doubt that the hydrogenation products obtained either by the treatment of coal or the tars produced from coal, lignite, and kindred substances are entirely suitable for petrol engine use. The same applies also to petrol made by the hydrogenation of heavier petroleum fractions.

The chemistry of the products made by the hydrogenation of coal by the Bergius process has been the subject of an investigation by Ormandy.

The hydrogenation of lignite tars has been carried out on a large scale in Germany at Leuna, a production of 200,000 tons of benzine being obtained and a pressure of 100 atmospheres being employed.[1]

The type of conditions used for hydrogenation can be judged from some of the patents. For instance, one patent (E.P. 272,556 I.G.), which describes the production of low-boiling liquids from coal oils and tars by destructive hydrogenation with flowing gases under high pressure, gives as an example that the crude oil is atomised in a vertical high pressure reaction chamber lined with aluminium over a catalyst composed of chromium and molybdenum oxides, temperature being 475° C., pressure 200 atmospheres. It will be noted that the temperatures utilised in this type of process are very close to those used in ordinary cracking.

Plant for the hydrogenation of petroleum products on a large scale has been built by the Standard Oil Company of New Jersey, who are operating large plants which are capable of converting heavy petroleum into over 100 per cent. by volume of gasoline, using pressures in the region of 3,000 lbs. per sq. in. Hydrogenation as applied to petroleum is now an established refinery process. It is applied to almost any quality of crude oil, being capable in all cases of producing petrols having high octane numbers, *i.e.*, good anti-knock properties. It also materially reduces the sulphur content of the products, the catalysts employed being sulphur-resistant. Its advent also ensures increased yields of light-stable, non-gum-forming, sulphur-free petrols and good burning quality kerosenes from crudes which would normally be suitable only for fuel oil or asphalt production.

PROCESSES FOR REDUCTION OF CARBON MONOXIDE.—By the reduction of carbon monoxide with hydrogen in the presence of a catalyst, synthetic fuel consisting largely of methyl alcohol can be made. The mixture produced in this way is known as " synthol," the process having been developed in Germany by Fischer. The composition of the mixture can be varied by the conditions under which the reduction is carried out, or by varying the composition of the catalyst, but at the present time production is not on a

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[1] Weinberg, *Petr. Zeit.*, 1929, xxv., p. 147.

sufficiently large scale to provide any serious quantities for fuel purposes.

PROCESSES FOR THE CONDENSATION OF GASEOUS HYDROCARBONS.—The quantity of gas available at oil-fields is extremely large, and for many years enormous quantities of gas have been wasted on account of its occurrence in districts where there are no industrial outlets and from which costs of transportation are high. During recent years a great deal of attention has been drawn to this, with the result that the use of large quantities has been facilitated by the laying of large pipe lines for the transportation of the gas from the production fields to towns where it can be used for heating, illuminating, and power production. In addition to this, a further quantity of gas is being utilised after compression in cylinders so that it can be employed as a substitute for acetylene in welding processes, etc. Certain of the condensable hydrocarbons are also compressed into the liquid form which is eventually vaporised, mixed with air, and used in this form for illumination, heating, etc.

It has recently been found possible to convert gaseous hydrocarbons into liquids by the action of heat and pressure, in some cases with the assistance of a catalyst. The gas utilised is generally either natural gas or a mixture of hydrocarbons obtained from cracking plants and distillation units. The subject has been investigated by Stanley and Nash[1] and by Wheeler and Wood.[2]

The mechanism of the fractional decomposition of normal paraffins is treated by Hague and Wheeler.[3] Similarly the decomposition of ethane, ethylene, propane, and propylene has been described by Frey and Smith.[4]

The condensation of natural gas containing paraffins into aromatic hydrocarbons has been patented by Wheeler, Dunstan, and the Anglo-Persian Oil Co.,[5] and a plant for the manufacture of motor spirit by the condensation of Persian natural gas has been installed in Persia. This plant is operating on a commercial scale, and the synthetic fuel produced is blended with the fuel produced by the older distillation and cracking methods.

Fischer[6] has patented a process for the polymerisation of methane. Catalysts such as chromium, zinc, aluminium, their oxides, and manganese chromate are mentioned in a patent for the process of manufacturing aromatic hydrocarbons from non-aromatic hydrocarbons in the presence of hydrogen.[7]

It is also possible to prepare olefines and acetylene by the treatment of methane.

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[1] *Nature*, 1928, vol. cxxii., p. 725.

[2] *J.S.C.I.*, 1929, vol. xlviii., p. 1. T.

[3] *Fuel*, 1928, vol. vii., p. 525.

[4] *Ind. Eng. Chem.*, 1928, vol. xx., p. 948.

[5] E.P. 309,455.

[6] E.P. 319,340.

[7] E.P. 281,291 (I.G.).

Such condensation processes are not purely confined to the production of motor spirit, but may be employed for the manufacture of heavier oils suitable for lubrication. The fuels made by the treatment of natural gas are generally high in aromatic content, and at the present time those made commercially are being used in the form of blends. At present the production of such fuels is comparatively small, but as the amount of gas available is very large, there is little doubt that this form of synthesis will be an important method for the production of more volatile fuels in the future.

PART III

THE RELATION BETWEEN THE CHEMICAL AND PHYSICAL PROPERTIES OF FUELS AND ENGINE EFFICIENCY

WHEN fuel is burnt in a furnace, that is to say utilised for external combustion, the chemical and physical properties of the fuel are important. The fuel should have heat value ; its viscosity should be sufficiently low to allow it to be readily atomised, and it should be substantially free from water and other extraneous impurities. The efficiency of the fuel for furnace firing does not vary greatly with different fuels, except in so far as the heat value itself varies. When the fuels are intended for internal combustion, the physical and chemical properties are more closely related to the suitability of the fuel and on the efficiency with which it can be utilised for power production.

Internal-combustion engines employing liquid fuel can be divided into two classes ; firstly, carburetter or vaporiser engines, in which the fuel and air enter the cylinder in the form of a mixture which is afterwards compressed and exploded by spark-ignition. This type of engine covers the petrol engine and engines using kerosene or vaporising oil. In their general features the latter are similar to the petrol engine, except that they are fitted with special heating appliances to volatilise the comparatively heavy fuel.

The second class of engine, usually known as compression-ignition or Diesel and semi-Diesel engines, are those in which the air is drawn into the cylinder on the suction stroke and compressed, the fuel only being introduced into the cylinder towards the end of the compression stroke. Such engines are employed for burning fuels heavier than kerosene which are not readily volatilised. The properties desirable in the fuels for the two types of engine are fundamentally different.

For use in petrol engines it is necessary to have a fuel which will volatilise readily in a current of air to form an explosive mixture. Volatilisation of the heavy oils used in Diesel engines is to a large extent unnecessary, though, no doubt, a certain amount of volatilisation takes place when the oil is injected into the heated cylinder. The properties of the various fuels used on these engines will be dealt with in a later section as each fuel is considered separately, but there is one particular property of fuels which has an important bearing on the construction of the engine, to understand which it is necessary to have some knowledge of thermo dynamics. As this subject is applicable to both types of engine, it is proposed to deal with it as a separate section.

Heat engines are operated by the expansion of the heated gaseous products of combustion, and the efficiency of the engine is dependent upon the expansion ratio, that is to say the ratio of the volume of the cylinder above the piston in its " top dead-centre " position and the volume above the piston when it is at its " bottom dead-centre." Since in all existing types of internal-combustion engines the expansion ratio and the compression ratio are dependent upon each other, it is usual to refer to this ratio as the compression ratio. Taking petrol engines as an example, a certain volume of explosive mixture is drawn into the cylinder ; this is then compressed during the compression stroke, and at about the end of the compression stroke this mixture is exploded. The heat generated increases the pressure of the gases in the combustion space, and these force the piston outward through the expansion stroke. Work is done by the fact that during the expansion stroke the pressures on the piston are higher than during the compression stroke ; the actual energy required for compression is stored in the moving parts from one cycle to the next.

Heat and work are both forms of energy. These have been correlated by Joule, who established the equivalents denoting how many foot-pounds of work were equivalent to a British Thermal Unit of heat. Joule's equivalent, therefore, gives the relationship between a quantity of heat and the corresponding quantity of work, which is : 1 B.Th.U. of heat is equivalent to 778 ft.-lbs. ; 1 H.P. is 33,000 ft.-lbs. per min. Working from these two constants one finds that 1 H.P. per hour is 2,545 B.Th.U.

If an engine gives perfect efficiency, that is to say 100 per cent. efficiency, it would require fuel containing 2,545 B.Th.U. in order to give 1 H.P. hour. In practice, the efficiency of internal-combustion engines is very much lower than this, but by measuring the heat in the fuel given to the engine and measuring the amount of work done by the engine, it is possible to state the overall thermal efficiency in terms of a fraction or percentage. The losses which occur in internal-combustion engines are partly due to friction and heat loss due to radiation, etc., but a large proportion of the loss is unavoidable as it is dependent upon the properties of the operating cycle of the engine. If the compression ratio of the engine were infinitely high, and all frictional and heat losses, by conduction, radiation, etc., were avoided, the efficiency would reach 100 per cent.

In an engine operating on the constant volume cycle, the theoretical efficiency may be calculated from the formula $E=1-\left(\frac{1}{r}\right)^{n-1}$, in which r is the expansion ratio and n is a constant, representing the ratio between specific heat of the gas at constant pressure and constant volume. The value n for the air cycle is 1·408 if no allowance is made for heat being lost. In practice, heat is lost during compression, and the value actually becomes 1·35. If one accepts the value for n as 1·25 it will allow for frictional losses and losses due to gas friction, and this formula approximates to the absolute maximum efficiency which can be obtained in practice.

In the case of the constant-pressure cycle engine, represented by the Diesel type of engine, this formula is modified by the effect of the cut-off ratio (R), and the nearest theoretical formula then becomes, according to Chalkley :—

$$E=1-\left(\frac{1}{r}\right)^{n-1}\times\frac{R^{n-1}}{n(R-1)}.$$

As already stated, in the constant-volume cycle engine, such as gas engines and petrol engines, ignition is effected by means of a spark, but in the Diesel engine and the cold-starting mechanical-injection engines, which are usually also classed as Diesels, ignition is effected by the heat of compression. In the latter case the timing of the ignition is obtained by timing the valve which admits the fuel into the cylinder. In spark-ignition engines the spark itself is timed. When gases undergo compression there is a tendency for their temperature to increase. If the rate of compression is extremely slow and the heat is thereby dissipated, one approaches " isothermal compression." The rapid compression obtaining in internal-combustion engine practice causes a rise in temperature. If no loss of heat took place from the system the compression would be referred to as " adiabatic compression." Actually in engines a certain amount of loss of heat takes place, but the conditions more closely approach adiabatic conditions than isothermal conditions. Now, the temperature of a gas after adiabatic compression can be determined by the formula :—

$$T_2=T_1\left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}}$$

where, under perfectly adiabatic conditions, the value of $n=1{\cdot}408$. Under engine conditions, with a certain amount of heat loss and therefore not true adiabatic conditions, the temperature can be calculated by this formula, accepting the value of n as being 1·35. These compression temperatures are important inasmuch as there is a certain temperature at which a fuel-air mixture will spontaneously ignite.

The minimum temperature at which the spontaneous ignition takes place is known as the temperature of spontaneous ignition, and the actual experimental figure obtained for the spontaneous-ignition temperature of the fuel depends considerably upon the conditions of experiment. The experimental side of this question is dealt with in another portion of this book. The lowest temperatures determined experimentally are those obtained with Moore's apparatus under conditions in which the fuel, together with oxygen, is allowed to be heated for a considerable period under such conditions as allow both fuel in the liquid and vapour phase to be present at the time of the ignition. Experiments in which the fuel is entirely vaporised give higher results. Experiments in which air is used instead of oxygen also give higher results. If the time permissible for the reaction is reduced this also affects the results, tending to raise the temperature necessary to produce ignition.

As the temperature in the cylinder of an engine is a function of the compression ratio, it is obvious that in the constant-volume cycle, where an explosive mixture is compressed in the cylinder and ignition is effected at the correct time by means of a spark, it is absolutely essential that the compression ratio employed shall not be sufficiently high to bring about spontaneous ignition. Otherwise one would experience ignition before the end of the compression stroke, and it would also result in irregular firing. The compression ratio employed in a constant-volume engine is therefore limited by the spontaneous-ignition temperature of the fuel. The converse applies to the conditions in a Diesel engine. There the temperature in the cylinder at the end of compression must be sufficiently high to ensure instantaneous ignition when the fuel is injected into the combustion space. If the compression ratio is not sufficiently high to bring about a temperature considerably in excess of the spontaneous-ignition temperature of the fuel, then one will obtain irregular firing or misfiring. In actual practice it is necessary to employ a very much higher compression ratio as a minimum for Diesel engines than the maximum which is possible on engines of the constant-volume cycle. This is in spite of the fact that the fuels used on Diesel engines have actually a lower ignition temperature than the more volatile fuels used on petrol engines. The actual limiting maximum compression ratio permissible with engines of the constant-volume type is not alone affected by the spontaneous-ignition temperature of the fuel, but is also limited by another property of the fuel which becomes noticeable at temperatures approaching the spontaneous-ignition temperature.

If a high compression ratio is employed in a petrol engine, a phenomenon known as "pinking" or detonation may occur, even if the compression ratio is not sufficiently high to produce spontaneous firing (*i.e.*, without the aid of a spark). Detonation occurs at a compression ratio very considerably lower than that which would be required to produce spontaneous firing in the engine. Many theories have been put forward to explain the exact nature of detonation, and although some difference of opinion may exist on the exact nature of this phenomenon, all authorities are agreed that it is a result of extremely rapid flame propagation within the cylinder. The phenomenon of detonation produces a sound which suggests the striking of one metal against another ; it is most prevalent in petrol engines when running at low speeds and open throttle setting. The sound is not actually produced by metal to metal contact or shock, but is the effect of gas pressure upon the walls of the cylinder. When an engine is detonating, instead of the combustion occurring during an appreciable portion of the cycle, it actually takes place almost instantaneously with an extremely rapid rise in pressure. The effect is not only to produce an unpleasant sound in the engine by suddenly developed high pressures within the cylinder, but also to cause a falling-off of the power generated by the engine.

We therefore find that in actual practice it is the phenomenon of detonation which limits the maximum compression ratio which can be employed with an engine of the constant-volume type. There is every advantage in employing high compression ratios with engines of the constant-volume type, provided detonation can be avoided. Not only does high compression ratio result in a high efficiency, but it also affords greater power output from an engine of given dimensions.

It is therefore the practice in designing petrol engines to employ the highest compression possible, but at the same time the compression is kept sufficiently low to avoid detonation even when the engine is running under adverse conditions, and has had its compression ratio somewhat raised by the formation of carbon deposits within the combustion space. The compression ratio that can be employed on petrol engines is governed by the following factors : the nature of the fuel, the size of the engine, the weakness or richness of carburation, the speed at which the engine operates, and to a very large extent by the design of the combustion chamber. Other influences have some slight effect, such as the barometric pressure, temperature of the outside air, temperature of cooling water, etc. The majority of these factors are in nowise connected with the fuel. Nevertheless, the fuel itself is variable, and therefore it is desirable that petrol engines should be supplied with fuel which can be used without causing detonation.

It has been found in practice that the various volatile liquid fuels employed in petrol engines show great variation in the tendency towards detonation, and it is important to be able to measure this property. Although the property may be estimated with a certain amount of accuracy by means of a chemical analysis of the fuel, at the present time there is insufficient information on the subject to permit a really close estimation to be made of the anti-detonation properties of the fuel from its chemical composition. It is preferable, therefore, to determine the anti-knock properties by direct experiment. The only satisfactory method of determining the anti-knock properties experimentally is to test the fuel on a specially constructed engine in which the compression ratio may be varied. One can then determine the maximum compression ratio, which can be employed with a given fuel before detonation commences.

VARIABLE-COMPRESSION ENGINES.—There is no doubt that for many years past firms manufacturing automobiles and motor cycles have experimented to determine the practical effect of operating their engines at different compression ratios. Gas-engine manufacturers also have had considerable experience of the effect of various fuels on the behaviour of high-compression engines. The subject, however, was not thoroughly investigated until Ricardo, working on behalf of the Asiatic Petroleum Company, built a special engine so designed that the compression ratio could be varied whilst the engine was in operation. This engine was a single-cylinder vertical overhead-valve engine. The cylinder, instead of being fixed to the crank-case, was held in position by means of a collar which could be used to raise or lower the cylinder, in order to increase or decrease the distance between the cylinder block and the crankshaft. In this way a wide range of compression ratios could be explored on each of a large variety of fuels to be tested.

Since that time many other variable-compression engines have been made expressly for the purpose of measuring the knock rating of fuels. Such engines are usually mounted with a delicate dynamometer to enable the generated power to be measured with accuracy. The type of dynamometer which has been found most favourable for this purpose is the swinging-field dynamo. If a normal dynamo is employed for measuring the load, in order to calculate the load on the engine from the electrical output of the dynamo, it is necessary to know the overall efficiency of the dynamo. With a given speed and a given load the efficiency is fairly constant, but as test engines are required to operate at varying loads and varying speeds one meets with considerable variation in the efficiency of the dynamo itself, thus making it practically impossible to obtain the engine output with the required degree of accuracy. In order to overcome the error introduced by variation in dynamo efficiency, the swinging field dynamo was evolved. In this machine the field magnets of the dynamo are mounted on ball-bearings concentrically with the armature, and by allowing a slight amount of movement of the dynamo field and employing a yard-arm working at a known radius from the centre of the dynamo, it is possible to make a direct measurement of torque on the field magnets. Any losses produced by windage between the armature and the field magnets also affect this torque, so that the torque of the field magnets may be taken as the torque generated by the engine. The electrical efficiency of the machine does not enter into the matter.

With such a machine the calculation of the horse-power generated is a simple matter. All the data that one requires is : the load required to hold the yard-arm in position, the radius at which this load operates, and the number of revolutions per minute made by the engine.

The determination of the compression ratio at which detonation commences under a given set of conditions may be measured in several ways ; the point at which the " pinking " sound becomes audible may be considered the detonation point. This method, however, has a serious drawback because there is no very clearly marked point at which detonation becomes audible. Different observers may hold widely different views as to whether an engine is " pinking " or not ; with the same observer and the same engine one can get a fair degree of concordance in different trials, but the point cannot be sharply discerned on many engines even when the observations are made by the same person.

Another method is to calculate the maximum power output of the engine at a given number of revolutions with all conditions fixed except the compression ratio, and plot a curve showing maximum power output against the compression ratio. By this means one can obtain a curve which shows the maximum power output at a given compression ratio, the power falling off as the compression ratio is increased beyond the point at which violent detonation takes place. Results obtained in this manner are not always concordant, and the writer does not consider it a satisfactory method of making examinations. A better method is to plot the compression ratio against the overall thermal efficiency, but even this method gives somewhat erratic results.

Probably the best method employed so far is the " bouncing-pin " method first employed by Midgley and Boyd.[1] These observers fitted an engine with an opening in the upper portion of the combustion chamber. Into this opening was fitted a spring-loaded piston, so arranged that the pressure of the explosion applied to the under surface of the piston whilst the spring pressed it from the upper side. Resting on this piston from the upper side is a heavy steel spindle. The spring pressure and weight of valve are such that the normal pressure of explosion only produces a very small amount of movement. The high pressure generated by detonation, however, produces such a movement on the piston that the spindle or

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[1] *J. Ind. Eng. Chem.*, 1922, No. 7, p. 589.

bouncing-pin is thrown upwards until it comes into contact with an electric " make-and-break " fitted with platinum points, and thereby closes an electric circuit. This circuit includes a battery and a simple hydrolysis cell in which water is decomposed into hydrogen and oxygen. The quantity of gas generated can be measured in a pipette. This electrolytic cell is a simple method of integrating the number of detonations and the magnitude of the detonations, since the period at which the electric circuit is closed is dependent upon the amount and intensity of detonation. By taking a given rate of gas evolution in the electrolytic cell, one can obtain a very delicate indication of the point at which detonation sets in, or of the intensity of detonation under fixed operating conditions.

Detonation, as previously mentioned, is affected by a very large number of different engine features, such as the valve timing, magnitude of the cylinder, temperature of the induction system, ignition timing, etc., and consequently all these must be standardised for a series of tests. As the results are affected by the dimensions, speed of the engine, and the design of the induction system, one does not obtain the same figures in terms of compression ratio with different test engines. It is therefore not satisfactory to employ compression-ratio figures as standards, but it is necessary to interpret the results backward into terms of the fuel mixture.

By taking two fuels, one possessing a strong tendency towards detonation and the other a high anti-detonating value, one may make mixtures the proportions of which are varied so as to have a detonating point anywhere over the range of commercial fuels. The procedure, therefore, in testing fuel on variable-compression engines is to use the engine as an instrument for matching the sample to be investigated against a synthetic fuel of known composition, and the results are stated in terms of a heptane-benzole mixture or some other synthetic mixture consisting of two pure bodies, the anti-knock characteristics of which are well known. Ricardo has used toluene as a basis for working out anti-knock property. At the present time the mixtures used for commercial testing are generally those of heptane and iso-octane, the heptane being a paraffin hydrocarbon with general characteristics similar to those of petroleum spirit except that it has a very strong tendency to detonate.

Iso-octane is not a straight-chain hydrocarbon, but is a trimethylpentane, consequently the length of chain is only five carbons instead of eight, as would be the case with normal octane. It is for this reason that iso-octane has a greater anti-knock property than heptane, in spite of its higher molecular weight.

Iso-octane can be obtained in the pure state, and is therefore used as a standard. The knocking tendency is expressed as an

"Octane Number," that is the percentage of iso-octane in an iso-octane-heptane blend which has the same knocking intensity as the fuel under test.

As the results obtained on variable-compression engines are affected very considerably by general details of engine design and by the operating conditions, a joint committee of the scientific societies interested in this work has arranged for the adoption of a standard variable-compression engine for making tests of the anti-knock property of fuels. This engine, known as the Co-operative Fuel Research, or C.F.R. engine (also known as the Horning engine), is being manufactured by the Waukesha Motor Company, Waukesha, Wisconsin ; it possesses a bore of 3¼ in., stroke of 4½ in., giving a displacement of 37·4 cub. in. Other details are as follows : the engine is steam-cooled, which gives a jacket temperature of about 208° F., and is capable of giving very high compression ratios, the range being between 3 : 1 and 30 : 1. The carburetter, which has been designed by the Co-operative Fuel Research Committee in conjunction with the U.S. Bureau of Standards, is of the air-bled fuel-jet type, with fixed fuel jet and adjustable air breathe. It is equipped with either two or four float chambers to allow instant change-over from one fuel to another.

The recommended speed for testing (Research method) is 600 revs. per min. The standard testing set at the time of writing is equipped with a three-phase iso-synchronous motor.

No dynamometer is employed. The load carried by the engine is not measured except in so far as the carburetter conditions are stabilised. It has been found in practice that very accurate control of the engine speed is a primary consideration in fuel testing, and that the majority of dynamometers do not allow of a sufficiently close control of this factor, consequently in the C.F.R. testing set a synchronous motor is employed which has the effect of controlling the speed of the engine by keeping it in phase with the periods of the mains. When the engine is working under load the current is being absorbed by the electric mains which are connected up to this set. All readings are based on the primary standards of heptane and iso-octane. When testing fuels possessing anti-knock properties higher than pure iso-octane, tetra-ethyl lead mixtures are usually employed as standards.

In view of the high cost of pure heptane and pure iso-octane, these fuels are not generally used for ordinary commercial tests, but they are used as primary standards, and from them a series of secondary standards are prepared. Mixtures in the secondary standards are then used in the normal practice of testing against ordinary fuels. The secondary standards are at the present time prepared by the Ethyl Gasoline Corporation, and are known as

"A.2," "B.2," C_6, C_7, and C_8. These standards are supplied together with a curve showing the relationship between mixture composition of these two liquids and the octane number. Results

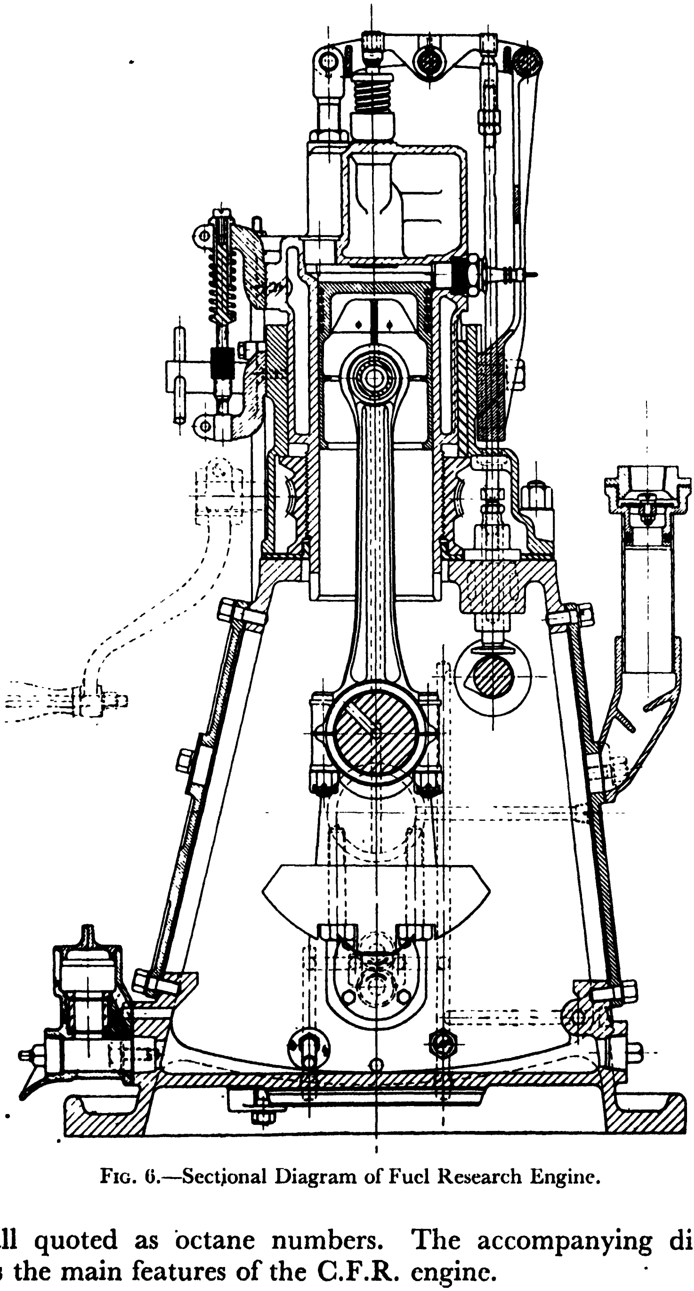

FIG. 6.—Sectional Diagram of Fuel Research Engine.

are all quoted as octane numbers. The accompanying diagram shows the main features of the C.F.R. engine.

The conditions under which tests are carried out in the C.F.R. engine affect the results very considerably, in spite of the fact that the procedure is purely one of matching commercial samples against certain reference fuels. For instance, it does not follow that because reference fuel B.2 matches a certain commercial spirit under C.F.R. test conditions that B.2 will match the same spirit under slightly altered conditions. A slight change, for example, in the induction air temperature will have the effect of making the two samples no longer a match but of making one knock more rapidly than the other ; consequently, it is important that the conditions used foı standard testing should approach as closely as possible to the conditions existing in automobile engines, and with this in view various investigations have been carried out in the United States

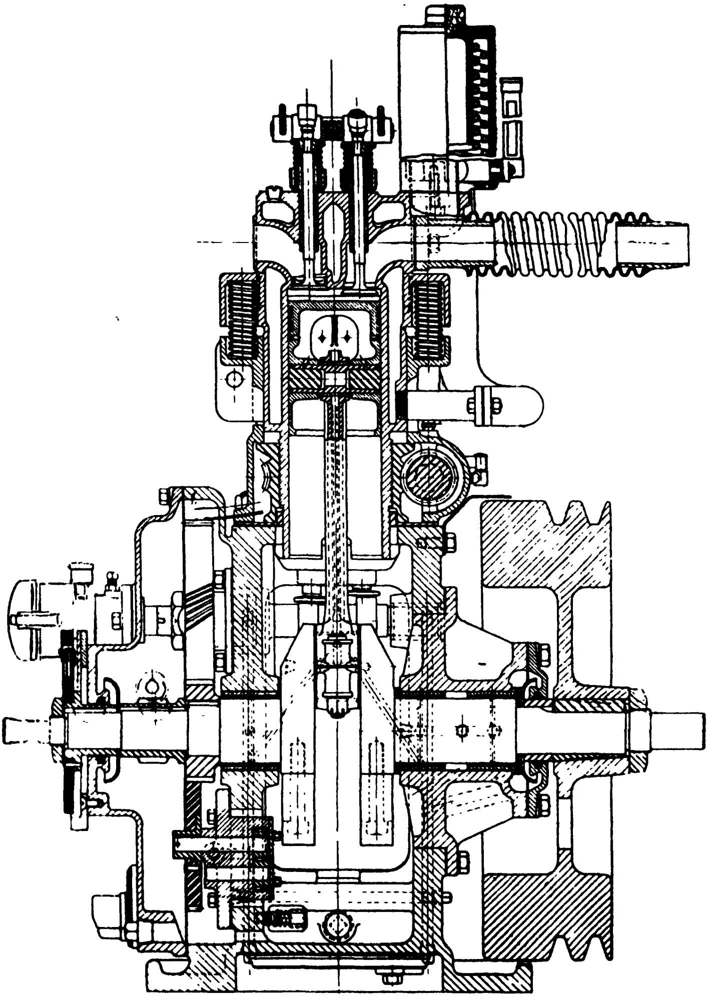

FIG. 7.—Fuel Research Engine.

comparing the results on automobiles with the results by the C.F.R. Research method.

As certain discrepancies were found, a modified procedure, which is generally known as the C.F.R. Motor method, has been developed. This method is supposed to give results more closely corresponding to experience in automobiles. There has been, however, a considerable amount of dispute as to whether the results obtainable by the Motor method are really more representative of actual car performance, and it is certainly the writer's experience with British cars that the C.F.R. Motor method shows a much greater variation from automobile performance than the Research method.

This is particularly noticeable when testing spirits of high olefine content, which are rated far too low by the Motor method ; this criticism also applies to tests of spirits containing percentages of alcohol. In the latter case, automobile experience indicates that alcohol has a very much greater anti-knock effect than is registered by the Research method of testing, and the Research method itself gives a much greater value to alcohol than the Motor method, so that the Motor method is very widely out of accord with actual automobile experience. The difference between the Research and Motor methods of testing on vapour-phase cracked spirit can be as much as sixteen octane numbers, whilst the difference on alcohol mixtures is not much less. The conditions employed in the Motor method are similar to those in the Research method, except that heat is applied to the air intake of the engine, and the speed of the engine is increased from 600 to 900 revs. per min.

At the present time the standardised conditions of the Motor method call for an air inlet temperature of 300° F. and a slightly increased spark advance over that employed in the Research method. A smaller jet is also used in the carburetter. The Air Ministry, in their specification No. D.T.D.230 for aviation fuels, employ the Motor method, only modifying the carburetter intake temperature to 260° F.

It is probable that this matter will be reconsidered, and a third procedure developed in the near future.

The technique of the operation of variable-compression engines and the relationship between various engine conditions and the operating results are very complex, and would occupy too much space to warrant their being dealt with in detail in the present work. A very comprehensive review of earlier work is to be found in Section II. of the " Report of the Empire Motor Fuels Committee," published by the Institution of Petroleum Technologists, in which a great deal of information obtained by Ricardo is compiled. Since this time, however, a mass of literature on this subject has appeared in technical periodicals, particularly in the American journals.

ANTI-DETONATORS.—From the earliest days of the petrol industry it has been known that certain fuels can withstand a higher compression ratio than other fuels, and it was known, for instance, that when burning coal-tar products a higher compression ratio could be used than when burning petroleum products. It was only when the subject became more carefully investigated that the actual determination of the anti-knock tendencies of various fuels was made. As Midgley and Boyd were investigating various fuels on behalf of General Motors Corporation they widened the field of their investigations and tested mixtures containing certain other bodies not generally regarded as fuels.

Midgley and Boyd employed an engine fitted with a " bouncing-pin." No arrangement was made for varying the compression ratio whilst the engine was in operation, but by closing down the engine and changing parts, it was possible to explore a range of different compression ratios. By employing a high compression on the engine and then utilising a fuel possessing distinct detonating tendencies such as kerosene, and then trying the influence of various bodies admixed with the kerosene, it was possible to tabulate various bodies in terms of the anti-knock properties they could give to the kerosene. It was at that time known that benzole, toluol, xylol, and alcohol, when added to normal fuel, would improve its anti-detonating properties. Midgley found that xylidine possessed this characteristic to a more pronounced extent than the previously mentioned bodies. Using the " bouncing-pin " as a measure of detonation and varying the percentages of the various bodies mixed with a standard kerosene, Midgley was able to obtain figures giving the relative knock-suppressing property of these various bodies. He found that toluene is better than benzene, xylene slightly better than toluene, and absolute alcohol better than the aromatic hydrocarbons. Midgley then found there were a number of substances which could suppress detonation ; some of these possessed this property to a very high extent. He also discovered that certain other bodies could induce detonation, for example, he discovered that bromine, oxygen, ethyl nitrite, and ethyl nitrate induced detonation, but iodine, selenium di-ethyl, and tellurium di-ethyl, and the tetra-ethyl compounds of tin and lead suppressed detonation.

The most remarkable of the products discovered was lead tetra-ethyl which, in terms of the number of molecules present in the fuel, possesses 1,400 times the anti-detonating effect of benzene. When referred to in terms of volume, 0·04 per cent. of lead tetra-ethyl is as effective as 25 per cent. of benzole—in other words, lead tetra-ethyl in terms of volume per cent. is 625 times as effective as benzene.

Following the publication of Midgley and Boyd's first paper in 1922, a large amount of work has been done on the subject of anti-detonators, practically the whole field of organo-metallic derivatives and many other compounds having been investigated. Iron carbonyl has been used to a certain extent for this purpose on the Continent, but though the original discovery of Midgley and Boyd, namely, tetra-ethyl lead, has met with considerable success, no other body possessing all the necessary characteristics to the same extent has been discovered. A satisfactory anti-detonator must be capable of being manufactured at an economical price, must be soluble in the spirit, and must have no appreciable deleterious effects on the engine. Lead tetra-ethyl is now used in large quantities, and its two main drawbacks, namely, its poisonous nature and the tendency to deposit lead on the walls of the combustion chamber, have not proved serious. After many investigations on the effects of the exhaust gases from engines burning tetra-ethyl lead, it has been found that the poisonous nature of the lead compounds produced is not sufficiently serious to interfere with its use, whilst the tendency to deposit lead compounds, particularly on the sparking-plug points, is overcome by using a halogen derivative such as ethylenedibromide in admixture with the fuel. The addition of this body enables the lead to leave the engine in the form of its halogen derivative.

It has been shown on thermo-dynamic grounds that the theoretical efficiency of an engine either of the standard volume type or of the Diesel type increases with increase of compression ratio. In practice, however, it is found that whereas there is every incentive to utilise the highest possible compression ratio on petrol engines which in any case operate at comparatively low compression ratios, there is no such advantage in utilising very high ratios on Diesel engines.

In the Diesel engine the *maximum* compression ratio is not limited by the fuel, but the ignition temperature of the fuel places a limit on the *minimum* compression ratio which can be used. With the comparatively high compressions employed in Diesel engines, one finds that an increase in compression ratio over and above the minimum requirements results in an increase in frictional loss due to the fitting of tighter or more numerous piston rings, in a necessity for building larger bearings, and an engine of heavier construction to withstand the higher pressures. This all results in increased frictional loss which is sufficiently great to neutralise any advantage gained by increase in the theoretical efficiency. In addition to this, it makes a more costly engine and one which is somewhat more liable to break down.

The incentive in Diesel engine construction, therefore, lies not in the direction of utilising the highest possible compression, but in using as low compression as possible compatible with certainty of ignition. The possibility of using minimum compression ratios is very important with the high-speed Diesel engines, which have to be of light construction. There is, therefore, at the present time, an incentive towards discovering agents which will have an effect almost the direct opposite of anti-detonators in that they will reduce the ignition point of the fuel and make it possible to utilise a lower compression on high-speed Diesel engines. Such special bodies have not been widely investigated to the time of writing, though many years ago the author investigated this subject and tested out the ignition point of mixtures of fuels containing two fuels, one of low and the other of high ignition point. He also tried the admixture of bodies such as paraffin wax, which possesses a particularly low ignition point, but found that the effects were not very pronounced unless large quantities of the low ignition-point fuel were employed. He also discovered that the effect of a comparatively small admixture of low ignition-point fuel might be very pronounced on the spontaneous-ignition tester, but was not so pronounced on the behaviour of engines when he tested out such mixtures on a slow-speed Diesel engine at various compression ratios. The engine which he employed was not a variable-compression engine, but was a standard Diesel engine in which the compression was varied by the introduction of special packings between the connecting-rod on the big-end bearing, this having the effect of raising or lowering the piston position relative to the cylinder.

The writer understands that knock promoters such as amyl nitrite have a more pronounced action than the normal fuels, but this is a department of research which has not yet been very widely investigated. There is every indication, from practical experience, that the ideal compression for Diesel engines is somewhere in the neighbourhood of 300 lbs. per sq. in. ; this takes into consideration both efficiency and cost of construction.

PART IV

FUELS FOR INTERNAL COMBUSTION

CHAPTER I

NOTES ON FUELS FOR ENGINES FITTED WITH CARBURETTERS AND VAPORISERS

In the present volume it has been deemed advisable to consider both carburetter and vaporiser engines simultaneously, as both types operate in the same manner, and it is usual even in petrol engines to use some form of heating in the induction system. The vaporiser is only a form of carburetter in which a comparatively large amount of heat is added to the fuel, and the distinction between a carburetter and vaporiser has become less clearly marked during recent years.

Under the term " vaporiser " the writer is considering purely the appliance for forming a heated mixture of fuel and air to be supplied to engines which operate on a constant-volume cycle. Hot-bulbs and such vaporising and ignition appliances which are used on engines, in which the fuel is introduced at the end of compression, are nowadays rarely referred to as vaporisers, and are not included in the present chapter. These are dealt with in the section devoted to Diesel engines and other engines operating on a constant-pressure cycle.

The history of the petroleum industry has been very closely connected with the development of the internal-combustion engine (particularly the petrol engine), both being almost entirely dependent upon the other. The petrol engine could not have been developed had it not been for the availability of adequate supplies of motor spirit, whilst the petroleum industry could not possibly have approached its present magnitude without the development of the petrol engine, which consumes more than one-third of the present production of crude petroleum. In view of this relation, and the fact that the quality of motor spirit has been very intimately connected with the economic position, it is advisable to make a brief historical survey in order to understand fully the present position.

The actual quality of motor spirit supplied at any particular time is not entirely dependent upon the requirements of petrol engines, but is very considerably affected by the demand for other petroleum products and the amount of crude oil available. For example, in a time of over-production there is a tendency to use volatile spirit of comparatively narrow boiling range. When there is a petroleum shortage, there is a tendency to enlarge the petrol fraction at the expense of the kerosene fraction, thus altering the boiling range. There is also a tendency to crack fuel oils so as to generate motor spirit at the expense of the fuel-oil production.

In the earlier days of the petroleum industry medicinal oils and lubricating oils were the most important products manufactured. The invention of the safety-lamp to burn petroleum oil opened a suitable market for the sale of products boiling from 150° to 300° C. This fraction was known as the kerosene fraction, and had to be kept roughly to within these limits, because the inclusion of lighter products—that is to say products of lower boiling point—would have reduced the flash point and made the oil unsafe for use in lamps. The inclusion of heavier fractions would have caused greater refining difficulties and would have made the product inferior in burning properties, that is to say a product more likely to develop smoke in the lamps and to form deposits on the wicks. As the more volatile spirits had to be removed from the lamp-oil fraction (they could not be included in any other marketable fraction), stocks of these low boiling fractions accumulated and had to be destroyed as there was no outlet for them. It was not until the petrol engine was developed that a remunerative market could be found for them.

The petrol engine itself is a development of the gas engine, being practically a gas engine for which the explosive mixture is made from a volatile liquid instead of from a fixed gas. The use of a volatile liquid makes it possible to carry a considerable quantity of fuel in a comparatively small volume, which would be impossible when using a permanent gas. The lighter products of petroleum, usually called petrol, possess a sufficiently high vapour tension to make them volatilise easily in air at ordinary temperatures, thus forming an explosive gaseous mixture. The nature of the fuel and the simplicity of the process lend themselves to the production of engines working at high speed and giving high powers for a small weight of engine. Such engines are chiefly used for land installations, marine work, aeroplanes, airships, and automobiles, the latter being at present by far the largest consumer.

In the earlier designs of carburetters the air was drawn over the surface of the spirit, or bubbled through the spirit so as to form a rich mixture of volatilised fuel, to which more air was added until the air-fuel ratio was correct for use in the engine. For this type of carburetter it was essential that the spirit should be capable of evaporation at normal temperature, and if the spirit contained any considerable proportion of high boiling constituents they would not evaporate with sufficient rapidity and would be left behind in the carburetter. This type of carburetter, known as a surface carburetter, had therefore the strong objection that on account of the possibilities of selective evaporation it could only be employed when burning readily volatile fuel. Whilst this carburetter was in use, one therefore finds that the motor spirit, all of which was obtained by direct distillation of crude oil, possessed a comparatively low end point, usually from 120° to 150° C. As the automobile industry developed and the demand for this fuel increased, refiners were desirous of increasing the range and of utilising some of the heavier fractions in the motor spirit. It was practically impossible to increase the boiling range until the discovery of the jet carburetter provided an instrument which, being so designed as to overcome any possibility of selective evaporation, enabled the refiner to include heavier fractions. The jet carburetter is almost universally used at the present time. It is operated by suction from the engine, it is extremely simple and reliable, and yields good results with suitable fuels. The principle of the jet carburetter is as follows.

The air is drawn by the engine through a slightly restricted aperture over a jet in which petrol is maintained at a constant level by means of a chamber containing a float, which automatically operates a needle-valve in the petrol inlet pipe. The partial vacuum caused by the suction of the engine suffices to spray the fuel into the air, as in a scent spray, thus making a mixture which is supplied to the engine through the induction pipe. A valve or throttle in the induction pipe is controlled by the driver or attendant, and regulates the supply to the engine. Various modifications and additions are used, such as separate small "pilot jets" for slow-running and extra-air fittings ; the principle, however, remains the same.

The object of the carburetter is to give approximately the same mixture strength, that is to say the same air-fuel ratio at all conditions of speed and load, and the maximum economy is obtained when the mixture strength is close to the minimum concentration which will give regular firing. In order to obtain maximum power a somewhat higher proportion of fuel is employed, and in modern carburetters there is usually a device for increasing the ratio of fuel present during the period of acceleration. In such carburetters an extra fitment, frequently known as the accelerator well or accelerator pump, gives an additional supply of fuel to the mixture when the throttle is suddenly opened. This results in a richer mixture being available during the period of acceleration than during the period of regular running at the same throttle setting.

The jet type of carburetter is much more suitable than the older surface carburetter for a wide range of fuels, because in the former the fuel is sprayed into the induction system, and therefore selective evaporation in the induction pipe can only take place to a very small extent. Furthermore, any unvaporised fuel that may exist in the induction pipe at any time must ultimately reach the engine. Fuel which is incompletely volatilised in the induction system would pass into the cylinder where it would be heated by the warm engine. It would also be subjected to the comparatively high temperature produced by compression. It would, therefore, have ample facilities for further volatilisation. In any case, should it remain in the form of globules in the cylinder until the time of ignition, it would then be burnt in globular form.

When the use of automobiles increased rapidly between the years 1910 to 1920, a comparative shortage of petrol was a result. This situation was to some extent relieved by widening the temperature limits when distilling crude in such a way that use was made of some of the constituents which had hitherto been included in the kerosene fraction. The original distillation range of petrol had been from normal temperature to 150° C., but during this period the temperature limits were increased so as to give a spirit with a final boiling point of about 200° C. These alterations reflected themselves in the changes in the specific gravity of the petrols. The spirit used on the surface carburetter possessed a specific gravity of 0·690. The increase in the distillation range referred to changed the specific gravity of the equivalent grade of spirit to over 0·720.

From 1920 up to the present time the rapidly increasing demand for motor spirit has been met largely by an increase in the production of crude oil and by two technical improvements. These were the development of the cracking process by which oils of high boiling point can be converted into products of lower boiling range, and the extraction of volatile fractions from natural gas.

Natural gas as obtained from oil wells contains a certain amount of volatilised spirit, which can be removed either by compression and cooling or by absorption in oil or with carbon. The product obtained in this manner is known as casing head or natural gasoline, and, being extremely volatile, it can be used for blending with heavier distillates to manufacture motor spirit. Though a motor spirit famine has often been predicted, the production of crude at the present time is so great, and the technical developments allow such a high yield of spirit to be made from the crude, that there is no danger of shortage in the near future. This is reflected in the fact that the price of motor fuel is extremely low.

By far the bulk of the fuel employed in internal-combustion engines of the petrol engine type has been derived from petroleum, but one must also bear in mind that quite a considerable quantity of benzole from the coal-tar industry has also been employed. Benzole, on account of its narrow distillation range, and its high anti-knock properties, is advantageously used in the form of mixtures with petroleum spirit, and though it is only available in comparatively small quantities, it is nevertheless of great service for improving the latter product. In Germany and France, alcohol obtained by the fermentation of vegetable products has been employed to a considerable extent. It is doubtful whether alcohol would have been used to any considerable extent had it not been for certain tariff advantages made in favour of alcohol in countries which do not possess their own petroleum supplies, and where the authorities consider it advantageous to encourage home-produced fuels. A certain amount of alcohol has been used in South Africa, because transportation costs for petroleum products are particularly high, and where the necessary raw material used for the manufacture of alcohol is available in large quantities. The use of alcohol in this country has increased recently, partially due to the tax position, which makes it possible for alcohol to be sold at an economic price in competition with petrol, and also due to the construction of plants in this country capable of manufacturing anhydrous alcohol.

Spirit prepared from shale oil has not been used to any great extent, as the shale industry has suffered very severely from the competition of low-priced petroleum products. The history of the Scotch shale industry (the oldest and most highly developed industry of this type) has indicated that it has been impossible to compete with imported products since the fall in market prices which took place a few years after the war.

Oils derived from the destructive distillation of lignite, and by low-temperature carbonisation of coal, have been used for motor spirit, and in several countries, most notably Germany and Britain, small quantities of oil have been made by the low-temperature carbonisation of bituminous coals. These products have only been marketed in very small amounts, and have been employed as substitutes for benzole, that is to say in the form of blends with petroleum spirit. The volatile constituents of low-temperature tar possess very high anti-knock values but require careful refining, as otherwise they are liable to be unstable and to possess a tendency to form gums.

Properties of Motor Spirit.—The following list includes the main properties which have a bearing on the performance of motor spirits :—

1. Specific gravity.
2. Fractional distillation.
3. Gum test.
4. Colour.
5. Approximate composition of hydrocarbons.
6. Anti-knock property.
7. Calorific value.

8. Elementary composition.
9. Latent heat of vaporisation.
10. Vapour tension.
11. Vapour density.
12. Explosive range.

Although all these properties are of fundamental importance in connection with the behaviour of motor spirits, it is not necessary in the majority of cases to determine these properties when making commercial evaluations. Petroleum spirit is often sold on specifications which contain only the specific gravity, distillation test, gum test, and colour. Such a modified specification is only possible, however, when the origin of the spirit is known, so that the other properties are not liable to great variation. If the origin of the spirit were unknown, it would be necessary to make engine determinations for octane number. For commercial requirements note is also made of the odour of the spirit, although this property has no bearing on the performance but may have very considerable bearing on sales.

The reason that commercial evaluations can be made on the results of comparatively simple tests is because in the majority of cases the properties are very closely inter-related, and a knowledge of the results of one or two tests gives one information which makes the testing of other properties superfluous. Other properties are similarly inter-related.

Specific Gravity.—The specific gravity is of considerable importance in the evaluation of motor spirit as it has a direct bearing on performance, and further gives to the experienced chemist a considerable insight into the constitution of the spirit. It is of great importance in the measurement of incoming cargoes of motor fuel, in that the relationship between volume and weight is dependent upon the specific gravity, that is to say, the number of gallons present in a ton of petrol is variable and is dependent upon the specific gravity. From the consumer's point of view it is the converse which is of primary interest. The consumption of fuel in an automobile engine is dependent upon the heat value, and the heat value of petroleum spirit is almost a constant when determined on a unit weight of fuel.

There is, however, considerable variation in the specific gravity, and as motor spirit is bought by volumetric measure, that is to say by the gallon, the weight of fuel bought is dependent upon the specific gravity of the fuel. One gallon of water weighs 10 lbs., therefore 1 gal. of petrol, specific gravity 0·700, weighs 7 lbs.; 1 gal. of heavier fuel with a specific gravity of 0·760 will weigh 7·6 lbs. Benzole has a lower heat value than petrol, but the difference in heat value is comparatively small and the difference in specific gravity is very great. If, therefore, we work out the heat units contained in 1 gal. of petrol of specific gravity 0·700, and in 1 gal. of benzole, specific gravity 0·880, it is found that :—

1 gal. petrol weighing 7 lbs. contains $7 \times 18{,}500 = 129{,}500$ B.Th.U. net.
1 gal. benzole weighing 8·80 lbs. contains $8{\cdot}80 \times 17{,}100 = 150{,}480$ B.Th.U. net.

Thus, if the price per gallon of the two products be the same, benzole is the cheaper fuel, though it possesses a lower calorific power than petrol.

With the majority of hydrocarbon fuels the heat value is slightly lower with the higher specific gravity, but as the variation in specific gravity is much greater it is found as a general rule that the higher the specific gravity the lower the consumption of fuel, that is to say, the greater the mileage obtained on an automobile. This rough rule is only applicable, however, to hydrocarbon fuels ; with other fuels it is necessary to take account of both the specific gravity and the heat value in order to calculate the heat units per gallon.

The specific gravity has a slight bearing on the adjustment of carburetters as it affects the level of fuel in the float chamber. A high-density fuel gives increased buoyancy to the float, and consequently the fuel supply to the float chamber is cut out at a lower level when a fuel of high specific gravity is employed. This means that the level of fuel in the jet varies according to the gravity of the fuel, and very wide variations in specific gravity may necessitate an adjustment in float setting.

When evaluating motor spirits of petroleum origin a high specific gravity is generally an indication of the presence either of cracked or of aromatic compounds, as the olefine hydrocarbons which are present in cracked spirit possess a higher density than the corresponding paraffins. Aromatic compounds are higher in density than either olefines or paraffins of the corresponding boiling point. It is, however, necessary in estimates of this nature to take account of the distillation range, as the higher boiling hydrocarbons of paraffin, naphthene, and olefine origin have higher densities than lower boiling compounds of the same series.

FRACTIONAL DISTILLATION.—Fractional distillation is a commercial test of the greatest importance in the evaluation of motor spirits. The test consists of distilling the spirit and noting the temperature at which various proportions of the spirit are distilled over. It is, therefore, a measurement of the boiling point of the constituents and of the quantity of the constituents. The Engler distillation which is used as a standard method of testing does not give the true fractional distillation of the spirit, but only a rough-and-ready test obtained by using apparatus of certain standard dimensions. There is reason to believe, however, that for the purpose of evaluation, the rough-and-ready commercial method of test has certain advantages over a more complex fractional distillation which can only be carried out by using special appliances.

The exact relationship between Engler distillation and performance is extremely complex, and has been the subject of many investigations.[1] Space will only permit a brief survey of the subject in the present volume. The initial boiling point is closely related to the vapour tension exerted by the spirit, and it is often considered as a measure of the ease of starting obtainable from a given spirit. The latter consideration is really only a half-truth, as ease of starting is more closely related to the quantity of spirit which is distilled at temperatures in the vicinity of 60°, 70°, and 80° C.; although as a general rule the percentage distilled at these temperatures is closely connected with the initial boiling point, in exceptional cases it is possible to get a low initial boiling point due to the presence of a very small quantity of volatile matter, which is insufficient to bring about ready starting on an automobile engine, particularly in cold weather.

As the vapour pressure is closely related to the initial boiling point, it is found that the loss of spirit by evaporation during transport and storage is largely a function of its initial boiling point, that is to say, spirits of low initial boiling point give comparatively large storage and handling losses.

The initial boiling point of spirits used commercially in this country is generally between 35° and 45° C., and buyers often prefer that this figure shall not exceed 40° C. The preference for low initial boiling point, however, does not always apply in other countries; in Roumania it is generally considered that a 45°-50° C. initial boiling point is the ideal. The initial boiling point of various spirits on the British market will be seen from the accompanying tables. As this property can be adjusted over fairly wide ranges by the blending of small quantities of casing-head gasoline in motor spirit mixtures, we may take it that the figures given by the analyses indicate the properties which the oil companies consider to be most satisfactory.

Extremely low initial boiling points are not desirable; not only do they cause "vapour-lock" trouble in some conditions of engine operation, but they bring about high losses in storage and transport, and also increase the danger in storage, as spirits of extremely low initial boiling point give off large volumes of gas when subjected to a slight rise in temperature. On this account it is usual to demand a fairly high initial boiling point when purchasing casing-head gasoline. As casing-head gasoline is extremely volatile, its initial boiling point is liable to be extremely

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[1] A very comprehensive study of this property will be found in "The Volatility of Motor Fuels," by George Granger Brown, Department of Engineering Research, University of Michigan.

low. When it is first collected from the stripping plant on the oil-fields, in order to overcome the tendency to gas, or " wildness," it is usual to treat this gasoline in a stabilisation plant which removes the light ends. Stabilisation plants are fractionating columns operated under pressure, in which the lower boiling constituents of the casing head can be driven off as an overhead product, leaving a " stabilised casing-head gasoline " with an initial boiling point in the region of 30° C.

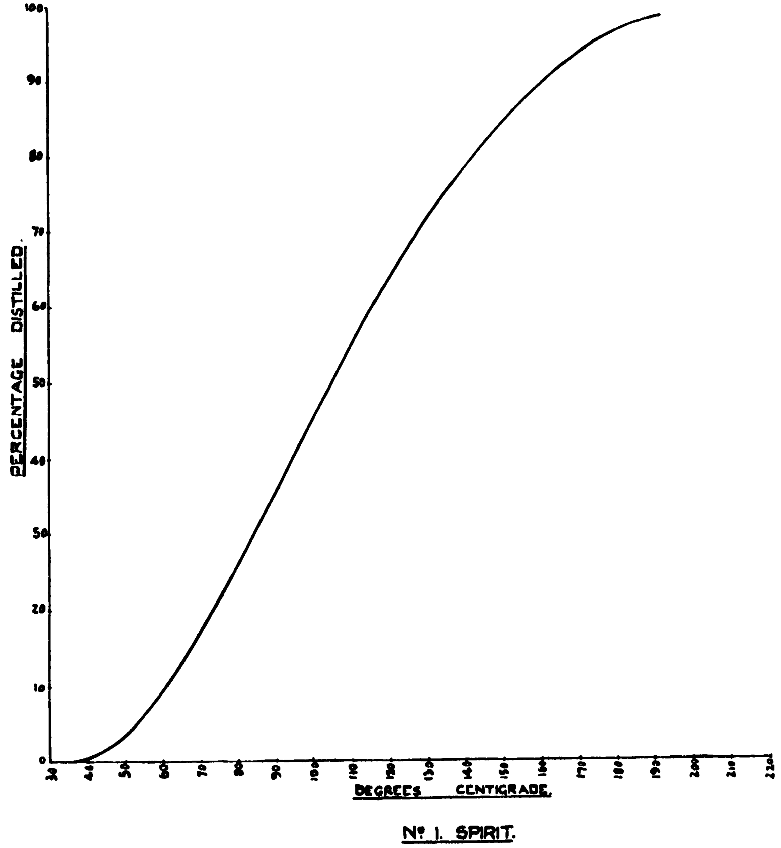

FIG. 8.—Distillation Curve.

The results of Engler distillation tests are best shown in the form of a curve in which temperature is plotted against the volume distilled. The yield at each particular temperature has some significance in the valuation, and the result or curve has to be considered as a whole. In commercial work particular note is usually made of the percentage distilled at 100° C. ; this is often referred to as volatility. There is no particular significance in this figure, but it happens to be a convenient point for indicating the general direction of the curve, and is a rough measure of the flexibility of the spirit. The term flexibility refers to the property of the spirit to give rapid acceleration on an automobile when the engine is cold.

It must be borne in mind, however, that intermediate points between the initial boiling point and 100° C. have a very great bearing both on starting and on flexibility. Motor spirit used throughout the world generally gives a yield by Engler distillation at 100° C. of between 25 and 60 per cent.; 25 per cent. is about the usual lower limit for commercial spirit, though in exceptional cases lower figures are encountered. Average commercial spirits in this country yield about 30 per cent. at 100° C.; first-quality motor spirit (No. 1) generally yields 36 to 45 per cent. at 100° C., whilst aviation spirit yields from 50 to 60 per cent. at 100° C.

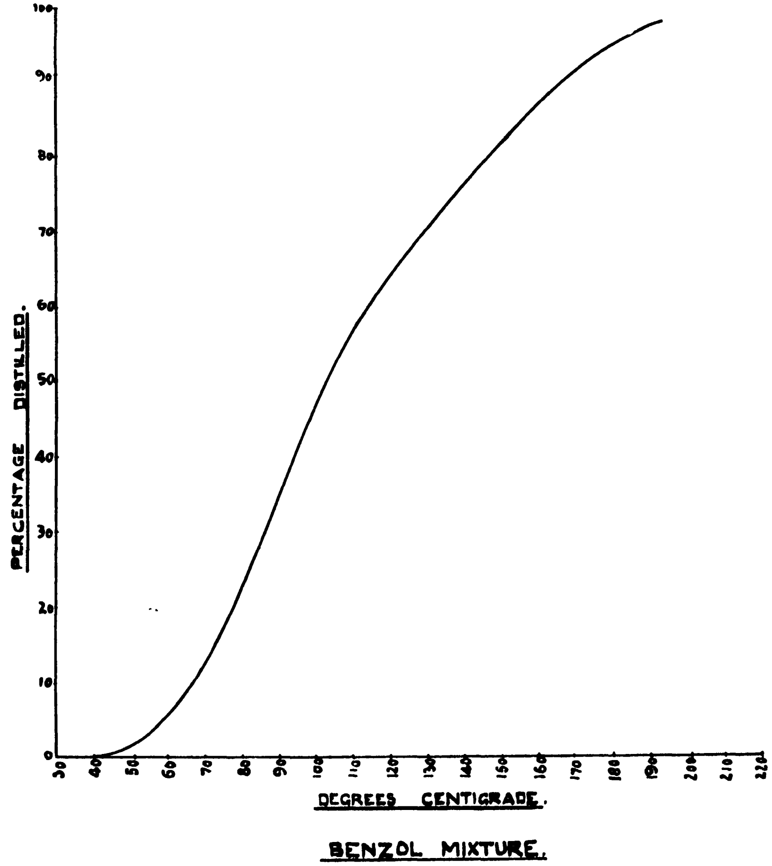

FIG. 8A.—Distillation Curve.

Another point which is frequently considered is the temperature at which 50 per cent. of the spirit distils. This is occasionally referred to as the mean boiling point, although this term is not quite correct as the mean boiling point should be taken by integrating each portion of the curve and finding the average boiling point of the whole mixture. The equilibrium boiling point referred to by refiners is the temperature at which the whole fraction is driven over from the top of the dephlegmating column on a continuous still, and is not the same as either the 50 per cent. point or the average distillation point.

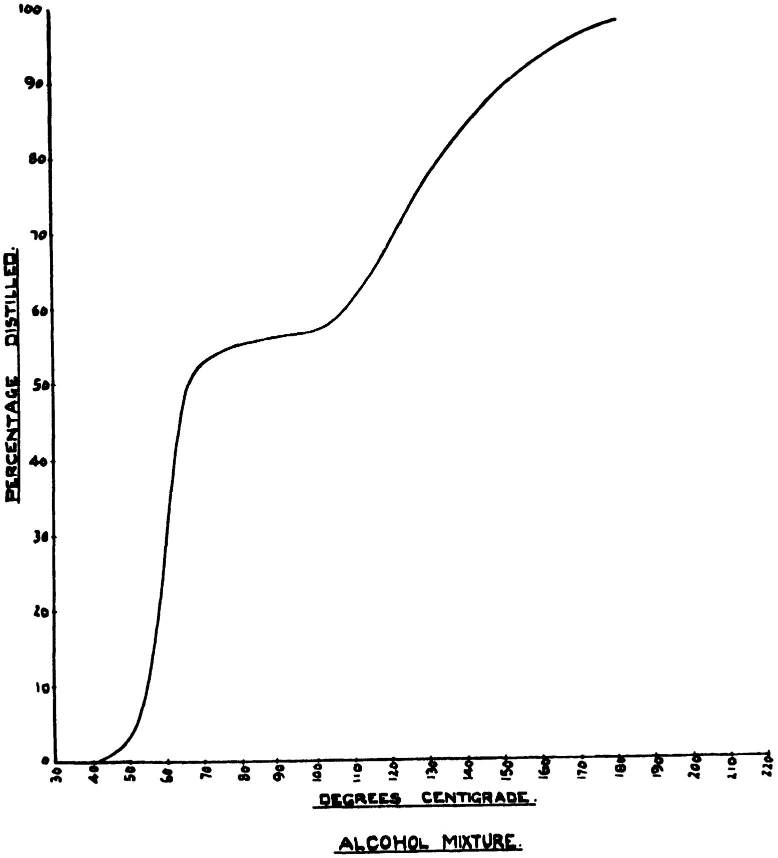

FIG. 8B.—Distillation Curve.

The end point of the distillation curve is of considerable importance primarily, as it is a measure of the liability of fuel to cause crank-case dilution. High end-point spirits give a greater amount of crank-case dilution than low end-point spirits. This dilution is brought about in the following manner : under running conditions, and to a greater extent under starting conditions in automobile engines, a certain amount of the fuel passes down the cylinder wall and becomes admixed with lubricating oil in the crank-case. As the crank-case is warm, and a certain amount of air and combustion gas passes through the crank-case, a partial distillation takes place, so that after a lubricating oil has been in use for a period it is found to have become contaminated with a certain amount of fuel ; the fuel having been partially evaporated, the contaminant is found to be mainly the higher boiling-point fractions of the fuel. If a fuel is light with a low end point it should be almost entirely evaporated, but if the end point is very high, large quantities of a body distilling between 100° C. and the end point of the spirit will be found in the crank-case. In actual practice, after an engine has been running for a period, depending upon the operating conditions, the dilution almost reaches an equilibrium, that is to say, the rate of evaporation of the diluent from the crank-case oil almost counterbalances the rate of contamination.

At one time it was common practice in the United States to use a quality of spirit known as U.S. Navy gasoline. This fuel was considerably less volatile than the average grade in use to-day. It usually distilled about 20 per cent. at 100° C. and had an end point in the region of 220° C., being fractionated to meet the U.S. Navy specification, which calls for an end point of 225° C. With this spirit in cold weather the dilution was very serious, samples of crank-case oil often containing as much as 20 per cent. of fuel residues.

Dilution to a small extent is not of much practical importance, but heavy dilution markedly reduces the viscosity of the lubricant and interferes with its satisfactory operation. Crank-case dilution is much more serious in engines fitted with vaporisers, as the fuel employed on these engines has an end point usually of between 250° and 300° C., and in certain cases dilutions as high as 50 per cent. are found. On account of this it is common practice to use very thick lubricating oil for vaporising engines, in order to compensate for dilution, but even when this precaution is taken lubrication is often unsatisfactory.

It is insufficient to take note solely of the end point when considering crank-case dilution. Motor spirit which has been run from antiquated plant containing poor fractionating equipment always contains a small amount of high boiling-point products which have been passed over during the bad fractionation. The quantity of these products is small, but they are sufficient to affect the end point. Modern equipment possessing a high degree of fractionation gives a sharp end point, but a fraction distilled with this equipment contains considerable quantities of bodies boiling close to its final boiling point, that is to say, there is no straggling portion at the end, but a sharp cut.

In fuel used on engines fitted with vaporisers the distillation curve is equally important and the end point is of very serious consequence, because a high end point generally has the effect of reducing the anti-knock properties of the fuel. The anti-knock properties of the different fractions from any particular crude vary considerably; they are usually much superior in the lower boiling-point portions, and fall off rapidly as the boiling point (and with it the molecular weight) increases; for this reason the anti-knock properties of kerosenes are usually much lower than those of spirits prepared from the same crude. It is also desirable in fuels for vaporisers to have a low initial boiling point and as short a boiling range as possible, as although heat is available for bringing about vaporisation, the vaporisation is still effected more thoroughly when dealing with low boiling fractions.

There is no particular object in making Engler distillations of the one or two pure liquids which are occasionally used as fuels; for example, alcohol or pure benzene. Alcohol has a definite unvarying boiling point, so that there is no distillation range to be determined; benzene in the pure state similarly has a definite boiling point. Commercial benzole, on the other hand, is a mixture, and purchasing specifications dealing with it always contain an Engler distillation test.

GUM TEST.—Hydrocarbon fuels such as petrol and benzole, when in the crude state, contain certain complex bodies which have been carried over during the distillation or formed by oxidation or polymerisation after the distillation. These bodies are to a large extent removed by refining treatment, but a small amount is liable to remain in the refined product. A certain amount of gum is also formed after refining by further oxidation or polymerisation, and this is particularly accentuated when the refining process has not been very effective.

Straight-run petroleum spirits contain very little gum even in the crude distillate stage, and the spirits from sweeter crudes such as the majority of the Roumanian and Russian crudes do not require any refining treatment but can be sold as finished products straight from the stills. Other straight-run spirits contain a little sulphur and require refining; as a general rule, however, after a light refining treatment the gum test of these spirits is negligible.

Cracked spirits are much more chemically active than straight-run products of the corresponding boiling point. The presence of olefines and di-olefines makes them particularly liable to both polymerisation and oxidation; their gum contents are not only usually considerably higher than the straight-run products, but they also tend to increase their gum contents during long periods of storage. Benzole requires a substantial degree of refining treatment before the gum test is sufficiently low for the commercial market.

Various methods of gum tests give results of different magnitudes, figures obtained by the copper dish test being much greater than those obtained from glassware, and the superiority of any particular method for motor spirit valuation is still a subject for discussion.

The gums are complex organic bodies which do not evaporate or distil, but, on heating, form either sticky deposits or coke. The main difficulty in automobile engines when burning fuel of high gum test is the formation of deposits on the inlet valve and inlet valve stem ; in some cases deposits also occur in the induction pipe. The writer's experience has indicated that gum troubles are much more pronounced in engines in which the induction system is so designed as to allow reflux condensation in the induction pipe ; for example, a vertical induction pipe with a carburetter at the lower end, and in which the engine is fed from the upper end, operates with the walls of the pipe continuously wet with fuel, which may remain in this position exposed to the up-going stream of air for some time. These conditions tend to form gums, and engines in which such a phenomenon can occur generally experience greater gum trouble. Undoubtedly, in such cases, it is not the initial or preformed gum in the fuel which is primarily responsible, but gum formed while the spirit is refluxing up and down the induction system.

Anhydrous alcohol supplied for use with motor spirit is practically free from gum prior to the addition of denaturent, and in the majority of cases the gum is not severe after the addition of the denaturent. Mixtures of alcohol and motor spirit frequently give a gum test considerably over the figures obtained from either product separately, and when blending such mixtures a special study has to be made of this subject.

In addition to refining, the gumming propensities of the present-day motor spirits are reduced by inhibitors. These are bodies which, when present in very small quantities, are capable of reducing the tendency to form gums, and they are supposed to act by prevention of the formation of peroxides. Cresols, hydroquinone, and other hydroxy and amino organic compounds have been found to possess this action, and have been used to a large extent by refiners as gum inhibitors.

Colour.—The colour of motor spirits is not of great importance at the present time, although in the early days a water-white colour was required. Colour frequently has a relationship with the gum test, a yellow colour accompanying a high gum content. In the days before gum tests had been investigated very thoroughly the colour was therefore used as a measure of efficient refining, but recently less importance was attached to the colour. Many spirits, in fact, are now dyed before distribution, sometimes as a means of distinguishing them from other spirits, and occasionally as a method of disguising the yellowish tinge which the spirit might possess. Straight-run spirits are, however, generally water-white, but cracked spirits are frequently liable to change colour at very short notice, some going yellow when kept in the dark and reverting to white when exposed to light, whilst others go yellow in the light and regain their colour when stored in the dark.

APPROXIMATE COMPOSITION OF HYDROCARBONS.—The majority of spirits contain a very great variety of hydrocarbons, and for analytical purposes these are divided into four main classes—paraffins, olefines, naphthenes, and aromatics. This division is only rough as it is possible to have hydrocarbons which belong to two classifications simultaneously ; for instance, a naphthene may have an unsaturated side chain and therefore be an olefine as well as a naphthene, and similarly aromatic olefines exist. The rough division into four hydrocarbons is, however, useful, provided one understands the analytical method by which these have been determined.

Paraffin hydrocarbons are generally stable against oxidation or other forms of chemical change. They are lower in specific gravity than the aromatic hydrocarbons of the same boiling point, whilst the naphthene and olefine bodies come intermediate in specific gravity. The paraffins are not usually considered desirable bodies in motor spirit as their anti-knock properties are very poor. They are, however, very clean burning and therefore considered desirable in illuminating oils. Possessing comparatively low spontaneous-ignition points, they are a desirable constituent of gas oil or fuel oils which are required for Diesel engine work.

The olefines are much more chemically active than the other three classes of hydrocarbons, and certain classes of olefines are very liable to form gums by oxidation or polymerisation. On the other hand, carefully refined motor spirit containing high olefine content can be quite satisfactory. Olefines are not present to any large extent in straight-run distillates, but are formed in large quantities by the cracking process. Spirits cracked by liquid-phase treatment usually contain over 20 per cent. of olefines, whilst products of vapour-phase cracking contain about 50 per cent. of olefines. Olefines have marked anti-knock characteristics, and they are not generally present in large quantities in kerosene, gas oil, or fuel oil. Olefines usually possess a characteristic odour.

Naphthenes are extremely stable bodies, in many cases more stable even than the paraffins. They have a higher anti-knock property than the paraffins and are easily refined so as to be free from gum. They give reasonably good burning oil for purposes of illumination, although not quite so good as the paraffins. They are present in large quantities in certain Russian and Roumanian oils, and also in certain special crudes which are widely distributed.

Naphthenes are present to some extent in nearly all crude oils, but the proportion varies greatly according to origin.

Aromatics are bodies possessing a much higher density than the other three classes of hydrocarbons. Though to some extent chemically active, they are very stable to heat and consequently impart to a petroleum fraction a high anti-knock value. They contain a higher proportion of carbon than the other hydrocarbons, and consequently burn with a smoky flame which makes them undesirable constituents of kerosene. On this account they are frequently removed from lamp-oil fractions by means of washing with liquid sulphur dioxide (Edeleanu process) in order to give the kerosene good burning properties. The extract so obtained can be fractionally distilled and the lower fractions added to motor spirit and higher fractions added to vaporising oil. These extracts are desirable constituents of fuel for carburetters and vaporisers on account of their anti-knock properties. The proportion of aromatics present in crude oil varies very greatly, certain oils, particularly those from the Dutch East Indies, being high in aromatic content and consequently of great value for use in petrol and vaporising engines.

Anti-knock Property.—The method of determining anti-knock property has been dealt with in another section, and the anti-knock property of the various types of hydrocarbons is referred to in the preceding paragraphs. This property is of fundamental importance in motor spirit valuation, and though it is desirous to use high-compression engines in order to obtain the maximum effect from the anti-knock property of fuels, there is still an advantage in using a high anti-knock fuel on an engine which will operate with satisfaction on a fuel of lower octane number. The advantage arises from the fact that the limiting low speed at which an engine can be operated is generally decided by the point at which pinking becomes so obvious as to make running irregular or rough, and it is therefore found that when operating on a fuel of higher octane number drivers do not so readily change down in gear as when the pinking of the fuel is more pronounced. As high gears give lower fuel consumption, general experience of drivers operating on two different fuels with the same car is that they get better consumption from the higher anti-knock fuel.

Motor spirits at present on the market are in nearly all cases blends in which various ingredients have been mixed in such a way as to yield the necessary starting, flexibility, and anti-knock properties, and the latter property is the most difficult and the most expensive to obtain. The use of cracked spirit has been greatly increased during recent years, and the main object in using cracked spirit has been to obtain high anti-knock products from crudes which would otherwise yield spirits of low octane number.

For blending purposes alcohol is the most effective fuel for raising anti-knock, and for this purpose it is approximately twice as effective as benzole ; benzole and toluene are also very effective anti-knock fuels and are preferable to the olefines. Vapour-phase cracked spirit which is very rich in olefines gives very high octane numbers, usually over 80 by the Research method, although they yield lower figures by the Motor method. In this instance the writer considers that the Research method is much more representative of general car performance.

The high anti-knock property of vapour-phase spirit is almost independent of the nature of the raw material from which the cracked spirit has been prepared. Liquid-phase cracked spirits containing only about half as much olefines as the vapour phase are not so high in their anti-knock properties ; these properties are to a greater extent dependent on the raw material from which they originate.

Some of the naphthene-base straight-run spirits have quite high values, for example, an aviation spirit of naphthene origin from a particular field in Roumania possesses an end point of 150 and an octane number of 79 both by the Research and Motor methods, whereas a corresponding spirit from a paraffin-base oil would give an octane number of below 65. The actual anti-knock property of the naphthene is not clearly known, and is certainly very dependent on the particular type of naphthene hydrocarbon present, and it is therefore unsafe to estimate anti-knock property by assuming any figure for the naphthene content as obtained by analysis—in fact, all attempts at computing anti-knock by estimation from the basic types of hydrocarbons present in the motor spirit is liable to very great error and in consequence is unsatisfactory.

Anti-knock is greatly dependent on the boiling range of the product, and a crude which yields an aviation spirit of over 60 octane number may yield a kerosene of less than 10 octane number. There appears to be a greater gap in octane number between naphthene-base kerosenes and paraffin-base kerosenes than there is between petrols from the same two bases. Special vaporising fuels distilling in the lower kerosene range may possess octane numbers as high as 80. This can be brought about by using highly aromatic distillates and adding further aromatics in the form of Edeleanu extracts.

Of special organic compounds used in small quantities for producing anti-knock properties, the only one which has been successful on a large scale has been tetraethyl lead, and in small quantities this is extremely effective. There is, however, a limit to the amount of this compound which may be employed. A small quantity produces a large anti-knock effect, but the further addition of the same quantity brings about a smaller rise in anti-knock property and it is not expedient to use large quantities of lead ; therefore, if extremely high anti-knock properties are required, it is necessary to start with a fuel of high octane number and then raise the anti-knock characteristics by the further addition of tetraethyl lead. In this way results can be obtained which could not possibly be obtained by the action of lead alone on a low anti-knock fuel.

Special spirits used for racing generally employ alcohol, benzole, and tetraethyl lead in addition to petrol. In such mixtures the lead is purely an anti-knock agent, the alcohol is simultaneously an anti-knock agent, and a body used for increasing the latent heat of the mixture ; the benzole gives anti-knock properties and at the same time a heat value which helps to keep the consumption from becoming excessive, whilst the petroleum spirit gives the necessary volatility for starting and flexibility. Racing mixtures are often more complicated by having more than four ingredients.

The spirits obtained from crudes in different parts of the world are so large in number and so variable in characteristics that no general rules can be made as regards their anti-knock properties. Some of the Russian spirits possess high octane numbers, whilst others are very low. Californian spirits are frequently high in octane number ; mid-Continental and Pennsylvania spirits are generally low. Spirit from the Dutch East Indies is generally high, due to the aromatic content ; Roumanian spirits are very variable, as even in the same field one finds both naphthene and paraffin-base oils, whilst the content of aromatics varies considerably.

CALORIFIC VALUE.—The power generated by a given quantity of fuel is dependent upon its heat value. Properties such as anti-knock, latent heat of vaporisation, etc., allow one to convert a greater or less proportion of this heat into the form of work, but the work obtainable is fundamentally dependent on the heat value. Under the most favourable conditions in petrol engines, about one-quarter of the heat present in the fuel can be converted into work. If the engines were 100 per cent. efficient it would be necessary to use 2,545 B.Th.U. to generate 1 H.P. per hour. Special engines operating on alcohol will yield about one-third of the heat of the alcohol in the form of work, and such engines have extremely high compression ratios.

There is very little difference in heat value in different samples of petrol. The heat value of the low specific gravity light paraffin-base petrols is slightly higher than that of petrol of higher gravity. Straight-run spirits are slightly higher in heat value than cracked spirit. The maximum variation is only about 5 per cent., and the heat value is generally in the neighbourhood of 20,000 B.Th.U. per lb. It is a property that is not usually worth estimating, as, when dealing with spirits of similar grades and general properties, the heat values are so close as to be almost within the range of experimental error.

The highest heat values are found in the hydrocarbons with the highest hydrogen content. Commercial benzole which contains about half the hydrogen content of petroleum spirit gives a heat value of about 17,789 B.Th.U. per lb. Pure benzene possesses a heat value of 18,090 B.Th.U. per lb. Pure alcohol gives a heat value of 12,697 B.Th.U. per lb.

The above figures are all gross, that is to say, are the entire amount of heat which can be obtained from the fuel when the products of combustion are cooled down to normal temperature. The net calorific value is the figure obtained by calculation from the gross, by making allowance for the fact that in the majority of circumstances it is impossible to cool the products of combustion to below 100° C., and that consequently the latent heat of vaporisation of the water which has been formed during combustion is lost. The net calorific value, therefore, is a lower figure than the gross calorific value, and the difference is proportional to the hydrogen content of the fuel.

The heat value of kerosene is lower than that of motor spirit, and again, with refined kerosenes, is not liable to great variation. The gross heat value of kerosene is usually in the region of 20,000 B.Th.U. per lb. or very slightly lower. Bodies containing oxygen, such as methyl and ethyl alcohol, are very much lower in heat value than hydrocarbons.

ELEMENTARY COMPOSITION.—The elementary composition of petroleum motor spirits shows very slight variation. They are practically pure hydrocarbons and contain about 16 per cent. of hydrogen, the remaining 84 per cent. being carbon. In spirits of high aromatic content or cracked spirit the hydrogen content is slightly less. Coal-tar derivatives contain approximately half the amount of hydrogen of petroleum derivatives, pure coal-tar benzene containing 7·7 per cent. of hydrogen and 92·3 per cent. of carbon.

The elementary composition of fuels rarely requires testing. The analytical procedure for the determination of the elementary composition is complicated, and the results do not give one much guidance as to the properties of the fuel. Fuels of high oxygen content possess low heat values, and this property is much more easily determined by a calorimeter.

LATENT HEAT OF VAPORISATION.—This property is of considerable importance in connection with carburetter design, and has considerable bearing on the maximum power output obtainable from a fuel. The latent heat of vaporisation is the amount of heat required to convert the liquid into a gas ; conversely, one may say it is the amount of cooling effect produced on vaporisation.

An exposed carburetter and induction system will operate at a much lower temperature than that of the atmosphere due to the latent heat of the fuel ; with petrol the latent heat of about 80 cals. is not very great, but, nevertheless, the cooling effect is quite noticeable, and sometimes this results in the formation of " snow " on exposed carburetters. Where smooth running is the main consideration and high power output is not particularly important, the cooling effect is not desirous, and it is common practice to heat the induction system in order to ensure more effective vaporisation. Where large power output is required, as in racing, the induction system is kept as cool as possible so that the shrinkage brought about by cooling will result in a heavier charge entering the engine. This is a point of particular note when dealing with alcohol, where the latent heat is particularly high.

Oxygen compounds possess a higher latent heat of vaporisation than hydrocarbons ; there is little variation in the latent heat of vaporisation of petrols from different bases, although the latent heat decreases as the fractions become higher in boiling point ; for example, Russian spirit fractions of 40° C. boiling point and 0·640 specific gravity possess a latent heat of 80 cals. per kg., whereas a fraction boiling at 175° C., specific gravity 0·813, gives only a latent heat of 51·6 cals. per kg. Intermediate fractions possess intermediate latent heats. Several formulæ have been given connecting latent heat with boiling point. The latent heat also varies with the temperature, being less as the temperature increases.

VAPOUR TENSION.—Liquids give off a vapour pressure below the boiling point. Usually this pressure is very small at temperatures far from the boiling point and rises as a curve, the boiling point being the temperature at which the pressure exerted by the liquid is equal to the pressure of the atmosphere. It therefore follows that if the pressure is reduced, boiling will take place at a lower temperature, and if the pressure is increased, the boiling point will be higher, these being points on the vapour-pressure curve.

The possibility of evaporating liquids in carburetter or vaporiser systems depends upon the partial pressure generated by the liquid. If the liquid gives off insufficient vapour at the temperature of the carburetter system, an explosive mixture will not be formed. For this reason kerosene cannot be used on the ordinary automobile engine, but by fitting a vaporiser, *i.e.*, raising the temperature of the fuel and the air until the temperature is one at which sufficient vapour pressure is exerted, it is possible to obtain an explosive mixture. As the vapour pressure of hydrocarbons is dependent upon the boiling point, the general behaviour of fuels can be taken from the distillation curves, which are more easily determined and more useful as a general measure of their performance.

There are, however, circumstances in which vapour pressure has to be taken into consideration in the normal valuation of fuels.

A petrol possessing a high vapour pressure may, under exceptional conditions either of high temperature or of low pressure, generate vapour in the piping, pumps, or other parts of the system connecting between the fuel tank and the carburetter jet. If gas is generated in this way, for example, in the feed-pipe to the carburetter, the bubble of gas will pass to the jet, and for a time the flow of petrol from the jet will cease and the engine "cut out." Such a phenomenon has been known to occur very frequently and is known as "gas-lock." Gas-lock is generally caused by an unsatisfactorily designed fuel system, and in the majority of cases can be cured by redesigning the system in such a way as to prevent overheating at a particular point which is causing trouble.

Fuels required for aircraft have to operate at very much reduced atmospheric pressure at high altitudes ; this means that there is a much greater tendency to generate gases, and the gas-lock problem is much more serious. It is therefore usual to specify certain maximum vapour pressures for aircraft fuels ; the vapour pressure is generally closely connected with the initial boiling point of the spirit, a low initial boiling point giving high vapour pressure.

The vapour pressure of pure bodies can best be determined by apparatus designed on the lines of a barometer, but when dealing with mixed bodies, such as petroleum fractions, the quantity of spirit used for the experiment affects the result, and therefore an empirical method consisting of heating a quantity of spirit and air in an enclosed space and noting the rise of pressure on a pressure gauge is found more satisfactory. The apparatus in general use at the present time is the Reid vapour tension apparatus, and aircraft specifications include an upper limit by the Reid vapour-pressure method ; for example, British Specification D.T.D.230 gives an upper limit of 7 lbs. per sq. in. at 100° F.

Vapour-pressure limits are also frequently included in specifications for casing-head gasoline. This spirit, which is the most volatile of the liquid fuels and is used for blending purposes, possesses a very high vapour pressure when it is first collected, and special fractionating equipment is employed in order to stabilise this body by removing certain of the lighter hydrocarbons. The presence of extremely volatile hydrocarbons has a disadvantage in that the rate of evaporation, both of the casing head and of blends afterwards made from this casing head, may be excessively high, and also that the storage and transport of products of high vapour tension increases the fire hazard by their giving off inflammable gases ; also that the high vapour tension is an undesirable characteristic in the fuel which is afterwards to be made from the casing head. The vapour tension is therefore used as a measure of ensuring that the casing-head gasoline has been efficiently stabilised.

Vapour Density.—The vapour density of any compound is dependent upon the temperature and the molecular weight, and it can be calculated from the molecular weight. The volume occupied by a molecule of gas is the same at any given temperature, regardless of the nature of the molecule, therefore 2 gm. of hydrogen, the molecular weight of which is 2, occupy the same volume as 78 gm. of benzole of molecular weight 78. If the molecular weight in grams of any substance is evaporated, the volume occupied at 0° C. and atmospheric pressure (760 mm.) will be 22·4 litres. This is known as the gram molecular volume. From this it will be seen that the higher the molecular weight of a body the more dense will be its vapour. This has a certain bearing on the performance of fuels in an engine in that the quantity of fuel which can be burnt in the cylinder is dependent upon the amount of air which can be taken in with the fuel into the cylinder, therefore a substance of high molecular weight giving a dense vapour occupies less space in the cylinder, and therefore a slightly greater weight of fuel can be employed. It follows that a greater power can be obtained from a fuel of higher molecular weight, other conditions being equal. The difference is not very great when dealing with ordinary fuels because the volume of air required is much greater than the volume of fuel, so that a slight alteration in the volume occupied by the fuel vapour does not increase the quantity of air which can enter the cylinder to any large extent. This accounts for the observation often made by drivers of low-compression engines that when using heavy fuels they can get greater power.

Explosive Range.—Fuel-air mixtures can only be exploded over a comparatively narrow range of concentration. Insufficient or excessive proportions of fuel result in a mixture which is non-inflammable. The experimental measurement of the range of fuel-air concentrations which is explosive is very dependent on the conditions of the experiment. For example, determinations made at atmospheric pressure give different results from those obtained at high pressures. Observations made in small vessels give a narrower range than those obtained in larger vessels. The limit at which a mixture will burn in a downward direction is different from the limit at which mixtures will burn in an upward direction, and therefore the actual figures given for explosive ranges as determined experimentally at atmospheric pressures have not a very direct bearing on engine conditions. The ranges are, however, in any case very small, and when studying carburetter design this point has to be borne in mind. It also has a very direct bearing on the difference in efficiency obtained between carburetting and vaporising engines operating on the constant-volume cycle and Diesel engines. If it is desired to obtain a low load from an engine fitted with a carburetter, it is impossible to obtain this by reducing the proportion of fuel present, as this would bring about a non-explosive mixture, and therefore to reduce the load one must restrict the total volume of explosive mixture to the engine. This means that the induction system must operate at a partial vacuum whilst the exhaust of the same engine is being discharged against full atmospheric pressure. This throws an artificial load on the engine, the work of pumping from a partial vacuum into a full atmosphere being a form of brake on the engine. This is the main reason why the fuel consumption of petrol engines at low loads is very high.

In the Diesel engine the matter of explosive range does not enter into consideration. In all circumstances a full charge of air is drawn into the cylinder, the induction system being approximately atmospheric pressure. If a small load is required, then only a small amount of fuel is injected and a small amount of air so situated that it comes into contact when the fuel is burnt. There is therefore no artificial load in the form of a pressure difference between induction and exhaust systems thrown on the engine, and the engine, therefore, is much more efficient at low load.

There is not a great deal of difference between the actual efficiency of petrol and Diesel engines at full load. One finds that the fuel consumption of a Diesel engine omnibus on a busy London circuit is less than half the fuel consumption of a similar petrol vehicle operating under identical conditions. This very large difference is in part brought about by the comparatively high fuel consumption of the petrol engine under idling and low load conditions.

With a knowledge of the vapour density and the ultimate composition of the fuel it is possible to calculate the exact amount of air required for combustion, and thereby calculate the percentage of volume of fuel mixture which will give complete combustion of the air with no excess of fuel. This mixture is always within the explosive range which includes mixtures containing both excess air and excess fuel. Eitner determined the limits for downward propagation of flame in a Bunte burette, and has given the following figures showing the gas volume limits for the explosive range for the following bodies :—

	Lower Limit.	Upper Limit.
	Per Cent.	Per Cent.
Alcohol	3·95	13·65
Ether	2·75	7·7
Benzene	2·65	6·5
Pentane	2·4	4·9
Benzine (petrol) . . .	2·4	4·9

It is essential in carburetter and vaporiser design that the mixture delivered to the engine should always be within the explosive range, irrespective of load conditions and irrespective of speed. As mixtures at the rich end of the explosive range result in the waste of fuel, it is undesirable that such mixtures should at any time pass to the engine. Mixtures on the weak side of the theoretical combustion mixture give maximum economy, whilst maximum power output is obtained by mixtures very close to the theoretical mixture. Mixtures at the thin end of the explosive range give very poor acceleration and power output and are therefore undesirable.

It will therefore be seen that the actual satisfactory working range of a fuel mixture which has to be delivered by a carburetter is extremely narrow, and as this has to be delivered under conditions of no load and extremely low speed when idling, full torque and low speed when climbing in high gear, full torque and high speed when driving full speed on the flat and also at high engine speeds with low torque when cruising, it will be seen that the design of a carburetter is by no means a simple matter. In actual practice it is desirous to so design a carburetter that the mixture is slightly richer in the idling position than under full load conditions. This gives more certain ignition and more rapid response for acceleration. Many carburetters also have auxiliary devices by which the mixture is enriched when the throttle is suddenly opened. This allows one to obtain the acceleration which is only obtainable with a reasonably rich mixture and at the same time effect the economy which can be obtained by using a fairly lean mixture when the throttle is being held open.

COMPETITIVE WINTER GRADES OF MOTOR SPIRITS ON THE BRITISH MARKET, OCTOBER 1933.

Grade.	Specific Gravity 60° F.	Engler Distillation (I.P.T.)															
		10% at °C.	I.B.P.	50° C.	75° C.	100° C.	125° C.	150° C.	175° C.	200° C.	225° C.	250° C.	F.B.P.	Rec.	Res.	Loss.	Octane Number.
			°C.	%	%	%	%	%	%	%	%	%	°C.	%	%	%	
Regent	0·7497	62	37	4½	17	32	52½	72½	90	97½	...	...	205	99	1	...	71·9
Regent Super	0·7385	57	36	5½	21½	38	56½	76	91	97½	...	...	204	98½	1	½	70·7
Regent Benzole Mixture	0·7449	60	36	4	20½	41½	60	77	89½	97	...	...	207	99	1	...	74·0
Shell	0·7431	63	38	2½	17½	36½	62	83	95	...	...	...	195	98½	1	½	69·6
Shell-Mex	0·7456	69	38	2	14½	33	56	77	92	...	...	...	199	99	1	...	66·9
Shell Racing	0·7794	67	41	1½	15	56½	79	90½	96	...	...	...	190	98	1	1	80·0
Pratts High Test	0·7366	62	36	3½	20	37	56	76	92	...	...	...	195	99	1	...	68·5
Pratts Commercial	0·7353	69	39	1½	14½	37½	62	82	93	...	...	...	196	99	1	...	64·8
Pratts Ethyl	0·7348	62	38	4	19½	39	62	83	96	...	...	...	191	99	1	...	78·2
Pratts Benzole Mixture	0·7640	70	44	1½	14	42	62½	78	91	97½	...	...	205	99	1	...	74·5
Power Premier	0·7365	58	35	4½	20½	36	55	75	91	...	...	...	197	98½	1	½	71·6
Power No. 3	0·7456	70	40	2	13	30	51	76	92	...	...	...	194	98	1	1	69·4
B.P. Commercial	0·7450	65	37	2	17	33½	57½	78	93½	...	...	...	198	99	1	...	67·9
B.P. Ethyl	0·7378	64	40	1	19½	40½	63	83	95	...	...	...	196	99	1	...	78·5
R.O.P. Commercial	0·7432	77	47	...	9	26½	53	81	95½	...	...	...	191	99	1	...	65·3
R.O.P. Zip	0·7369	69	44	½	14½	34½	62	82½	95½	...	...	...	190	98½	1	½	65·3
Redline Commercial	0·7449	68	38	2	14½	32	53	73	90	...	...	...	200	99	1	...	65·7
Redline Super	0·7340	60	33	5½	20½	37½	60	78	91½	...	...	...	194	98	1	1	66·6
Blue Spot (Universal)	0·7338	61	37	4	18	36½	57	75	90½	...	...	...	203	98½	1	½	63·2
Dominion	0·7360	69	38	1½	14	34½	60½	80½	92½	...	...	...	195	98½	1	½	63·8
Cleveland No. 1	0·7409	58	33	6	19½	33	48	64	84	97½	...	...	204	99	1	...	69·5
Aero Spirit	0·7390	63	35	3½	17	32½	52	70	86½	96½	...	...	205	98½	1	½	63·0
Corys No. 1	0·7357	65	39	3	17½	36½	60	78½	92½	...	...	...	200	99	1	...	64·6
Corys Commercial	0·7385	67	39	2½	16	35	57½	77	93	...	...	...	195	98½	1	½	64·1
Corys Benzole Mixture	0·7528	65	40	3	17	43	66	80	93	...	...	...	197	98	1	1	67·8
Aero Benzole Mixture	0·7540	68	39	1½	19	35	56	73	89	95	...	...	221	98	1	1	63·8
Glico Ethyl	0·7357	63	39	3	19	38	61	82½	96	...	...	...	187	98½	1	½	78·2
Glico Commercial	0·7435	60	33	5	19	35	58	73½	90	...	...	...	200	98	1	1	66·1
Citex Koolmotor	0·7526	59	45	2	48	52	65	79½	92	...	...	...	199	99	1	...	79·3
Citex Commercial	0·7346	59	32	5½	21	38	60	76	92	98	...	...	202	98½	1	½	63·6
National Benzole	0·7813	75	50	...	10	47½	71	85	94½	...	...	...	195	99	1	...	76·2
Aviation Plus Brittol	0·7468	69½	37	2½	13½	33	54	77	93	98½	...	...	205	98½	1	½	63·0
Alliance Motor	0·7480	73	43	1	8	25	50	72	90	...	...	...	200	98	1	1	56·0
Blue Star	0·7389	61½	33	5	18	33½	52	75	90½	...	...	...	201	98	1	1	63·6
G.O.P. No. 1	0·7501	74	39	1½	11	27½	52½	73	81½	92	95	97	255	98	1½	½	61·6
Anglo-Scottish	0·7487	79	45	1	7½	26½	59½	84	95	...	...	...	193	98	1	1	65·2

Competitive Summer Grades of Motor Spirit on the British Market, June 1933.

Grade.	Specific Gravity 60° F.	Engler Distillation (I.P.T.).													Octane Number.
		10% at °C.	I.B.P.	50° C.	75° C.	100° C.	125° C.	150° C.	175° C.	200° C.	F.B.P.	Rec.	Res.	Loss.	
			°C.	%	%	%	%	%	%	%	°C.	%	%	%	
Shell No. 1	0·7382	62	37	2½	22½	42½	65	84½	95	...	195	98½	1	½	67
Shell Mex	0·7401	68	38	1	14½	34	54½	77	92½	...	198	98½	1	½	65
Shell Racing	0·7986	80½	61	...	4	55	82	94	97	...	178	98	1	1	84
B.P. Plus	0·7364	63	42	1½	18½	39	58½	78	90½	...	202	98	1½	½	73
B.P. Commercial	0·7418	63	36	3	17½	35	52	70	87	...	199	98	1	1	67
Pratts High Test	0·7345	61	31	5	19	39	61	79½	93½	...	193	98	1	1	68
Pratts Commercial	0·7425	64	34	3	16½	32	52	72	89	...	202	98½	1	½	67
Pratts Ethyl	0·7358	63	38	2	20	42	66	84½	95	...	194	98½	1	½	77
Pratts Benzole Mixture	0·7581	67	40	2	16	40	63	80	92½	...	194	98	1½	½	72½
Cleveland No. 1	0·7383	58	33	6	20½	35½	51½	69½	86	96½	205	98	1	1	68
Regent Commercial	0·7574	66	36	3	14½	30	48	67	85	96	208	98½	1	½	72
Regent Super	0·7400	56	34	5½	23	42½	62½	79½	91	97	204	98½	1	½	75½
Regent Benzole Mixture	0·7496	61	36	2½	22	44	65	80	91	97½	204	98½	1	½	77
Glico-Ethyl	0·7351	61½	33	4½	19½	42½	67½	86½	96	...	186	97½	1	1½	76½
Glico Commercial	0·7435	63	34	4	16½	33½	53	71½	89	...	199	98	1	1	67
National Benzole	0·7814	77	50	...	8½	47½	70½	85½	95½	...	192	99	1	...	78
Citex Koolmotor	0·7539	59	40	2	45	50	68	83	94	...	196	97½	1½	1	79½
Citex Commercial	0·7354	66	35	2½	16	35	59	79	94	...	202	99	½	½	63
Power Premier	0·7348	58	33	5½	21	38	58	78	91	...	196	98	1	1	74½
Power Commercial	0·7434	66	37	2½	15½	31	50	72	91	...	198	98	1	1	68
R.O.P. Zip	0·7426	75	43	1½	10	34	63	84	96	...	198	98½	1	½	67
R.O.P. Commercial	0·7407	65	33	3½	16	32	54	80	95	...	191	98	1	1	69
Corys No. 1	0·7292	59	34	4½	19	38	60	80	93½	...	196	98	1½	½	61½
Corys Commercial	0·7329	62	34	4	18	36	56	77½	93	...	196	98	1	1	62½
Corys Benzole Mixture	0·7372	62	37	2½	20	43½	66	84½	95	...	191	98	1	1	66
Dominion	0·7315	65	37	2	16	41	70	86	95	...	185	98	1	1	62½
Redline Super	0·7341	60	35	5	18½	40	62	80	94½	...	190	98	1	1	65
Redline Commercial	0·7470	67½	35	4	17½	30	53	69½	88	...	202	98	1	1	67
Bowrings Spirit	0·7351	59	30	6	18½	35	53½	69	85	95½	203	96½	1½	2	63
Aero Special	0·7364	71	40	1	12½	31	57½	80	95	...	200	99	1	...	60
Blue Star Super	0·7321	65½	33	4½	17	38½	64½	85	96	...	183	97½	1	1½	61½
G.O.P. No. 1	0·7363	64	33	4	17	34	57	77	90	95	227	97½	1½	1	60
G.O.P. Commercial	0·7387	65	35	3½	16	33½	56	76	89	94	227	97½	1½	1	62½
Silkol Spirit	0·7401	78	48	...	8	32	63	87	...	...	174	98½	1	½	61

These are the results of tests taken in the author's laboratory on samples purchased in the open market.

During the past year a new alcohol fuel named " Cleveland-Discol " has been marketed in this country by the Cleveland Petroleum Products Co. The author carried out much of the experimental work on this particular blend, and trials were made including tests on a large number of automobiles. The fuel has properties quite different from normal petrols, although in many respects resembling " Koolmotor " marketed by Cities Service Oil Co. The properties of a typical sample of " Discol " are as follows :—

Specific gravity at 60° F.	0·7524
Distillation—	
Initial boiling point at	38° C.
5 per cent. at	50° C.
10 ,, ,,	55° C.
35 ,, ,,	68° C.
48 ,, ,,	75° C.
52 ,, ,,	100° C.
65 ,, ,,	125° C.
80 ,, ,,	150° C.
92 ,, ,,	175° C.
Final boiling point at	195° C.
Recovery	98 per cent.
Residue	1 ,, ,,
Loss	1 ,, ,,

Octane number (Research method)—80
Vapour pressure (Reid) —9·5 lbs.

Although this fuel contains between 15 and 20 per cent. of alcohol, the actual consumption tests carried out indicate that the mileage obtained on an average English car is almost exactly the same as the mileage obtained by premium grade spirits of entirely petroleum origin. On high-compression engines the consumption with " Discol " was found to be slightly superior.

It will be noted that the octane number by the Research method is given as 80. Tests by the Motor method give a slightly lower figure, but in the author's opinion neither figures give a true indication of the anti-knock properties of this fuel, as numerous trials on sports cars fitted with high-compression engines (compression ratio about 7 : 1) indicated that this blend was almost an exact match in anti-knock quality with a mixture consisting of 50 per cent. of premium grade spirit of 78 octane number blended with 50 per cent. of commercial benzole. Experience on sports cars showed that " Discol " was definitely superior to a mixture of 60 per cent. of 78 octane number spirit with 40 per cent. commercial benzole. This indicates that the performance on sports engines of the types used is very much higher than one would anticipate from an 80 octane number spirit, as the same engines practically refuse to run on premium grade spirit containing tetraethyl lead possessing an octane number of about 78 by the Research and Motor methods. The author is therefore of the opinion that both the Research and the Motor methods give comparatively low readings on alcohol mixtures.

The comparatively low consumption of this mixture is rather surprising as the heat value of the alcohol mixture is undoubtedly considerably lower than that of a straight petrol, but the author found that the percentage of carbon monoxide in the exhaust gases of engines running on " Discol " was much lower than when the same engines operated under the same conditions on petrol, and it is probably this increase in the efficiency of combustion which is counteracting the low heat value. The mixture in question gave starting tests both on the road and in a special " startability " motor which were quite equal to the best grades on the market. Flexibility was equally good, and the engine has a tendency to run somewhat cooler and gives, generally, a smoother running condition than with normal petrol.

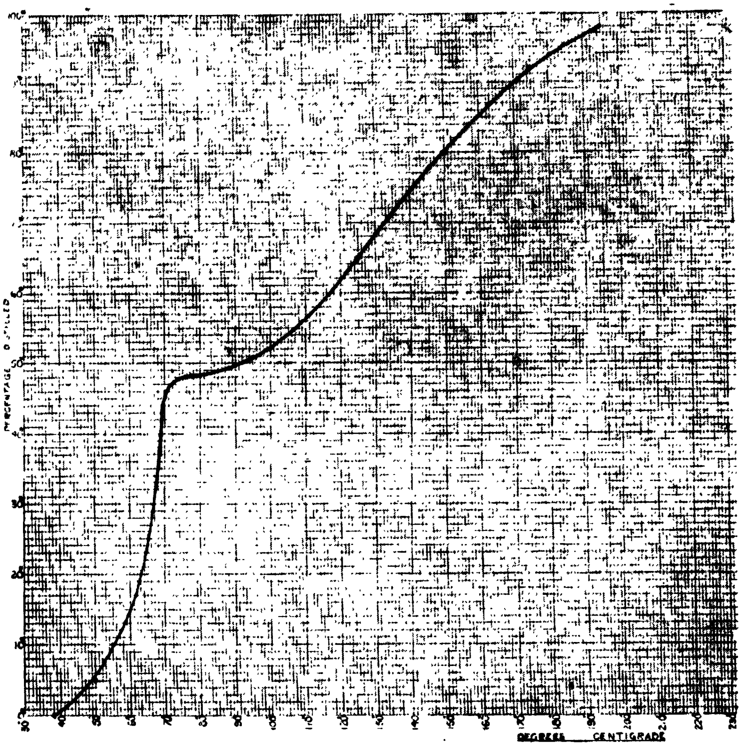

Fig. 9. "Cleveland-Discol."

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CHAPTER II

NOTES ON FUELS FOR ENGINES FITTED WITH ATOMISERS

In this section we are dealing with engines in which the fuel is injected into the cylinder towards the end of the compression stroke. In the majority of such engines ignition is obtained by the heat of compression, and the engines are generally referred to as Diesel engines. In some engines of this type hot bulbs or hot plates are used to assist ignition, and such engines are often known as hot-bulb engines or semi-Diesel engines. Some time ago it was common to classify engines in which the fuel was injected by means of compressed air as Diesel engines, whilst those fitted with mechanical injection were referred to as cold-starting engines. The tendency at the present time, however, is to call both these types Diesel engines, and to refer to the general class including hot-bulb engines as heavy-oil engines.

These types of prime movers all operate on the constant-pressure cycle or on a modified form of constant-pressure cycle. The fuel is not injected instantaneously in the cylinder but takes a definite period to enter, therefore the combustion is not in the nature of an explosion but is more in the form of a torch burning inside the cylinder from the injecting mechanism. The indicator card of such engines, therefore, does not show a sudden jump in pressure from the pressure of compression to the pressure of explosion, but usually shows a certain amount of rise in pressure over and above the normal compression, and the pressure is maintained with a slight increase or decrease during the period in which fuel is injected, quite an appreciable portion of the cycle having elapsed before normal expansion commences.

The temperature in the cylinder of an engine starting from cold is a mathematical function of the degree of compression, and if the compression is high enough the resulting temperature is sufficiently great to ignite the fuel immediately it enters the cylinder. When this means of ignition has to be employed it is necessary to use a high compression ratio, and the compression pressure at the end of the compression stroke in Diesel engines is usually from 350 to 600 lbs. per sq. in. If it is desired to use a lower compression, then it is necessary to take other means for effecting ignition ; some portion of the combustion-chamber wall must be raised to a higher temperature by some external device, such as a blow-lamp. For this type of cycle it becomes obvious that the fuel does not need to be evaporated prior to entry to the cylinder, therefore it is not essential to use a volatile fuel.

The problem of detonation, or knocking, does not arise, as the conditions which bring about knocking in a petrol engine do not exist in a heavy-oil engine, that is to say the cylinder is never full of explosive mixture. The high compression makes it easier for this type of engine to burn fuels containing asphaltic or gumming material, and as heavy-oil engines usually operate at a lower speed than petrol engines there is more time available for combustion. The high compression also makes this particular type of internal-combustion engine very efficient, and the overall thermal efficiency of Diesel engines may exceed 35 per cent.

The accompanying diagram shows a good example of the indicator diagram of a slow-speed Diesel engine injecting with compressed air. It will be noticed that the top of the indicator card in this case is flat. The high-speed mechanical-injection engines do not give flat indicator cards of this type, but give a card intermediate between this and the usual petrol-engine card.

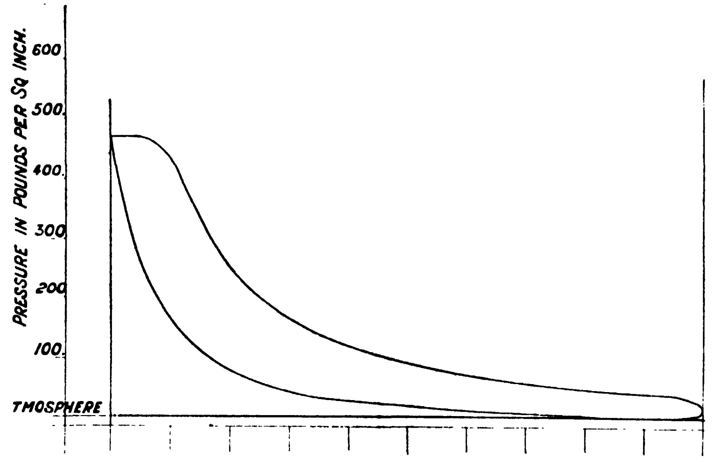


Fig. 10.—Indicator Diagram of Diesel Engine.

The fuels mainly used for Diesel engines are of petroleum origin and may be either distillates or residua. Shale oils, lignite oils, and sometimes coal-tar oils are also employed with success. Animal and vegetable oils will operate quite satisfactorily on Diesel engines, but are very rarely used on account of cost.

Though Diesel engines are capable of utilising much higher boiling fractions than petrol engines, and are also capable of burning asphaltic or resinous material, they are nevertheless quite distinctly sensitive to certain impurities, particularly water and ash. As

Diesel oils are often of fairly high gravity and medium viscosity it is possible for them to hold up water in suspension, and the presence of such water is very undesirable. If the water were in solution and thereby finely distributed it would not have any pronounced effect, but in hydrocarbon oils water is totally insoluble and, when suspended, is not always in a fine state of division. The result is that globules of water may enter the fuel pump, eventually resulting in a charge of water being passed to the engine. This causes misfiring or irregular running. On engines fitted with governors this results in the falling of the governor and an overload charge of oil entering at a later stroke, the effect of this heavy charge of oil being to dirty the engine by carbonisation.

When tar oils of high tar acid content are used a certain amount of water is in solution in the tar acid ; this water being finely distributed does not cause trouble, and it is only the suspended water which is injurious.

Oils of higher viscosity frequently contain small quantities of suspended matter part of which may be combustible, such as particles of carbon ; other portions are incombustible matter, such as sand, and these bodies being insoluble in benzole are estimated as mechanical impurities. The portion which is incombustible is determined by the ash content, although the weight of ash is not exactly the same as the weight of incombustible material present, as some materials increase or decrease in weight on heating during the ash test ; for instance, particles of calcium carbonate are incombustible, but on ignition give off carbon dioxide and leave a residue of lime which is of lower weight than the original calcium carbonate. Metal particles, such as iron, on ignition absorb oxygen to form oxides, and therefore increase somewhat in weight.

The mechanical impurities of heavy oils consist mainly of carbon, rust, and sand, but a certain amount of very finely divided inorganic material, originating possibly from the oil itself, is sometimes found. On large engines of the stationary type mechanical impurities to the extent of about one-tenth of 1 per cent. can be handled by the filtering apparatus, or, if very small, pass through the engine. In high-speed Diesel engines of the type used for road vehicle propulsion any mechanical impurities cause serious trouble, and the oil should be completely free from these as there is always a risk of a certain amount of dust or rust from piping getting into the oil. There are usually elaborate filtering devices in the fuel supply system, but these are not large and are not capable of handling much impurity, only being intended as a final assurance that no mechanical impurities can get to the very delicate fuel pump and injector system.

Inorganic impurities, which are denoted by the ash content of the fuel, are a very serious drawback to any type of heavy-oil engine fuel. The major portion of the ash is burnt and blown out through the exhaust valve, causing no trouble, but if a small proportion of it becomes mixed with the lubricant on the cylinder wall it will cause heavy wear of the piston, cylinder, and piston rings ; also, on being passed towards the exhaust it is liable to remain under the exhaust valve (in poppet valve engines), when it results in pitting of the exhaust-valve face. This may be brought about either by incompletely burnt organic matter such as coke, or by inorganic matter such as sand and rust.

Practically no ash is permissible in fuel for high-speed Diesel engines. Slow-speed engines, particularly large sizes, may burn fuels containing small percentages of ash, but the quantity should never exceed 0·05 per cent. The fuels used for high-speed Diesels at the present time are nearly always gas oils or mixtures of gas oil and kerosene. Some of the gas oils used are of fairly high boiling range, the higher boiling constituents of which closely approach crude lubricating oil distillate. At the present time the average oil used on this type of engine may be considered as a light gas oil. The distillate oils, being extremely mobile and comparatively free from colloidal matter, do not carry mechanical impurities or ash content, and separate from water fairly readily. There is, therefore, little difficulty in keeping such oils clean.

At the time of writing the bulk of the oil used on heavy Diesel engines is either heavy gas oil, mixtures of heavy gas oil with residual fuels, or light residual fuels alone. The tendency is, however, to employ oils of quite reasonable viscosity, where mechanical impurities are very rarely found in excessive amounts and the ash content is usually very much below the maximum limit of 0·05 per cent.

It is not essential to use very thin oils for slow-speed Diesel engines, and a few years ago the use of heavy residua, such as Mexican residue with a specific gravity of 0·950 and sometimes Mexican residue as much as 0·980 specific gravity, was fairly common. Although the design of engines has improved since that date, and it would be possible still to use oil at least as heavy as previously, the tendency recently has been to use much thinner products. This tendency has been brought about primarily by a change in economic conditions ; with heavy production in the petroleum industry there has been no difficulty in obtaining large quantities of distillate oils ; also, the increased use of asphalt for road-making has resulted in an outlet for this product, from the manufacture of which gas oil is made as a by-product. It is therefore found that the asphalt which used to be burnt in Diesel engines is now being used on the roads, and comparatively clean and mobile gas oils are being made available to the fuel market at low prices. It is probable also that some of the troubles experienced in the burning of heavy asphaltic oils has made engineers more insistent in obtaining thinner oils as fuels for heavy-oil engines.

Diesel engines are capable of burning fuel oils containing considerable quantities of asphalt, but the quantity which can be burnt satisfactorily is largely dependent on the nature of the asphalt present in the fuel. Asphaltic bodies are incapable of being distilled, and therefore one may assume that this portion of the oil is burnt whilst in the state of finely divided liquid particles.

It is common when testing fuel oils to use two methods for asphalt determination ; one is the Holde soft asphalt by which all bodies insoluble in an alcohol-ether mixture are estimated as asphalt. The other method is the hard asphalt determination by which bodies insoluble in light petroleum spirit are classed as asphalt. The product of the latter test is referred to as " hard asphalt." As a general rule the figure obtained by the soft asphalt test is considerably larger than that obtained by the hard asphalt test, and includes practically the whole of the bodies precipitated by the hard asphalt test in addition to certain bodies which are soluble in the petroleum spirit and therefore do not register in the hard asphalt test. We may therefore consider the soft asphalt test as yielding all types of asphalt or total asphalt, whilst the hard asphalt test yields bodies more insoluble contained within the total asphalt figure. This assumption is not exactly correct as the two solvents have distinctly different actions, and there are isolated cases in which the hard asphalt figure may exceed the total, which would not be possible if the entire hard asphalt were precipitated by the alcohol-ether solution. Generally, however, it may be considered that petroleum spirit yields a comparatively high melting asphalt and that the alcohol-ether solution precipitates the same material as the petroleum spirit but, in addition, refuses to dissolve certain asphaltic portions of the oil which are of a lower melting point or softer structure and which are soluble in the petroleum spirit.

It is usually found that oils containing a high hard asphalt content are frequently rich in sulphur, and it is the more heavily polymerised sulphur-containing asphalts which are precipitated from petroleum spirit solutions. There is no regular relationship between the two values, and on occasions oils may be found in which all the asphalt may be classed as hard asphalt. In such oils the soft asphalt, or total asphalt, is approximately equal to the hard asphalt figure. In other oils the content of soft asphalt may be quite high, whilst the content of hard asphalt may be extremely low. For convenience in making evaluations of this nature it is easier to refer to the results of the soft asphalt test as total asphalt, and use the term " soft asphalt " as referring to the difference between the total asphalt and the hard asphalt.

The following are analyses of four oils which have been used to a considerable extent on Diesel engines :—

	Specific Gravity.	Conradson's Coke Test.	Total Asphaltum.	Hard Asphaltum.	Soft Asphaltum.
			Per Cent.	Per Cent.	Per Cent.
Heavy Mexican oil .	0·966	12·37	20·58	16·43	4·15
Egyptian oil . .	0·959	10·48	19·55	13·05	6·50
Fuel oil ex-Barbados	0·970	6·22	5·80	1·02	4·78
Comodoro Rivadavia	0·942	7·38	23·9	5·86	18·04

It will be noted that the heavy Mexican oil, which incidentally is of high sulphur content, contains comparatively little soft asphalt, and it is an oil which is distinctly difficult to burn in Diesel engines, as, unless the working conditions are very favourable, there is a tendency for the oil to burn late and combustion will be taking place when the exhaust valve opens. This is demonstrated simply by the presence of sparks in the exhaust and the comparatively large quantity of sparks which will emerge from the indicator cock if this is open whilst a slow-speed engine is running on this fuel.

Although the Comodoro Rivadavia oil contains a higher total asphalt, the asphalt in this oil consists mainly of soft asphalt, and experience has shown that it is a much easier oil to burn. It will also be noted from these figures that an oil containing hard asphalt gives a higher coke value than an oil containing a similar quantity of soft asphalt. From this it may be assumed that if the asphalts are not going to be classified it is better to use the coke value alone as an indication of the suitability of Diesel oils.

Coal-tar distillates are comparatively free from mechanical impurities or ash, but many of the creosote oils contain naphthalene, which at lower temperatures separates out in the form of solid crystals. Naphthalene is a perfectly good fuel, but is liable to cause obstruction of the fuel system ; it also tends to cause trouble during storage and handling. Oils which are comparatively free from naphthalene are therefore preferred, and if tar oils rich in naphthalene have to be burnt it is necessary to arrange for the oil to be kept hot all through the fuel system. For several years practically no tar oil has been used in this country on heavy-oil engines, but there may be a tendency towards increase of such products on account of the taxation of imported petroleum oil.

The presence of cresols in coal-tar products necessitates the use of steel pipe instead of copper pipe in all fuel leads as the latter are liable to corrosion.

The presence of paraffin wax in petroleum oils has the effect of making the oil solidify at higher temperatures, and where much wax is present oil may solidify in ordinary cold weather. Paraffin wax itself burns quite freely, but the presence of paraffin wax, as denoted by high cold test, is mainly objectionable on account of difficulties in storage and handling. It does, however, raise another indirect difficulty in that oils rich in paraffin wax may be partially solid during storage, and therefore do not give the same opportunity for mechanical impurities to settle out in the main store tanks. We therefore find that oils of high cold test are occasionally liable to have unexpectedly high ash contents.

Lignite tars and lignite-tar distillates are not used in this country although they have been employed as Diesel-engine fuels to quite a large extent in Germany. They burn quite readily in spite of their high tar acid content. The presence of a special type of paraffin gives them a high cold test which presents certain storage and handling problems.

The ignition qualities of Diesel-engine fuels are very variable and present by far the most difficult problem in the study of fuels for this purpose. This problem may be considered as in some way corresponding to the anti-knock property in motor spirit. As previously explained, it is essential that the fuel shall ignite in a heavy-oil engine when it is exposed to compressed air at the temperature of the cylinder at the end of the compression stroke. Fuels, however, differ in the temperature requisite to bring about their ignition, and practically all forms of heavy-oil engines have been designed primarily to operate on petroleum products, the ignition qualities of which present very little variation.

When unusual fuels, such as coal-tar products or petroleum oils from very exceptional aromatic crudes, are to be employed ignition difficulties are encountered. In pre-war days it was well known that slow-speed Diesel engines which gave perfectly good ignition on petroleum oils would refuse to start on coal-tar creosote. After a considerable amount of experimental work it was proved by Holm, Constam, and Schläpfer that this difficulty was due to the very high temperature of spontaneous ignition possessed by the coal-tar products. Holm and Constam and Schläpfer both devised experimental means for testing the minimum temperature at which oils would ignite ; the apparatus was rough and the results very erratic, but they were sufficiently accurate to demonstrate clearly the large difference between coal-tar products and petroleum products. A new form of apparatus was designed by Moore and a large number of spontaneous-ignition temperatures determined with considerable experimental accuracy. After Moore's experiments many forms of ignition apparatus have been employed, each giving slightly different results, some of the more modern types of which are claimed to give slightly more concordant results than the original instrument.

The temperature of spontaneous ignition as defined by Moore is the minimum temperature at which the fuel will burst into flame when brought into contact with oxygen at the same temperature. Determinations can be made both in air and in oxygen, but as the air figures are liable to a larger degree of experimental error the oxygen figures have been generally employed. The pressure at which experiments are carried out in the Moore apparatus is normal atmospheric pressure.

These experiments show that whereas petroleum fuel oils ignite at temperatures of from 250° to 270° C. in oxygen, coal-tar oils require a temperature of from 400° to 500° C. to bring about ignition. It can also be demonstrated that in order to obtain certainty of ignition under starting conditions, *i.e.*, with a cold engine, it is necessary to employ a compression on the engine calculated to give a very much higher temperature than the temperature of spontaneous ignition of the fuel. The calculated temperature obtained by compression is not attained under starting conditions, as the value of 1·35 for the exponential n, although correct for an engine in operation, is undoubtedly too high for the cold cylinder and slow speeds encountered under starting conditions.

In engines using compressed air for atomising purposes there is a very pronounced cooling effect brought about by the expansion of the air when leaving the atomising system and entering the cylinder. We therefore find that the compression ratio, or the maximum compression pressure necessary in heavy-oil engines to bring about ignition, is very much higher than one would anticipate from a study of the ignition point of the fuel.

Low boiling petroleum products possess higher spontaneous ignition points than high boiling products. Oils rich in asphalt appear to have rather higher ignition points than the distillate oils ; coal-tar products made by low temperature carbonisation, or obtained from vertical retort tars which operate under conditions approaching low temperature conditions, are lower in ignition point than the products of high temperature retorts. Shale oils give ignition points very close to those of petroleum oils, whilst lignite products are usually a little higher in ignition point than petroleum bodies.

The writer has made many investigations on the spontaneous-ignition temperatures of mixed fuels, and curves produced showing percentage composition against ignition point indicate that the ignition point of the mixture cannot be calculated, and it is not an arithmetic function of the ignition point of the two components. The type of curve obtained on such experiments varies, but usually mixtures containing up to half of the lower ignition point constituent show ignition points very little over that of the lowest component. With a larger proportion of the higher ignition component the test on the mixture increases very suddenly and becomes fairly close to that of the higher ignition point component. Tests on engines made by varying the compression indicate that the engine performance does not fall into line with these curves, but that the ignition qualities as shown on engines more closely approach to an arithmetic relationship.

The utilisation of high ignition-point fuels on Diesel engines has been the subject of a great deal of research for the past twenty-five years, and briefly one may state that the following is a summary of the results of investigators. The normal compression pressure used on engines employing mechanical injection is in the region of 400 lbs. per sq. in., although sometimes pressures as low as 300 lbs. per sq. in. are employed. The actual compression required is dependent on many other features of the engine ; for instance, large engines lose less heat to the cylinder wall, and one can therefore use slightly lower compression pressures to effect ignition. The speed of the engine, the minimum temperature which it will encounter in use (particularly under starting conditions), whether two-stroke or four-stroke cycle, and so forth, all bear certain influence. Engines using compressed air usually employ a pressure in the neighbourhood of 500 lbs. per sq. in. when using petroleum.

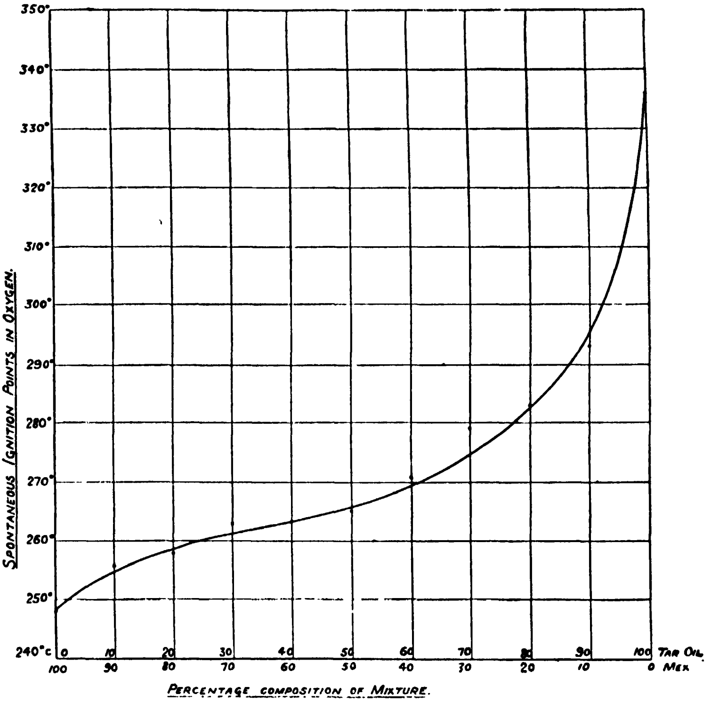


FIG. 11.—Ignition Points of Mixtures of Tar Oil and Petroleum Residuum.

The results are again affected by other features of the engine, and ease of starting is very much influenced by the nature of the fuel-injection system ; for instance, large orifices which allow the use of comparatively big quantities of air with the fuel charge tend to cool the cylinder and interfere with starting. Conversely, small orifices facilitate starting. When burning fuels whose ignition points are only slightly higher than the normal oil for which the engine was originally designed, any slight difficulty or uncertainty in starting can be overcome by increasing slightly the compression. The only fuels which possess sufficiently high ignition points to cause real difficulty in starting are coal-tar products, and in order to burn them it has generally been found advisable to use pilot ignition gear.

The simple expedient of using very high compression is not practicable as it would involve putting excessive strain on the engine, which is primarily designed to use petroleum oils. The mixing of coal tar and petroleum oils is generally unsatisfactory because the proportion of petroleum oil required is over 50 per cent., and also, unless the two oils are exceptionally clean distillate products there is a tendency in such mixtures for the formation of precipitates of petroleum asphalt and coal-tar pitch. The latter phenomenon is due to the tar acids in the coal-tar oil dissolving the asphalt from the petroleum oil and forming a solution which is insoluble in the main body of hydrocarbon oil.

With the pilot ignition system the engine is provided with an extra fuel pump. Tar oil is introduced into the cylinder in the usual manner, but the extra fuel pump delivers a smaller charge of some easily inflammable oil (any shale oil or a good quality petroleum oil). The ignition oil is led to the atomiser in such a way as to lie between the fuel valve seat and the main charge of tar oil. Thus, when the fuel valve opens a small separate charge of the more easily inflammable oil first enters the cylinder (before inner dead centre) and heats the combustion space to a sufficiently high temperature to cause immediate and regular ignition of the tar oil. The ignition pump does not require to be under the control of the governor as the quantity of ignition oil required is the same for all loads. This method yields excellent running at all loads. The proportion of ignition oil required is approximately 6 per cent. at full load. The accompanying diagram shows clearly the arrangement of the fuel pumps on an engine fitted for burning tar oil on the pilot-ignition system. The indicator cards obtained when an engine is running on the pilot-ignition system generally show a distinct mark where the ignition oil ceases and the tar oil commences to burn. Two typical indicator diagrams obtained by the use of pilot ignition are shown in Fig. 13.

The use of specially designed fuel valves, which allow a small portion of the tar oil to enter the cylinder prior to a main charge of the same fuel, have met with some success on larger engines. The introduction of a small quantity of the tar oil in advance of the full charge causes the ignition to be more regular, but in the author's experience the tar-oil pilot charge is not nearly so satisfactory as a petroleum oil used with special fuel pump.

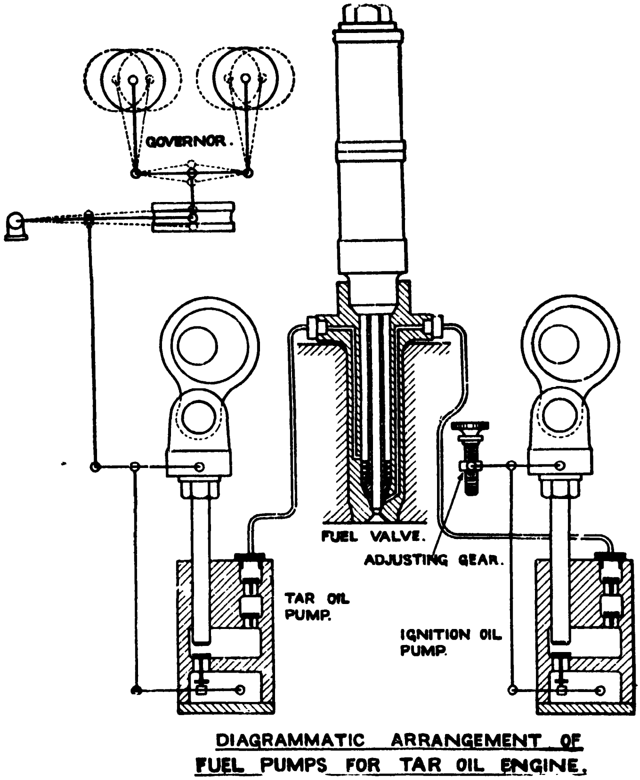


FIG. 12.

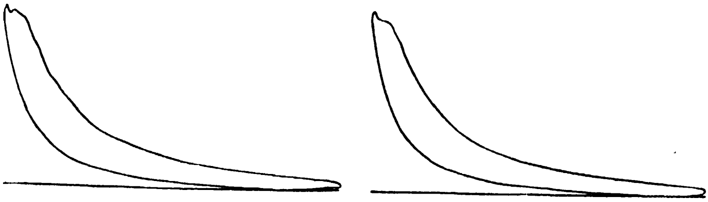


FIG. 13.—Tar Oil with Petroleum Oil Ignition.

The accompanying drawing (Fig. 14) shows a device made by the author. It is a ported bottom fuel casing, the piece fitting into the standard bottom fuel-valve casing and forming a seat for the fuel valve.

The lower end of the fuel valve is turned so as to have a shoulder which closes the ports marked A until the valve has been raised a short distance. One port is made specially deep to reach below the shoulder, and provide a passage to the fuel-valve face when the fuel valve is closed. When the needle valve is on the seat there is no way through to the combustion space, but on being slightly raised, there is a very restricted way through the single port B. On raising the fuel valve farther the several ports A are opened simultaneously, and the main charge of tar oil is introduced. The fuel cam is set to give the opening of the ports A about inner dead-centre, when

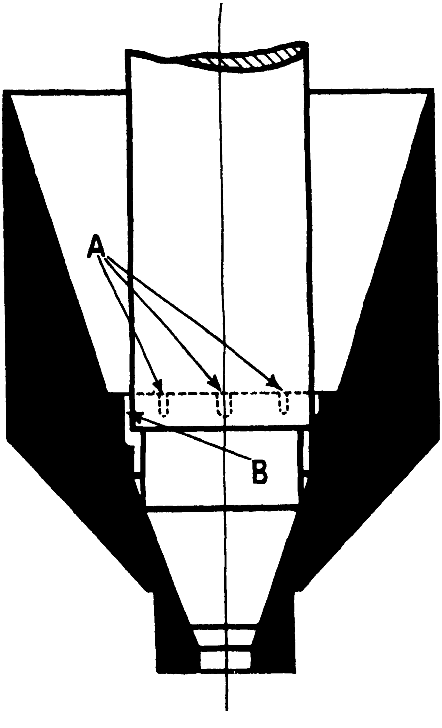


Fig. 14.

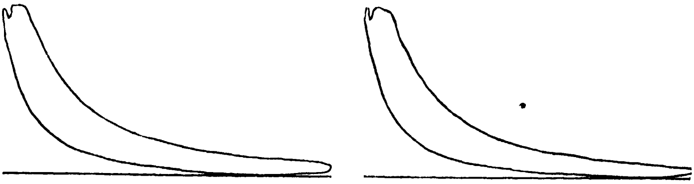
B should commence to operate some 15° before inner dead-centre when the valve first opens. Thus a small charge of tar oil is introduced into the cylinder prior to the main tar-oil charge. This device certainly improved ignition, and the writer considers that the explanation of the improvement is because, from the nature of the design, the small charge of oil which first entered the cylinder was unaccompanied by compressed air, and therefore more closely approached conditions of mechanical injection, being uncooled by the refrigerating action of the expansion of the air.

The employment of catalytic agents as a means of promoting ignition has been advocated, but to the best of the writer's knowledge no invention of this type has proved satisfactory. A considerable amount of research is being carried out at the present time to discover substances which will promote ignition when added in small quantities to fuel oil. The writer experimented many years ago on this subject, using ether, carbon disulphide, paraffin wax, and other bodies of low ignition point, but none of the substances was sufficiently effective to be of practical use. Amyl nitrate is claimed to be effective as an ignition promoter, but no body possessing ignition-inducing properties of the same order as the anti-knock properties of tetra-ethyl lead has yet been discovered.

The oils usually used are the creosote and anthracene oil fractions. These oils are quite mobile distillates, although they are both liable to solidify or deposit crystals on cooling. The creosote fraction is rich in naphthalene, whilst the anthracene oil is rich in the hydrocarbon anthracene. Both naphthalene and anthracene are fuels in themselves, and, apart from their tendency to separate as solids, there is no objection to them as fuels.

Although raw coal tars have been burnt on various occasions with more or less satisfaction, it is very questionable whether these bodies containing considerable quantities of free carbon will ever become employed in normal practice.

When burning raw coal tars the difficulties of ignition may be overcome by the methods already enumerated for tar oils, but additional difficulties are encountered on account of the tars generally containing free carbon, frequently accompanied by water and ash. The free carbon is the most serious consideration with raw tars. Small percentages of free carbon may be burned without difficulty, but when over 10 per cent. of this substance is present the exhaust valve becomes very badly pitted, the exhaust temperature is high, and there is often a smoky exhaust. This action is due to the slow burning of the particles of free carbon, which, when not completely consumed during the working stroke, pass from the engine in a glowing state. This can be proved by opening the indicator cock of the engine, when it will be noticed that the number of sparks bear a direct relationship to the free carbon content of the fuel. These glowing particles of carbon become trapped under the exhaust-valve face and produce an appearance similar to beaten metal-work. The free carbon does not consist of pure carbon, but is best considered as coke in an exceedingly finely divided state. The removal of free carbon is very difficult, though it has been found possible to extract two-thirds of the free carbon from water-gas tar by centrifugal treatment. The removal of free carbon by filtration presents many difficulties, mainly on account of the large quantities of this body which have to be handled. The commercial extraction of free carbon from horizontal retort tars by filtration is not very promising, as even if the removal could be completely and economically effected the reduction in the quantity of tar is a serious consideration. In practice it is impossible to prevent the loss by tar being removed together with the free carbon. To make this process successful with tars containing 25 to 30 per cent. of free carbon, it would be necessary to find a market for this by-product. Hitherto it has been usual among Diesel engine users only to employ such tars as contain a sufficiently low percentage of free carbon to allow of them being burned without any treatment. The tars obtained from vertical retorts are generally low in free carbon content, and have been employed on a large scale in Germany, where the Dessau vertical retorts are largely used for gas manufacture. Vertical retort tars also contain large quantities of aliphatic hydrocarbons, which to some extent aid their ignition and combustion. Fig. 15 shows two indicator diagrams taken from a 50-B.H.P. Mirrlees-Diesel engine, when running on vertical retort tar with kerosene as ignition oil.



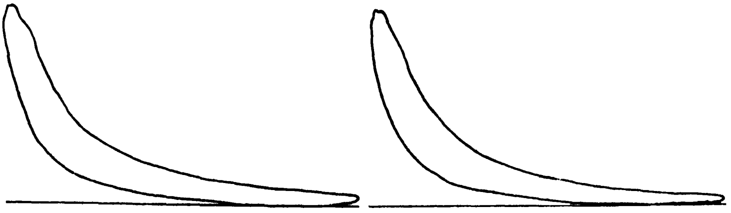
VERTICAL RETORT TAR WITH KEROSENE IGNITION.

FIG. 15.

The tars of this country are generally higher in free carbon content than those produced on the Continent, as the majority of British gas works employ horizontal or inclined retorts, which yield heavy viscous tars containing 15 to 30 per cent. of free carbon. The high viscosity of these products is also an undesirable feature. The newer installations in this country are, however, mainly vertical retort plants. Some of the coke-oven tars can be used in Diesel engines, but different types of coke oven yield tars of widely varying properties. The author has run a 50-B.H.P. Mirrlees-Diesel engine in trials extending over six months on raw tar from Simon-Carvé coke ovens. A typical indicator card taken during this trial is shown in Fig. 16.

FIG. 16.—Coke-oven Tar with Petroleum Residuum for Ignition.

The tar produced from carburetted water-gas plants, although a product of gas works, is not a coal tar, but is the residue left after cracking petroleum or shale-gas oils. It is therefore different in composition from other tars. It is known as carburetted water-gas tar, or as oil-gas tar. It is mainly composed of aromatic hydrocarbons, but contains a sufficient quantity of other hydrocarbons to give it a comparatively high hydrogen content (about 7 per cent.).



OIL GAS TAR WITH KEROSENE IGNITION.

FIG. 17.

During recent years the question of the quality of Diesel fuel has been studied in America with a view to framing a Diesel fuel classification for the guidance of users. The various methods of rating Diesel fuels have been examined, namely, spontaneous-ignition temperature, cetene number, critical compression ratio, etc. It has been found that the correlation between physical properties determined in the laboratory (such as specific gravity and aniline cloud point) and the utility of the fuel in service conditions may be expressed in the form of an equation, which is :—

$$\text{Diesel index number} = \frac{(\text{A.P.I. gravity at } 60^\circ \text{ F.}) \times (\text{aniline point }^\circ \text{ F.})}{100}.$$

The results of the investigations carried out by Technical Committee "C" of the A.S.T.M., Committee D. 2, have enabled them to prepare a classification for differentiating types of fuel oils suitable for Diesel-type engines. It is pointed out that this classification is not intended to be used for purchase specifications, but as a means of determining the usefulness of oils purchased.

METHODS OF TESTING.—The properties listed in this classification are determined in accordance with the following methods of testing :—

(a) *Flash Point.*—In absence of legal or local requirements, the minimum flash point shall be determined in accordance with the Standard Method of Test for Flash Point by means of the Pensky-Martens Closed Tester (A.S.T.M., Designation D. 93) of the American Society for Testing Materials.

(b) *Viscosity.*—Standard Methods of Test for Viscosity of Petroleum Products and Lubricants (A.S.T.M., Designation D. 88) of the American Society for Testing Materials.

ANALYSES OF COAL-TAR FUELS

Description.	Specific Gravity at 15° C.	Water.	Ultimate Composition.				Ash.	Coke.	Net Calorific Value.		Free Carbon.
			C.	H.	O. & N.	S.			Calories.	B.Th.U.	
Horizontal retort tar	1·180	1·75	91·5	5·2	2·6	0·5	0·20	24·0	8,645	15,561	18·2
Inclined retort tar	1·157	1·11	89·9	6·0	3·6	0·5	0·02	18·5	8,671	15,626	14·0
Vertical retort tar	1·089	2·25	88·0	6·8	3·8	0·6	0·03	6·1	8,664	15,613	1·7
Otto Hilgenstock coke-oven tar	1·208	6·00	90·0	5·4	3·8	0·8	0·02	26·8	8,624	15,523	23·9
Simon-Carvé coke-oven tar	1·090	0·50	88·1	5·6	6·1	0·2	0·07	6·0	9,261	16,670	Traces
Chamber-oven tar	1·082	1·29	88·2	6·9	4·6	0·3	Traces	7·3	8,737	15,727	3·0
Low temperature carbonisation tar	1·058	3·00	85·8	8·1	5·49	0·09	0·11	8·2	8,776	15,797	2·2
Water-gas tar	1·054	0·59	92·2	6·8	0·4	0·6	Traces	18·7	8,647	15,563	6·8
Blast-furnace tar	1·172	3·00	89·5	5·75	0·55	0·84	0·36	23·4	8,288	14,918	9·5
Blast-furnace tar oil	0·974	None	87·25	9·8	2·59	0·36	None	1·05	9,243	16,637	None
Oil distilled from low temperature tar	0·884	,,	85·6	11·4	2·48	0·4	,,	0·84	9,558	17,204	,,
Horizontal retort tar oil	1·065	1·00	90·1	6·8	2·4	0·50	0·2	3·0	9,243	16,637	,,
Pennsylvanian petroleum fuel oil	0·889	None	86·7	12·55	0·11	0·64	Traces	0·60	10,108	18,194	,,

Diesel Fuel Oil Classification

Grade of Diesel Fuel.	Flash Point, ° F.	Water and Sediment, per Cent. by Volume.	Viscosity Seconds.			Carbon Residue per Cent. by Weight.	Ash per Cent. by Weight.	Pour-point, ° F.	Sulphur.	Ignition Quality.
			Saybolt Universal at 122° F.		Saybolt Furol at 100° F.					
	Min. (*f*).	Max.	Min.	Max.	Max.	Max.	Max.	Max. (*h*).		
1-D. (*a*) A distillate oil for use in engines requiring a low viscosity fuel	115 or legal	0·05	32	50	...	0·2	0·01	35	(*i*)	(*j*)
3-D. (*b*) A distillate oil for use in engines requiring a medium low viscosity fuel	150	0·2	32	70	...	0·5	0·02	35	(*i*)	(*j*)
4-D. (*c*) An oil for use in engines requiring a medium low viscosity fuel	150	0·6	...	500	...	3·0	0·04	35	(*i*)	(*j*)
5-D. (*d*) An oil for use in engines permitting a medium high viscosity fuel	150	(*g*)	...	...	100	6·0	0·08	40	(*i*)	(*j*)
6-D. (*e*) An oil for use in engines of special design for high viscosity fuels and after engine manufacturers' recommendations only	150	(*g*)	...	...	300	10·0	0·12	40	(*i*)	(*j*)

(*a*) Grade No. 1-D. is recommended for mechanical (solid) injection engines of the high-speed type; in general, for engine speeds over 1,000 revs. per min.

(*b*) Grade No. 3-D. is recommended for mechanical (solid) injection engines of the medium-speed type; in general, for engine speeds from 360 to 1,000 revs. per min.

(*c*) Grade No. 4-D. is recommended for air-injection engines, both two and four stroke cycle types, with speeds not over 400 revs. per min. Grade No. 4-D. can be used for mechanical (solid) injection engines with cylinder diameters over 16 in. and speed under 240 revs. per min., but approved heating equipment furnished by the engine manufacturer is recommended.

(*d*) Grade No. 5-D. is recommended for air-injection engines of the slow-speed type; speed under 240 revs. per min. Manufacturer should be consulted for approved heating equipment.

(*e*) Grade No. 6-D. is not regularly used for Diesel engines, and is not recommended unless tested and approved by engine manufacturer. The purchaser should be informed regarding high maintenance cost of engines and operating problems involved in the use of this grade of fuel.

(*f*) Minimum flash point as stated or as required by local fire regulations, fire underwriters or state laws.

(*g*) To be inserted later.

(*h*) Lower pour-points may be specified whenever required by local temperature conditions to facilitate storage and use, although it should not be necessary to specify a pour-point of less than 0° F.

(*i*) So far as known, sulphur content need not be considered as regards combustion characteristics. However, a maximum of 2 per cent. is suggested to purchasers operating engines intermittent service to limit corrosion.

(*j*) See discussion under "Methods of Testing," paragraph (*g*), Ignition Quality.

(c) *Carbon Residue.*—Standard Method of Test for Carbon Residue of Petroleum Products (Conradson Carbon Residue) (A.S.T.M., Designation D. 189) of the American Society for Testing Materials.

(d) *Ash.*—Place 10 gm. of the fuel oil in a weighed uncovered platinum crucible of a capacity not greater than 100 millilitres and heat gently with a Bunsen burner until the oil fires and continues to burn when the flame of the burner is applied to the surface of the oil. Allow the oil to burn without further application of heat. The oil will continue to burn until practically all of it has disappeared. The time required will be about fifty minutes. Then place the platinum crucible in a gas or electric furnace and heat to a bright red heat until all carbon is consumed. Cool, weigh, and report the residue as ash expressed as a percentage of the original 10-gm. sample.

(e) *Pour-point.*—Standard Method of Test for Cloud and Pour-points (A.S.T.M., Designation D. 97) of the American Society for Testing Materials.

(f) *Sulphur.*—Standard Method of Test for Sulphur in Petroleum Oils by Bomb Method (A.S.T.M., Designation D. 129) of the American Society for Testing Materials.

(g) *Ignition Quality.*—According to present opinion, combustion knock in a fuel-oil injection engine is caused by the accumulation of fuel in its cylinders prior to ignition. Even under conditions that insure ignition, the fuel may not ignite instantaneously but only after a definite delay. The longer this delay, the more fuel accumulates in the cylinders, which then burns unevenly, finally causing audible knock. If the delay is extreme, the engine will fail to operate with the fuel. It is significant that every factor which tends to aggravate knocking in a spark-ignition gasoline engine tends to suppress it in Diesel engines. Fuels of paraffin base, consisting chiefly of saturated straight-chain hydrocarbons, give the smoothest combustion in general, while naphthenes and aromatics burn roughly at low compression ratios. It is known that highly cracked products give trouble and also that the amount of trouble is increased as the speed of the engine is increased. Turbulence in the charge mixture reduces the delay period, and turbulence is a controlling factor in engine speed. It is now generally agreed that ignition quality is one of the most important characteristics of Diesel fuels.

The Committee realises the impossibility of reducing all types and designs of engines to a common rating for fuel-burning characteristics. Engine factors, such as combustion-chamber design, turbulence, spray characteristics, compression ratio, injection timing, and engine speed, vary greatly in different engine makes. Tests of ignitibility on various types of engines have no theoretical significance but have provided practical data for the types and sizes of engines on which the tests were performed. Fuel characteristics are based on a study of field-engine performance correlated with laboratory ratings of various test fuels. Ignitibility, one of the most important characteristics from the standpoint of satisfactory engine operation, has been measured by such indices of performance as Diesel index number, cetene number, and critical compression ratio.

DIESEL INDEX NUMBER.—Diesel index number is calculated from aniline point and A.P.I. gravity by the following formula :—

$$\text{Diesel index number} = \frac{(\text{A.P.I. gravity at } 60^\circ \text{ F.}) \times (\text{aniline point } ^\circ \text{F.})}{100}.$$

Aniline point is the lowest temperature at which equal parts of volume of freshly distilled aniline and the test sample of oil are completely miscible. It is determined by heating such a mixture in a jacketed test tube to a clear solution and noting the temperature as turbidity appears as the mixture is cooled.

For A.P.I. Gravity see the Standard Method of Test for Gravity of Petroleum and Petroleum Products by Means of the Hydrometer (A.S.T.M., Designation D. 287) of the American Society for Testing Materials.[1]

CETENE NUMBER.—Cetene number was first proposed by Boerlage and Broeze, of the Bataafsche Petroleum Maatschappij,[2] and is the percentage of cetene in a blend of cetene and alphamethylnaphthalene which has the same ignition quality (measured in a specified engine under a definite set of engine conditions) as the fuel under test. It may be determined from the critical compression ratio by determining this ratio for various blends of cetene and alphamethylnaphthalene and plotting the curve.

CRITICAL COMPRESSION RATIO.—The critical compression was first proposed by Pope and Murdock, of the Waukesha Motor Co.[3] It is determined on a C.F.R. engine modified to run as a Diesel engine by replacing the ignition system with a fuel pump and fuel injection valve and also replacing the regular piston with one of special design. The operating conditions are as follows :—

Speed	600 revs. per min.
Fuel feed	9 millilitres per min.
Injection advance angle	12° before true dead-centre.
Injection pressure	1,500 lbs. per sq. in.
Jacket temperature	212° F.
Air inlet temperature	100° F.

The critical compression ratio is obtained by motoring the engine at the selected speed and noting the compression ratio at which firing occurs (as judged by the sound of the exhaust) within three seconds after the fuel is injected.

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[1] See p. 149 (A.S.T.M., Designation D. 287-33).

[2] Boerlage and Broeze, " Ignition Quality of Diesel Fuels as Expressed in Cetene Numbers," *Jour. Soc. Automotive Engrs.*, July 1932.

[3] Pope and Murdock, " Compression Ignition Characteristics of Diesel Fuels," *Jour. Soc. Automotive Engrs.*, March 1932.

None of these methods has been sufficiently correlated with service performance to justify setting definite limits. Field investigators are urged in reporting results to state whether the following limits, if set, would be satisfactory for Diesel oils, Grades Nos. 1-D., 3-D., and 4-D.

	Oil Grades.		
	No. 1-D.	No. 3-D.	No. 4-D.
Diesel index number (minimum)	45	30	20
Cetene number (minimum)	50	40	30
Critical compression ratio (maximum)	8·1	8·8	9·8

These methods are not considered practicable for determining the ignition quality of Diesel oils, Grades Nos. 5-D. and 6-D. It is doubtful whether any test other than an actual engine test would be satisfactory for these heavy oils.

Some of the experimental results quoted by various authors or by various workers who have investigated the relationship between the different methods of rating Diesel fuels have been collected together in the following table, which should serve as a guide to the reader in judging the Diesel quality of his own fuel.

RELATIONSHIP BETWEEN DIESEL INDEX AND SPONTANEOUS-IGNITION TEMPERATURE AND CRITICAL COMPRESSION RATIO FOR A WIDE RANGE OF FUEL TYPES.

Fuel.	A.P.I. Gravity.	Specific Gravity at 60° F.	Aniline Point, ° F.	Spontaneous Ignition Temperature.[1]	Diesel Index.	Critical Compression Ratio.
1	36·1	0·8443	212	...	76	6·82
2	41·2	0·8193	172	461	71	6·95
3	37·8	0·8358	176	462	68	7·07
4	41·7	0·8170	166	468	69	7·18
5	31·2	0·8697	171	...	53	7·40
6	37·8	0·8358	129	488	49	7·88
7	29·4	0·8794	131	490	38	8·21
8	33·6	0·8571	111	488	37	8·35
9	28·2	0·8860	117	489	33	8·45
10	31·0	0·8708	109	...	34	8·52
11	24·8	0·9053	113	...	28	8·61
12	22·2	0·9206	120	496	27	8·93
13	20·0	0·9340	92	495	18	10·09
14	17·4	0·9503	...	516	...	11·03
Cetene	48·6	0·7857	161	456	78	6·87
α Methylnaphthalene	...	...	too dark	over 700	...	very high
Normal heptane	74·1	0·6882	158	468	117	7·35
Iso-octane	71·6	0·6967	181	602	130	16·5

[1] Bomb apparatus of Moore type used.

Oxygen flow . . . . . 100 c.c. (minimum).
Drop size . . . . . 2 mm. diameter.
Rate of temperature rise . . . . 1° F. per min.

One-minute interval between drops for oxygen to clear the bomb cavity.

PART V

FUELS FOR EXTERNAL COMBUSTION

CHAPTER I

PETROLEUM LIQUID FUELS FOR EXTERNAL COMBUSTION

Liquid fuels available from petroleum for external combustion are almost innumerable, because any liquid product obtained by simple methods of separation, or as a by-product in a refining process, is utilised as a fuel oil if it can be burnt and if it cannot command a selling price higher than that of fuel. They may be distillates or residues of distillation of crude oil or by-products from its treatment.

Petroleum liquid fuels comparatively unknown outside America are the petroleum gases (constituting natural gas) which are compressed into the liquid state. One of these is known in America as " Bottled Gas " and is sold in pressure containers, some of which are similar to the well-known compressed-air or oxygen cylinders. " Bottled Gas " is composed of 95 to 99 per cent. propane, and is available in the U.S.A. in quantities ranging from tank-car lots down to containers of 4 lbs. net. The properties of this commercial propane are :—

Vapour pressure at 70° F. (21·1° C.)	120 lbs. per sq. in. gauge.
„ „ 105° F. (40·55° C.)	210 „ „ „
„ „ 130° F. (54·44° C.)	300 „ „ „
Initial boiling point	−45° F. (−42·5° C.).
Final boiling point	−40° F. (−40° C.).
Weight per U.S. gallons of liquid at 60° F.	4·24 lbs.
Specific gravity of liquid at 60° F. (water=1)	0·508
„ „ vapour (air=1)	1·52
Cubic feet of vapour per lb. of liquid	8·49
„ „ „ U.S. gallon of liquid	36·0

The rapidly increasing importance of " Bottled Gas " as a fuel is indicated in the following table, which quotes the total sales in U.S. gallons for each year from 1922 to 1932 :—

Annual Sales of " Bottled Gas " in U.S.A.

Year.	U.S. Gallons.	Year.	U.S. Gallons.
1922	222,641	1928	2,600,000
1923	276,863	1929	5,900,000
1924	376,488	1930	11,800,000
1925	403,674	1931	15,294,648
1926	465,085	1932	17,000,000
1927	1,091,005		

Liquefied commercial butane is another important liquid fuel available in America for external-combustion purposes. It is used in many industrial heating operations and for gas-making.

Commercial butane is composed of 90 to 95 per cent. isobutane and normal butane, and has the following properties :—

Vapour pressure at 70° F. (21·1° C.) .	30 lbs. per sq. in. gauge.
„ „ 105° F. (40·55° C.) .	63 „ „ „
„ „ 130° F. (54·44° C.) .	95 „ „ „
Initial boiling point . . .	17° F. (−8·3° C.).
Final boiling point . . .	30° F. (−1·1° C.).
Weight per U.S. gallon of liquid at 60° F.	4·8 lbs.
Specific gravity of liquid at 60° F. (water=1)	0·576
„ „ vapour (air=1) . .	1·95
Cubic feet of vapour per lb. of liquid .	6·7
„ „ „ U.S. gallon of liquid	32·0

This liquid fuel increased in importance from 1928 onwards, as is shown in the following table of total sales in U.S. gallons for each year from 1928 to 1932 :—

ANNUAL SALES OF LIQUEFIED BUTANE GAS IN U.S.A.

Year.	Industrial and Miscellaneous.	Gas Manufacture.
1928	400,000	1,500,000
1929	1,500,000	2,500,000
1930	2,200,000	4,000,000
1931	7,023,516	6,185,655
1932	8,000,000	7,000,000

Both "Bottled Gas" and liquefied butane are gasified before entry into the burning equipment consuming them.

The petrol or gasoline fractions of petroleum, which are used in greatest quantities as motor fuels (internal combustion), also figure in industry as liquid fuels for external combustion, but only to a comparatively limited extent ; other special low boiling fractions of the petrol yield of crude oils are also manufactured for use in external-combustion units. These petrol-like products have important applications as external-combustion fuels, which depend on their ease of volatilisation as compared with kerosene. With them are formed gas-air mixtures, which are burnt in numerous appliances for the production of heat and light.

Kerosene, familiarly known as "paraffin" or "paraffin oil," is more important than any of the foregoing. Like petrol or gasoline, kerosene is a refined distillate ; it boils between 150° and 300° C. (approximately), has a flash point of 100° F. and above, a low sulphur content (approximately 0·05 per cent.), and is refined carefully so that it shall not yield "char" in heating or lighting appliances operating on the "wick-fed" principle. Large quantities are sold annually all over the world for the production of light and heat.

As a source of heat, it finds a large measure of popularity in domestic circles as a substitute for coal, gas, and electricity, and it also competes with these forms of energy in cooking appliances.

The gas-oil fraction of crude oils is obtained directly by distillation immediately after the removal of the petrol and kerosene fractions ; it is not submitted to any special refining process before distribution on the market. Its " body " or " viscosity " lies between kerosene on the one hand and thin spindle lubricating oils on the other ; it is too viscous for use in the conventional wick-fed heating and lighting appliances, and is not sufficiently viscous to be serviceable as a lubricant ; frequently it is not amenable to chemical treatment, which would lead to the production of a premium-priced commodity. It is used throughout a large number of industries as a fuel, one of its large outlets being in the carburetting of water gas which is mixed with coal gas prior to its distribution through company gas mains.

A rapidly growing application of this low-priced material is domestic heating, for which the less odorous, low sulphur-content grades are reserved. The higher sulphur-content gas oils serve as thinning or blending agents for reducing the viscous black residual fuel oils to a wide range of fuel oils, made to suit the requirements of the different oil-burning equipment. These fuel oils constitute the major sources of liquid fuels for external combustion. At the same time, the consumption of fuel oils for domestic purposes has become increasingly important within comparatively recent years.

In appearance by reflected light, gas oils vary from a straw-yellow to dark red in colour, and from a very faint light-blue fluorescence to a dull green or brownish-black. Average physical properties of the gas-oil type of liquid fuel are :—

Specific gravity at 60° F.	0·85 to 0·89
Flash point (closed Pensky-Marten)	160° to 200° F.
Viscosity at 60° F.	40 to 100 secs. (Redwood No. 1 viscometer).
Pour-point (A.S.T.M.)	Zero° F. to 25° F.
Total sulphur	0·2 to 1·5 per cent.
Conradson carbon residue	Negligible.
Hard asphalt	Negligible.
Water and sediment	Nil.
Calorific value (gross)	19,600 B.Th.U.

Residual fuel oils, as the name implies, are residues of crude-oil distillation ; they remain in the crude-oil stills or pass from the bottom of the " flashing " tower after " topping " or skimming operations. These may be complete when all the petrol and kerosene fractions have been removed, or when these products and the gas-oil distillate have been separated. They vary in viscosity according to the viscosity of the crude oil charged to the stills and with the percentage of overhead distillates removed. The so-called " fuel oil " crudes usually have high sulphur contents, high specific gravities, and also relatively large, hard asphalt contents. In the ordinary way these crudes are not suitable for the production of lubricating oils ; in other instances, if such crudes should contain lubricating-oil fractions of low quality, obtainable only by expensive refining, they are devoted to fuel-oil production according as the price structure of the market for refined products dictates.

Typical analyses of a number of residual fuel oils are given in the following table :—

Country of Origin.	Specific Gravity at 60° F.	Closed Flash (Pensky-Marten).	Viscosity at			Pour-point, A.S.T.M.	Sulphur.	Gross Calorific Value.
			60° F., Redwood No. 1.	100° F., Redwood No. 1.	122° F., Saybolt Furol.			
		° F.	Secs.	Secs.	Secs.	° F.	Per Cent.	B.Th.U.
S. America (Aruba) .	0·991	190	...	2,800	155	10 to 15	2·2 to 2·4	18,400
,, (Curacao)	0·965	250	...	5,700	290	25	1·9 ,, 2·0	18,650
,, (Mexican)	0·968	230	...	2,900	150	15	3·3 ,, 3·5	18,600
,, (Venezuela)	0·976	235	...	5,700	290	35	2·0 ,, 2·5	18,500
Roumanian . .	0·950	200	...	1,300	71	55	0·3 ,, 0·4	18,800
Russian (Baku) .	0·910	230	120	300	...	15	0·1 ,, 0·2	19,200
,, (Grozny) .	0·909	160	730	172	...	35	0·1 ,, 0·2	19,250
Trinidad . . .	0·985	210	...	1,050	60	10 to 20	1·0 ,, 1·2	18,400

The appearance of such products is usually that of a black fluid.

The most important property mentioned in the above table is the gross calorific value : these values are manifestly very similar, although the other properties lie between comparatively wide limits. Slight variations in the calorific value of fuel oils are to be expected, the value generally increasing as the specific gravity and viscosity decrease ; the converse of this is the rule when the subject is viewed from the standpoint of " heat units per gallon of oil "—the higher the specific gravity the more are the heat units available from the gallon of oil.

These different fuel oils are utilised in oil-burning equipment either as they are obtained from the distillation units or after having been " thinned out " by gas oil to the viscosity requirements of the burning equipment in which they are to be utilised. It is to be expected, then, that the general term " fuel oil " covers a vast number of products that vary mainly in their viscosities. The following tables describe many standard fuel oils sold in America. These commercial specifications were adopted by the interested parties in 1929.

Refinery by-products also contribute material serviceable as fuel ; they are many in number and possess different fuel values according to the manner in which they are derived.

Cracking plants, on the one hand, produce not only low boiling products, such as petrol, but also high boiling fractions which are devoted to the augmentation of fuel-oil supplies. Solvent extraction processes, employed for the improvement of lubricating-oil stocks on an ever-increasing scale, reject considerable amounts of material to fuel-oil storage. On the other hand, the current wide use of

PROPOSED COMMERCIAL STANDARD SPECIFICATIONS FOR FUEL OILS

At a meeting of Technical Committee " C " in Atlantic City on 25th June 1924, the following Commercial Standard Specifications were approved for adoption by Section 1 of Technical Committee " C," and the action of Section 1 was approved by Technical Committee " C." In the tabulation below, the proposed specifications are given first, followed by present specifications (C.S. 12-33).

Grade Number.	Flash Point.		Water and Sediment. Maximum.	Pour-point.[1] Maximum.	Ash. Maximum.	Distillation Test.			Carbon Residue. Maximum.	Viscosity.		Remarks.
	Minimum.	Maximum.				10 per Cent. Maximum.	90 per Cent. Maximum.	E.P.		Minimum.	Maximum.	
Proposed No. 1. (A distillate oil for use in burners requiring a volatile fuel)	° F. 100 or legal	° F. 150	Per Cent. 0·05	° F. 15 [1]	Per Cent. ...	° F. 420	° F. ...	° F. 600	Per Cent. 0·02	S.U. at ...	100° F. ...	...
Present No. 1 (C.S. 12-13). (A distillate oil for use in burners requiring a volatile fuel)	110	165	0·05	15 [1]	...	420	...	600	...	...	...	...
Proposed No. 2. (A distillate oil for use in burners requiring a moderately volatile fuel)	110 or legal	190	0·05	15 [1]	...	440	620	600	0·05	...	...	...
Present No. 2. (A distillate oil for use in burners requiring a moderately volatile fuel)	125	190	0·05	15 [1]	...	440	620	...	...	...	...	...
Proposed No. 3. (A distillate oil for use in burners requiring a low viscosity fuel)	110 or legal	200	0·1	15 [1]	...	...	620 [3]	...	0·15	...	70 secs.	...
Present No. 3 (C.S. 12-33). (A distillate oil for use in burners requiring a low viscosity fuel)	150	200	0·1	15 [1]	...	460	675	...	...	...	55	...
Proposed No. 4. (An oil for use in burners requiring low viscosity fuel)[2]	150	...	1·0	...	0·1	...	...	...	...	70 [4]	500	...
Present No. 4. (An oil for use in burners requiring low viscosity fuel)[2]	150	...	1·0	...	...	...	...	...	...	...	125	Present specifications permit a maximum flash point not greater than 250° F.
Proposed No. 5. (An oil for use in burners equipped with preheaters permitting a medium viscosity fuel.) (Bunker B)	150	...	1·0	...	0·15	...	...	...	...	S.F. at 25	122° F. 100	...
Present No. 5. (An oil for use in burners permitting a medium viscosity fuel.) (Bunker B, Federal Specification 2D)	150	...	1·0	...	...	...	...	...	...	...	100	...
Proposed No. 6. (An oil for use in burners equipped with preheaters permitting a high viscosity fuel.) (Bunker C)	150	...	2·0 (See remarks)	...	...	...	...	...	...	100 [5]	300	A deduction in quantity to be made for all water and sediment in excess of 1·0 per cent.
Present No. 6 (C.S. 12-33). (An oil for use in burners permitting a medium viscosity fuel.) (Bunker C, Federal Specification 2D)	150	...	2·0 (See remarks)	...	...	...	...	...	...	...	300	Present specifications provide a maximum sediment of 0·25 per cent. A deduction in quantity to be made for all water plus sediment in excess of 1 per cent.

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[1] Lower or higher pour-points may be specified whenever required by conditions of storage and use. However, these specifications shall not require a pour-point less than 0° F. under any conditions.
[2] Pour-point may be specified whenever required by conditions of storage and use. However, these specifications shall not require a pour-point less than 15° F. under any conditions.
[3] This requirement shall be waived when the carbon residue is more than 0·07 per cent. and less than 0·15 per cent.
[4] This requirement shall be waived when the carbon residue is more than 1 per cent.
[5] This requirement is waived when the carbon residue is 4 per cent. or more.

sulphuric acid in the refining of the better-priced products introduces into refineries large amounts of black viscous acid sludges, the disposal of which has always been a subject of much concern to refiners. Their conversion into forms which are usable as fuel has been successfully achieved, so that these sludges may now be consumed as fuel under boilers, stills, etc.

The process employed for the disposal of acid sludge is determined by the type of oil stock which has been acid-treated and by the point whether the refinery produces sufficient acid sludge to warrant the installation of acid-recovery plant. If the latter factor obtains, then the process resolves itself into one of acid recovery and utilisation of the hydrocarbon residue as fuel.

Acid sludge from cylinder-oil acid treatment is not always easy to convert into fuel in that the temperature at which the treatment takes place plays an important part in the subsequent process for conversion into fuel. If the treating temperature is above 160° F. (approx.) the acid sludge is more difficult to resolve, because it becomes harder the higher the treating temperature. Acid sludge of suitable quality may be converted to fuel by mixing it at about 120° F. with about an equal volume of any kind of fuel oil, such as gas oil or slops, by air agitation, and heating with dry steam coils up to a temperature of 180° to 200° F. With some acid sludges, air agitation may cause the formation of lumpy products, in which cases agitation is better produced by steam in the absence of air. In this manner the acid sludge may be successfully fluxed into a product that can be burnt advantageously through pressure burners in shell or tube-still furnaces.

A typical analysis of a final product obtained in this manner is :—

Specific gravity	0·977
Ash	0·15 per cent.
Acidity	1·0 ,, ,,
Calorific value	16,800 B.Th.U.

The comparatively high ash content does not cause any trouble in the setting as most of it is ejected through the stack ; on the other hand, corrosion by the acid is not experienced so long as the combustion products are not allowed to cool below or to their dew point. Suitable provisions are necessary to prevent the creation of nuisance by the stack gases, which may contain high contents of sulphur oxides when acid-sludge fuel is burnt ; this is mainly achieved by making the chimney stack of such a height that the emerging flue gases are not brought down near their point of entry to the atmosphere by eddy currents caused by wind-impingement against neighbouring high structures (down-draught).

When acid recovery is possible, the acid sludge is split by steam and water into weak acid, fuel oil, and solid sludge or sludge coke. The fluid portion of the acid-sludge fuel can be successfully consumed in a pressure fuel-oil burner, whereas the wet sludge, which is sometimes semi-solid, can be consumed in special burners, such as the Duncan Rotary Sludge burners (Illinois Stoker Co., Alton, Ill., U.S.A.) which can handle up to 4,000 lbs. of wet sludge per hour.

It is estimated that in 1930 American petroleum refineries consumed about four million barrels of acid sludge as refinery fuel.

CONSUMPTION OF FUEL OIL IN THE U.S.A.—The many industries utilising gas oil and fuel oil, and the avenues through which these products are consumed, are illustrated in the following tables. It places the users in the order of magnitude for the year 1929, and is based upon statistics issued by the U.S. Bureau of Mines, " National Survey of Fuel-oil Distribution in 1929." The quantities are expressed in terms of barrels containing 42 U.S. gallons each.

DISTRIBUTION OF GAS OIL AND FUEL OIL IN THE U.S.A. (1928-29)

Uses.	1928.	1929.
Steamships (including tankers)	89,942,155	92,042,365
Railroads	70,680,111	75,965 760
Used as fuel by oil companies	50,044,106	56,206,214
Gas and electric power plants	30,901,657	31,478,020
Iron and steel products	19,429,514	20,318,526
Commercial heating	16,427,105	17,692,851
Other manufacturing processes	10,023,352	13,548,032
Miscellaneous uses	12,757,596	11,719,583
Domestic heating	5,971,556	7,190,556
Smelters and mines	6,897,642	7,049,965
Food industries	6,488,288	6,924,603
U.S. Navy, Army Transport, etc.	8,368,577	6,392,336
Textiles and their products	4,586,306	4,721,481
Chemicals and allied industries	3,400,011	4,191,852
Cement and lime plants	5,223,887	3,031,046
Automotive industries	3,628,493	3,224,410
Paper and wood pulp	2,792,752	2,992,800
Ceramic industries	2,995,531	2,376,046
Logging and lumbering	2,673,234	2,248,215
Total domestic deliveries	353,231,875	369,584,661
Exports and other shipments	44,428,220	39,150,832
Total distribution	397,660,095	408,735,492

The foregoing table does not classify under the appropriate heading the total consumption of all the types of fuel oil utilised for purposes of domestic heating, which is an important outlet for fuel oils in the U.S.A. and a growing outlet in other countries.

The following table illustrates more clearly the magnitude of the domestic fuel-oil market, and also the increasing tendency of domestic oil-heating units towards the use of the heavier grades of fuel oils—a sane and commendable movement.

CONSUMPTION OF FUEL OILS FOR DOMESTIC HEATING IN THE U.S.A. (1921-30)

(*Barrels of* 42 *U.S. Gallons each*)

Year.	Light Furnace Oil.	Heavy Furnace or Gas Oil.	Total.
1921	500,000	100,000	600,000
1922	640,000	400,000	1,040,000
1923	2,260,000	560,000	2,820,000
1924	3,855,000	1,165,000	5,020,000
1925	6,860,000	1,970,000	8,830,000
1926	6,805,000	2,910,000	9,715,000
1927	7,366,000	5,484,000	12,850,000
1928	8,369,000	8,834,000	17,203,000
1929	10,278,000	12,869,000	23,147,000
1930	12,420,000	17,370,000	29,790,000

The consumption of fuel oil in this country is on a much smaller scale, but statistics indicate that although there is a tendency for kerosene imports to be reduced there has been a steady rise in the quantity of fuel oil imported over the last ten years. Import statistics for gas oil are rather erratic, and there is no direct indication as to whether the figures are on the increase or decrease. Import figures for 1932 and 1933 are as follows :—

	Kerosene.	Gas Oil.	Fuel Oil.
	Gals.	Gals.	Gals.
1932 . .	216,720,695	97,116,670	493,438,269
1933 . .	185,340,654	114,886,956	570,232,175

In addition to the above imports, a considerable amount of kerosene, gas oil, and fuel oil was manufactured from imported crude, from which one might expect a yield of about 50 per cent. of combined kerosene, gas oil, and fuel oil. The importations of crude oil for 1932 and 1933 were as follows :—

1932	368,502,111 gals.
1933	391,563,021 ,,

The production of fuel oil from shale is comparatively small, but there is no doubt that during the last year or two there has been a considerable increase in the use of coal-tar oils for fuel purposes. This has been brought about largely by the import tax of 1d. per gallon on imported oils which has maintained a higher price level, thereby assisting the production of coal-tar products which have hitherto found difficulty in competing with the low prices of imported oils.

CHAPTER II

THE CHEMISTRY OF COMBUSTION

Any combustion process needs two participants : (1) the combustible material—fuels such as gas, coal, oil, wood, etc. ; and (2) the supporter of combustion—oxygen in the air or substances known as oxidisers that will supply oxygen. For power generation in industry, the supporter of combustion is atmospheric oxygen, and the fundamental reactions are those of oxidation of the fuel.

Commercial fuels—coal and oil—are complex substances mainly composed of carbon and hydrogen in chemical union, so that first considerations of combustion reactions are those dealing with the mechanism of the interaction of carbon, hydrogen, and oxygen. These reactions are conveniently represented by chemical equations which contain the reactants on the left and the products on the right of the sign of equality.

A simple reaction taking place during combustion is :

$$C+O_2=CO_2 \quad . \quad . \quad . \quad . \quad (a)$$

This expresses briefly that one atom of carbon (C) combines with one molecule of oxygen (O_2) composed of two atoms of oxygen (O) to yield one molecule of carbon dioxide (CO_2). Equation (*a*) conveys the further information that twelve units by weight (*e.g.*, pounds) of carbon require 32 parts by weight (pounds) of oxygen in order to burn completely to 44 parts by weight (pounds) of carbon dioxide (atomic weight of carbon=12 ; of oxygen=16).

Equation (*a*) is incomplete, however, inasmuch as it does not include details of the heat energy liberated when carbon is burnt—a truth that is admissible from common knowledge—so that an addition has to be made to the right of this equation to make it theoretically complete ; properly written, the equation becomes :

$$C+O_2=CO_2+Q \quad . \quad . \quad . \quad . \quad (b)$$

in which Q represents the quantity of heat energy involved in the reaction, and the positive sign before the quantity Q indicates that the energy is liberated and may be utilised for power generation. A reaction of this type is classified under the general heading " exothermal reaction "—one in which the heat energy is liberated. The opposite class of heat reaction is known as the " endothermal "—one in which heat is absorbed from an external source, without which the reaction could not proceed. A typical example is the production of carbon disulphide from carbon and sulphur, which is effected by the addition of heat to the system. Both types of reactions form parts of the general picture of chemical processes functioning during the combustion of hydrocarbon fuels. Of both types the following are the most important. The equations are written so that they express whether the reaction is exothermal or endothermal in character, and also the number of heat units are written as British thermal units involved when a " pound-mole " of the combustible is consumed in the reaction. (A pound-mole is the molecular weight of the combustible expressed in pounds weight. A pound-mole of carbon is 12 lbs. ; of hydrogen, 2 lbs., etc.) It should be remembered, too, that the quantity of heat involved in the following reactions is calculated on the assumption that combustion takes place at constant pressure (the opposite of combustion in an enclosed space such as a calorimeter bomb, a petrol engine, etc., in which the conditions are those of constant volume), and also that both the reactants and the products of combustion are at 60° F. before and after combustion respectively.

The complete theoretical and ideal process of combustion of a hydrocarbon fuel (methane) is expressed as :

$$CH_4+2O_2=CO_2+2H_2O+384,000 \quad . \quad . \quad (1)$$

but it does not state adequately all the possibilities. Some fuel (methane) in favourable circumstances may attain a high temperature and, in the absence of oxygen, " crack " into elementary carbon and hydrogen :—

$$CH_4=C+2H_2-36,800 \quad . \quad . \quad . \quad (2)$$

Such a process takes place in almost all hydrocarbon combustions in which the flame is luminous, the luminosity or yellow colour arising from the incandescence of carbon liberated inside the flame. The presence of free carbon in luminous flames is readily demonstrable by causing the flame to impinge on a cold surface on which the carbon would deposit itself—a process of " sooting." Any such luminous flame, however, does not deposit soot outside the flame unless there is insufficient oxygen around it (secondary air) to cause the carbon to burn into invisible oxides of carbon. Similarly, the liberated hydrogen in luminous flames would burn to water. Equations may therefore be written in another sequence :—

$$CH_4=C+2H_2-36,800 \quad . \quad . \quad . \quad (2)$$
$$C+O_2=CO_2+174,600 \quad . \quad . \quad . \quad (3)$$
$$2H_2+O_2=2H_2O+246,200 \quad . \quad . \quad . \quad (4)$$

The heat balance of equation (1) is obviously equal to the sum of the heat quantities contained in equations (2), (3), and (4) :—

$$174,600+246,200-36,800=384,000$$

The combustion of fuels in the majority of practical conditions, unfortunately, does not attain the ideal expressed in equation (1) because other side reactions occur in degrees of magnitude depending upon the prevailing conditions of temperature, ratio of fuel to air, etc. A brief discussion of these and the consequences of their enactment follows.

Some carbon formed by the effect of heat (already produced) on a part of the unburnt fuel may encounter hot carbon dioxide. If they meet at a temperature of approximately 500° C. they form some carbon monoxide, but if the temperature is about 1,000° C. the free carbon will react with an equivalent proportion of carbon dioxide to give the corresponding quantity of carbon monoxide :—

$$CO_2+C=2CO-70{,}200 \quad . \quad . \quad . \quad (5)$$

The two reactions (3) and (5), which are complementary one to another, may be written as one :—

$$2C+O_2=2CO+104{,}400 \quad . \quad . \quad . \quad (6)$$

although the first end product of carbon combustion is generally accepted to be carbon dioxide, which may or may not react with incandescent carbon to yield carbon monoxide. A comparison of equations (3) and (6) shows that equation (6) represents the result of insufficiency of oxygen for complete combustion of the fuel. A typical example of practical circumstances under which equation (6) dominates equation (3) is that of a petrol engine operating with a " rich " mixture (of petrol and air), which is so favoured by many because the power generated in each combustion is greater than with a lean mixture.

Carbon monoxide is also formed when carbon dioxide is heated to very high temperatures, at which temperature carbon dioxide dissociates into carbon monoxide and oxygen ; but carbon monoxide is frequently a product of the interaction of incandescent carbon and the superheated vapour of the water of combustion (steam) which has been formed in a manner depicted in equation (4) :—

$$C+H_2O=CO+H_2-70{,}000 \quad . \quad . \quad . \quad (7)$$
$$C+2H_2O=CO_2+2H_2-71{,}600 \quad . \quad . \quad (8)$$

Equation (7) is the well-known " water-gas " reaction, so called because its principle is exploited commercially for the production of gas by the passage of superheated steam through incandescent coke.

The influence of steam at very high temperatures in flames and combustion products in complicating the process is shown by equation (9) :—

$$CO+H_2O=CO_2+H_2-700 \quad . \quad . \quad . \quad (9)$$

which states that carbon monoxide can derive oxygen from the steam to burn into carbon dioxide and hydrogen, but with the reduction of the heat units available for power generation. The carbon monoxide produced in flames, or in excessively hot zones of the combustion chamber, will revert to carbon dioxide if given the opportunity provided by the influx of secondary air :—

$$2CO+O_2=2CO_2+244{,}800 \qquad (10)$$

A brief survey of the possible chemical reactions enumerated above indicates forcibly that the carbon-monoxide content of the products of any combustion process should be kept down to a minimum if the thermal efficiency of the unit is to attain a high value. This statement assumes greater significance if the heat produced in the four main reactions is calculated not on the pound-mole basis but reduced to a more practical method, namely, the heat produced when 1 lb. weight of the combustible is consumed. The four equations then become :—

$$C+O_2=CO_2(+14{,}500) \qquad (11)$$
$$2C+O_2=2CO(+4{,}350) \qquad (12)$$
$$2CO+O_2=2CO_2(+6{,}120) \qquad (13)$$
$$2H_2+O_2=2H_2O(+61{,}550) \qquad (14)$$

Expressed in this form, the equations imply, amongst other things, that if 1 lb. weight of carbon is burnt entirely into carbon monoxide, the heat liberated would be only 30 per cent. of the heat freed by the combustion of 1 lb. weight of carbon into carbon dioxide.

Equation (14) conveys very important information, and, when compared with equation (11), it is apparent that hydrogen, when burnt in oxygen, produces slightly more than four times the quantity of heat than the same weight of carbon burnt completely into carbon dioxide, other conditions being identically the same. It is evident, therefore, that a hydrocarbon fuel derives a very important part of its heat-producing ability from its hydrogen content.

This method of approach points out one of the reasons (*a*) why petrol engines are so inefficient thermally (carbon monoxide is a prominent constituent of petrol-engine exhaust gas, especially when they operate on rich mixtures which are favoured generally because of the greater horse-power output per cylinder obtained with rich mixtures as opposed to lean or theoretical mixtures) ; (*b*) why Diesel-engine combustion is more efficient than petrol-engine practice (the presence of carbon monoxide in Diesel-engine exhaust gases is the exception rather than the rule) ; (*c*) why it is common practice to measure the carbon-monoxide content of flue gases in order to judge the combustion or furnace efficiency of power units (the lower the carbon-monoxide content, the better is the fuel being utilised).

The preceding discussion of combustion and the chemical reactions involved has been simplified by putting aside for the time several important factors which are encountered in practice, for which provision is made below. The three assumptions which have been made are :—

1. That the fuels burn in oxygen.
2. That the products of combustion are brought to the original conditions of temperature (60° F.) and pressure (1 atmosphere).
3. That liquid fuels are composed of hydrogen-carbon complexes.

None of these obtains in practice, and when they are taken into consideration, the general aspect is considerably altered.

Firstly, although the main reactions involved occur between the organic constituents of a fuel and oxygen, the oxygen is supplied as atmospheric air, that is, the oxygen is diluted mainly by nitrogen. Air has the following composition :—

APPROXIMATE COMPOSITION OF ATMOSPHERIC AIR

Constituent.	Percentage.	
	Weight.	Volume.
Oxygen	23·1	20·9
Nitrogen	76·9	79·1

so that equation (*a*), when written to include the nitrogen accompanying the oxygen necessary for the complete combustion of carbon, would be :

$$C+O_2+3.76N_2=CO_2+3.76N_2 \quad . \quad . \quad (c)$$

The nitrogen gas, therefore, passes through the reaction without any value as a heat-raising reactant ; the presence of nitrogen is, on the other hand, a cause of heat loss, as is pointed out in the next section.

Secondly, there is no constancy of temperature and pressure as they relate to the fuel and air entering a power unit, and the products of combustion after the optimum fraction of the available heat energy has been abstracted from them. The effect of this inconstancy of temperature and pressure on the efficiency of the utilisation of theoretically available heat energy is as follows :—

Heat engines of the petrol and Diesel types inhale cold air (in some conditions the intake air is preheated by exhaust hot-spot devices), and they exhaust the products of combustion at high temperatures and substantially elevated pressures. Similarly, stack gases emanating from all power units operating with external combustion are hot for two reasons : in natural-draught settings the motion of air through the furnace is induced by the negative pressure produced in the stack by virtue of the lower density (higher temperature) of its contents as compared with that of the outside air ; in both natural and forced-draught units it is not economical to recover the total heat content of the flue gases. The heat content of these gases, therefore, is lost.

This heat loss may be divided into two quantities : the one is the heat required to raise the inert nitrogen and the oxides of carbon from the atmospheric to the exhaust or stack temperature, and the second is the amount of heat contained in the water of combustion. The latter in turn may be subdivided into three quantities : (*a*) the heat required to raise the equivalent amount of water at 60° F. from that temperature to the boiling point of water (212° F.) ; (*b*) the heat which has to be provided in order to change the water at 212° F. into steam at 212° F. (a function of the latent heat of vaporisation) ; (*c*) the heat necessary to elevate the temperature of the steam from 212° F. to that of the exhaust or stack gases (at constant pressure).

The loss of heat in the " water of combustion " (freely quoted as the " hydrogen loss "), which leaves the power unit above the boiling point of water, explains why the calorific values of fuels are sometimes expressed as " net " calorific values. This quantity is smaller than the gross calorific value (as determined by the calorimeter-bomb method) by that amount of heat required to convert the water of combustion at 60° F. into steam at 212° F. It is obvious at once that a comparison of the heat values of fuels is more rational if based on their net calorific values. Such a comparison is none the less arbitrary because it does not take into account the sensible heat lost in the normally gaseous products of combustion, etc., namely, carbon dioxide, nitrogen, excess oxygen, and the sensible heat in the steam, all of which usually enter the stack at temperatures above 212° F.

Care has to be exercised, therefore, because any attempt to rate the efficiency of a combustion process in a plant will be inadequate if based on an estimate of the input of heat units from a knowledge of the weight of fuel used and its " net " calorific value. This mistake is so often made that it is advisable to accept for this purpose " gross calorific values " together with information of the " hydrogen content " of the fuel ; these quantities and the temperature of the flue gases, etc., provide a suitable starting point for the calculation of the " hydrogen loss " and the net heat input into the furnace.

Reverting to equation (*a*) it will be seen that 1 lb. of carbon theoretically requires $11\frac{1}{2}$ lbs. of air $\left(\frac{32}{12}\times\frac{100}{23\cdot1}\right)$ for its complete combustion into carbon dioxide. In practice, however, complete combustion is not possible when only the theoretical amount of air for the combustion of the fuel is provided, because practical conditions are not sufficient to ensure that every particle of fuel encounters its quota of oxygen. Consequently, excess air is always provided, and this usually ranges from 10 to 25 per cent. of the theoretical amount. This is important to bear in mind, since an additional loss of heat results from this excess air carrying away useful heat from the power unit into the atmosphere. The heat loss due to excess air is involved, especially in Diesel engines and in power units operating with external combustion.

The third assumption made in the earlier discussion of combustion reactions was that fuels were composed only of carbon and hydrogen. In the case of most fuels this is far from the truth ; most commercial fuels contain many other constituents, the most important of which are sulphur (combined, and occasionally some is free), nitrogen (as organic nitrogen compounds), oxygen (as organic compounds or as water), and inorganic impurities known as the " ash " content of the fuels. All these have a significance in any discussion of the heat-producing qualities of fuels.

The sulphur compounds occurring in coal, coal tars, tar oils, and liquid petroleum fuels are complex bodies composed of organically combined carbon, hydrogen, and sulphur ; it occurs as hydrogen sulphide in some, notably natural, gas ; in special fuels it may be present as free sulphur. In general, however, the sulphur content of the fuel would burn to form sulphur dioxide :—

$$S+O_2=SO_2+Q \quad . \quad . \quad . \quad . \quad (d)$$

the reaction being exothermal in character.

Nitrogen compounds are present in some petroleum fuels in small amounts, and to a much greater extent as pyridines in coal-tar fuels. They burn into carbon dioxide and water, and the fate of the nitrogen depends upon the conditions in which the fuel is burnt. In ordinary external combustion the nitrogen content of the fuel probably leaves the combustion chamber as nitrogen gas, but when the fuel is burnt under pressure in a calorimeter bomb, for example, it probably forms nitrogen oxides which dissolve together with the sulphur oxides in the cooled water of combustion to form nitrogen acids and sulphur acids. The formation of these acids by solution of the gases in the water produces heat, so that in any accurate estimation of the net calorific value of a fuel, allowances have to be made not only for the water formed but also for the formation of these mineral acids.

Organically combined oxygen present in fuels reduces the calorific value because part of the heat-producing avidity of the fuel for oxygen is satisfied before the fuel enters the combustion zone. This applies more especially to coal-tar fuels which contain amounts of organically combined oxygen (as phenols, etc.), which are appreciable in comparison with the oxygen content of petroleum fuels which is usually very small.

The inorganic constituents of a fuel also reduce the calorific value, but over and above this fact, if the ash content is appreciable, it introduces other objectionable features such as air pollution, clinker formation, glazing of furnace brick linings, etc., to which reference will be made later.

CHAPTER III

THE UTILISATION OF LIQUID FUELS FOR EXTERNAL COMBUSTION

The utilisation of liquid fuels as sources of heat energy requires the use of mechanical appliances, which are designed to apply the fuel in a manner appropriate to the end in view. This may take many forms ; the heat generated by combustion may be required for lighting purposes, for direct application to vessels containing commodities of various forms and types, for steam generation, or for heating media such as air, oil, and water, which in turn are circulated to the zones or units requiring their heat content.

These many uses of liquid fuels cover domestic, commercial, and industrial applications, all of which require special mechanical units. In each of these are processes of operation fundamentally common to the others ; a quantity of fuel has to be stored conveniently at hand and in sufficient amount to satisfy the demands of the unit for a reasonable interval of time ; the fuel has to be moved from the storage vessel to the zone of combustion, and the fuel has to be burnt. The most important stage in any heat-generating unit is the combustion process, but the efficiency of this depends on preceding operations ; these comprise the preliminary treatment or handling of the fuel, the method by which the combustible is introduced to the supporter of combustion (atmospheric oxygen), the nature of the flame, furnace, or boiler design. The two latter are outside the scope of this manual, and attention will be directed, therefore, to the other factors.

It has already been indicated that the combustion of a fuel is made up of a series of reactions between the carbon-hydrogen complexes in the fuel and the oxygen in the air ; it is therefore an oxidation process which must be rapid, and hence every effort should be made to bring both the liquid fuel and the air into most intimate contact ; also, ignition has to be aided or started, and adequate provision should be made for its effective continuance. Many everyday and well-known occurrences may be cited to emphasise these points.

A thin wood-shaving may be regarded as a source of heat energy ; it can be ignited by bringing it into contact with a hot body, and, subsequently, it may continue to burn with flame formation or it may continue to glow and be consumed slowly. The glowing condition can be transformed into rapid combustion with flame by placing the glowing wood into an atmosphere of oxygen ; in such circumstances the dull red end becomes white-hot, bursting eventually into flame. Combustion then proceeds rapidly, because the rate of heat generation is sufficient to stimulate the more rapid combustion of the unburnt wood so that flame formation continues. The glowing end of the wooden strip may be induced towards flame formation and rapid combustion also in air by adequate artificial draught. The net effect in both cases is the same, because in each the glowing combustible is afforded greater opportunity for encountering oxygen that is free to combine with the fuel and liberate heat energy at a more rapid rate. The question of heat-raising through the agency of fuels and air, therefore, becomes one of promotion of rapid oxidation.

A less obvious example that may be instanced in this connection is that of rust formation—rust being oxides of iron. A piece of iron will become coated with rust in a comparatively short time if it is allowed to remain in the open air, but the rate of rust formation decreases rapidly as the rust layer becomes thicker and prevents easy access of oxygen to free iron. It is common knowledge, too, that the amount of rust formed by a given amount of iron in unit time can be increased by subdividing the iron mass into small particles. The speed of rust formation will be enormously increased if the piece of iron is reduced to the form of a powder. If this process of subdivision is continued to the limiting condition, that is, if metallic iron particles are prepared by the decomposition of pure iron compounds in the absence of air, the metal possesses such a large surface that when it is scattered in air the oxidation to oxides of iron is so rapid, and the heat of oxidation is produced so rapidly, that the iron particles become incandescent and appear as a shower of sparks. This is an example of how effective is extreme subdivision of an oxidisable material in assisting the rapid interaction of the substance with the surrounding oxygen (air).

Each of these examples corresponds to measures adopted in combustion engineering ; the former case is typical of how the rate of combustion of a hot bed of coal is increased by artificial draught, each lump of coal having to undergo combustion from the outside and towards its centre of mass, mainly by the consumption of successive outer layers. The latter exemplifies the measures taken to promote rapid combustion of coal, firstly by reducing it into the form of a powder, and secondly by mixing it mechanically with air before its entry into the combustion space ; it also supports the practice of reducing the bulk of liquid fuel into fine spray which is mingled with the air, so that each particle may have every facility for encountering its quantum of oxygen.

The most effective method for ensuring rapid combustion of liquid fuels in air is to convert the liquid into the gaseous or vapour form, which is then mingled with the most economical proportion of air ; the mixture is then conveniently and most readily burnt.

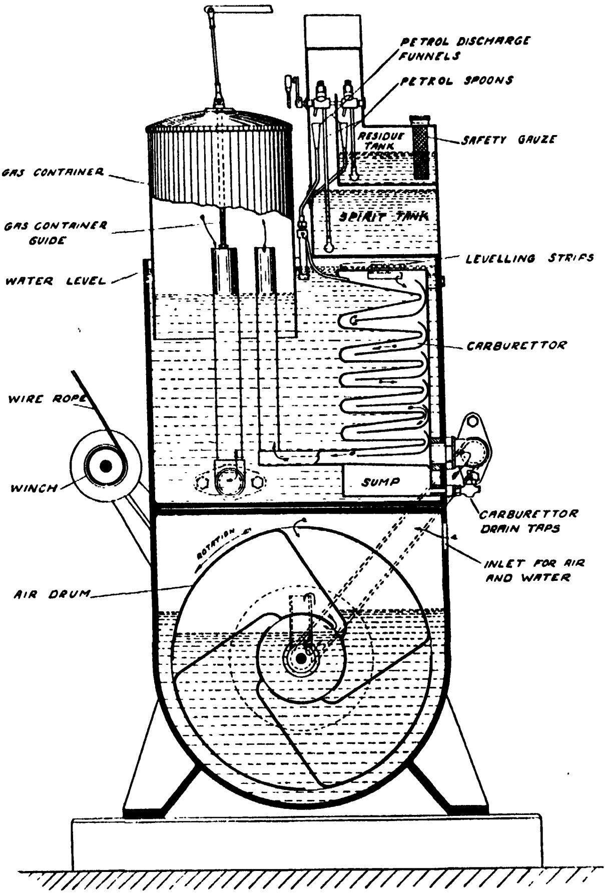
The manner in which a liquid fuel is prepared for combustion is decided, however, by the general properties of the particular fuel and the application to which it is put. If gasification is simple to perform, then the liquid fuel is gasified, but if the fuel is not easily vaporised cold, it may be possible to approach near to the ideal by utilising part of the heat of combustion to vaporise the fuel by radiation. On the other hand, this may not provide complete satisfaction when the fuels are of very low vapour pressure ; in such cases the oil is mechanically reduced to a spray, which burns more readily because it has a larger surface area per unit weight of fuel from which to vaporise and with which to meet the oxygen in the air. The following chapters describe some of the outlets for liquid fuels and methods available for their preparation for combustion on various scales and for a number of different purposes.

LIQUEFIED PETROLEUM GASES.—Propane and butane, and mixtures of both, in the form of liquids under pressure are being employed on an ever-increasing scale in the U.S.A. For domestic purposes, liquid propane is the most useful and most widely used of the two because it is self-vaporising at temperatures below —40° F. and atmospheric pressures. It is transported in cylinders to be gasified at a central station, whence it passes through pipes to serve a community ; or it may be serviced to individual dwellings in small " bottles " (small metal cylinders) which contain sufficient hydrocarbon for their needs until the " service van " repeats the circuit, replacing empty cylinders with full ones. This " bottled gas " distribution is invaluable to those who live in districts which cannot be connected economically to gas or electricity company's mains. No elaborate vaporisation apparatus is needed.

The commercial butanes in liquid form are employed in industrial plants where the fuel consumption of large-scale heating operations is large. It is particularly valuable where an economical, clean, and easily controlled fuel is needed. They are used for the enrichment of manufactured gas, the efficiency in the cold being 100 per cent. Here the fuel replaces gas oil, which would otherwise be used for carburetting the water gas or other gases of low heat value ; alternatively it may be used in conjunction with gas oil during periods of sudden demands for gas of statutory heat value.

Alternatively, these liquefied gases may be the base material for manufactured gas, that is, to give heat value to inert gases (diluents) such as exhaust or flue gases, or air. They can also be " reformed " or cracked to give gas of low density and the desired B.Th.U. content.

PETROL FRACTIONS.—The principle of utilising easily vaporised petroleum fractions for the preparation of air-hydrocarbon gas mixtures intended for domestic and industrial uses has been practised in this country since about 1904. An apparatus available for the manufacture of petrol gas is illustrated sectionally in the accompanying figure, which operates on "Aviation" petrol. The mechanism can be actuated by gravitational pull on weights suspended over a pulley and joined to a winch attached to the machine. (These may be raised manually or by an automatically operated electric motor.) The unit can also be arranged to be worked automatically by electric motors without the falling weights.



By Courtesy of Spensers (London) Ltd.

FIG. 18.—Spenser's "Silverlite" Generator. Model *de luxe*.

A push-rod oscillates the petrol spoons which pick up measured volumes of the aviation petrol ; this flows down the petrol discharge funnels along the tortuous path of a carburetter, through which pass volumes of air carefully metered by the rotating wet air drum in the base of the unit. The resulting gas-air mixture enters the gas-holder and raises it to a certain height, when a retarding force is applied through a brake drum and ratchet which slows down or stops the mechanism. The unit restarts when consumption of gas lowers the gas container, so that the ratchet and brake band are released. Any unvaporised petrol is drawn from the base of the petrol carburetter and poured into a residue tank at the top ; from this it is fed by another spoon into a residue carburetter, through which the air passes before it enters the petrol carburetter.

The petrol vapour-air mixture made thus is consumed in burners, not employing the Bunsen principle because the requisite amount of air (oxygen) has already been added to the hydrocarbon gas ; uniform and efficient utilisation of the heat content of the original liquid hydrocarbons is assured and maintained without any need for hand control of primary air ports in the burner.

A similar device may be used for vaporising the more volatile special (low boiling) petrol fractions having specific gravities round 0·680, which are more costly than aviation petrol.

For industrial heating operations, which require large volumes of gas, electrically driven units are employed, and these work under much greater pressures than the unit described.

KEROSENE (paraffin oil or paraffin).—Kerosene is probably the liquid petroleum fuel that has been used for the longest period of time and in the largest quantities ; during the early days of the petroleum industry it was the product made in largest quantity, but it is still a very important petroleum product because of the enormous number of ways in which it is used either for lighting or heating purposes.

This liquid fuel is employed in appliances which fall under two main headings :—

1. Wick-fed Appliances.
2. Vaporising Appliances.

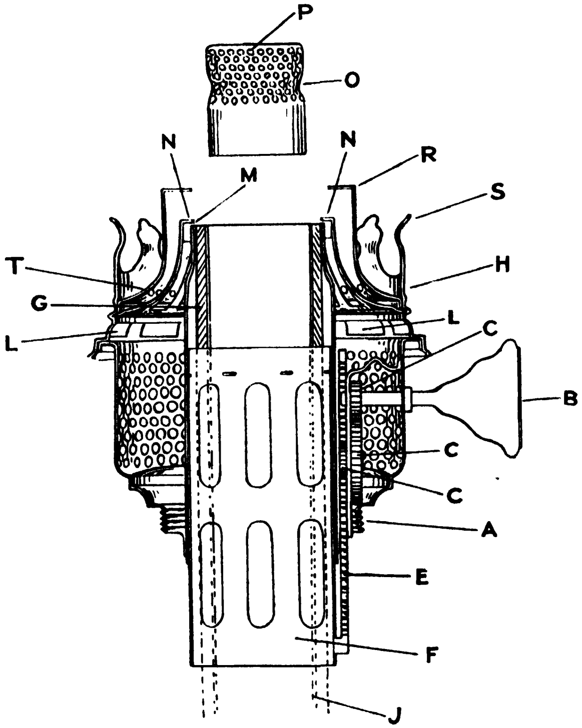
The Wick-fed Principle underlies the convenient utilisation of kerosene in the household lamp which has served humanity all over the world with light (and heat indirectly as well) during the last eighty years ; it is also employed in the many domestic heaters, cookers, etc., which produce heated air and products of combustion, the heat content of which enters the area to be warmed or the oven in which articles of food undergo cooking processes. These heated gases are also utilised in many other appliances for storage water-heating, etc.

There are many forms of units for a specific use, but the underlying principle of each remains the same ; the low viscosity of the liquid and its high capillarity enable it to ascend from a reservoir through a plaited fibre wick at the top of which it is exposed over a comparatively large surface favourable to easy ignition by small flames. Having been ignited, the flame provides the heat needed for the continuous vaporisation of the fuel that continues to creep along the interstitial channels in the wick.

In the small appliances, such as the domestic kerosene lamp, the air supporting combustion surrounds the flame, which for that reason is luminous. Brilliance of flame is imparted to it by surrounding the flame with a transparent (glass) globe or chimney, which induces draught, so that the flame temperature rises sufficiently to make incandescent white the carbon particles formed inside the flame by thermal decomposition of the hydrocarbons. The amount of light radiated by one of these units can be varied by raising or lowering the wick in its metal holder (suitable mechanism being provided such as gear-wheels, rack and pinion, etc.) so that more or less surface area of wick is enveloped by the flame at its base. A maximum flame, however, obtains for each form of equipment, and if this is exceeded, more kerosene is fed into the flame than there is air to burn it completely ; in such a condition the flame becomes dull and emits smoke (carbon). An optimum flame-height is a characteristic of burners consuming kerosene on the wick-fed principle. In addition, kerosenes of different composition (carbon-hydrogen ratio) can be burned properly in lamps of certain construction with flame-heights peculiar to each fuel. In general, therefore, the maximum useful flame-heights obtainable with kerosenes of different carbon-hydrogen ratios, and lamps having differently constructed burners and chimneys, are a function both of the chemical composition of the fuel and the construction of the appliance. These lamps are designed to produce luminous flames.

Other wick-fed burners are designed to produce heat, so that arrangements are made that the flame is semi-luminous to non-luminous ; also, in order that concentrated heat is available, greater quantities of fuel are burned in unit time in unit combustion space by employing a circular wick. This also necessitates provision of extra air for combustion. The air is usually fed into the kerosene flame at the wick-top so that the air mingles readily with the vaporised fuel on top of the wick. The wick tube is therefore made hollow, and in this way the flame is fed both by central air draught and by air surrounding the outside of the flame. Special precautions are taken also to maintain a thin flame by means of a flame-spreader placed in the central air-draught column. This flame-spreader possesses circular rows of small holes opposite the top of the wick, so that the central air draught is split up into a series of fine jets which liberally feed the kerosene flame. By these and similar means good mixing of hydrocarbon vapour and air is assured, so that a semi-luminous or non-luminous flame ensues. The mechanical details of a wick-fed burner operating on the semi-luminous or non-luminous flame principle are shown in the accompanying sketch.

The satisfactory operation of these burners for a lengthy period depends to a great extent on the care given to and the behaviour of the wick (excluding influences which some badly refined kerosenes have in forming char or crusts on the top of the wick). The conditions tend to be more severe the hotter the flame, because high temperatures tend to decompose the wick. A properly designed burner will protect the wick from such deterioration for a remarkably long time.



By Courtesy of Falk, Stadelmann & Co. Ltd.

Fig. 19.—" Famos " (Incandescent) Burner.

Wick-fed lamps are also specially designed for the production of wholly non-luminous flames. This type is represented by the " Famos " lamp, the non-luminous flame of which is enveloped by an incandescent mantle, the end effect being abundant white light. These appliances call for very special designing to obviate the least tendency towards a smoky flame, which would seriously impair their continued use for lighting purposes. The accompanying sketch details the essential constructional features of the " Famos " burner.

The threaded male A attaches the burner to the reservoir below.

B is the outside wick winder which actuates a train of three wheels C on a ratchet E attached to the wick-carrier F, the circular wick being represented by G. The holder H carries both the chimney (glass) and mantle, and is lifted off for lighting wick G. Air passes up the centre tube J and through air ports L. Air from L source is deflected sharply on to the outer side of the flame burning at M just above the point of ignition by the baffle N. Immediately above this point the flame receives a charge of air on its inner side at O through the holes in the air diffuser P, and again a little higher on the outer side by the inner turned edge of cone R. These means establish a pure blue oil-gas flame which, by reason of its intense heat, makes the superimposed mantle (not shown) incandescent. The mantle holder and mantle (removable for renewal) fit on cone R.

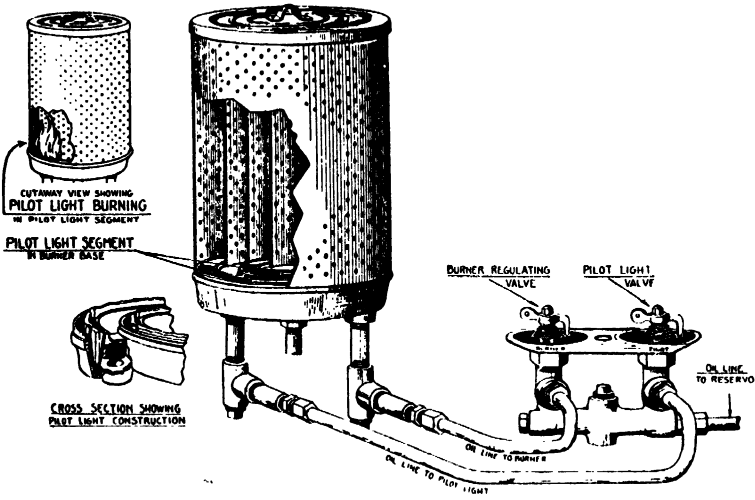
The air draught is induced by a 12½-in. long chimney held in position by clips S. Air also passes through cone R to supply a body of air between the outer side of the mantle and the inner side of the chimney to keep the latter cool (T).

This form of incandescent lamp serves a useful purpose in providing outlying districts (or rooms not serviced with gas, etc.) with artificial light when gas and electricity are not obtainable ; in other circumstances they compete with these sources of light.

Special types of wick-fed burners operating on kerosene or somewhat heavier refined distillates are also available for remarkably heavy duty and large heating potentialities ; the nature of their main functions has forced the makers to discard the conventional type of wick in favour of the more lasting asbestos type. These are a main feature of the Gilbert & Barker range oil burner, many of its unique points being described below.

The burner base is formed of two or more annular fuel vaporising grooves with alternate air channels. In the fuel grooves are situated short asbestos cylinders, and on each side of these wicks stand tall perforated sleeves made of thin high-chromium alloy steel. The kerosene or range oil is maintained at a uniform or constant level in the fuel grooves by suitable exterior arrangements fed from a fuel reservoir. The operating method is to remove the cover and deflector top so that a lighter-torch can be applied to the wicks. These become lit all round and burn in between the pairs of perforated cylinders, which gradually attain a dull red heat, the cover having been replaced. As soon as the cylinders are sufficiently hot, the fuel regulating valve is opened so that extra fuel is fed to the wicks. The flame now leaves the wick-top and extends along the space between the cylinders. Under normal operating conditions and maximum oil consumption, therefore, the kerosene or stove oil is fed through the heated asbestos wick from which it vaporises. The vapours partly burn in the annuli, and as they ascend the remainder is mixed with extra air which enters the burner through the base and along the alternate air channels. Complete combustion takes place at the top of the burner in the form of a non-luminous flame. These units can be fitted in ordinary coal-fired ranges, or they may be incorporated in specially designed units such as storage-water heaters, circulating warm-air room heaters, etc.

The novel features are : (1) the means available for efficient vaporisation of the fuel ; (2) the manner in which excess air is directed into the fuel vapour ; (3) the red-hot cylinders radiate heat along their length to the sides of the grate or oven, and the ascending heat serves to heat hot plates which can deal with exterior utensils requiring bottom-heat ; (4) manual control of the fuel valve makes it possible to vary the heat generated ; and (5) in the "pilot-light" models quick response to sudden demand for heat is possible.



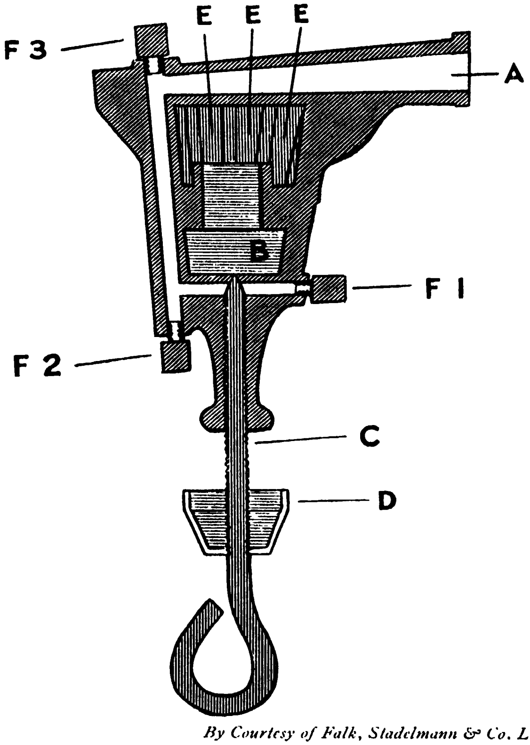
By Courtesy of Gilbert & Barker Manufacturing Co. Ltd., Springfield, Mass., U.S.A.

FIG. 20.—" G. & B." Stove Burner (with pilot light). *De luxe* model.

When properly fitted and operated on normally refined kerosenes or stove oil these units are free from the troubles arising out of wick deterioration, carbonisation, or tar formation at the base of the burner, and soot formation in the flue passages. Modifications of the simpler units provide a range of appliances capable of generating from 30,000 to 100,000 B.Th.U. hours under conditions of maximum oil consumption.

Kerosene is also used in wickless units for the production of moderately small quantities of heat ; some of these small appliances possess all the essential characteristics of large domestic and commercial oil-burning equipment, as will be observed by a comparison of the details immediately following and those given later for the larger installations.

The well-known " Barrow Lamp " is a typical example of a spray type of oil burner producing a luminous flame. The treatment given to the kerosene resembles in many ways the procedure adopted on large-scale plant that burns hundreds of tons of fuel oil per day. For example, kerosene is stored in an elevated tank and is fed under pressure (hydrostatic head) through a pipe. It enters the burner at A and follows the channels bored in the casting (dotted line shows the direction of oil flow) until it reaches B, where it is checked by the screw valve C.



By Courtesy of Falk, Stadelmann & Co. Ltd., London.

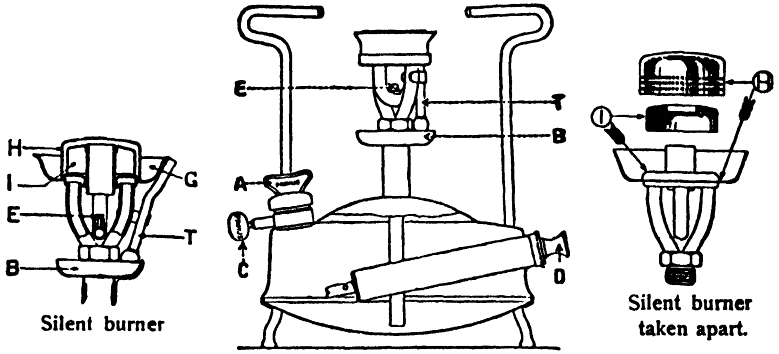
FIG. 21.—" Barrow Lamp."

In normal operation the kerosene is heated by the hot metal casting and is metered by adjustment of the screw valve C seated on an orifice B. Through B the kerosene vapour and heated kerosene are sprayed against the flat top of the casting, and the deflected stream of kerosene vapour and air with which it has been partly mixed at B is split into various jets through the open ports E. The incomplete mixing with air allows the flames to be luminous.

To start the burner the cup D is partially filled with a piece or two of loose string, and valve C is momentarily opened until oil flows over the burner and into cup D, where it is lit. When the flame has almost expired valve C is opened, and the flame will light or the vapours can be ignited at the ports E. More frequently, perhaps, the burner is started by preheating it over an ignited piece of paper, shavings, etc., flooded with paraffin.

The screw-nuts F can be removed if necessary for cleaning out the channels should they become encrusted with carbon.

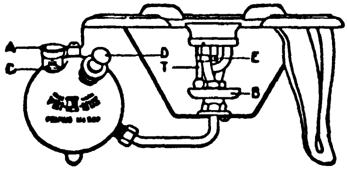
In the lesser-used "naphtha" (gasoline) pattern the entrance



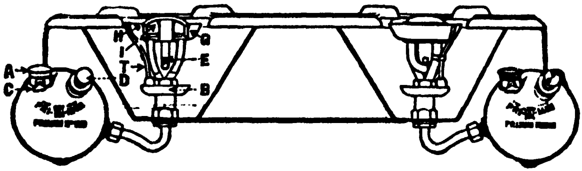
Silent burner

Roarer pattern stove.

Silent burner taken apart.



Range with one roarer burner.



Range with two silent burners.

Fig. 22.—"Primus" Wickless Kerosene or Paraffin Oil Stoves.

A is plugged and the fuel enters at F1, since it is not necessary to heat the petrol by passing it through heated channels as in the paraffin pattern just described.

The principles detailed above also govern the method of operation of many other kerosene spray burners, some of which are of large capacity.

The "Primus" types of kerosene burner, on the other hand, aim at complete gasification, efficient admixture of excess air, and the production of an intensely hot non-luminous flame.

In these the kerosene is contained in a vessel under air pressure generated by a small piston displacement pump. The kerosene is forced under pressure through a central vertical column leading from a point near to the base of the container to a series of U-tubes, in which it is completely gasified. The gas then passes through a fine orifice under such high pressure that it is efficiently mixed with air by the time it impinges against a superimposed dome-shaped spreader. The latter is perforated by several rows of small holes, from which the oil-gas air mixture burns as a series of small non-luminous Bunsen flames. These appliances produce intensely hot flames ideally suited to the heating of utensils such as those used for cooking, solder melting pots, etc. The same sequence of operations—the flow of kerosene under pressure, gasification in heated tubes, the formation of a high-velocity gas jet, admixture with air and combustion with non-luminous flame—is followed in other units such as the painter's blow-lamp and larger forms of similar apparatus used for supplying heat to heavy fuel oil in the starting up of large oil-burning installations from cold, etc.

GAS OILS, DOMESTIC FUEL OILS, MEDIUM AND HIGH-VISCOSITY FUEL OILS.—The utilisation of these liquid fuels demands the use of methods and appliances which have to perform a task more difficult than in any of those described above ; the low boiling petrol fractions are readily vaporised without leaving troublesome residues ; the same applies almost equally to kerosenes which could not be used satisfactorily in kerosene burners were these liquid fuels less refined than the high degree of refining to which they are subjected to-day. Their clean water-white condition enables them to undergo drastic heat treatment without the appreciable formation of tarry or solid residues, and their comparatively low boiling range and sharp final boiling points fit them for complete gasification in kerosene-vaporising burners.

The liquid fuels forming the subject heading of this section, on the other hand, have more extended and higher boiling ranges ; they are not always given refining treatment, though the necessity for partial refining of some of them at least is being more and more observed by sections of the petroleum industry. These radical differences in physical properties reflect themselves in the methods adopted for their preparation for combustion. They are comparatively very fluid (their viscosities range from about 40 Redwood No. 1 secs. at 70° F. to 200 secs. at 100° F.) and can therefore be forced through fine orifices, usually in the cold state. The general principle of most domestic oil burners, therefore, is to pump these fuels under pressure through fine nozzles so that the issuing oil jet breaks into a fine spray which is easily ignited. A few units, however, operate on the " surface-vaporisation " principle, but the majority employ the " atomisation " method. Among the various designs of domestic fuel-burning units (which are legion) are to be found several different mechanical methods of effecting this atomisation, so that the fuel may burn completely and continuously without much attention.

The burner or atomising unit is fitted to a boiler or air heater, both of which are parts of a larger system. Common to most are the following : small storage tanks which are conveniently situated so that they may be filled by the oil companies' road wagons under bulk-delivery terms ; the oil may be fed from this supply to the burner by gravity, but mainly by a small pump through an efficient filter designed to hold back particles which may tend to clog the fine orifice in the oil burner. A very large number of units contain an electric fan or impeller which supplies, under force, the air necessary to support the combustion of all the oil consumed in the boiler furnace ; there are others which supply, under pressure, only that amount of air required to assist the atomisation of the oil and to give it " direction " and " volume," which severally affect the shape and length of the flame ; and finally, a number of units depend entirely on natural draught to provide the burning oil with air for its combustion.

Most of the modern efficient units contain numerous automatic controls which operate electrically ; a thermoregulator placed in a space to be heated may decide the times when the burner is " cut-in " or " cut-out " ; another in the flue or stack can stop supply of oil fuel to the burner if the atomised oil fails to ignite ; or a boiler regulator may maintain a constant water temperature or steam pressure in the boiler by affecting the oil pump, etc., directly.

Common to all is a luminous flame which should completely fill the furnaces so that maximum heat radiation to the furnace walls is attainable ; at the same time the flame should not be allowed to impinge on cool surfaces, otherwise carbon deposits (soot) or the production of smoky fuel gases may result and so reduce the efficiency of heat transfer and fuel utilisation.

Typical members of several classes of domestic oil burners (in most cases they would be more correctly described as " atomisers ") are briefly described below :—

1. Surface vaporisers (forced draught) " Prior " burner.
2. Rotary atomisers (natural draught) " A.B.C."
3. Pressure-jet (forced draught) " Gilbert & Barker " burner.
4. Pressure-jet (forced draught) " Frother " type Williams " Oil-o-Matic."
5. Pressure-jet (natural draught) " Automestic " burner.

SURFACE VAPORISATION.—A simple burner operating on this principle (the " Prior " burner) takes the form of an open cast-iron trough having hollow walls in which mechanically propelled air necessary for combustion of the oil is preheated.

The oil is fed by gravity to the trough through the base by an inlet pipe which projects about $\frac{1}{2}$ in. above the bottom of the trough. A thin layer of oil is maintained in it by an overflow connection in the bottom.

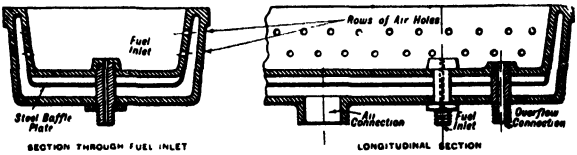


Fig. 23.—" Prior " Oil Burner.

The air required for combustion is fed by a blower fan at a pressure of 2 to 4 in. water-gauge pressure into the hollow walls where it is preheated, thence it is supplied to the vaporising fuel through the inner wall by rows of staggered holes situated above the oil surface. The oil vapour is caused thus to burn as a series of vertical tongues of flame similar to that depicted in the accompanying sketch.

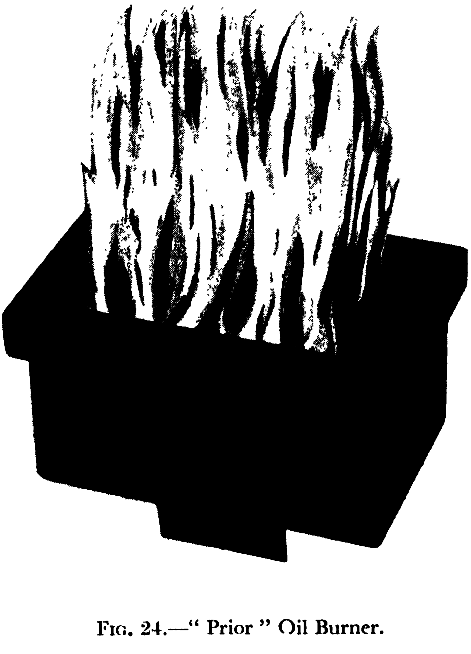


Fig. 24.—" Prior " Oil Burner.

It will be seen, therefore, that the oil vapours rising from the oil surface are produced by heat radiated downwards by the flame and heat conducted from the same source through the metal casting to the oil layer.

The burner, when operated automatically, functions on the "high-low" principle, flame regulation being possible between the ratios of 8 to 1. Different sizes of burners (that vary in the area of the casting bottom) have maximum oil consumptions varying from about 1½ to 180 lbs. of oil per hour.

It is apparent that very heavy fuels which are not readily volatilised as a whole or those which contain "hard asphalt" are not suitable for burners of this type. In the event of heavy fuels being used, the tacky residue that may form in greater or less quantity must be removed periodically. The burner is capable of handling satisfactorily light fuels which have distillation ranges that do not "tail off" to very high temperatures.

Rotary Atomisation.—Several units adopt this principle in various forms ; in some the oil is atomised by being whirled radially outwards from a rotary disc ; in others, such as the "A.B.C." burner, a similar effect is produced by a cup rotating at high speed. In this particular design the cup is sustained by the hollow shaft of an electric motor ; the shaft at its lower end dips into an oil reservoir which is maintained full of oil to a level controlled by a constant-level device. When the shaft rotates, the oil ascends the hollow shaft by virtue of centrifugal force inasmuch as the hollow channel in the shaft increases gradually in diameter towards its (wider) upper end. When the oil reaches the cup it travels along its surface and is thrown as a spray from its edge. The oil mist mixes with air propelled outwards by small vanes in the top of the cup.

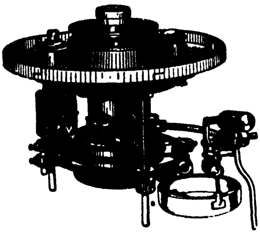


Fig. 25.—"A.B.C." Oil Burner.

The bulk of the air required for combustion is induced naturally and enters the boiler base after having moved over the electric motor and through suitably arranged hollows below the cup. When fitted the burner top protrudes above a fire brick or clay base built into the furnace in the form of a shallow basin. Ignition is initiated by a small gas pilot light or by high-tension electric arc. The flame produced under normal conditions is annular in form since there is a lag between the time the oil leaves the edge of the cup and when it reaches its ignition temperature.

The burners described in the following sections are designed for special duties and can be classified into three main categories :—

1. The pressure-jet system.
2. Air atomisation : (*a*) low-pressure air, (*b*) high-pressure air.
3. Steam atomisation.

The Pressure-jet burners depend solely on turbulence in the oil for the disintegration of the oil jet ; this is produced by forcing the oil through passages of various designs and eventually through an orifice.

Atomisation by Air Pressure is accomplished by organised impact between an oil stream and one or more jets of air, both the oil and air being under high or low pressure before entry into the atomiser.

The Steam Atomising units employ steam in a similar manner as air is used in the second type described above.

Each type has its commendable features which fit it for use in particular spheres, ranging from small domestic through the medium-sized industrial plants to the large commercial (land and marine) power generating units.

The qualities of each type are most obvious if their suitability for very large commercial plants working at high rates of oil consumption is examined. For units of this size air atomisation requires large air-pumping accessories, which is a disadvantage as there are more mechanical parts to maintain or cause trouble through partial failure ; other considerations, such as noise and consumption of steam to drive these accessories, rule out air atomisation. Atomisation by steam removes the need for air-pumping accessories, but the system suffers from disabilities in other directions ; the steam used to atomise the fuel reduces the useful steam-generating capacity of the boiler unit ; also, more fresh water is needed to replace that converted into steam for the atomising burner. This aspect is a definite disadvantage in large plants like marine boilers, which operate under conditions demanding the utmost economy of fresh water ; this applies equally to land boilers, for which the available water must be softened or chemically treated before entry into the boiler. In general, therefore, large steam generating units are most efficient from a fuel consumption point of view, and in their economical use of boiler feed-water when they are operated on the pressure-jet system.

These advantages are less obvious as the size of the plant decreases, and the pressure-jet system frequently falls into disfavour on that account ; another reason for this disfavour is that the primary cost of air-atomising burners, for example, is less than the pressure-jet burners. In any circumstances, however, it should be observed by prospective users of oil-burning equipment that there are pressure-jet systems which can operate on each or several of the liquid fuels on the market, and that if a pressure-jet burner suitable for their plant can effectively deal with the heavy viscous petroleum fuels this is an advantage, because these fuels are produced in the largest quantities, are available at the lowest prices, and have the highest British Thermal Units per gallon.

In the following sections will be found descriptions of many excellent burners suitable for domestic, industrial, and commercial units ; the details will enable the reader to decide to which of the three main systems each burner belongs.

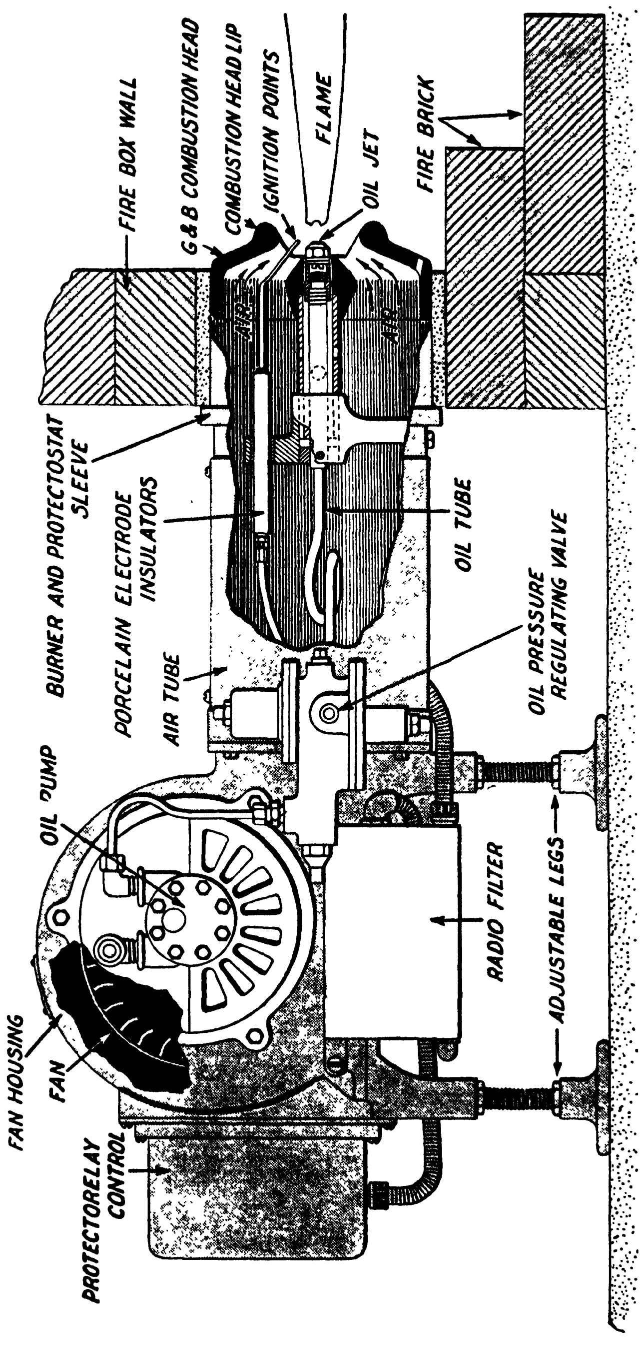
A typical example of the " gun " type or complete domestic oil-burner unit is the Gilbert & Barker " Flexible Flame " oil burner. The whole assembly contains a motor which propels a fan for supplying to the furnace all the air required for combustion ; it also provides the motive force to the oil pump which feeds the oil under constant pressure to a nozzle centrally placed in an air tube. The atomised oil is ignited by an electric spark of the continuous type, formed at the ends of non-fouling porcelain-insulated electrodes. The transformer supplying these with current is specially housed in a radio filter, so designed that there is no interference with radio sets in the building. The unit is fully automatic, the burner being turned on and off as required by thermostats operating in the areas being heated, in the boiler if the pressure gets excessive, etc.

The novel feature is the flexibility of the flame which is produced by a specially designed combustion head in conjunction with nozzles of varying spray-angle. Two streams of air, one from above and one from below, are directed into the atomised oil. As these air streams pass over the horizontal, broad flat lips of the combustion head they are flattened out and, meeting the oil stream, produce a flat flame. The use of a nozzle of wide spray-angle produces a wide short flame, and, as the angle of the spray from the nozzle is reduced, the flame becomes narrower and longer. Thus the shape of the flame can be definitely controlled and fitted to the shape of the fire-box in which it is used, a provision that is essential for greatest economy and efficiency in operation.

Another requirement which this burner fulfils is that when the oil pump stops (heating no longer being required) there is a positive quick cut-off, resulting in a rapid stopping of oil flow to the nozzle and absence of " dribbling " at the nozzle. Any gun-type burner of this form which is in the least way prone to " dribble " at a " cut-off " can readily have its efficiency impaired later by the formation of carbon or tarry matter from the " oil dribble " under the action of heat radiated on to the nozzle by the refractory lining of the furnace.

THE (WILLIAMS) " OIL-O-MATIC " BURNER employs a somewhat different method for bringing the oil into intimate contact with air, which consists essentially of two stages, one taking place between the pump and burner nozzle and the other at the nozzle. The unit functions as follows :—

The oil-circulating pump draws oil from a storage tank and sends it to an oil strainer, the excess oil going along the " overflow " back to the tank. The oil required for combustion passes from the automatic shut-off valve to the oil-feed metering pump. This

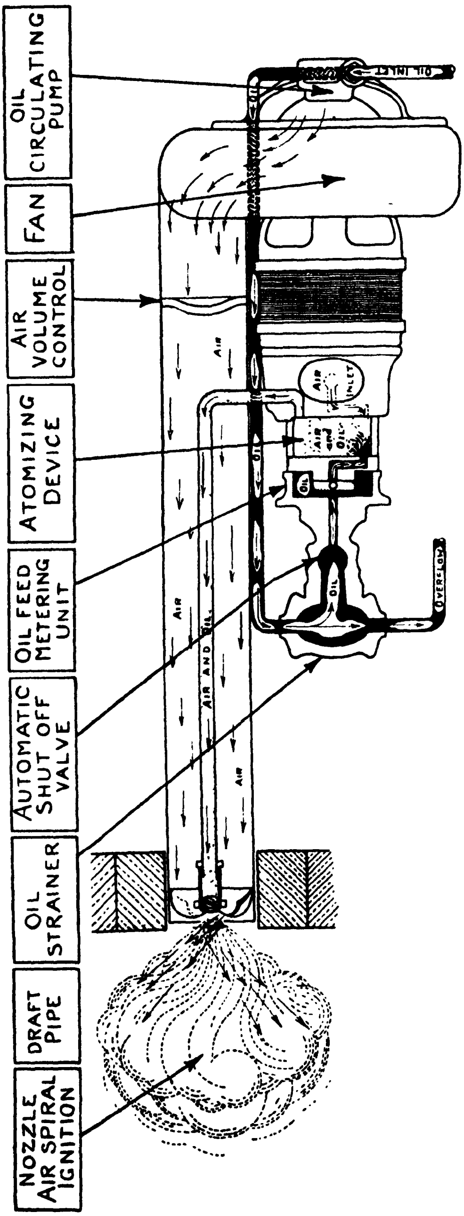


Cross Section of "BS" Model G&B *Flexible Flame* Oil Burner Showing Various Units of Construction and Design

By Courtesy of Stemco Ltd., Camden Town, London.

FIG. 26.

displacement pump can be adjusted quickly to give any desired output within reasonable limits. The oil is then discharged into an atomising device, which is a rotor placed eccentrically in a cylindrical housing, vanes being fitted in the rotor which fly outward under centrifugal force; the air which is mixed with the oil at this point is drawn through a muffler marked " air inlet " on the

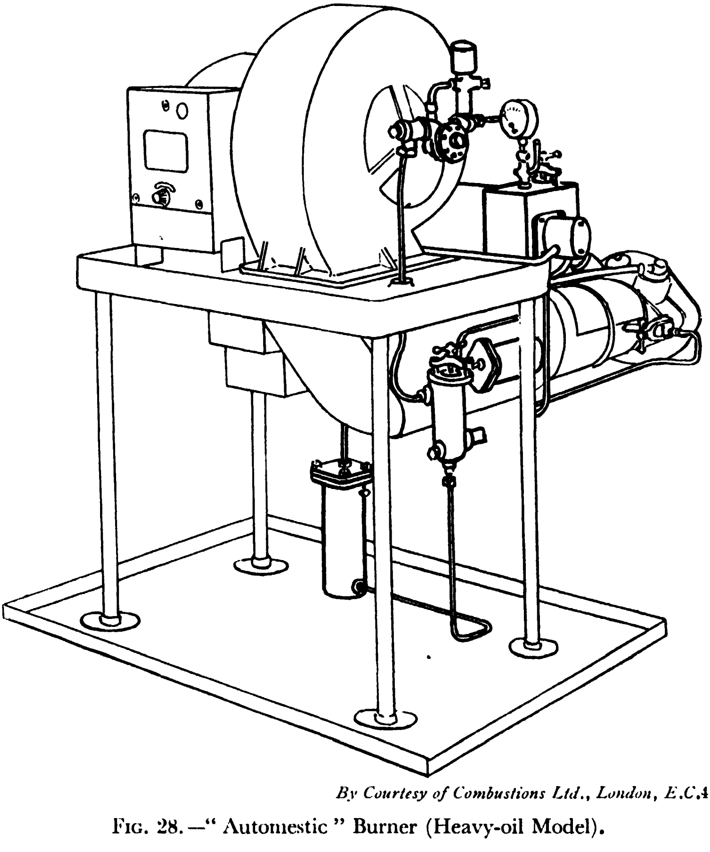


By Courtesy of G. N. Harden & Sons Ltd., London, W.C.2.

FIG. 27.—" Oil-o-Matic " Burner.

drawing. The "froth-like" air-oil mixture is impelled towards the nozzle, at the end of which is fixed a spiral which imparts a rotating motion to the oil and air mixture as it passes through the orifice. The issuing stream is met by the air for complete combustion, which rotates in the reverse direction. This motion is given to the combustion air by stationary air vanes which fit closely in the annulus between the draught pipe and central nozzle.

The partial admixture of oil and air in the unit is thus completed on the furnace side of the nozzle.



By Courtesy of Combustions Ltd., London, E.C.4.

FIG. 28.—" Automestic " Burner (Heavy-oil Model).

THE " AUTOMESTIC " BURNER belongs to the pressure-jet type, with electric ignition, and can be obtained in two forms, one to burn light domestic fuel oil and the other heavy industrial fuel oil of 200 secs. viscosity at 100° F. (Redwood No. 1 viscometer).

The " Heavy Oil " unit, illustrated below in outline, embodies a number of interesting devices (patented) which enables the unit to overcome the difficulties usually associated with the burning of heavy oil on a fully automatic oil burner.

The main function of these devices is to prevent cold oil being forced through the orifice after the burner has been idle. For example, when the plant is restarted by the action of a control thermostat a few seconds elapse before oil issues from the pressure nozzle and the ignition of the oil. This time-lag is arranged to ensure that only warm oil at the correct pressure shall issue from the orifice.

The path taken by the oil can be traced by reference to the illustration, in which the important components are enclosed by the heavy lines. The oil enters the suction strainer (situated below the platform and between the two right-hand legs) and passes upwards to the suction side of the pump, from which it is fed through a thermostatically controlled preheater (on which the pressure gauge is mounted) and a discharge strainer before it reaches the burner proper. When the unit is started from cold or after a long "cut-off" period, the cold oil in the oil-ways is prevented from being ejected from the burner nozzle by a patented shut-off valve, which is set so that it opens just below the final working oil pressure. Pressure is being gradually built up, and in the meantime the cold oil passes into the patent receiver (in the centre of the figure on the base of the unit) ; by the time the oil pressure in the piping between the discharge side of the pump and the receiver has built up to approximately 80 per sq. in., all the cold oil has been displaced into the receiver by hot oil. When this pressure has been established, the burner shut-off valve opens and warm oil immediately issues from the orifice and is ignited by the electrodes.

When the plant shuts down a piston in the patent receiver forces the hot oil out of the piping between the burner orifice and the heater, and thereby assists in preventing oil from dribbling and carbonising at the nozzle so that a clean start is possible when the unit commences the cycle of operations again.

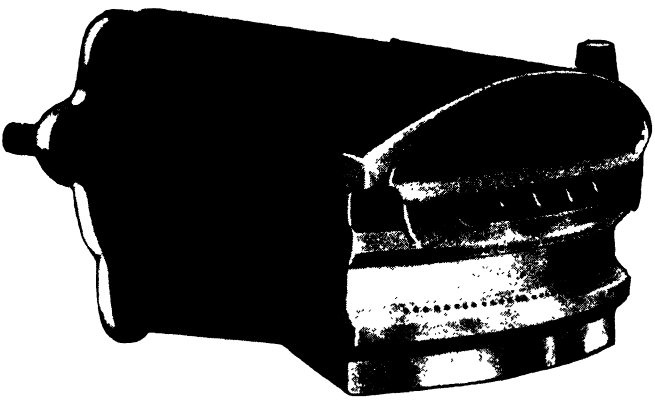
Various sizes of " Automestic " burners are available for outputs ranging from 100,000 to 2,000,000 B.Th.U. per hour.

THE " FILMA " COMPRESSED-AIR OR STEAM TYPE.—The general principles governing the operation of one of the " Filma " burners are : (1) the controlled flow of oil over a weir so that a thin film of oil falls across, (2) the path of a series of steam or air jets.

The oil is supplied to the top compartment of the burner, which is carefully set in a horizontal position. The oil flows along the floor of this chamber and spreads out as a film, which proceeds down the gentle slope to the front ; at the same time it widens out. The attenuated oil film then flows over a lip, the edge of which is purposely scalloped so that the oil does not concentrate into one or more narrow streams.

The falling oil film encounters the air streams which emerge from the upper row of holes in the lower compartment of the burner, which is fed with air under pressure. These air streams slope gently downwards and deflect and partly atomise the dropping oil film. At a point slightly below and in advance of this point of impact of oil with the upper air jets, the air issuing from the lower row of holes meets the other air streams at right angles. At this point the atomisation of the oil film is completed. The resulting cloud of oil floats forward under the influence of the natural draught of the furnace and is readily ignited.

The burner does not contain any narrow passages, and can function on an oil which is fluid enough to flow through the supply pipes. The oil should be supplied at a gravity head of about 4 ft., but this depends on the viscosity of the fuel, etc. If the fuel oil is very viscous, its free flow and spread in the burner should be assisted by preheating. Various sizes of burner are available for oil consumptions ranging from 0·5 to 55 gals. per hour.



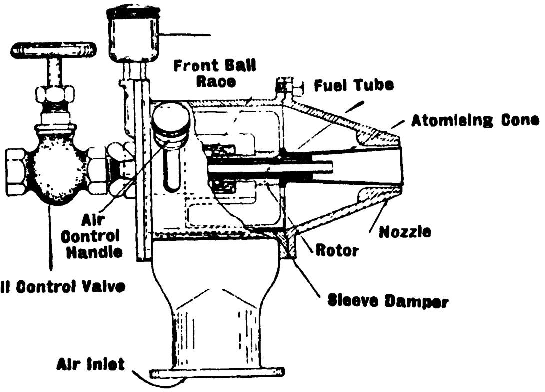
By Courtesy of Filma Burners Ltd.

FIG. 29.—" Filma " Burner.

THE " ROTAMISOR " BURNER.—The atomisation of the liquid fuel in this burner depends upon the centrifugal action of a spinning cone-frustum on an oil film of circular cross-section as distinct from the " Filma " burner just described, in which an almost flat oil film is broken up by a series of air or steam jets.

The " Rotamisor " burner is essentially a low pressure air burner, since it operates with air at an average pressure of 10 in. water gauge (5·8 oz. per sq. in.). The cross-section below illustrates the mechanism of the unit.

The air enters at the flange marked " Air Inlet," which is placed tangentially to the main body of the burner. The air therefore impinges tangentially on the blades of a rotor which rotates at a very high speed a hollow shaft on which it is mounted. This motion is also imparted to the atomising cone since the rotor, hollow shaft, and cone are solidly connected one to the other. The fuel oil, which may be fed to the burner either by pump or gravity, flows through the central fuel tube on to the inner surface of the rotating atomising cone ; the oil film is thus evenly distributed around the cone and becomes thinner as it travels towards the outer edge of the cone. Eventually the oil is thrown off the periphery as a very fine mist and immediately encounters the enveloping rotating air, both being intimately mixed at the end of the nozzle. The finely divided oil spray and low pressure air combine to produce a soft flame which gives exceptionally even heat distribution without the danger of damaging the boiler plates or furnace brickwork. In addition, since the unit contains no jet or fine orifice, the danger of choking and carbonising is eliminated. Furthermore, as both the oil and air supplies are under positive control, an oxidising, neutral, or reducing flame can be obtained as desired in accordance with the demands of the industrial and metallurgical furnace work to which the unit may be applied.



By Courtesy of Combustions Ltd., London.

Fig. 30.—" Rotamisor " Burner.

In certain cases it may be an advantage to operate the burner from existing compressed-air supplies (up to 100 lbs. per sq. in.) ; when this obtains a patented device can be attached to the air inlet. If required, too, thermostatic controls can be added so that the oil and primary and secondary air supplies can be regulated automatically.

Different sized burners cope with oil consumptions varying between 0·5 to 80 gals. of oil per hour. In the smaller sizes all the air for combustion is passed through the burner, and in the larger forms from 15 to 30 per cent. of the air passes through the burner as primary air, the remainder being introduced into the fire-box by specially designed natural-draught or forced-draught air directors.

The " Parwinac " Industrial Oil Burner.—The " Parwinac " burner consists of an outer barrel in which a hollow tube is fixed centrally ; air is fed under pressure through this annulus. The central tube encloses a solid rod, which forms an inner annulus through which the fuel oil is fed under a gravity head or small pressure pump. The oil is caused thus to flow along the inner annulus and emerges at the front end of the gun to be spread outwards by a small cone frustum and radial members slightly in advance, all of which are parts of a front member. This consists of a larger cone frustum, the diameter increasing towards the mouth of the unit ; attached to this cone are outer vanes, suitably pitched so that when they encounter the forward moving air stream this front member is caused to rotate very rapidly. The splayed oil film meets the inside of the spinning cone frustum and is impelled towards the front, where it is whirled off the periphery. Immediately on reaching the front edge of the spinner and on leaving it the oil film meets a sharply rotating air stream, which is turned into the path of the oil by the Venturi-shaped mouth of the outer barrel.

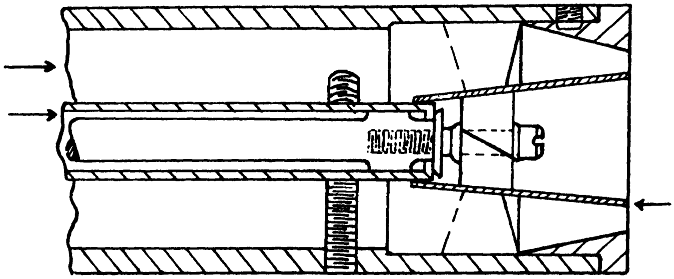


FIG. 31.—" Parwinac " Industrial Oil Burner.

The centrifugal action of the spinner and the attenuating effect on the oil of the enlarging diameter of the inside of the spinner, together with the rapidly rotating air stream, all contribute to the atomisation of the oil fed into the inner annulus.

In this case, also, the oil may be preheated more or less according to the viscosity of the oil, which may lie within a very wide range at room temperature and still be successfully atomised by the unit. The rate of flow of oil into the burner is hand-controlled by a valve in the oil line at the rear of the unit. These burners can deal with up to 25 gals. of fuel oil per hour.

URQUHART'S INDUSTRIAL PRESSURE-JET BURNER.—This burner is fed with oil under pressure which flows along two longitudinal channels between a central sheath (containing a central rod) and the outer tube. The oil enters a small annular chamber and then meets a bush which snugly fits the central rod bearing a three-start spiral thread. The depth of these threads varies from nothing to a maximum along their length ; when, therefore, the rod is moved forward or backward in this bush by hand manipulation of an outer control wheel, the area of the three oil exit ports is increased or reduced so that more or less oil is allowed to flow through the bush. In doing so a high-velocity whirling motion is imparted to the oil on its way to the nozzle, which may therefore be somewhat larger than is normally the case. The regulation of rate of oil flow through the nozzle is controlled within the burner and not by variation of pump pressure and/or change of one orifice for another of different size.

The control hand-wheel at the rear of the burner works in a substantial square thread, and a guide to the rate of oil flow is possible by observation of a dial plate with indicating pointer attached to the control wheel.

Means are also provided for circulating hot oil through the burner right up to the nozzle or jet, so that cold oil residing in the branch pipe from the circulating main at the burner can be displaced before starting up from cold. This obviates the possibility of injecting a volume of cold oil into the furnace before ignition takes place.

This atomising unit can cope with the cheapest and heaviest grades of fuel oil with the assistance of suitable oil preheaters, and, when cleaning is necessary, the centre spindle may be removed without having to take the atomiser from the boiler front. It is used with a Cyclone Air Register which is suitable for natural, forced, or induced-draught plants.

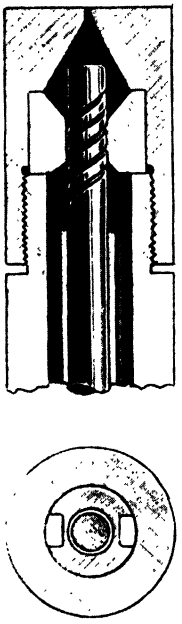


FIG. 32.—Urquhart's Industrial Pressure-jet Burner.

PRESSURE-JET SYSTEM OF OIL BURNING.—The pressure-jet system of oil burning is most usually employed in large steam-raising plants where large oil consumptions take place, and where high rates of evaporation are essential. In these circumstances the pressure system is the most efficient. Other considerations, however, make the pressure system indispensable in special cases ; for example, marine systems invariably adopt the pressure-jet method in order to avoid the consumption of steam for steam atomisation in steam atomising systems or for operating the compressed-air plant. The same disqualification of steam or air atomising systems applies to land installations which are so placed that the feed water is of bad quality. It is necessary here, also, to keep down to the minimum (1) the quantity of make-up feed into the boilers ; (2) the cost of chemical treatment of boiler feed-water.

Boiler plants of large size are operated at lowest cost by the burning of the cheapest fuel oil, which is the high-viscosity heavy grade of the residuum type. Such products, therefore, require special handling and treatment before entry to the pressure-jet burners ; they have to be preheated (1) to reduce power costs of the oil-pumping units ; (2) to facilitate rapid and efficient filtration so that the danger of clogging the exit holes of the pressure burners is reduced to a minimum ; (3) to permit thorough and complete resolution of the oil into a fine mist immediately it emerges from the pressure burner.

Essential accessories of a pressure system, therefore, are pumps, heaters, and filters. Many forms and types are available ; the following illustration shows a Duplicate Unit Plant made by Swinney Brothers Ltd. It consists of two pumps, two heaters, and a duplex discharge filter, so arranged that either pump or heater or filter can be used while the other is acting as a " stand-by." The pumps are long-stroke, double-acting, and of the vertical pattern ; the heaters are the patent " Everclean " type which are fitted with a quick, simple, and efficient cleaning device, and they employ the straight-tube principle. The heating element is of the double straight-tube type, the tubes being held at one end only so that they are free to move at will on contraction or expansion.

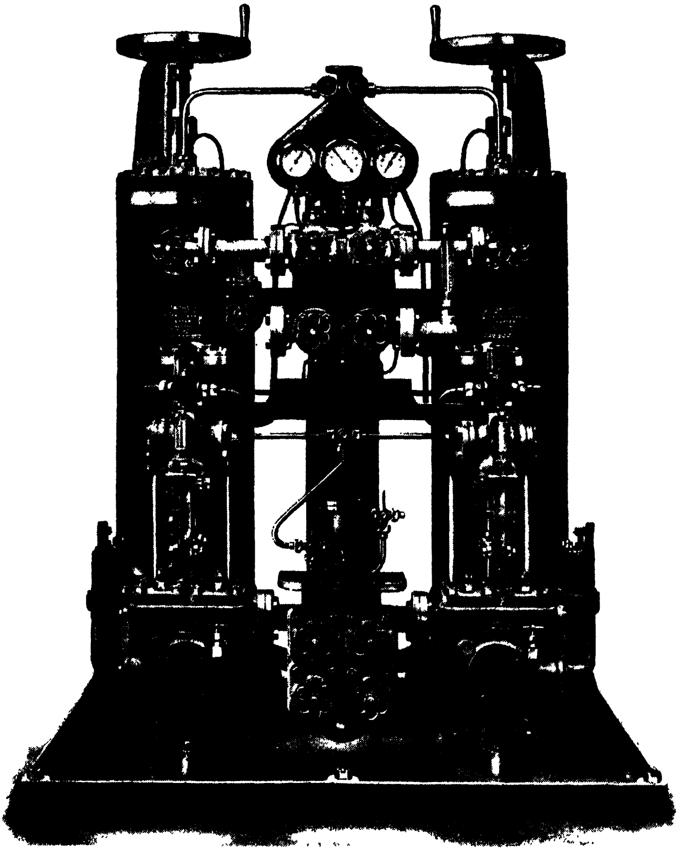
The discharge and suction filters (the latter is not shown on the illustration because it is fitted separately) are both of the duplex type and are fitted with special quick-release covers for rapid cleaning. The filter elements operate on the sleeve principle, which positively extracts all dirt and solid particles from the oil. Such units as the one, illustrated are neat, compact, and possess the essential feature of accessibility. The operations and regulations are all controlled from the front, no fittings or valves being at the sides or back.

Where necessary single-type units may be employed ; they differ from the above in that there is only one pump, one heater, and one duplex filter incorporated in the unit ; if desired also an electrically driven pump may be added.

Such installations are thoroughly reliable, operate at high efficiencies, and are suitable for all kinds of fuel oil, including the heaviest very viscous fuel oils.

A system such as this usually depends upon steam for operating the oil pumps and heaters, so that special provisions are necessary in order to permit operation of the oil burners in the absence of boiler-steam pressure when starting up a cold boiler and setting.

Many different methods are available for this starting-up process ; some installations have stand-by electric heaters for preheating the oil, which may be fed by gravity if the head is sufficient or by a small electrically driven pump until sufficient steam has been raised to operate the main pressure system. In others, such as the Swinney Brothers marine units, the fuel oil is drawn from the oil bunkers by a special hand-pump and circulated in the usual way through the whole of the system, including a patent starting heater, until the required oil temperature is reached. The starting heater is of the straight-tube type and is heated by self-heating paraffin burners. These burners are supplied with paraffin from the reservoir to which they are fitted, and in which pressure is supplied to the paraffin by a small hand-pump. When the desired oil temperature has been reached the oil is fed to the burner, which is kept in operation by the hand-pumps until sufficient steam pressure has been generated for the operation of the steam pumps and steam oil heaters.



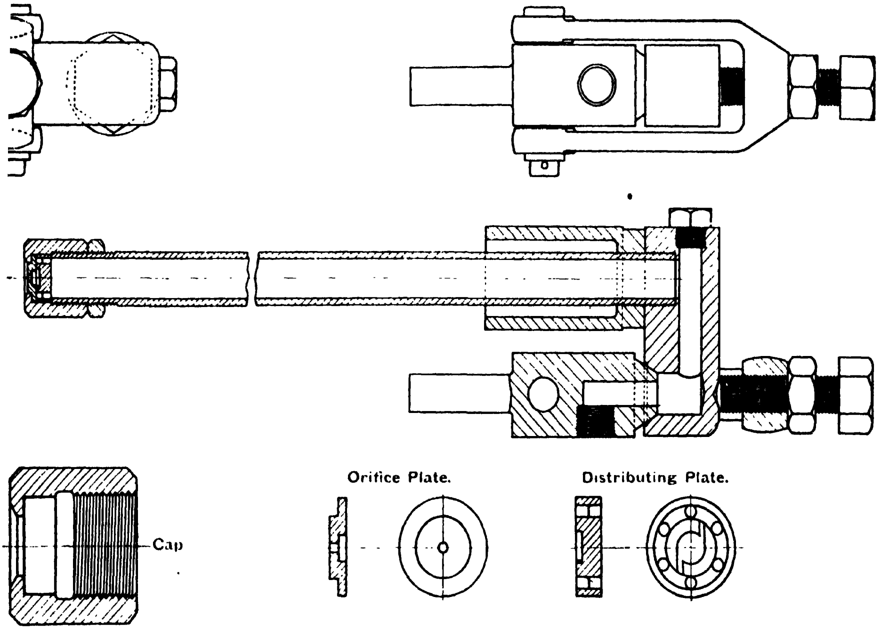
By Courtesy of Swinney Bros. Ltd.

Fig. 33.—" Swinney " Duplex Heating and Pumping Unit.

THE "BABCOCK & WILCOX" PRESSURE-JET BURNER.—This design of burner atomises the oil by pressure applied directly to the fuel without the use of air or steam as an atomising agent.

The essential parts of the unit from an atomisation standpoint are the distributing plate and orifice plate, both of which are situated at the end of the burner barrel and held in position by a cap nut screwed up tightly. The construction of these parts is shown in the enlarged views below.

It will be seen that when the distributing plate is held up against the back of the orifice plate the slots across the face form a passage through which the oil is compelled to pass on its way to the orifice. These passages are arranged tangentially to the circumference of the cylindrical recess in the centre of the distributing plate, so that the oil naturally rotates at high speed in this chamber ; the oil is also rotating as it is discharged from the orifice, and consequently the discharge is conical in form.



Oil Fuel burner on the pressure system. Arranged with quick release clip in order that the burner may be dismantled without disconnecting the oil supply piping.

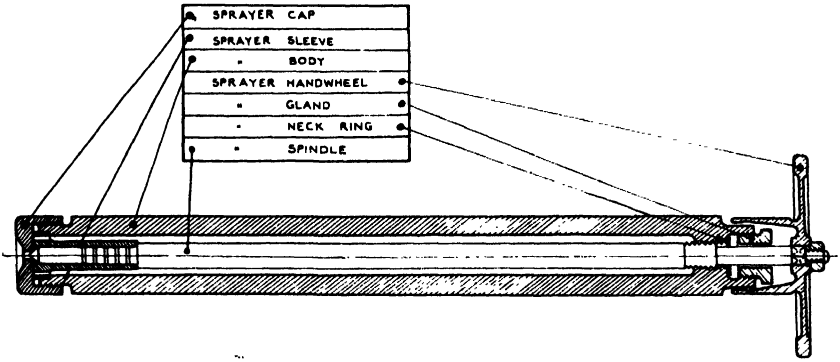
By Courtesy of Babcock & Wilcox.

FIG. 34.—"Babcock & Wilcox" Pressure-jet Burner.

The *angle* of this cone depends upon dimensional factors in the design of the distributing and orifice plates, on the relation of the areas of the various passages to each other, on the diameter and depth of the cylindrical recess, and other factors which determine the design of the parts.

The *quality* of the spray in turn depends upon the velocity of the oil through the passages, which is a function of the oil pressure and the viscous properties of the oil. Very viscous fuel oils of the "residual" type must therefore be preheated to render them to flow more readily under the available pump pressures. It is important to note also that the quality of the spray is affected by the "finish" of the nozzle parts.

Different distributing and orifice plates are obtainable, the differences being in the dimensions of the essential features, so that the burner can be made to operate at various oil consumptions. These plates are interchangeable with each other and will fit the same cap nut and barrel ; with the orifice plate the variation can only be on the diameter and length of the orifice, but the distributing plate is varied both in the size and number of slots. The burner as a whole is secured in its working position by a clamp-coupling which enables the burner to be withdrawn and replaced by another in a very short space of time.



By Courtesy of Thornycroft & Co.

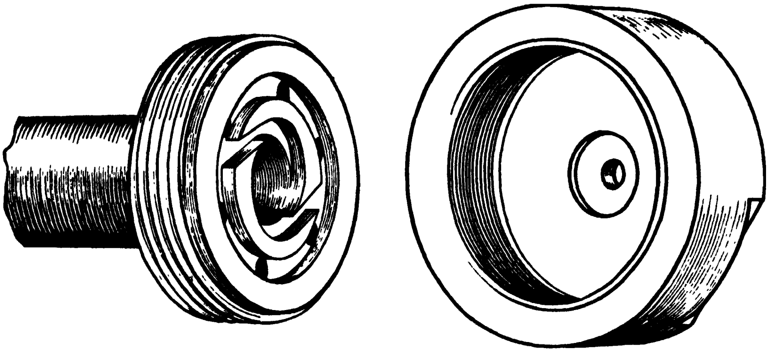
FIG. 35.—"Thornycroft" Patent Oil-fuel Sprayer.

THE "THORNYCROFT" PATENT OIL-FUEL SPRAYER.—This consists of an outer steel tube and central spindle of tool steel, the latter being fitted with a fine thread for adjustment of the point in the exit hole.

At the end of the tube is a sprayer head which is made in two parts, the sprayer sleeve and the cap. In the sleeve are cut two spiral grooves leading tangentially into a whirl chamber round the axis. It will be noted that *both* edges of the grooves are tangential to the whirl chamber, and that the exit hole is at the centre of the cap.

The heated oil flows under pump pressure along the tube into the outer circumference of the cap and then through the two grooves cut in the cap centre ; it then enters the whirl chamber, and by the time the oil reaches the exit hole the angular velocity is very considerable. The oil, therefore, passes through the exit hole with a spiral motion, and on leaving the hole centrifugal force disintegrates the oil so that it flies out as a cone of oil spray.

The sprayer works well from pump pressure of 50-60 lbs. per sq. in. up to 150-200 lbs. per sq. in. Different sprayers are available with maximum oil outputs of 200, 300, 400, 500, 700, and 1,000 lbs. per hour, but as the central spindle may be adjusted by the control wheel small variations in the output are possible, though the principal function of the spindle end is the breaking up of obstructions in the cap. When large outputs of about 2,000 lbs. and above are required for special purposes, such as cement kilns, sprayers can be made to suit these large demands.

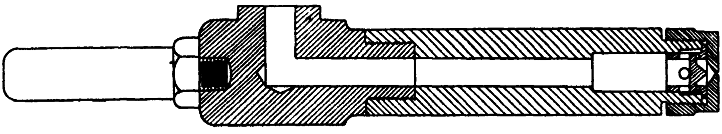


By Courtesy of Thornycroft & Co.

FIG. 36.—" Thornycroft " Pressure Burner.

The sprayer is readily detachable for cleaning purposes, the oil-pipe connection being under a hand-screw, so that as soon as the screw is released the sprayer can be removed and, when it is screwed up again, the joint is remade.

SWINNEY BROTHERS PRESSURE-JET BURNER.—The four component parts of this burner (see Fig. 1) are the body, the diaphragm, the nozzle, and the handle. Atomisation of the oil is based on the true " vortex " principle in that a rotary motion of exceedingly high velocity is imparted to the preheated oil, which is forced under pump pressure through tangential holes in the diaphragm before entering the swirl chamber. This rotary motion causes the oil to



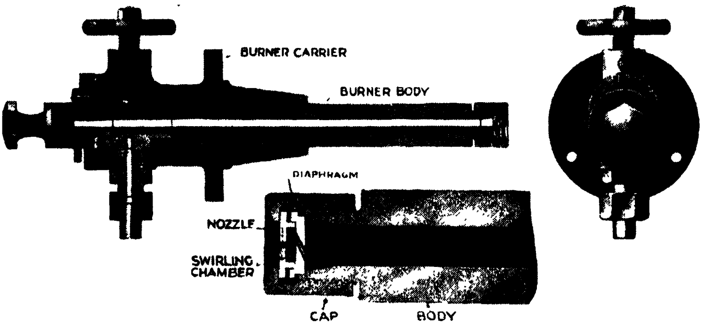
By Courtesy of Swinney Bros. Ltd.

FIG. 37.—" Swinney " Pressure-jet Burner.

break up on issuing from the nozzle into a hollow cone of oil vapour or mist which lights up immediately, without noise or explosion, on application of a lighted torch.

The burner is held in position in the furnace fronts or air directors by a special holder. If necessary the burner may be fixed in a patent holder, which prevents fire and scalding by hot oil in so far as the burner cannot be removed while the oil is turned on, nor can the oil be turned on while the burner is out of the holder.

"WALLSEND" PRESSURE-JET BURNER.—Another member of this class is illustrated below in Fig. 38, which shows a cross-section of the complete burner, a rear-end view of it, and an enlarged cross-section of the nozzle end. The most important components are the body, diaphragm, and nozzle, which are held together by the threaded cap.



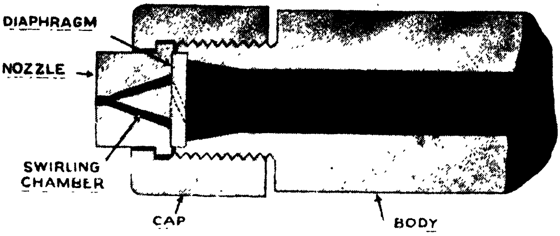
By Courtesy of Wallsend Slipway & Engineering Co. Ltd.

FIG. 38.—"Wallsend" Pressure-jet Burner.

It will be seen that the holes are drilled nearly tangentially through the diaphragm, and these cause the oil to spin rapidly in the swirling chamber. Consequently, upon issuing from the nozzle the oil opens out into a fine conical spray by reason of the centrifugal forces operating.

The burner is supported by a carrier into which it is fixed by a clamp, a mitre joint being formed between the burner and its carrier, thus making a perfectly oil-tight joint. This allows the burner to be removed without breaking any joints when desired for cleaning or other purpose.

The carrier in turn is mounted on an air director on the furnace front, the function of the director being to direct the air required for combustion of the finely atomised oil in such a manner that intimate mixture of oil and air is obtained ; this ensures rapid and efficient combustion—an extremely important requirement, especially when individual burners have to deal efficiently with large quantities of oil. This is particularly the case in furnaces fitted with water-cooled walls—here there is very little assistance from radiant brickwork in maintaining temperatures necessary to sustain combustion. Fig. 39 shows an enlarged cross-section of

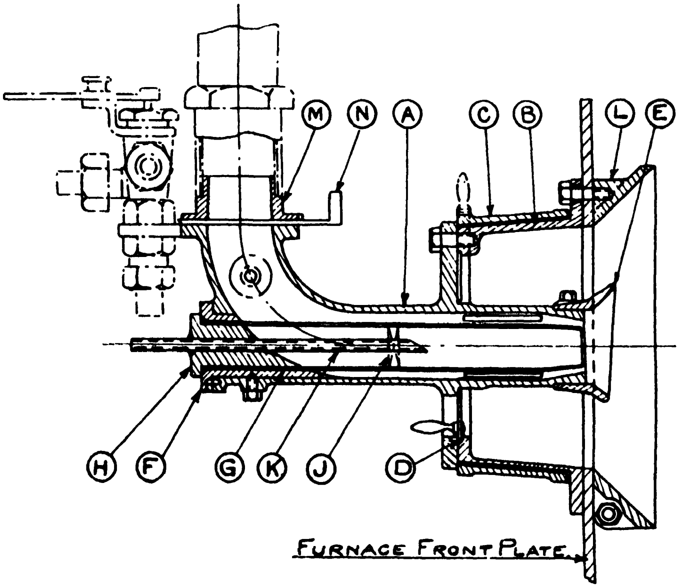


By Courtesy of Wallsend Slipway & Engineering Co. Ltd.

FIG. 39.—" Wallsend " Pressure-jet Burner.

another form of pressure nozzle which utilises a different type of swirling chamber.

LOW PRESSURE AIR-ATOMISING OIL BURNER.—A typical burner of this class is shown in the detailed cross-section below which is



By Courtesy of White's Marine Engineering Co.

FIG. 40.—Arrangement of "Turbinia" Burner. Type W. 2.

specially suitable for small boilers, industrial furnaces, galley ranges, etc. It operates on the gravity system, the oil being led from an overhead supply tank about 7 ft. above the burner—a height which has been found to give ample oil pressure to ensure a steady flow to the burner.

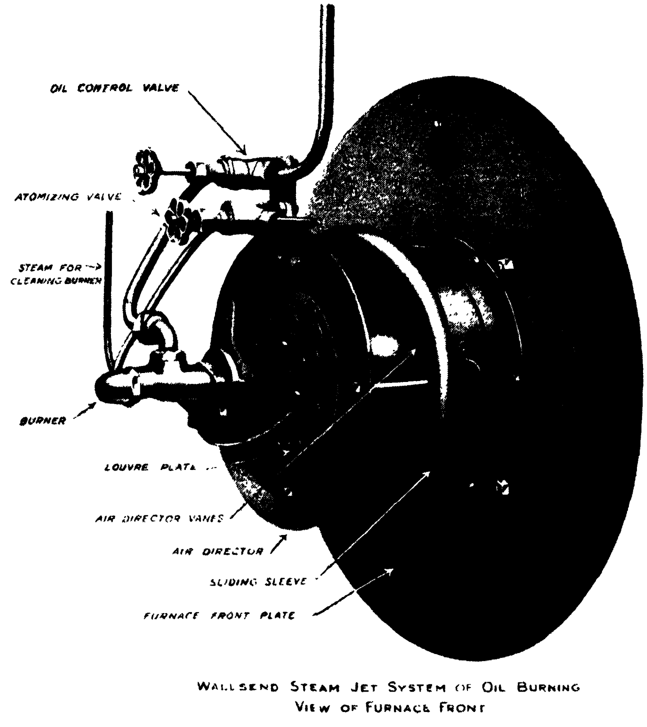
The supply or gravity tank is provided with a small steam-heating coil which maintains the oil at a temperature required to facilitate its flow to the burner, usually around 100° to 120° F., and this is regulated by means of a thermostat.

The air necessary for atomisation and for supporting the combustion process is supplied by a blower which discharges air under a pressure of 12 to 14 in. static water gauge. The manner in which the air atomises the oil is as follows : the air moves at high velocity past the end of central oil tube and thereby creates a partial vacuum at that point ; when the oil leaves the end of the pipe it is blown into a spray or cloud of finely divided particles which are readily ignited. The burner design is very simple, comprising three concentric cylindrical passages and a series of fixed vanes inside the vaporising chamber. The last named impart a rotating motion to the air which conduces to the formation of a cylindrical incandescent flame from which soft heat radiates throughout the whole furnace. Complete smokeless combustion takes place at the mouth of the burner, which can burn any grade of oil from the lightest to the heaviest.

STEAM-JET BURNER (Wallsend-Howden).—The accompanying sketch illustrates the Wallsend-Howden Steam-jet Burner, as manufactured by the Wallsend Slipway and Engineering Co. Ltd. The figure has added interest in that the burner is shown in position in an air director. It will be appreciated from this illustration that the air-director vanes are set at an angle so that as the air passes through the director a rotary motion is imparted to it. Since this direction is the reverse of that taken up by the rotating oil-steam mixture expelled from the burner efficient mixing of oil and air is assured.

A special feature of this burner is that it is designed to give the same conical form of spray as the pressure burner described on p. 184. This being the case, the same type of air director is used for admitting and controlling the combustion air. The spray being in the conical form permits more effective use to be made of the combustion-chamber volume than with those steam-jet burners which inject the oil into the furnaces as fan-shaped or flat type of sprays.

Reference to Fig. 41 will indicate that both the atomising steam and oil feeds are controlled by valves conveniently placed ; in addition, there is a second steam connection to the burner, the object of this being to permit the admission of steam to the oil passage in the burner in order to clean it by blowing out any oil remaining in the burner when shutting down. This is a very important operation, because it prevents carbon forming in the burner nozzle when shutting down burners which have been operating in furnaces of high temperature ; any oil remaining in the burner would carbonise under the effect of heat radiated from the furnace, and if carbonisation such as this were permitted to proceed unchecked, trouble would probably arise when attempts would be made to relight the burner.



By Courtesy of Wallsend Slipway & Engineering Co. Ltd.

FIG. 41.—" Wallsend-Howden " Steam-jet Burner.

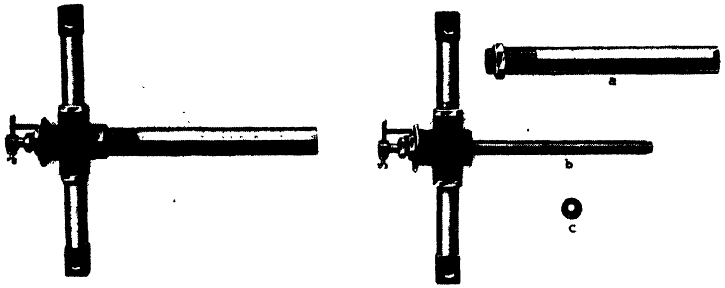
STEAM-JET SYSTEM (Clyde Oil-fuel Systems Ltd.).—Another form of steam-jet burner is shown in Fig. 42, p. 188 ; the view on the left shows the assembled burner, which is connected to the steam and oil supply pipes by quick-release arrangements which permit rapid removal of burner and its replacement. The handle on the left end is a hand-manipulated oil regulator.

The view on the right depicts the component parts, *a* being the outer casing, *b* the oil tube carrying the valve, central oil tube, steam and air extensions, and *c* is the atomiser. The mechanism is as follows : the oil flows past the valve and along the inside of the tube shown in *b*, the quantity being regulated by the oil regulator. Steam under a pressure from 5 lbs. per sq. in. upwards passes through the annulus between the oil tube and the outer casing, and eventually emerges from the atomiser through a series of holes drilled tangentially in the nozzle. These steam jets play on the oil flowing through the central hole in the atomiser and create a swirling motion which breaks up the oil stream into very fine particles.

The burner is fitted in an air director provided with pitched vanes which give a swirling motion to the air opposite to the direction given by the steam to the oil.

A notable feature of the unit is that it contains no restricted oil passages which permit its use with fuels ranging up to the heaviest.

The burners which are made to cope with oil consumptions from 5 to 500 lbs. of oil per hour can operate also with air instead of steam at pressures from 10 to 15 lbs. per sq. in. upwards, which may be supplied by an air compressor or by an existing main.



By Courtesy of Clyde Oil-fuel Systems Ltd.

Fig. 42.—" Clyde " Steam-jet System.

THE COMPARISON OF OIL AND COAL AS FUELS FOR STEAM-GENERATING PLANTS.—Coal has been and continues to be consumed in far greater quantities throughout the world than oil, which is a comparatively modern fuel for external combustion. The production of both commodities during 1932 serves as a guide in this matter; approximately 1,000 million tons of coal were produced in that year, which is a considerably greater amount than the 180 million tons covering the world production of crude petroleum during the same period; of the latter amount only a comparatively small fraction is sold for external-combustion purposes.

Both fuels have competed with each other, and during the last half-century many important outlets for coal have been lost in favour of oil.

The explanation of the change over from coal to oil, or the immediate acceptance by an industry of oil as its best fuel, resides in the physical condition of the products ; coal is a solid and oil fuels are liquids, and out of these differences arise the arguments that sway consumers in the direction of liquid fuels. To these may also be added other considerations of almost equal value.

The advantages of liquid fuels in comparison with coal for external combustion may be detailed as follows :—

(*a*) The storage of oil is not attended by a loss of space encountered when lump coal (and the voids) occupies the same storage volume ; being a liquid easily pumped through pipes, oil can be stored in any vacant tank or space which would be entirely unsuitable for storing coal were it used. These are important points for marine steam-generating plants, the oil being stored in false bottoms or bilges if necessary.

(*b*) The higher calorific value of liquid petroleum fuels (18,500 to 19,000 B.Th.U. per lb.) as compared with that of coal (13,000 to 15,000 B.Th.U. per lb.) adds further importance to the first point ; it is a vital argument from a marine viewpoint in that less weight of oil fuel than of coal need be carried for a given sea voyage. The benefits accruing from these two features are : (1) increased space for profit-earning cargo, and (2) a larger radius of action for a ship using oil fuel.

(*c*) It is possible to utilise the heating powers of oil fuel more efficiently ; in addition, the combustion of oil fuel is more easily regulated, and more important from most points of view is the fact that full power can be reached very rapidly, or sudden demands for large increases or decreases in the amount of steam generated are rapidly accommodated by oil fuel burning installations. There is also no necessity for banking (coal) fires and a loss of fuel when the plant is shut down for overhaul, etc. (when coal is the fuel employed).

(*d*) The use of oil fuel permits a reduction of boiler-room staff, cleaner working conditions for the necessary firemen, and no ashes or clinkers remain for clearing away, and atmospheric pollution by dusty (ash) particles is reduced to a minimum.

(*e*) The benefits of oil fuels reflect themselves in boiler design. There is no need for grates, fire-bars, ash-pits, etc., so that the weight of boilers and the overall volume of a boiler for a given steam generation are less for oil-fired boilers than for coal units.

(*f*) Special facilities are afforded by liquid fuels used in ships. Being a liquid, the entire bunker requirements can be quickly transferred by pumping from land installations or large barges to the ship. This dispenses with the necessity when coaling a ship for the entire personnel to handle the coal over the longer fuelling period required. This advantage in favour of oil is important in naval circles, for oil fuelling allows the ratings to preserve their physical energy for the more important tasks that are part of their duties in times of war.

(*g*) Oil-fired ships also possess the advantage of being able to maintain an even keel by transferring rapidly oil from one tank to another ; this removes the necessity for admitting water to the vessel.

(*h*) Oil can be stored indefinitely without deterioration or loss of calorific value, whereas coal tends to " weather " and lose part of its calorific value in the process. Equally important is the fact that coal is prone to spontaneous combustion, whereas oil is not.

Many of the advantages of using oil as a fuel apply especially to marine use and do not apply to land installations. In this respect coal utilisation on land has been encouraged by the development of mechanical stokers and chain-grates which make the use of coal more continuous than the older hand-fired coal-burning units. In the latter the continual need for opening the furnace doors is a definite drawback, and where the boiler units are not large enough to warrant the expense of mechanical stokers oil continues to possess the advantage under discussion.

The efficiency of coal combustion has been continually increased by improvements in coal utilisation, chief among which is the growing use of pulverised fuel. This has enabled coal to be fired in a manner very similar to the air-atomisation oil burners. In further amplification of this development is the endeavour to make commercially possible the combustion of oil/pulverised coal mixtures, erroneously described as " colloidal " oil-coal fuels. These have many attractive possibilities, but so far their stability or freedom from coal settlement in the oil medium is not satisfactory. These oil-coal mixtures can be burnt in appliances very similar to pressure burners for oil. Their effective utilisation, however, is a matter awaiting solution in the future, and will be problematical until stability of the mixture over a lengthy period is demonstrable.

PART VI

SIGNIFICANCE OF TESTS AND ANALYTICAL METHODS

CHAPTER I

SIGNIFICANCE OF TESTS OF LIQUID FUELS FOR EXTERNAL COMBUSTION

Specific Gravity.—This property is defined as the ratio of the weights of equal volumes of oil and water at a temperature arbitrarily chosen as 60° F. The corresponding measure commonly used in the United States is the A.P.I. (American Petroleum Institute) gravity scale. The A.P.I. gravity is related to the specific gravity by the expression

$$\text{Degrees A.P.I.} = \frac{141{\cdot}5}{\text{Specific gravity at } 60^\circ \text{ F.}} - 131{\cdot}5.$$

Persons who are accustomed to the use of " specific gravity " and acknowledge that a unit volume of oil weighs *more* as the numerical value of the specific gravity increases, should therefore bear in mind that the reverse is the case when the gravity is expressed in degrees A.P.I.—the larger the numerical value of the degrees A.P.I. of an oil the less is the weight of a unit volume of the oil.

The main uses of " gravity " are in the calculations of weight corresponding to known values of volume ; in those countries acknowledging the imperial gallon as the commercial unit of volume the weight of 1 gal. of oil is ten times its specific gravity. Consequently, if the weight of oil is known its volume in gallons may be calculated if the specific gravity of the oil is available (and vice versa).

It also serves as a means of checking the constancy of a suitable oil obtained periodically from any source, but too rigid insistence on small variations in specific gravity is not commendable as such an attitude is a hindrance to commercial dealings. It has no direct relation to the quality of any fuel.

It may be a serviceable criterion when a choice between different oils is possible in that some fuel oils become mixed with water when stored in certain places, such as false bottoms of sea-going vessels ; in such cases a low specific gravity oil is to be preferred, since the lower the specific gravity of the oil the easier will it be to free the oil from water by the centrifugal means usually adopted on board ships for this purpose.

Flash Point.—The "Closed Flash Point" is viewed as an indication of fire hazard, and for this reason the property and limits placed on it are freely quoted in legislative measures. The Board of Trade, for example, prohibit the use of fuel oil for marine purposes if its closed flash point is below 150° F. (Pensky-Marten). This attitude is adopted in the belief that this property is a measure of the temperature at which the oil is likely to form inflammable mixtures with air above the oil surface in a closed container, and because 150° F. is believed to be a safe low limit for marine users of fuel oil.

The closed flash point is frequently misused as an indication of the volatility characteristics of the product. This application of flash-point values is distinctly misleading, because very small quantities of volatile contaminants appreciably reduce the true closed flash point.

Distillation Tests.—When applied to kerosene distillation tests serve very little useful purpose, excepting possibly as a measure of constancy of type ; more importance is attached to the nature and amounts of the higher boiling fractions of a kerosene, because if it has too high a final boiling point, or if this is not clearly and sharply determinable, the product may be suspected of being able to cause "char" in wick-fed lamps, heaters, etc. In all such cases of doubt the best test is a trial burning test under the conditions of everyday use.

High "end points" or a fairly large percentage of high boiling fractions in the gas-oil type of No. 1 Light Domestic Furnace Oil are not favourable characteristics of fuels intended for "vaporising" burners employing no mechanical draught ; such burners require fuels that vaporise completely and without sluggishness, so that there shall be no gradual accumulation of fractions difficult to vaporise. Distillation tests are of very little use for judging "medium" and "heavy" fuel oils.

Viscosity.—The petroleum and liquid fuel industry quote the viscosity of an oil as a number of seconds at a certain temperature. This number of seconds is the time required for a certain volume of the oil at the specified temperature to flow through a cylindrical hole in the base of a standard apparatus under standardised conditions. Many different viscometers are employed throughout the world for measuring this property, so that the name of the viscometer used in the test should also be mentioned when the viscosity is quoted ; hence such expressions of viscosity as : 60 Redwood No. 1 seconds at 70° F. ; 40 Saybolt Universal seconds at 100° F., etc.

The viscosity of fuel oil is a very important property, because it is a measure of the ability of an oil to flow through the feed-pipes in an oil-burning system ; it is also closely related to the ease with which an oil may be atomised—if the oil is very "thin" (low viscosity) the oil will be more readily atomised than another more viscous fuel. Some fuel oils are so viscous at ordinary temperatures that they must be heated to a certain temperature range before the burner can utilise them properly, that is to say, the oil must be brought to a certain viscosity by heating before admission to the body of the burner. It is necessary in such instances, therefore, to know how the viscosity of the fuel oil changes with temperature alterations ; this knowledge is acquired by estimating the viscosity of the oil at a number of different temperatures. Having these different viscosity temperature values at hand, it is then possible by graphical methods to estimate the temperature to which a fuel oil must be preheated in order that its viscosity shall be suitable for the design of burner employed.

Cloud Point.—The "Cloud Point" is the temperature at which solid bodies (paraffin wax and/or asphaltic constituents) begin to form as the dry oil is cooled ; conversely, it is the temperature at which these bodies liquefy as the oil is warmed. Though difficult to determine on dark oils, such as the majority of fuel oils, it is an important property. Most fuel systems contain small-mesh gauze filters through which the oil flows or is pumped before it enters the oil burner, which may have a very narrow orifice ; filtration is provided so as to reduce to a minimum any risk of clogging the burner passages and orifice ; the gauze filters, however, are inclined to be clogged if the oil is fed to them at temperatures below its cloud point. With reasonable supervision, gauzes clogged by gradual accumulation of gelatinous or semi-solid bodies for the reason mentioned can be cleared by passing hot oil through them for a short period of time. The probability of clogging is normally very remote, because the gauze filters are chosen so that the size of mesh is as large as possible, and because oils are seldom fed to burners below their cloud point. The test has more significance during cold seasons and in cold climates.

Pour Point.—The "Pour Point" is a temperature which is almost invariably below the cloud-point value. The pour-point test is determined under standardised conditions in order that comparable estimates may be made of the temperature below which oils cease to flow. As a laboratory valuation test, it bears a loose relation to the temperature in service conditions at which the oil will flow or will be difficult to pump ; the test, therefore, is only a rough guide in comparing the pumpability of different fuel oils at low temperatures. In service conditions it is possible to pump oils at temperatures somewhat below their pour points, even though some paraffin wax may be present in the crystalline form. It is advisable, nevertheless, to be assured that the oil is stored in such conditions that it is not allowed to cool to or below its pour-point, in the absence of adequate means for raising the temperature of the oil-storage tank (by enclosed steam coils, etc.). The lowest permissible limit which can be placed on the pour-point of a fuel oil will vary with climatic conditions and whether storage tanks are above or below ground, in or out of doors, etc. Oils intended for cold regions must necessarily possess pour-points that are lower than those suitable for hot countries.

HARD ASPHALT CONTENT.—This quantity is only important in its relation to the carbon residue of the oil.

CARBON RESIDUE VALUE.—This is a measure of the tendency of an oil to form " carbon " when it is exposed to high temperatures. Usually high hard asphalt contents mean high carbon residue values. The test is of little moment in connection with the heavier fuel oils for external combustion in large power units, except that an oil having an exceptionally high carbon residue requires a little more care in the operation of the burner ; when such an oil is being used, the flame should be so adjusted that it is as far away as possible from the burner nozzle or tip, so that the furnace end of the burner can be kept as cool as possible ; otherwise " carbon " may form on the nozzle or orifice and interfere with the efficient operation of the burner. When reasonable care is exercised in this direction, oils having very high " carbon residues " can be burned with no inconvenience.

The situation is somewhat different in the case of fuel oil intended for domestic burning equipment, and especially when the unit belongs to the fully automatic type. Fuel oils destined for these units should have low carbon residues. Many of the fully automatic units operate on the " cut-in cut-out " principle, so that slight " drip " is liable to occur at the burner tip ; the oil-wetted tip may eventually be coated with a thin film of " carbon " as the furnace heat is reflected on to the burner. In the course of time, therefore, there is a tendency for this " coke " or " carbon " to build up to such an extent that efficient operation of the burner is jeopardised. Adequate measures are taken to provide for such possibilities by oil suppliers exercising due care in the selection of oils intended for domestic-burner consumption.

SULPHUR CONTENT.—The combined sulphur in fuel oils is not detrimental to their utility if the products of combustion are not allowed to cool below their dew point. Cooling of products of combustion to such an extent is seldom encountered in industrial fuel oil-burning units, and condensation of water of combustion is only realised when a high degree of " economising " is a feature of a furnace.

More significance is attached to " sulphur content " in domestic fuel oils because a high sulphur content frequently means that the oil will possess a strong, and sometimes an objectionable, odour.

For this reason domestic fuel oils are chosen so that their sulphur contents are low ; little danger then exists of objectionable odours penetrating to other parts of the buildings being heated.

Sulphur content is more important still when the fuel oil belongs to the kerosene type. These kerosene fuels should, and usually, have very low sulphur contents, because the products of combustion of kerosene appliances frequently are allowed to enter the free space of inhabited rooms, areas occupied by animals (chickens, etc.), in which appreciable amounts of oxides of sulphur would be harmful. The sulphur content of a kerosene is also believed to have some relation to the destruction of wicks, staining of glass chimneys, etc.

ASH CONTENT.—The ash content of a fuel oil arises from the incombustible matter present, such as grit, tank-scale, and the inorganic constituents normally present in crude oils. High quality, low viscosity fuel oils for domestic purposes generally possess negligible ash contents ; the heavier fuel oils, on the other hand, have measurable, though small, ash contents. In normal conditions these constituents are carried through the furnace by the moving gases, eventually to be ejected through the stack to the atmosphere. When high ash contents are found, the oils have a tendency to cause trouble, especially when the metallic radicals are sodium, potassium, and calcium ; these tend to form hard, brittle glazes on brick linings, arches, and baffle walls in the furnace settings. Such inconveniences are rare with oil fuels, and more often experienced with coal fuels, which invariably have ash contents greater than petroleum fuels.

WATER AND SEDIMENT.—This property is estimated by the centrifuge test when the fuel oils are " thin," and is considered to be a measure of the free water and sediment present in the oil. It should be regarded as a test of cleanliness and as an indication of freedom of the oil from sludging oil-storage tanks over a long period, during which the storage tanks are frequently replenished.

CALORIFIC VALUE.—The calorific value of a fuel oil is a measure of the amount of heat obtainable by combustion. Fuel oils of similar physical characteristics, such as specific gravity, viscosity, etc., have almost identical calorific values, even though their origins may be very different. A knowledge of the calorific value of a fuel is used mainly in calculations of combustion or furnace efficiencies.

The property is usually estimated by the Calorimeter-Bomb method, though, for practical purposes, it may be calculated approximately by the following equation and a knowledge of the gravity of the oil :—

$$\text{Gross calorific value} = 40\ (\text{A.P.I. gravity} - 10) + 18{,}320\ \text{B.Th.U.}$$

The specific gravity may be used for this purpose if it is converted into A.P.I. gravity by the formula given on p. 191, or by means of the conversion table on p. 248. As an example, assuming the specific gravity of an oil at 60° F. is 0·968, then, having converted this into the corresponding A.P.I. gravity, which is 14·7,

the gross calorific value=40 (14·7−10)+18,320=18,508 B.Th.U.

In some instances the calorific value is expressed in calories per gram ; this value can be converted into British Thermal Units per pound by multiplying it by 1·8.

The calorific value of fuels is also sometimes quoted as the net calorific value (see p. 151 for an explanation of the difference between net and gross calorific values).

Carbon and Hydrogen Contents.—Their estimation is carried out by " combustion " methods, and the quantities thus derived are useful in calculations of the net calorific value, boiler efficiencies, etc. Reference to equation 4 (p. 147) shows that 2 gm. of hydrogen form 18 gm. of water on combustion ; from this knowledge and the estimated hydrogen content of a fuel, the amount of water formed by a known weight of fuel oil can be estimated ; then by applying a correction recommended by the Institution of Civil Engineers the net calorific value of the fuel may be calculated, namely, deduct from the gross calorific value expressed in calories per gram an amount of heat equivalent to 586 cals. per gram of water produced on combustion.

CHAPTER II

METHODS FOR ANALYSIS AND VALUATION OF LIQUID FUELS

Sampling.—It is essential that a truly representative sample of a bulk of fuel oil or any other liquid product is procured for laboratory valuation of the bulk. The importance of obtaining an average uncontaminated sample cannot be over-estimated, because the properties of the sample must be representative of the tank's contents, so that the tests of a false sample may cause the rejection of satisfactory bulk stocks.

The precautions to be taken when sampling is done will vary with the circumstances. For instance, if there is any doubt that the contents of a storage vessel are not well mixed, as many samples as is practicable should be taken from different points in the tank. In such a case, samples taken from the top, middle, and bottom levels of the tank at north, south, east, and westerly positions, when mixed, should give a very good representation of the contents of the tank.

It is usually accepted as being sufficient for regular routine work to obtain samples from the top, middle, and bottom levels from only one vertical axis—usually the central one. Sometimes it is necessary for samples to be taken under other conditions. For example, should it be necessary to check the quality of an oil which is being pumped from a tank, samples would have to be drawn as near as possible to the outlet of the tank, which may be located very near the bottom. Alternatively, when a tank is fitted with a swing-arm, the sample should be drawn from a position adjacent to the outlet of the swing-arm.

Samples from different points of a tank may be examined separately, but wherever possible an average is prepared and an analysis made of the average.

In sampling a ship's cargo, true samples of each tank must be obtained, and, in order to prepare an average sample of the whole cargo, average samples representing the contents of each ship's tank must be taken, which are then mixed together in the proportions of the contents of each tank.

When such a method is adopted, care must be taken to stir each sample before use, so that each portion removed and the remainder may have the same properties. This is very essential when the oils contain water and sediment, which will tend to settle at the bottom of the sample.

The sample container may be made of glass, earthenware, or tinned iron, and should be fitted with non-porous stoppers. Samples intended for long journeys should be contained preferably in tinned-iron vessels. Care must always be taken that a container is clean before the sample is poured into it, because serious consequences may follow the use of a dirty container. Labelling a sample with full details should always be done, and reference samples should be sealed but not with sealing wax.

The better type of recognised apparatus for sampling bulk storage vessels consists of a weighted metal cage or carrier in which the actual sample bottle is inserted, so that the oil sample enters directly into the bottle itself. The bottle, before being lowered into the oil, is gently closed by means of a stopper or cork which is attached to a "snatch" cord. The term "snatch" implies that when the sample bottle has reached that position in the bulk of oil from which a sample is desired, the stopper is removed by jerking or snatching the cord. The oil then flows into the bottle and, when it is full (*i.e.*, when the escape of air bubbles at the oil surface has ceased), the bottle is drawn from the tank.

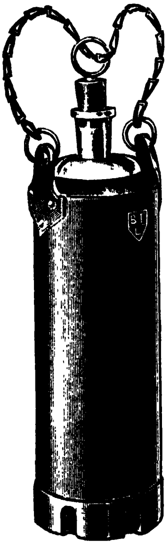


FIG. 43.—Metal Cage Sinker Type of Sampling Device (Baird & Tatlock).

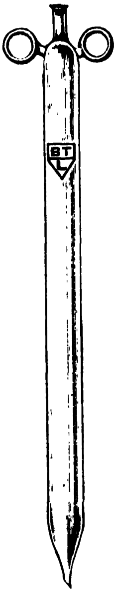


FIG. 44.—Thief Sampler for Barrels (Baird & Tatlock).

The foregoing remarks refer to the sampling of bulk stocks; when samples are to be taken from small containers, such as barrels, other means have to be employed. In this case it is recommended that the contents of the barrel or drum should be mixed by "rolling" or "up-ending" before the sample is drawn. Samples may be obtained from barrels or drums by careful pouring, but it is preferable that one use a glass "thief." This is a wide glass tube slightly drawn out at the top and bottom, which can easily be filled by suction from the mouth; when the thief is full, and after a finger is placed on the hole at the top, it is withdrawn from the barrel. The contents of the thief are then allowed, by releasing the finger, to run into a sample container. Samples can also be drawn conveniently from barrels or drums by means of the apparatus shown in Fig. 44.

THE EXAMINATION OF LIQUID FUELS.—The following is a list of the tests applicable to liquid fuels :—

Specific gravity.
Flash point (closed).
Flash point (open).
Fire test, or burning point.
Viscosity.
Pour-point (cold test).
Setting point.
Coke content (Conradson).
Coke content (Ramsbottom).
Calorific value.
Sulphur content.
Water content.
Sediment content.
Asphalt content (hard).
Asphalt content (soft).
Free carbon content.
Incombustible matter (ash content).
Boiling range or distillation test.
Carbon and hydrogen contents (ultimate analysis).
Iodine value.
Acidity.
Temperature of spontaneous ignition.
Latent heat of vaporisation.
Naphthene content
Anthracene content
Tar acids content
Tar bases content
These tests are only applicable to fuels containing tar oils.
Aromatic content.
Doctor test.
Fixed carbon content.

It is rarely necessary to determine all of these tests on one particular fuel, as usually the tests are selected to suit the requirements of a specification or any special purpose for which the oil may be intended.

Whenever possible the details of methods for obtaining the various physical constants given in the foregoing list will be accompanied by references to the two standard textbooks on the testing of petroleum products, namely, " Standard Methods of Testing Petroleum and its Products," published by the Institution of Petroleum Technologists (I.P.T.) ; " Method of Test Relating to Petroleum Products," published by the American Society for Testing Materials (A.S.T.M.). Fuller details of each test may then be obtained by reference to the books quoted.

SPECIFIC GRAVITY.—The specific gravity is the ratio of the mass of a given volume of the oil to the mass of an equal volume of distilled water at 15·5° C. or 60° F. For purely scientific purposes it is usual to take water at 4° C. (the point of maximum density) as unity.

The petroleum industry in this country has adopted the standard temperature of 60° F. or 15·5° C., and the results obtained should be expressed in terms of—

$$S\,\frac{60^\circ\text{ F.}}{60^\circ\text{ F.}}\ \text{(S being the specific gravity).}$$

This means that the specific gravity will be the ratio of the weight of a volume of the oil at 60° F. to the weight of the same volume of water at 60° F.

Whenever possible, and in order to avoid error, the determination should be carried out at a temperature of 60° F., but when this is not convenient the temperature of the oil should be noted and a correction applied for the difference between the temperature of the oil and the standard temperature of 60° F. The correction, which is added when the temperature is above 60° F. and subtracted when the temperature is below 60° F., is equivalent to the following list of corrections per 1° F. difference :—

Products lighter than kerosene, below 0·740	0·00048
” ” ” ” above 0·740	0·00044
Kerosene	0·00040
Gas oil	0·00036
Diesel engine fuels	0·00035
Heavy fuel oils	0·00034

When the specific gravity is required with accuracy to the fourth place of decimals, and has been determined by means of a specific-gravity bottle or pyknometer, it is necessary to apply correction for the buoyancy effect of the air.

APPARATUS.—Various types of apparatus can be used to determine specific gravity, including the specific-gravity bottle, pyknometer, hydrometer, and Mohr-Westphal balance.

Specific-gravity Bottle.—The usual form consists of a small glass vessel fitted with a ground-in glass stopper, which is pierced with a fine hole or capillary.

Specific-gravity bottles of different volumes can be purchased, and it is essential that with each bottle the weight of water, in grams at 60° F., it contains should be determined and used in all calculations when that bottle is employed.

To obtain the specific gravity of an oil, the specific-gravity bottle is filled to the top with oil, care being taken not to trap any air bubbles in the oil. The filled bottle is then allowed to stand for approximately half an hour, preferably in a water-bath maintained at a temperature of 60° F. On replacing the stopper, excess oil will escape through the capillary. Afterwards the bottle should be wiped clean on the outside and carefully weighed. The stopper should be immediately withdrawn and the temperature of the oil taken.

Having determined the weight of the oil contained in the bottle by subtracting the weight of the empty bottle from the weight of the bottle full of oil, the weight of the oil is divided by the weight of water which the bottle contains at 60° F. The result so obtained is the approximate specific gravity at the temperature of the determination, which may be corrected to give the approximate specific gravity at 60° F. by adding or subtracting the appropriate coefficient of expansion per 1° F. given above, according as the temperature of test is higher or lower than 60° F. Should an accurate specific gravity to the fourth place of decimals be required, allowance for buoyancy effect of the air should also be made.

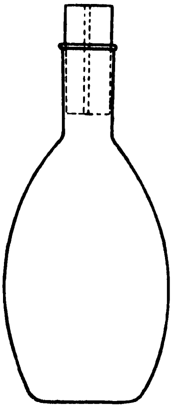


Fig. 45.—Specific-gravity Bottle.

Pyknometers.—These consist of tubes of various designs which are drawn into capillaries at each end. Fig. 46 shows the usual pattern.

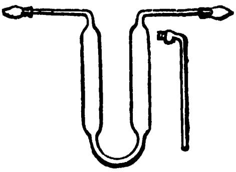


Fig. 46.—Pyknometer.

This instrument is filled by drawing in the oil by means of slight suction, up to fixed marks etched on the glass. The necessary calculations are the same as those employed for the specific-gravity bottle method.

Hydrometer.—The hydrometer (Fig. 47) is a float provided with a narrow stem and so made that only the stem projects from the

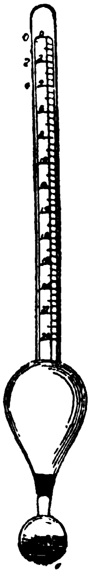
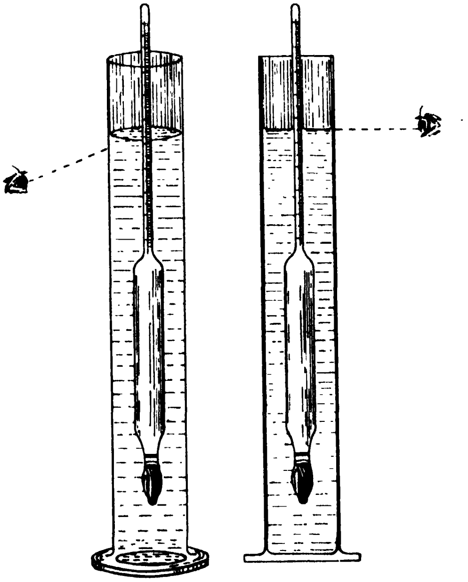


Fig. 47. Hydrometer.



A. B.

Fig. 48.—Method of Reading Hydrometer.

liquid under examination. As the weight of liquid displaced by a floating body is equal to the weight of the body, it is evident that the depth to which the hydrometer sinks will increase with light liquids and decrease with heavy liquids. The scale on the narrow stem is so graduated that the reading denoted by the meniscus of the liquid whose temperature is 60° F. gives the specific gravity of the liquid at 60° F. relative to water at 60° F.

Hydrometers can be purchased from either of four standard series, having the following limits of accuracy recognised by the Institution of Petroleum Technologists :—

	A.	*B.*	*C.*	*D.*
Tolerance of accuracy at any point on the scale	±0·0004	±0·0010	±0·0015	±0·0020

The maximum overall dimensions of these four series are :—

	A.	*B.*	*C.*	*D.*
Length not greater than	340 mm.	250 mm.	185 mm.	140 mm.
Diameter of bulb not greater than	40 ,,	30 ,,	25 ,,	20 ,,

The entire series of hydrometers cover a range of from 0·650 to 1·100 specific gravity, each hydrometer having a range of 0·05 specific gravity.

Hydrometers should only be used to determine the specific gravity of fuels which are reasonably mobile, such as oils of low or medium viscosity, because in very viscous liquids the hydrometer could not come to rest at the correct level in the liquid within reasonable time.

The procedure usually adopted for the determination of the specific gravity of a fuel by means of a hydrometer is as follows : the sample is poured into a clean, dry hydrometer jar, which is deep enough to enable the hydrometer to float freely without touching the bottom. Then the hydrometer, which should be cleaned by wiping carefully, is inserted in the oil with the weighted end downwards and allowing it to sink by its own weight. After the hydrometer has come to rest, submerge it by slight pressure about $\frac{1}{16}$ in. further and again allow it to come to rest. This procedure facilitates the formation of a uniform oil meniscus around the hydrometer stem. When taking the reading, the eye should be placed slightly below the plane of the surface of the oil and then raised slowly until the surface becomes a straight line.

Errors can easily be made by taking readings with the eye too high or too low. The hydrometer is a very convenient and speedy means of obtaining the specific gravity of suitable liquid fuels, and is certainly of especial value where readings are to be taken at control points in a refinery away from the laboratory itself.

There are other scales in common use in addition to the ordinary scale of readings based on the density of water. These are (1) the

Twaddell scale, which is used occasionally among tar distillers and soap-makers, and (2) the A.P.I. scale (American Petroleum Institute scale), as used in the American petroleum industry.

To convert degrees Twaddell into specific gravity for liquids heavier than water, multiply the degrees Twaddell by 5; add 1,000, and divide the result by 1,000, thus

$$12^\circ \text{ Tw.} = \frac{(12 \times 5) + 1000}{1000} = 1{\cdot}06 \text{ specific gravity.}$$

A convenient table is included in the Appendix for the conversion of A.P.I. degrees into specific gravity and vice versa.

Flash Point.—The flash point of an oil may be defined as the lowest temperature at which there is formed under standard conditions of test a mixture of air and oil vapour which will ignite momentarily upon the application of a small flame of standard size.

Flash points may be either " closed test " or " open test." The former is determined under such conditions that the sample under examination is entirely enclosed in the apparatus, or in other words, under " closed " conditions. The " open " flash point is obtained with the surface of the sample exposed to the atmosphere although carefully protected from draughts.

Usually the difference in temperature between closed and open flash points amounts to approximately 20° to 30° F., depending on the particular sample under examination. This relationship between closed and open flash points often serves to indicate contamination by an oil of much lower closed flash point than the liquid being tested. For example, if the closed flash of a certain fuel oil should prove to be much lower than the usual figure, and yet the open test temperature is normal for the quality of product under test, a conclusion can be drawn that the fuel oil has in some way become contaminated with a small quantity of oil of lower closed flash which, generally speaking, would not interfere with the open flash.

Both the closed and open flash tests can be obtained from the one heating of one quantity of oil unless it is specifically stated that the " open flash " should be obtained by means of apparatus solely designed for open flash and fire tests (to be mentioned later), for example, the Cleveland Open Cup, A.S.T.M., Designation D. 92-24.

In addition to the closed and open flash points, a property known as the " fire point " can be obtained by continuing the test. " Fire point " is the lowest temperature at which the oil will ignite at its surface and continue to burn for five seconds.

The apparatus used for the " closed flash " determination varies with the product. For kerosene and other oils flashing below 90° F., the Abel apparatus, as described in I.P.T., Serial Designation K. 7, is used, but kerosenes flashing between 90° to 120° F. require the same apparatus with a slight modification in the procedure of the test. On the other hand, kerosenes flashing above 120° F. are tested in the I.P.T. Pensky-Marten apparatus, as described in G.O. 7. The American standard apparatus for all kerosenes is the Tag Closed Tester, as described in A.S.T.M., Designation D. 56.

The details of the closed flash point test for fuel oils by the Pensky-Marten apparatus will be found in either I.P.T., Serial Designation F.O.7, or A.S.T.M., Serial Designation D. 93-22. The open flash test and fire point of fuel oils will be found in I.P.T., Serial Designation L.O. 7A, which describes a modification of the Pensky-Marten apparatus; A.S.T.M., Serial Designation D. 92-24, describes the method utilising the Cleveland Open Cup apparatus.

VISCOSITY.—Viscosity is the resistance of a substance to a change of shape. A viscous oil, or oil of high viscosity, is one which flows with difficulty; an oil of low viscosity is mobile and flows freely. It is expressed in terms of the "coefficient of viscosity," which is a number representing the value of the force required to move a plane of unit area with unit velocity relative to another plane (also of unit area) situated unit distance away, the space between both planes being filled with the fluid. The unit of viscosity is called a "Poise." (The viscosity of distilled water at 20° C. is almost equal to one-hundredth of a poise, *i.e.*, 1 centipoise.) Viscosity is also expressed in seconds for the efflux time of definite quantities of oils to flow through standard-sized orifices of apparatus called viscometers.

The amount of oil, the efflux time of which is noted, varies with the particular viscometer used :—

Redwood	50 ml.
Saybolt	60 ,,
Engler	200 ,,

The Redwood viscometer No. 1 and No. 2 are the recognised instruments in Great Britain, and a full description of these instruments, together with details of the method of their use, will be found in I.P.T., Serial Designation L.O. 8.

It should be noted that the Redwood No. 1 instrument is unsuitable for use when the time of flow is less than 30 secs., and when the time of flow exceeds 2,000 secs. the Redwood No. 2 instrument should be used. It should be noted that the time of flow obtained by means of a standardised Redwood No. 2 viscometer is one-tenth of the time of flow obtained with the standard Redwood No. 1 instrument at the same temperature.

When the viscosity in absolute units is required, the apparatus, as approved by the British Standard Institution, should be used. Either the U-tube or co-axial bulb type of viscometer is suitable. Each U-tube or similar viscometer is validly usable for a fixed range of viscosity, and therefore each has its one constant which is multiplied by the observed time of flow in order to obtain the kinematic viscosity in "stokes" (the unit of kinematic viscosity). Note also that the kinematic viscosity (stokes) multiplied by the density of the oil at the viscosity test temperature leads to the value of the absolute viscosity in "poises." The approximate absolute viscosity in poises (centimetre-gram-second units) may also be calculated from Redwood No. 1 seconds by the formula :—

$$n=d\left(AT-\frac{B}{T}\right),$$

where n=absolute viscosity of the oil in poises,

d=density at temperature of test,

T=time (seconds) for flow of 50 ml. (Redwood No. 1).

A and B are instrument constants.

For the standard No. 1 viscometer, the value of A is taken to be 0·00260 and that of B 1·7, which values are approximate for Redwood No. 1 instrument certified by the N.P.L.

To meet the requirements of certain specifications, it is sometimes necessary to convert the time of flow in seconds into so-called rape oil units. This is done in the following way : the time of flow in seconds is multiplied by 100 and divided by 535 ; the result is multiplied by the specific gravity of the oil at the temperature of the experiment, and then finally the result is divided by 0·915.

$$\frac{\text{Time of flow}+\text{specific gravity at temperature of viscosity}\times 100}{489{\cdot}525}.$$

The numbers 535 and 0·915 are, respectively, the supposed Redwood No. 1 time of flow and specific gravity of refined rape oil at 60° F. The number 489·525 is simply the product of 535×0·915.

The Saybolt Viscometer.—There are two Saybolt instruments for the determination of viscosity, namely, the Saybolt Universal and the Saybolt Furol Viscometers. These instruments are recognised in the U.S.A., and details of the instruments and the methods of test are contained in A.S.T.M., Designation D. 88-30. It is recommended by the A.S.T.M. that the Saybolt Universal Viscometer shall not be used for times of flow less than 32 secs.

The Engler Viscometer.—With regard to this viscometer, which is the recognised standard instrument for use on the Continent, the efflux time of flow of the oil in seconds is divided by the efflux time of flow for a corresponding quantity of distilled water at 20° C., the result being known as the Engler number. The Engler viscometer is operated in a similar manner to the Redwood viscometer. The apparatus is quite different in dimensions and shape, and the jet is in the form of a platinum tube closed by means of a wooden plug.

Tables for converting Redwood, Engler, and Saybolt viscosities are given in the Appendix.

Pour Point.—The pour-point of an oil is the lowest temperature at which the oil will flow or pour when it is chilled without disturbance under certain definite specified conditions. The details of the standard method of test can be obtained by reference to A.S.T.M., Designation D. 97-30.

Setting Point.—I.P.T., Serial Designation L.O. 11a. The application of this test will indicate the temperature at which an oil ceases to flow when submitted to a small definite pressure equal to a head of 5 cm. of water under definite conditions, from which mechanical disturbance is eliminated as completely as possible.

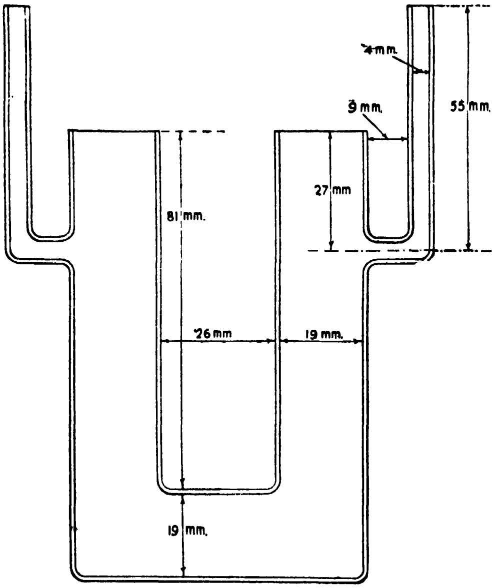


Fig. 49.—I.P.T. Setting-point U-Tube.

Apparatus.—The U-tube employed for the test shall be constructed from medium-walled glass tubing, the wall thickness of which is between 1 and 1·5 mm. The shape and dimensions shall conform with Fig. 49, tolerances of 1 mm. being permissible in each dimension indicated. The U-tube shall be suspended or supported in a vertical position in an air-bath consisting of a metal box 4 in. long by 4 in. wide by 6 in. high, provided with a suitable lid. A satisfactory support for the U-tube is conveniently made by cutting and bending a piece of sheet lead. The air-bath is capable of holding several U-tubes, so that several samples of oil can be tested in the course of a single cooling.

One limb of the U-tube is fitted with a rubber stopper which carries a thermometer. The thermometer shall be the "I.P.T. Setting Point" and shall conform to the specification laid down in the Appendix. When in position, the centre of the bulk of the thermometer shall be 2·5 cm. above the bottom internal surface of the U-tube and equidistant from the walls. The other limb of the U-tube is fitted with a rubber stopper which carries an indicator tube, the horizontal portion of which shall have an internal diameter of 2 mm. ±0·2 mm. In this tube is placed a small amount of coloured water to form an index of about 1 cm. in length.

To the side arm of the limb carrying the thermometer is attached a two-way glass tap, by means of which this limb may be connected with the source of pressure or with the atmosphere at will. To the side arm of the limb carrying the indicator tube is attached a glass tap, by means of which this limb may be connected with the atmosphere.

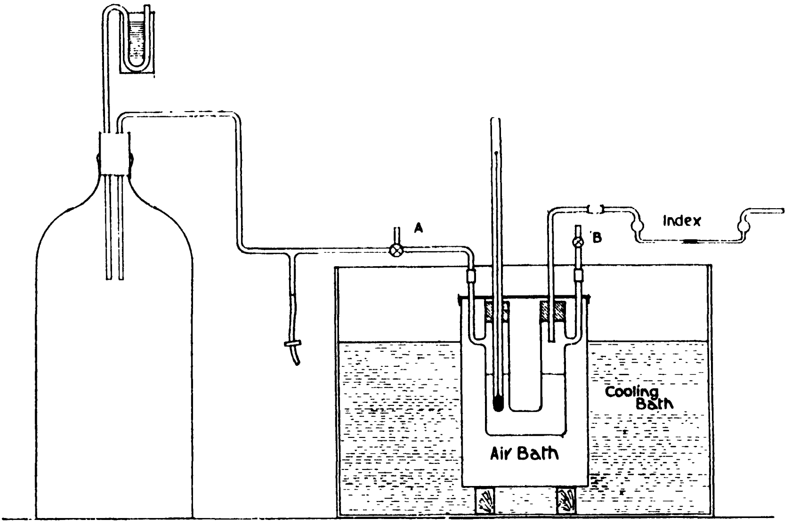


FIG. 50.—I.P.T. Setting-point Apparatus.

The air pressure employed in the test, equal to 5 cm. ±0·1 cm. of water, is conveniently obtained by blowing air into a Winchester quart bottle provided with a manometer and scale and connected with the U-tube.

The metal air-bath containing the U-tube shall be immersed in an outer bath containing an appropriate freezing mixture. This outer bath should be not less than 12 in. in diameter, and should be well lagged on the outside. The depth of the freezing mixture shall be such that it is approximately level with the junction of the side arms with the limbs of the U-tube.

Method.—In order to eliminate the effects of previous thermal hysteresis, the sample before testing shall be heated to 212° F. in a loosely corked bottle, and allowed to cool to a temperature at least 15° F. above the setting point. The oil is poured into the U-tube (previously fitted with its thermometer) to a height of 5 cm. above the lower inside surface of the tube. This level may conveniently be marked permanently on the tube. The apparatus is then assembled and the outer bath filled with a suitable cooling mixture.

For oils with a setting point above 40° F., crushed ice or a mixture of ice and water is a convenient medium. For oils with a setting point between 40° F. and −15° F., mixtures of ice with salt or crystallised calcium chloride may be used, while for those setting points below −15° F., alcohol cooled by solid carbon dioxide is the most suitable refrigerant. When the latter mixture is used, it will be found most convenient to place it in direct contact with the U-tube.

The temperature of the outer bath is so adjusted that when the oil is 10° F. above its setting point, the temperature of the oil is falling at a uniform rate of 1° F. per minute, and this rate shall be maintained until the setting point (or the lowest point of testing) is reached.

The air reservoir having been charged, the test is made by closing tap B and turning tap A to connect the air reservoir with the U-tube. Any movement of the oil is shown by the drop of water in the indicator tube. While the oil is relatively fluid, it is desirable to apply the pressure only momentarily in order to avoid excessive movement of the oil. Immediately after each application of pressure the taps B and A shall be turned to restore the pressure in each limb of the U-tube to atmospheric pressure.

The application of pressure shall be repeated at each 1° F. (*i.e.*, at each one-minute interval). As the setting point is approached, the movement of the water in the indicator becomes less marked until a temperature is reached when a very slight initial movement, followed by no further motion during a period of 10 secs., is recorded. This temperature is to be taken as the setting point of the oil.

COKE CONTENT OR CARBON RESIDUE.—(*a*) *Conradson Method.*—The coke content or carbon residue of an oil is the percentage of hard cokey residue which remains after careful evaporation of the oil in an enclosed space under carefully controlled conditions. Full details of this test will be found by reference to I.P.T., Serial Designation G.O. 9, with the proviso that the amount of coke remaining in the crucible must not exceed 0·4 gm. in weight, also that where the outside of crucible bears evidence of frothing the result shall be rejected. Details may also be obtained from A.S.T.M., Designation D. 189-30.

(*b*) *Ramsbottom Method.*—The principle of this test is similar to the Conradson method in that the oil is evaporated in the absence of air. The apparatus is entirely different, the evaporation of the oil being carried out in glass bulbs of definite shape and dimensions.

The temperature control of the Ramsbottom test is more accurate than in the Conradson method, as the glass bulb is placed in a metal sheath which is immersed in a molten metal bath maintained at a definite temperature of 550° C. This test is highly suitable for distillate oils and for refined oils such as lubricating grades. It is not recommended for residual oils such as heavy furnace oils, although it has been shown that, by modifying the standard procedure slightly, the method may be applied to heavy highly viscous residual oils. Details of this test are obtained by reference to I.P.T., Serial Designation G.O. 9A.

WATER AND SEDIMENT.—Water and sediment can be determined together by means of a centrifugal method. This method is not entirely satisfactory, however, because the total amount of water is rarely completely separated. The centrifuge, however, is widely used for this purpose, and details of the apparatus and method will be found in I.P.T., Serial Designation F.O. 14A ; A.S.T.M., Serial Designation D. 96-30.

An accurate determination of water is possible with the method of Dean and Stark, the one usually recommended. The method consists of heating a known quantity of the oil (100 ml.) with a low boiling medium (usually a particular water-free petroleum spirit or water-free toluol) in a flask fitted with graduated side limb and condenser. In this way the water distils off with the solvent vapours and condenses in the reflux condenser, becoming trapped in the graduated side limb. After adequate settling, the quantity of water which has been removed from the oil may be read directly. Full details of this test are given in I.P.T., Serial Designation F.O. 14 ; A.S.T.M., Serial Designation D. 95-30.

Sediment (*Mechanical Impurities*).—The term "sediment" refers to the material insoluble in benzole present in the oil. It can be accurately determined by the method recommended by the U.S. Bureau of Mines. This method consists of placing a weighed or measured quantity of the sample in a thimble made of Alundem cement of definite porosity. This thimble is suspended from the end of a small coil condenser in a flask containing boiling benzole. The benzole vapours fill the flask and, on reaching the top, are condensed by the small metal condenser ; the liquid benzole thus formed drops into the thimble at a controlled rate, thereby dissolving the oil which filters through the thimble, leaving any insoluble matter behind. When the filtrate leaving the thimble is almost colourless, that is, when all the oil has been removed, the thimble is removed, dried at 105° C. to constant weight, thus giving the amount of sediment in the quantity of sample taken. This should be converted into a percentage before reporting.

Note.—It is found that the use of crystallizable benzene instead of ordinary benzole will greatly assist in the rapid drying to constant weight of the thimble at 105° C.

HARD ASPHALT.—Determination of hard asphalt, I.P.T., Serial Designation F.O. 12.

Materials.—Petroleum spirit. The petroleum spirit to be used shall conform to the following specification :—

(*a*) It shall contain not more than 0·5 per cent. of aromatic hydrocarbons when tested by I.P.T., Method G. 30.
(*b*) At least 90 per cent. shall distil between the temperature limits of 60° and 80° C. when tested by I.P.T., Method G. 30.
(*c*) Its specific gravity at 60° F. shall be over 0·680 and below 0·690.

Method.—The procedure recommended for fuel oils is as follows : a quantity of the sample not exceeding 10 gm. as will give a weight of precipitated hard asphalt not exceeding 0·25 gm. shall be dissolved in the petroleum spirit, the volume of which shall be ten times the number of grams of the oil.

It is found that the amount of " hard asphalt " precipitated is affected appreciably by the ratio of solvent to oil, so that it is necessary to maintain a constant solvent/oil ratio in the estimation. In order to avoid delay in obtaining results, two or three different weights of oil should be taken, heated with their proper volume of spirit, and the estimation completed with the sample giving approximately 0·25 gm. of asphalt specified in the method. The oil and solvent should be thoroughly mixed and allowed to stand for twenty-four hours in the dark. The solvent is then decanted through an 11-cm. folded filter paper and the residue washed with successive quantities of petroleum spirit, which are mixed with the hard asphalt by means of a glass rod. The washings are passed through the filter paper and the process continued until the filtrate is free from oil. The residue in the flask shall then be dissolved in hot crystallizable benzene, poured through the filter, and the clean solution collected in a weighed conical flask. The filter paper is then washed free from all hard asphalt, and these washings likewise collected in the same flask. The benzene shall be evaporated on a water-bath and the hard asphalt dried in a steam oven, with occasional removal of the vapour in the flask by a gentle current of air, and then weighed.

SOFT ASPHALT (asphalt insoluble in alcohol-ether 1 : 2) (Holde method).—Five grams of well-mixed oil in a 300-ml. glass stoppered bottle are dissolved in 25 vols. of ethyl ether of specific gravity 0·72

(137·5 ml. calculated on the assumption that the specific gravity of oil is 0·9) at room temperature. With constant shaking, 12·5 vols. 96 per cent. alcohol (68·5 ml.) are then added slowly from a burette. After a final mixing by shaking, the flask is allowed to stand for five hours at 15° C., then the liquid is filtered rapidly through a pleated filter paper (white ribbon, S. & S. 589). The bottle and filter are then washed with a mixture of (96 per cent.) alcohol and ether (1 : 2) until about 20 ml. of the filtrate on evaporation give only traces of tarry matter. The washed asphaltic matter, which contains paraffin and soft resins, is dissolved from the sides of the bottle and from the filter paper by means of hot benzole into a tared glass dish, from which the benzole is evaporated and the solid residue is then weighed in the usual way.

Ash (incombustible matter).—Light fuel oils, such as distillate oils, are tested by the method described in I.P.T., Serial Designation G.O. 10.

The ash is determined by evaporating a suitable quantity of oil to a small volume, transferring the residue to a weighed platinum or silica dish, and cautiously continuing the evaporation to dryness by means of an Argand burner. Finally, all traces of carbon are removed by heating the dish to redness.

The actual quantity of oil to be used depends upon the amount of ash expected, but generally not less than 250 ml. should be taken. The weight of ash can then be obtained after cooling the previously weighed dish in a desiccator. The percentage of ash, by weight, is then calculated from the volume of oil taken and the specific gravity of the oil.

When the ash content of heavy residual fuel oils or medium viscosity furnace oils is required, it is impracticable to attempt to reduce the volume of the oil by distillation, with subsequent transference to a tared dish. Accurate results are obtainable by placing not less than 50 gm. of the sample in a tared platinum or silica dish. After cautious evaporation of the oil to dryness, the dish is finally ignited until all traces of carbon have disappeared. The weight of ash is then obtained, by difference, the result being reported as a percentage.

Fixed Carbon.—The amount of coke left after ignition of the oil in a closed crucible minus the ash is known as the fixed carbon.

Method (Lunge and Keane, vol. i., p. 334).—One gram of the sample is heated for seven minutes over a full Bunsen flame in a polished platinum crucible weighing 20 to 30 gm., which must be fitted with a tightly fitting cover.

The bottom of the crucible (supported on a platinum triangle) must be 6 to 8 cm. above the top of the flame. The flame, when burning freely, should be 20 cm. high. The under surface of the crucible cover should remain coated with carbon, but the upper surface must always be maintained free from carbon.

Total Sulphur.—I.P.T., Serial Designation G.O. 4 ; A.S.T.M., Serial Designation D. 129-27. (Of fuels other than petrol and kerosene.)

Apparatus.—The combustion of the oils should be carried out in a suitable type of bomb calorimeter. The inner surface should be of materials that are chemically and physically resistant to the products of combustion. The gaskets, insulating materials, etc., should not be liable to react with the products of combustion in such a way that any increase or decrease of the sulphur content of the liquids in the bomb shall arise. Particular attention is directed to lead gaskets which have been found to form lead sulphate if any appreciable area is exposed. The ignition wire should be of fine platinum (0·15 mm. diameter is suitable). Distilled water and all reagents should be sulphur-free.

Method.—The weight of oil to be used shall be not more than 1 gm. Ten millilitres of distilled water shall be placed in the bomb. Oxygen is then admitted to the bomb until the oxygen pressure is at least 25 atmospheres. The bomb shall be immersed in cold water, and the ignition wire is then fused by a suitable electrical current. After firing, the bomb shall remain in the water for ten minutes, so that complete absorption of the oxides of sulphur by the water may take place. The excess oxygen and products of combustion (excluding sulphur oxides) are allowed to escape slowly into the air.

The water in the bomb shall then be emptied into a beaker, and the interior, including the cover and all internal parts, washed out thoroughly with distilled water. If the collected contents and washings are not clean they shall be filtered, and the filter paper thoroughly washed with distilled water, the washings being added to the filtrate. The washings, filtrate, etc., should not exceed 300 ml.

Precipitation of the Sulphur.—Two millilitres of concentrated hydrochloric acid and 0·5 gm. of pure sodium peroxide (Na_2O_2) shall be added, and the solution well boiled. This procedure converts any sulphurous acid into sulphuric acid. Ten millilitres of barium chloride solution (100 gm. $BaCl_2 2H_2O$ per litre), after boiling in a test-tube, are slowly added to the boiling contents of the beaker. Boiling shall be continued for at least fifteen minutes. The solution shall be left on a hot-plate or steam-bath for not less than four hours. It is recommended that it shall stand all night with a clock-glass cover to prevent undue loss by evaporation. The precipitated barium sulphate shall be collected in a filter paper in the usual way, the paper and precipitate to be washed with water until free from all traces of chlorides. Finally, the filter paper is washed with a solution of ammonium nitrate (10 per cent.). (This treatment assists combustion of the paper later on and prevents reduction of the barium sulphate during ignition.) After placing the filter paper in a weighed crucible, and after drying, the paper shall be burnt off and the precipitate and paper ash ignited and weighed. From the weight of barium sulphate obtained, the amount of sulphur in the oil can be calculated. (Bromine water may be used in place of the Na_2O_2, but care should be taken to boil off the excess of bromine.)

EXAMPLES OF TOTAL SULPHUR CONTENT

Type of Oil.	Sulphur.
	Per Cent.
American gas oil	0·2
Persian gas oil	0·5
Roumanian gas oil	0·15
Russian gas oil	0·12
Texas fuel oil	0·9
South American fuel (Aruba)	2·2
Roumanian fuel oil	0·25
Russian fuel oil (Baku)	0·2
Trinidad fuel oil	1·1
Russian fuel oil (Grozny)	0·15
Light Mexican gas oil	1·9
Heavy Mexican gas oil	2·9
Mexican fuel oil	3·5

DISTILLATION TEST OR BOILING RANGE.—The term "boiling range" refers to the temperatures between which a substance boils. This applies to mixtures of liquids each having a different "boiling point." Petrols have a boiling range of 30° to 200° C., and kerosenes of 160° to 300° C. When the liquid consists only of one pure compound—for example, ethyl ether, hexane, alcohol, chloroform—it boils almost entirely at one temperature which is known as the "boiling point" of the substance.

The boiling range of a liquid is determined by a process known as distillation. During a distillation test the substance is heated under specified conditions in a "still" or distillation flask fitted with a thermometer, the bulb of which remains in the vapour only. The liquid is converted into a vapour which is condensed into the liquid state again, and by measuring the volumes of the distillate collected over prescribed temperature ranges, one is able to assign certain distillation characteristics to the product. For details of the method of determining the boiling range or distillation test of a gasoline or petrol, reference should be made to I.P.T., Serial Designation G. 3, or A.S.T.M., Serial Designation D. 86-30.

The same method is employed for kerosenes with two modifications, namely, that the thermometer used should be the I.P.T.

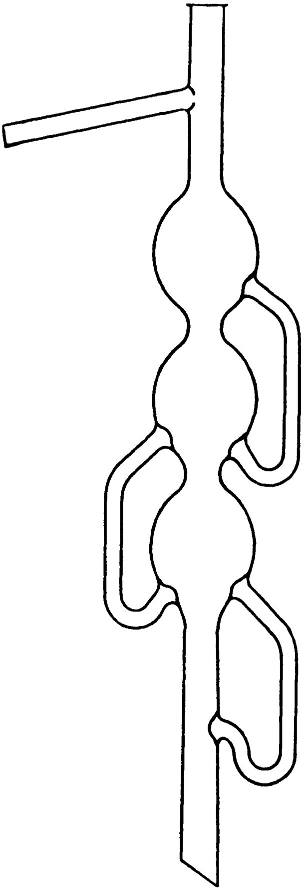
high-range distillation thermometer, and the hole in the asbestos board must be 1½ in. and not 1¼ in: as for gasolines.

Gas oils and Diesel fuels are tested by the method recommended for kerosene, with the exception that an even larger size hole in the asbestos board is necessary, such as, for example, a 2-in. diameter hole, when distilling 100 ml. in a 125-ml. Engler-pattern flask.

Fractional Distillation.—In certain cases a more precise separation of the components of a mixture may be desired, and in this case methods of fractional distillation are employed. Fractional distillation consists of separating the product by means of distillation into various more or less well defined fractions. It depends on the ultimate object of the test whether the fractions are volume percentages of the amount of oil taken, or whether the fractions are collected within definite ranges of temperature, as, for example, every 10° or 20° C.

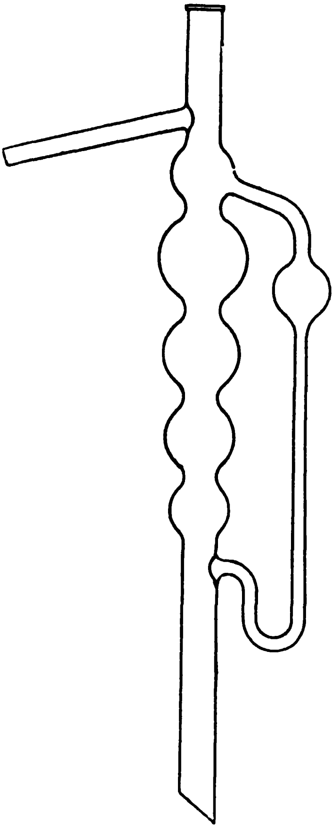
This type of experiment is carried out where an assay of a crude oil is desired, so that an accurate idea may be obtained of the amounts of products obtainable on a large scale. During such a test it is customary to determine the specific gravity or any other convenient property of each fraction, which can also be determined on the products of distillates obtained with a large-scale plant, thus ensuring proper separation of the fractions and rapid control.

Fractional distillation tests are usually carried out in round-bottomed flasks of the bolt-head type, fitted with a dephlegmator or fractionating column. The purpose of the dephlegmator is to obtain finer separation or sharper cutting of the different fractions. Dephlegmators are many in design, but they all function in a similar manner. To illustrate the advantage of the use of a dephlegmator, suppose that a mixture is made of equal quantities of two miscible liquids, one boiling at 100° C. and the other at 150° C., and which do not form an azeotropic mixture ; now, if these are distilled from an ordinary distillation flask until one-half of the mixture has passed over, it will be found that the distillate consists mainly of the lighter product and a certain quantity of the heavier product. Similarly, the residue would consist mainly of the heavier constituents boiling at 150° C., but would contain some of the liquid which boils at 100° C. By employing a dephlegmating column, the heavier product would be much more effectively removed from the vapour during distillation. The effect would therefore be that the first 50 per cent. distillate would be almost entirely the product of lower boiling point, whereas the residue would consist almost entirely of the liquid of higher boiling point. The reason for the incomplete separation of the constituents of a mixture when subjected to distillation is explained by a study of the effects of their vapour pressures. Consider the case of a mixture of two liquids undergoing distillation at normal pressure. The sum of the vapour pressures exerted by the two constituents is equal to the atmospheric pressure. The composition of the vapour immediately over the surface of the liquid will therefore be such that the amount of each constituent present will be proportional to the vapour pressure exerted by that constituent. If the mixed vapours are passed through a dephlegmator, an absorption of the higher boiling-point constituent takes place in the condensed mixture which is present in the dephlegmator, thus enabling vapours containing a higher proportion of the lower boiling constituent to ascend and pass through the apparatus to the condenser. Examples of the common forms of dephlegmators are given in Figs. 51 to 54.



LE BEL-HENNINGER DEPHLEGMATOR.

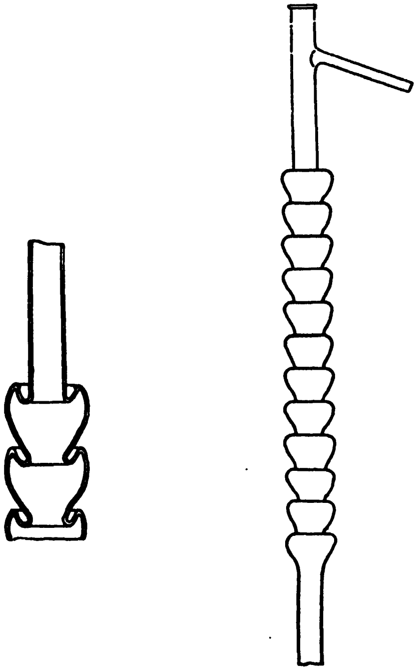
Fig. 51.



GLINSKY DEPHLEGMATOR.

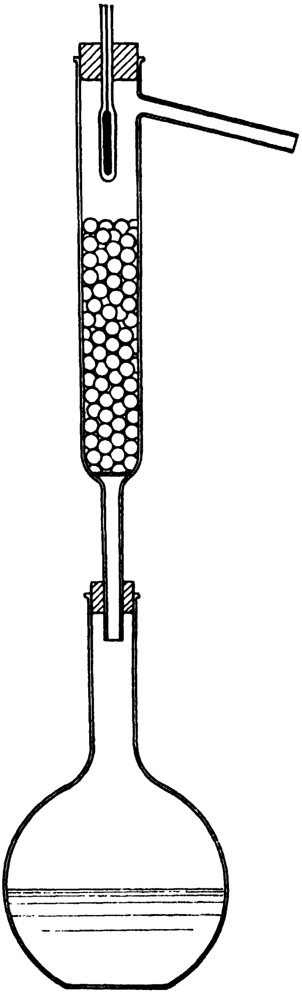
Fig. 52.

The results of distillation are best recorded in graphic form, from which it is possible to form an opinion of the distillation properties of the material. From such a curve it will readily be seen, for instance, whether the substance contains a large amount of constituents which boil over a very short range; on the other hand, when the curve has a uniform slope, the indications are that the liquid consists of a large number of evenly graded components which possess steadily increasing boiling points.



FRACTIONATING COLUMN (YOUNG)

FIG. 53.



BEAD COLUMN DEPHLEGMATOR.

FIG. 54.

It must be mentioned that the method adopted and the apparatus employed in making a distillation considerably affects the results obtained; to illustrate this point, curves are given in Figs. 55 and 56, the former showing distillation tests carried out on a motor spirit using an Engler flask, a Young's column attached to flask, and an ordinary type of retort as used for the

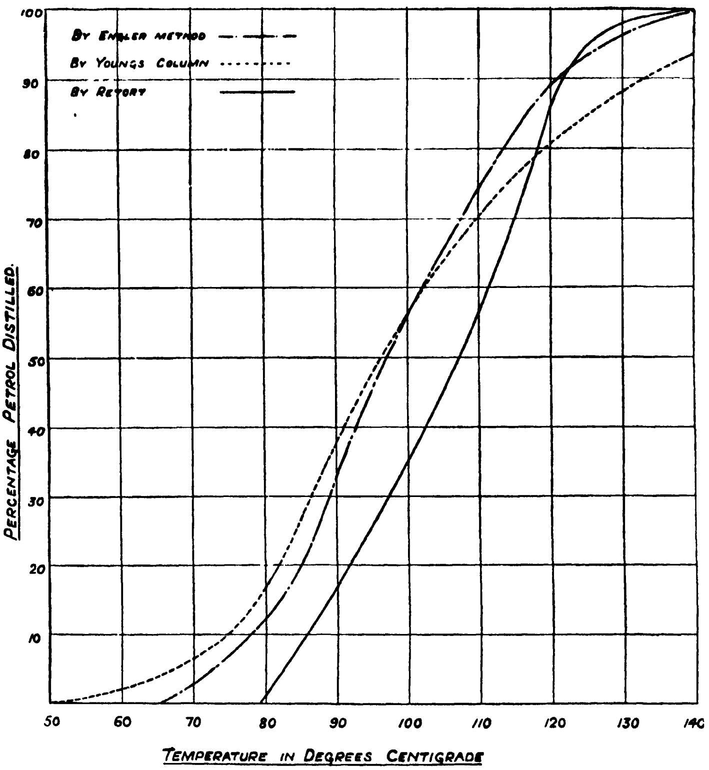


FIG. 55.

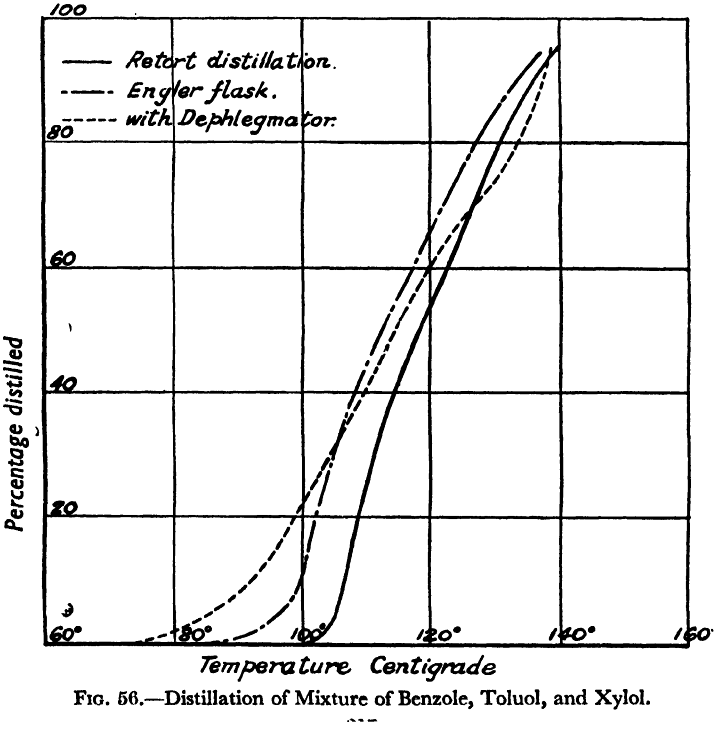


FIG. 56.—Distillation of Mixture of Benzole, Toluol, and Xylol.

distillation of tar. Fig. 56 shows the results of tests on a mixture of equal parts benzole, toluol, and xylol, using the Engler-pattern flask, a Le Bel-Hennige fractionating column, and retort.

The distillation tests adopted for raw tars with a view to their valuation are conducted on much larger samples. Copper vessels are frequently used as stills, because the water contained in many raw tars makes distillation very irregular. There is also a danger of glass vessels breaking by the bumping which takes place.

Tar Acids.—The determination of tar acids would be applied to fuel oils consisting of creosote or mixtures of creosote and petroleum fuel. Coal-tar distillates frequently contain acidic bodies, mainly phenol or carbolic acid (C_6H_5OH), and the three isomeric cresols ($C_6H_4CH_3OH$). These and other similar compounds are included under the term "crude tar acids." They may be estimated in the distillate obtained by distilling a quantity up to a vapour temperature of 280° C., and then either taking the whole of the distillate or an aliquot part and extracting it with successive quantities of 10 per cent. caustic soda solution until the tar acids are completely removed. The several soda extracts shall then be combined and boiled until the odours of tar oils and bases have disappeared. After cooling, the alkaline solution shall be acidified with concentrated hydrochloric acid, cooled again, and saturated with sodium chloride ; after sufficient time for settlement, the volume of tar acids is measured by suitable means.

Tar Bases.—Distillates of coal tar in the crude state contain basic compounds. These are mainly the various pyridines, quinoline, and isoquinoline, each of which contains one atom of nitrogen in the molecule. The effect of the presence of tar bases on the running of engines is not noticeable, because they burn satisfactorily. The tar bases are also used for the denaturing of alcohol, *i.e.*, in order to make the spirit unsuitable for drinking.

Tar bases may be determined on the clean washed oil, free from tar acids by agitation with sufficient 25 per cent. sulphuric acid to remove the bases. The aqueous solution shall then be separated, neutralised with strong clean aqueous caustic soda, and the mixture steam-distilled until the condensate shows only faint signs of opalescence. Caustic soda solution shall then be added to the distillate until the aqueous layer, after thorough agitation, attains a specific gravity of at least 1·38. It should be allowed to settle, and the upper layer, consisting of pyridine bases, shall be separated and allowed to stand over solid caustic soda for twelve hours, after which its volume shall be noted.

Naphthalene Content.—The estimation of naphthalene is of importance when analysing the higher boiling distillates of coal tars. It is rarely necessary to estimate this constituent, but its presence is indicated by its influence on the cold test or pour-point.

Naphthalene in oils can be determined best by distilling the liquid up to a temperature of 270° to 280° C., and after removal of tar acids the distillate is cooled to a temperature of 15° C. for about twenty-four hours to allow crystallisation to take place. The crystals are then filtered off, and any adhering oil removed by pressure between filter papers, after which the naphthalene may be weighed. This method, though only approximate, is sufficiently accurate for the purpose of fuel testing.

Naphthalene is an aromatic hydrocarbon having the formula $C_{10}H_8$. It is rich in carbon, containing only 6·2 per cent. hydrogen. When allowed to burn freely in the open air, it burns with a smoky, luminous flame. The pure hydrocarbon possesses a gross calorific value of 9,668 cals. per gram, melts at 79° C., boils at 218° C., and possesses a specific gravity at 15° C. of 1·145. Naphthalene has the property of subliming, use of which is made in its commercial purification.

Naphthalene as a constituent of heavy fuel oils is liable to cause obstruction of the fuel pipes, and has been associated with the formation of deposits in the atomising devices of Diesel engines. Apart from these difficulties, which may be overcome by mechanical means, naphthalene possesses valuable fuel properties. In normal times it is available in considerable quantities at reasonable prices. Oils containing crystals of naphthalene require heating in order to liquefy them completely before admission into the engine.

ANTHRACENE CONTENT.—It is not usual to estimate anthracene in petroleum fuel oils, though it is a component of most of the heavy distillates of coal tar. The anthracene content may be determined by collecting, cooling, and filtering the distillate obtained between 270° to 300° C. The crude anthracene is obtained by filtration. The proportion of the pure compound present in the crude product may be determined by oxidation with chromic acid in the presence of glacial acetic acid, whereby anthraquinone is produced. This test is known as the Hochst test.[1]

THE ULTIMATE ANALYSIS OF LIQUID FUELS.—When it is necessary to determine the quantitative ultimate composition of a fuel, a method involving a combustion furnace is used, as is customary for the determination of the ultimate analysis of all organic substances. The theory of the process is simple, but the manipulation is difficult, so that both extreme care and considerable experience are required in order to obtain accurate results. A full account of the theory and practice of this determination will be found in any textbook on practical organic chemistry.

The combustion determines the carbon and hydrogen present in a substance, and, provided that the sulphur content is known and

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[1] See Lunge, "Coal Tar and Ammonia," 1916.

that other elements are absent, the content of any oxygen present can be calculated by difference.

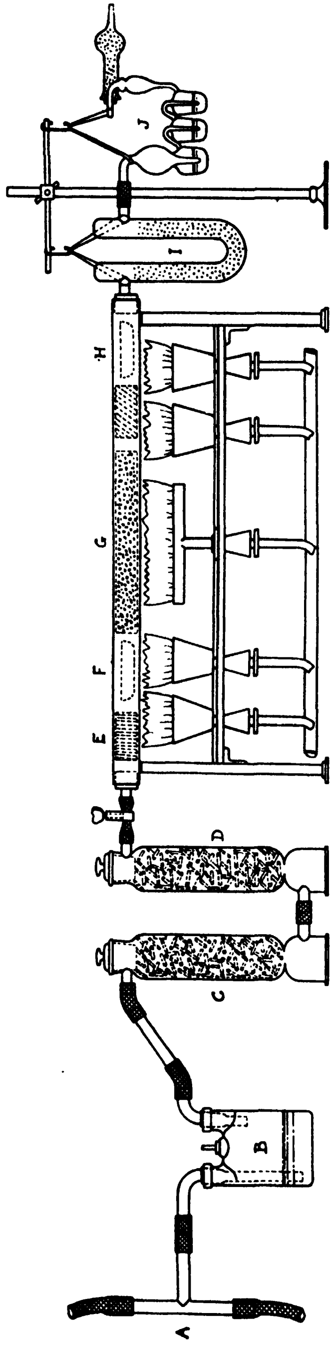

Fig. 57.—Combustion Apparatus.

The process consists of passing purified dry carbon dioxide-free air or oxygen over a weighed quantity of the substance in a heated tube, then collecting the water and carbon dioxide of combustion in weighed vessels containing suitable absorption materials. The increase in weight of these vessels represents the water and carbon dioxide formed by the complete combustion of a known weight of the material, and from these data the hydrogen and carbon contents can be calculated.

The substance to be analysed is burnt in a tube of hard silica about 30 in. long and ½ in. in bore. The tube is heated by a special combustion furnace, either gas or electrically heated, preferably the latter. The apparatus is shown in Fig. 57, and is so arranged that either air or oxygen can be admitted to the furnace from A into wash bottle B containing sulphuric acid, which serves as a drying agent and also as a bubble. After passing through the sulphuric acid, the air or oxygen is led through the towers C and D, where any carbon dioxide is removed by means of solid potassium hydroxide. The air or oxygen, now purified, is passed through the combustion tube in the furnace. It encounters first of all a coil of oxidised copper gauze E, which serves to prevent the volatile products of distillation from passing backwards in the tube. Then it passes over a small porcelain or platinum boat F, which contains the substance to be burned. The products of combustion are then passed through heated copper oxide G to ensure complete oxidation. A large porcelain boat H containing lead chromate is placed near the end of the tube to remove sulphur from the products of combustion. As any nitrogen occurring in the compound is also oxidised during the combustion, a spiral of copper gauze is placed in the end of the tube in order to decompose any oxides of nitrogen which may be formed, otherwise they would vitiate the carbon dioxide results. The products of combustion are next passed through a calcium chloride tube I which extracts the water, and thence through a potash bulb J containing a 40 per cent. solution of caustic potash which absorbs the carbon dioxide.

The apparatus must be carefully examined before use to ensure that all joints are gas-tight, and the furnace should also be heated for a period of several hours to facilitate the complete removal of water and dust from the tube by purified air which is passed through it meanwhile. The front portion of the tube is then allowed to cool, the calcium chloride tube and the potash bulb weighed, and about 1·5 gm. of the sample weighed into a boat which is placed in the combustion tube. The copper oxide coil is replaced in the tube, and the calcium chloride absorption tube and potash bulb returned to their respective positions. Air is slowly passed from a gas reservoir through the combustion train. The exit portion of the combustion tube is heated, and then the front end of the tube is also heated until the copper oxide is glowing, care being taken not to distil the oil from the boat until the coil is at a red heat. By slowly warming the tube in the neighbourhood of the boat, the oil may now be slowly burned, but the rate of burning must be very slow, and the speed of air such that about one bubble per second passes through the first bulb of the potash absorption vessel.

When the oil has almost completely distilled, the flame may be raised until the portion of the tube which surrounds the boat is at a bright red heat. Oxygen is then passed through the tube for half an hour to complete the combustion, after which air is passed through the apparatus for an hour to expel any carbon dioxide and water remaining in the tube, and also to displace the oxygen in the absorption tubes.

The absorption vessels are then weighed after cooling. The entire analysis requires at least six hours, and attempts to hasten the process only lead to failure. The weight of hydrogen in the oil is calculated from the increase in weight of the calcium chloride tube by multiplying by 0·1119. The carbon in the oil is calculated by multiplying the increase in weight of the potash bulb by 0·2727.

As the combustion is a difficult and lengthy procedure, and is generally not essential for the valuation of a liquid fuel, it is only carried out in special cases ; on the other hand, a knowledge of hydrogen content of a fuel oil may be required when the oil is to be employed simultaneously for power generation and other purposes, *i.e.*, in " lighter than air " craft water is condensed from the exhaust gases and used for ballast purposes—*i.e.*, to replace the fuel used—thus obviating the necessity of releasing hydrogen or helium as the

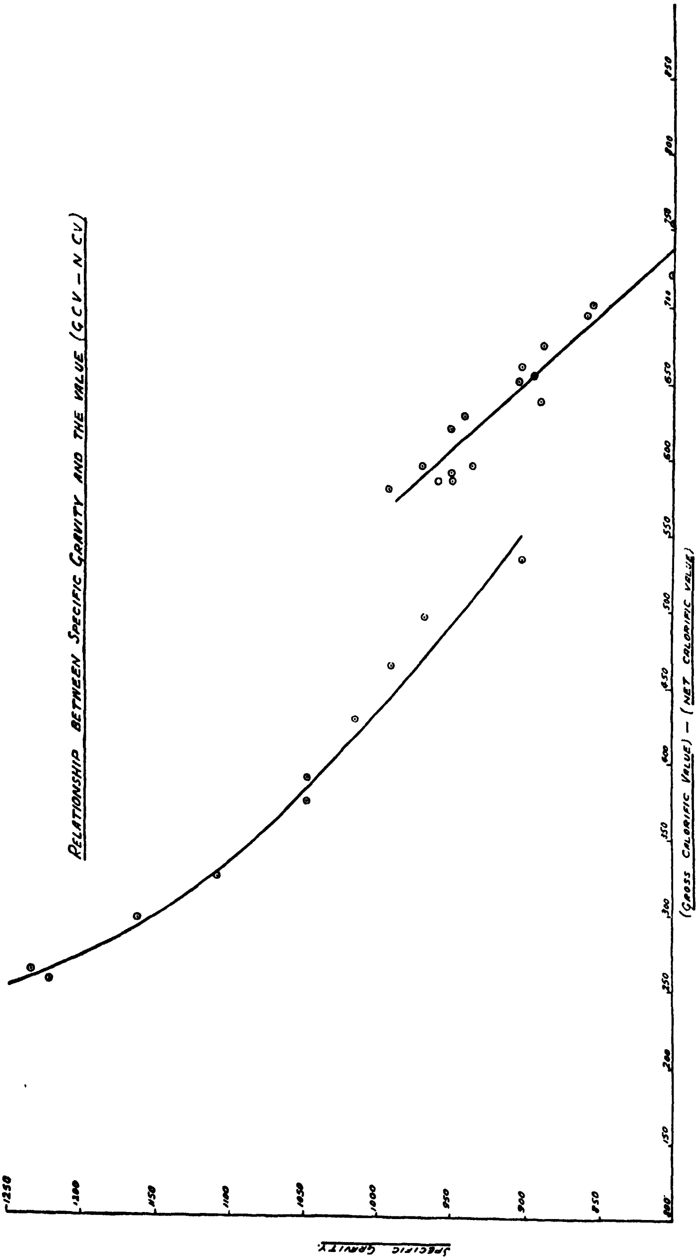

FIG. 58.

fuel is used. The greater the hydrogen content of the fuel in such cases, the greater the amount of water is there in the exhaust gases.

The elementary composition of a fuel oil does not vary greatly among oils of the same class. As a general rule, it is possible to estimate the hydrogen content of a liquid fuel with a fair degree of accuracy when its origin and its specific gravity are known. A calculation of *net* calorific values from the *gross* calorific values obtained by the calorimeter is more exact if the analysis by the combustion method has been determined. The curves in Fig. 58, based on experience with a large number of heavy coal-tar products and petroleum oils, indicates with a sufficient degree of accuracy the difference between the gross and net calorific values in relation to specific gravity.

The curve of lower specific gravity indicates the values for petroleum products, and the curve of higher specific gravity those of coal-tar products.

In those instances when oils are of doubtful origin and composition, that is, neither mainly aromatic (as obtained by high temperature destructive distillation of coal) nor entirely petroleum in origin, analysis by combustion becomes necessary in order to obtain (from the hydrogen content) an estimate of the proportion of compounds of each type present. Even in this case the experienced analyst can form a rough estimate of their composition by a comparison of the distillation curve with the specific gravity, but this latter method requires the previous collection of data from a large number of varying samples of oil.

The proportions of carbon, hydrogen, and oxygen present in a fuel indicate the amount of air necessary for its combustion, and to a small extent show the likelihood of carbon deposits that may be formed in the engine, fuels of high hydrogen content being least liable to promote carbonisation. Furthermore, Diesel oils having low hydrogen contents frequently present ignition difficulties, inasmuch as such oils generally have the higher spontaneous ignition temperatures ; this point is amply illustrated when we consider the superiority as Diesel fuels of petroleum oils over coal-tar oils (creosotes), the former having a much higher hydrogen content.

EXAMPLES OF RECENT CARBON AND HYDROGEN-CONTENT DETERMINATIONS

Type of Oil.	Carbon.	Hydrogen.	Sulphur.
	Per Cent.	Per Cent.	Per Cent.
Baku fuel oil	86·3	12·2	0·23
Californian Diesel fuel oil .	85·54	12·86	...
American domestic fuel oil .	86·5	13·04	0·17
Venezuelan pressure distillate .	86·40	12·57	0·47
Semi-Diesel fuel oil . .	86·5	12·04	0·51

ACIDITY.—Petroleum fuel oils rarely possess inorganic acidity to any great extent, although they usually give indications of organic acidity in a degree proportional to their naphthenic acid content. Compound fuel oils, such as blends of petroleum and creosote, would show higher figures for acid content because of the probable presence of phenolic compounds. It is usual and only necessary to examine fuel oils for inorganic acidity, although at times the content of total acidity is asked for.

Inorganic Acidity (I.P.T., Serial Designation F.O. 5).—One hundred grams of the oil shall be shaken vigorously in a tap funnel for one minute with an equal weight of warm distilled water. The water shall be allowed to separate and then run into a clean flask, cooled, and titrated with decinormal $\left(\frac{N}{10}\right)$ potassium or sodium hydroxide, using methyl orange as indicator. The result shall be expressed as the number of milligrams of potassium hydroxide necessary to neutralise the acidity of 100 gm. of the sample.

Total Acidity (I.P.T., Serial Designation L.O. 5).—Ten grams of the oil shall be weighed into a flask and 50 ml. of neutral 95 per cent. alcohol added. The mixture shall be heated to boiling on a water-bath, and well shaken to ensure solution of the acids in the alcohol. One millilitre of 0·5 per cent. solution of phenolphthalein shall be added, and the mixture titrated hot with $\frac{N}{10}$ potassium hydroxide (free from carbonate). The result shall be expressed as the number of milligrams of potassium hydroxide necessary to neutralise the acidity in 100 gm. of the sample.

The organic acidity of the oil may be obtained by deducting the inorganic from the total acidity.

VAPOUR DENSITY.—This is a test very rarely required in connection with motor fuels; an approximate figure can be obtained from a knowledge of the calculated average molecular weight of the fuel under review. Should it be necessary to make a determination, the method (also used for molecular weight determination) may be obtained in any textbook of physical chemistry.

LATENT HEAT OF VAPORISATION.—When a substance changes its physical state from a solid to a liquid, or from liquid to gaseous, a certain amount of heat is absorbed. When the change is from the liquid to the gaseous state, this quantity of heat is known as the latent heat of vaporisation. The value is mainly of interest in connection with the design of carburetters and vaporisers, where the cooling of the vaporising space is dependent upon the latent heat of vaporisation.[1]

[1] For the details regarding method and apparatus for determination of latent heat of vaporisation, see Holde, " Untersuchung der Kohlenwasserstofföle und Fette," p. 18.

Examples of latent heat of vaporisation are given in the following tables :—

Substance.	Formula.	Boiling Point.	Latent Heat in Calories.
ALIPHATIC HYDROCARBONS.			
Hexane	C_6H_{14}	69° C.	79·4
Heptane	C_7H_{16}	98° C.	74·0
Octane	C_8H_{18}	125° C.	71·1
HYDRO-AROMATIC HYDROCARBONS.			
Cyclohexane or hexamethylene	C_6H_{12}	80° C.	87·3
Dimethylpentamethylene	C_7H_{14}	90° to 92° C.	81·0
Methylhexamethylene	C_7H_{14}	98° C.	75·7
Dimethylhexamethylene	C_8H_{16}	118° to 119° C.	71·7
BENZENE AND ALCOHOL.			
Benzene	C_6H_6	80·4° C.	94·4
Ethyl alcohol	C_2H_5OH	78·5° C.	203·0

SPECIFIC HEAT.—Specific heat is the amount of heat required to raise 1 gm. of a substance 1° C. It is generally stated in terms of calories, 1 cal. being the amount of heat required to raise the temperature of 1 gm. of water through 1° C. Specific heat data is necessary in calculations connected with the construction of stills and condensers, and with the heating of fuel tanks and fuel supply lines. Some specific heat data for various fractions of petroleum have been published recently.[1]

In view of the number of examples given on a great variety of products by these authors, the necessity to carry out actual determinations hardly arises, as reference to the tables given in the papers should supply any information regarding the specific heats of most petroleum fractions.

A few results given by these authors for crude oils which have been topped to 100° C. are as follows :—

Product.	Specific Heat.	Mean Temperature.	Specific Gravity, 60° F./60° F.
	Calorie/Gram.	° C.	
Persian crude oil	0·4652/0·5154	13·7/85·5	0·8689/0·8694
Pennsylvania crude oil	0·4725/0·5316	11·1/93·0	0·8536/0·8544
Mid-Continent crude oil	0·5222/0·5428	15·0/94·7	0·8374/0·8379

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[1] Long, Jessel, and Steed, *J.I.P.T.*, 1930, xvi. 476 ; *ibid.*, 1930, xvi. 783 ; *ibid.*, 1931, xvii. 585.

Vapour Pressure.—Determination of the vapour pressure of gasoline is required in order to indicate the amount of very low boiling hydrocarbons, such as butane and propane, which may have been blended into petroleum spirits intended for sale as petrol. The determination of vapour pressure is carried out as a safeguard against explosion during transit.

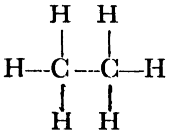
The method which is usually employed involves the Reid vapour pressure bomb, which is approved by the National Gasoline Association and the Bureau of Explosives (Institute of Commerce Commission), both of the U.S.A.

Details of the apparatus and method can be obtained by reference to the " Tag Manual," p. 99, which describes the determination of vapour pressure of natural gasoline.

For the determination of vapour pressure (absolute) of gasoline, reference should again be made to " Tag Manual," p. 102, where the Robinson vapour-pressure apparatus used for this test is described.

Iodine Value and Bromine Value.—Organic compounds which contain carbon atoms held together by more than one bond are known as unsaturated compounds, and are generally very reactive chemically. Bromine and iodine, when added to unsaturated compounds, usually form bromides and iodides by addition. To illustrate the difference in this respect between saturated and unsaturated compounds, the behaviour of ethane and ethylene with iodine may be taken as examples.

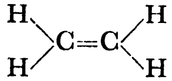
Ethane : formula



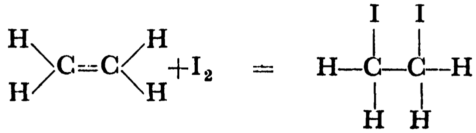
$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

This compound is a saturated hydrocarbon, which means that the carbon atoms are held together by only *one* bond. All the valencies of the carbon atoms are saturated, and therefore iodine or bromine cannot react with it to form additional products.

Ethylene : formula



This is an unsaturated hydrocarbon (a mono-olefine), and will readily absorb iodine (or bromine) in the following manner :—



Ethylene+Iodine = Ethylene iodide.

It is seen from this reaction that the compound has now become fully saturated.

Oils usually contain some unsaturated hydrocarbons, and a measure of the amount present may be obtained by an estimation of the quantity of iodine or bromine which they will absorb. By treating an oil under carefully controlled conditions with a measured excess of a suitable solution of iodine and then estimating the unabsorbed iodine, the amount of iodine which has combined with the oil can be accurately determined.

The data thus obtained are used for the calculation of the iodine value, which is expressed in terms of milligrams of iodine per gram of oil. The iodine value, therefore, represents the degree of unsaturation, or the proportion of double bonds present in the oil.

Of the different methods available for the determination of iodine value, such as Hanus, Hubl, and Wijs, the author has found that for quick and reliable results the method as described by Garner, *J.I.P.T.*, 1928, xiv., p. 700, is to be recommended. This method is based on Faragher, Gruse, and Garner's paper on the "Hanus Solution," *J. Ind. Eng. Chem.*, 1921, xiii., p. 1044. This is described as follows :—

Solutions Required.

Iodine solution—	
Iodine	25·4 gm.
Bromine	5·8 c.c.
Glacial acetic acid . . .	2,000 ml.
Decinormal sodium thiosulphate.	
Potassium iodide—	
Potassium iodide . . .	100 gm.
Distilled water . . .	1,000 ml.
Starch solution.	

Iodine Solution.—This is conveniently and rapidly prepared as follows : a small piece of glass wool is placed in the bottom of a glass funnel and the latter placed in the mouth of a Winchester quart bottle (2½ litres capacity). The glacial acetic acid is measured in a litre flask and transferred to conical flasks as required. The latter are warmed by immersion in hot water, and the hot acetic acid poured through the iodine, which is supported by the glass wool in the funnel. In this way the iodine is rapidly dissolved and the bromine is then measured out and added to the solution of iodine when the latter has cooled. It is not essential that the proportions should be absolutely exact, although, of course, it is desirable that no great divergence from these quantities should occur.

The iodine solution does not appear to alter if kept in the dark, even after three or four months. It is essential that the acetic acid shall be pure, otherwise erratic iodine numbers are obtained.

Method.—The iodine solution is standardised periodically in the regular determination of iodine numbers by a blank determination, that is, by titrating the mixture as described below, but without the addition of the gasoline. In general, when great accuracy is not necessary, the gasoline can be measured instead of weighed, and for this purpose the pipette devised by E. W. Dean (Bureau of Mines Bulletin, No. 181) may be employed. This pipette consists of a piece of capillary tubing, drawn out to a point, of which convenient dimensions are: bore, 1·5 mm.; length, 35 cm. Calibration marks showing the following volumes are etched on the pipette: 0·6, 0·4, and 0·2 ml. Wide-mouthed bottles (stoppered), and of about 400 ml. capacity, are used for the determinations.

Ten millilitres of carbon tetrachloride are placed in the bottle, a definite volume of the sample is measured out and run into the carbon tetrachloride from the pipette and washed out by drawing the carbon tetrachloride twice into the pipette, each time allowing to drain. Where the temperature differs greatly from 60° F. the temperature of the sample is taken, as the iodine number is based on the weight of sample used. As the method is, however, only accurate to about 2 per cent., the temperature correction can usually be neglected.

Twenty millilitres of the iodine solution are now added, and the pipette allowed to drain until one drop of the iodine solution has fallen into the bottle after the pipette has apparently emptied. The bottles are then placed in a dark cupboard for exactly fifteen minutes; 5 ml. of the potassium iodide solution are now added and the bottle shaken, about 200 ml. of distilled water added, and then standard sodium thiosulphate solution added from a burette until the solution is slightly yellow. It is necessary to shake the liquid vigorously as soon as the yellow colour fades in the aqueous layer in order to ensure that the iodine in the carbon tetrachloride at the bottom of the bottle may be removed. Starch solution is now added, and is followed by more thiosulphate solution until the blue colour is just removed by the last drop added.

Calculation of the Results.—The difference between the volume of sodium thiosulphate solution required in the iodine number determination and in the blank gives the amount of solution used up, and this corresponds to the weight of iodine absorbed by the sample.

$$\text{Iodine number} = \frac{\text{Millilitre sodium thiosulphate used up} \times 1{\cdot}27}{\text{Volume of sample} \times \text{specific gravity sample}}.$$

The specific gravity should be at the temperature at which the sample was measured out, but usually the specific gravity at 60° F. can be taken as sufficiently accurate. For routine work the iodine number may be calculated by means of an alignment chart based on the above formula. The volume of sample should be chosen so that about one-third of the iodine solution only is used up, *i.e.*, if the blank requires 40 ml. of $\frac{N}{10}$ sodium thiosulphate solution, then the actual titration figure of the sample should be only about 27 ml.

The chief advantage of this method is its quickness, because by having standard solutions ready for immediate use, a result can easily be obtained in less than one hour.

AROMATIC CONTENT.—This test is based upon the determination of the Critical Solution Temperature (C.S.T.) in aniline of the spirit before and after removal of the aromatics by means of sulphuric acid. Full details can be obtained by reference to I.P.T., Serial Designation G. 30.

Routine work is preferably carried out, however, with the "Aniline Cloud Point" test. This property is measured by observing the temperature at which equal volumes of *dry* aniline and *dry* petrol, kerosene, etc., are completely miscible. This value is the same as the result obtained by observing the temperature at which clouding (separation of aniline) occurs when equal volumes of aniline and the product are cooled from a temperature at which they are completely miscible. The C.S.T. method is tedious and no more reliable than carefully determined Aniline Cloud Points. There is a difference between the numerical values of both properties ; the difference is very small for some homologous series and large for other hydrocarbons. The differences are reasonably constant, so that a standardisation of aniline cloud-point methods would simplify the routine determination of aromatic hydrocarbons, etc.

DOCTOR TEST.—This test is applied to petrols and kerosenes, and is a qualitative measure of the sulphur compounds present which will react with sodium plumbite in the presence of a minute quantity of flowers of sulphur. Should the sample become discoloured, or if a darkening of the yellow colour of the sulphur film is markedly noticeable, the test is reported as "positive" (*i.e.*, the sample is sour). If the sample remains unchanged in colour, and the yellow film of sulphur remains light or only slightly discoloured by grey or black flecks, the test shall be reported "negative" (sweet gasoline). Full details can be obtained by reference to I.P.T., Serial Designation G. 33.

FREE CARBON.—This substance is best determined by Köhler's method : 10 gm. of tar are mixed with 25 gm. of glacial acetic acid and 25 gm. of toluene and boiled in a conical flask under a reflux condenser. The mixture is filtered through two counterpoised filter papers, and the precipitate washed with hot toluol until the washings become colourless. The precipitate is then dried at 120° C., the filters separated, and the difference in weight of filter papers is noted.

Constam and Schläpfer [1] analysed two samples of "free carbon," and found them to contain other elements than carbon.

	Carbon.	Hydrogen.	Oxygen and Nitrogen.	Calorific Value (Gross).
	Per Cent.	Per Cent.	Per Cent.	Calories.
First sample . .	92·7	2·6	4·0	8,271
Second sample . .	91·6	2·6	5·1	8,218

SPONTANEOUS-IGNITION TEMPERATURE.—The property of a fuel to ignite without the assistance of a flame or spark is known as spontaneous ignition, and the temperature at which this occurs is called the temperature of spontaneous ignition. This feature is of great importance in connection with fuels for use in compression-ignition engines.

It has no connection with "flash point" or "burning point," which are both dependent on the application of a flame to a sample of heated oil. Determinations of the temperature of spontaneous ignition of fuel oils have been made by Holm [2] and by Constam and Schläpfer,[3] and also by the author. Holm employed a vertical tube furnace, the determinations being made by dropping the substances on to a heated porcelain crucible cover, the temperature being measured by a thermocouple pyrometer. The results were of the greatest interest, and are therefore given here :—

TEMPERATURE OF SPONTANEOUS IGNITION IN OXYGEN, OBSERVED BY HOLM.

	° C.
Hydrogen	470
Petrol	415
Paraffin	380
Gas oil	350
Roumanian residuum .	380
Machine lubricating oil .	380
Compressor lubricating oil .	410
Paraffin (from lignite) .	370
Paraffin wax	310
Tar oil	530
Ethyl ether	400
Acetaldehyde	380
Ethyl alcohol	510
Acetone	570
Benzene	520
Xylene	500
Aniline	530
Cellulose	360
Anthracite	440

Constam and Schläpfer published the analyses of 220 fuel oils, together with their temperatures of spontaneous ignition. They also examined the effect of various heating surfaces on the ignition temperatures, and made duplicate experiments in atmospheres of oxygen and air. The apparatus employed for these experiments is shown in the accompanying diagram (Fig. 59). The majority of the determinations were made with a platinum crucible and in an atmosphere of oxygen.

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[1] *Zeits. Ver. d. Ing.*, 1913, p. 1439.

[2] Holm, "Ueber Entzündungstemperaturen (Zündpunkte), besonders von Brennstoffe," *Zeit. fur angew. Chemie*, 1913, p. 273.

[3] Constam and Schläpfer, *Zeits. Ver. d. Ing.*, 1913, p. 1489.

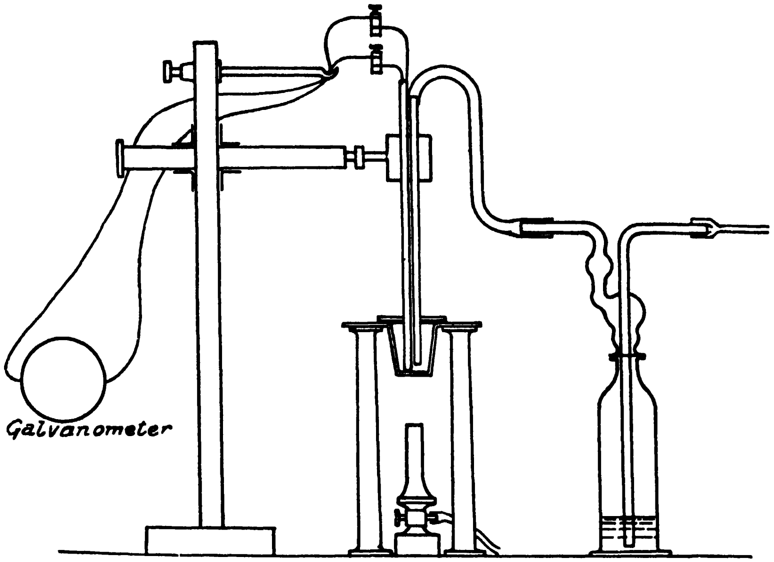

FIG. 59.

In order to obtain a uniform temperature in the heating space, a small platinum crucible was placed inside a larger crucible, and the intervening space of about 3 mm. was packed with ignited sand. The crucible was covered with an asbestos lid in which were holes to allow the passage of a platinum-rhodium thermocouple, and a tube to supply oxygen. The outer crucible was heated by a small Bunsen burner, and the oxygen slowly passed into the inner crucible. The thermocouple was protected by a thin tube, the lower end of which was situated 3 mm. above the base of the crucible (Fig. 60). Raising the thermocouple to 10 mm. from the base of the crucible only affected the temperature 10° C.

Oil was periodically dropped into the inner crucible by means of a drawn-out glass tube, and the temperature slowly raised until the oil-drop burst into flame. If an atmosphere of oxygen be employed, a distinct explosion is heard ; in air, only a light puff is noticed audibly. The oil at first vaporises a little, and then takes fire.

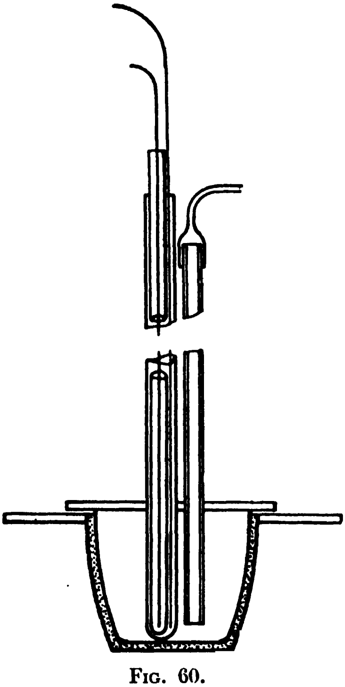

FIG. 60.

Oils of low asphalt content and lignite tar oils leave no residue when heated below their ignition point, but asphaltic petroleum oils, coal-tar oils, and tars leave a cokey residue. The results obtained by using nickel and platinum crucibles were found to agree closely, but porcelain crucibles yielded higher values. The temperatures were 50° to 100° C. lower when oxygen was employed than with air. Constam and Schläpfer claimed that their results have an experimental error of not greater than ±30° C.

The results of Holm and Constam and Schläpfer are in fairly close agreement for such fuels as were examined by both methods, as is shown in the following summary :—

TEMPERATURE OF SPONTANEOUS IGNITION.

	By Holm (in Oxygen).	By Constam and Schläpfer.	
		Platinum Crucible in Oxygen.	Platinum Crucible in Air.
Gas oil . .	350	350	400 to 460
Coal-tar oil .	580	550	590 to 650
Coal tar . .	500	480 to 530	600 to 630

The author had occasion some time ago to determine several spontaneous-ignition temperatures, and as no existing apparatus was sufficiently delicate to differentiate between the samples under examination, it was necessary to devise a special instrument for this purpose. This instrument was described in a paper read before the Society of Chemical Industry,[1] from which the following description is extracted :—

> " The instrument consists of a diffusion block of 4 in. diameter mild steel bar 3¼ in. deep, the base of which has been turned in order to afford a greater heating surface. The upper end of the bar has been machined so as to fit exactly the platinum crucible used for the estimation of the coking values of oils (dimensions : upper diameter, 35 mm. ; diameter of base, 22 mm. ; height, 37 mm.).
>
> " A screwed-on cover protects the upper end of the crucible from draughts. This cover is provided with two holes, one for the admission of oxygen or air, the other being the oil inlet. The oxygen or air is preheated to the temperature of the experiment by passing through a thin copper coil situated in a chamber inside the block. A thermometer and a thermocouple pyrometer are fitted into the diffusion block as close as possible to the base of the platinum crucible, and serve to show the temperature of the experiment."

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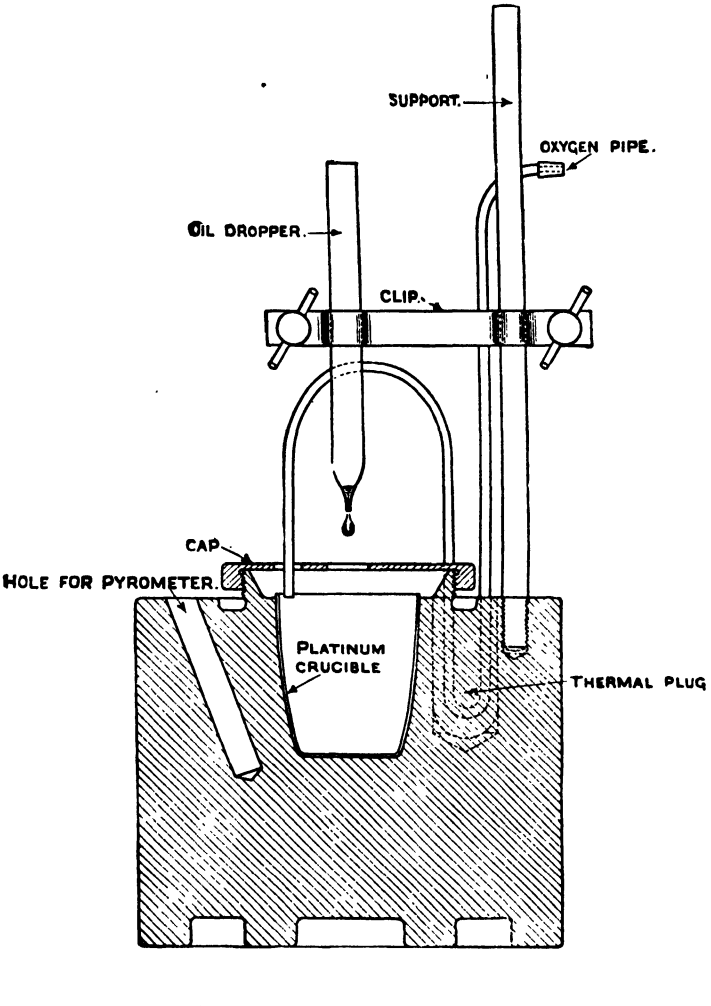
[1] *J.S.C.I.*, 15th February 1917, p. 109.

Method of Operation.—The block is heated to a given temperature, and if oxygen is being used, this is passed through the apparatus at a rate of three bubbles per second. The quantity of oxygen is observed by means of a wash bottle containing sulphuric acid (concentrated), which also serves to dry the gas. When the temperature of the block is constant at a desired temperature, one drop of the fuel under examination is allowed to fall through the hole in the centre of the cover of the instrument. If the temperature is much higher than the ignition point, a sharp



APPARATUS FOR TESTING IGNITION POINT.

FIG. 61.

explosion will occur almost immediately ; if below the ignition point no explosion takes place. When only slightly above the temperature of ignition, the explosion follows some ten to twelve seconds after the introduction of the oil. By repeating the experiments, the lowest temperature at which ignition takes place is rapidly determined. This temperature is the temperature of spontaneous ignition. The results obtained by different operators using the same apparatus agree to within 3° C.

A similar procedure, using air instead of oxygen, will give the ignition temperature in air, but in this case the explosion is much less violent and always follows one second after the introduction of the oil.

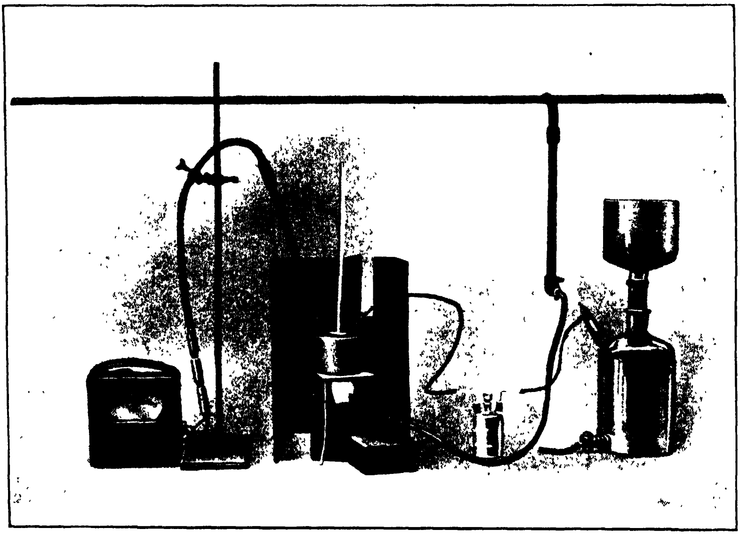


Fig. 62.

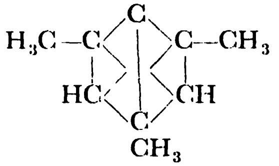
The construction of the original instrument is clearly seen from the accompanying drawing (Fig. 61). The arrangement of the instrument, with gas burner, thermocouple pyrometer, thermometer, oxygen container, and wash bottle, together with screen to protect the instrument from draughts, is shown in the illustration (Fig. 62). An improved type of this instrument is now marketed, the difference between this and the original form consisting in a reduction of the size of the crucible, as some trouble was experienced owing to the violence of the explosion in the larger sized crucible ; also, the thermometer pocket is deepened by drilling the hole obliquely past the side of the crucible.

The author considers that it would be advisable to adopt oxygen ignition temperatures as standard, as the results are more reliable and the determinations are clearer and more convenient.

Another type of spontaneous-ignition point apparatus is described in A.S.T.M., Serial Designation D. 286-30. This consists of a glass flask of standard dimensions, immersed to a certain depth in a molten metal bath. The temperature-recording device consists of a calibrated thermocouple, and the igniting atmosphere is simply the air contained in the flask. The fuel is admitted by means of a pipette drawn out to a very narrow diameter bore. The spontaneous-ignition temperature is the lowest temperature at which a gentle explosion occurs.

It is recommended that any ignition point apparatus should be calibrated by means of a reference fuel, and one which has been suggested is hexahydronaphthalene plus a percentage of ethyl nitrate to produce a standard value.[1]

Broeze [2] has selected cetene ($C_{16}H_{32}$), $CH_3—(CH_2)_{13}—CH\ .\ CH_2$, specific gravity 0·788, boiling point 274° C., as a standard of low spontaneous-ignition temperature, or, as he describes it, of high ignition quality when referring to it as a Diesel-engine fuel. Mesitylene (C_9H_{12}), specific gravity 0·863, boiling point 164·6° C.,



is suggested as a standard of high spontaneous-ignition temperature, or, in other words, of low ignition quality.

As the theoretical and practical efficiencies of engines operating on both the constant-volume cycle and the constant-pressure cycle are influenced by the engine compression pressure, the dependence of the compression pressure of the engine upon the ignition temperature of the fuel makes the ignition-point test one of the most important in the analysis of liquid fuels, especially fuels to be used in Diesel and semi-Diesel engines. Coupled with the necessity to know the temperature of spontaneous ignition is that of knowing also the " delay " period existing between the first injection of the fuel and its subsequent ignition in the combustion chamber of an engine. A very interesting attempt has been made to obtain data relating to the delay periods of fuels by means of the R.A.E. Spontaneous-ignition Temperature Apparatus, as described by Foord.[3] The apparatus, which is rather complicated in design, consists of (*a*) an electrically heated explosion vessel, (*b*) a fuel-injection system, (*c*) an ignition-timing mechanism, (*d*) an explosion-timing mechanism, (*e*) an electrical recording mechanism

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[1] Foord, *J.I.P.T.*, 1932, xviii., p. 547.
[2] *J.I.P.T.*, 1932, xviii., p. 570.
[3] Foord, *J.I.P.T.*, 1932, xviii., p. 535.

for indicating the ignition delay, and (*f*) a thermocouple for indicating the temperature of the air.

Method of Operation.—The temperature of the vessel having been raised to the highest point which it is desired to investigate, the current is cut off and sufficient time allowed for temperature conditions to become stable. A charge of cold air is then drawn into the vessel by means of a vacuum pump, the scavenging and circulation of the air being assisted by means of the tangentially offset induction port. Sufficient time is then allowed to elapse for the air temperature, as read on a calibrated thermocouple, to reach a maximum and commence to fall off. The fuel is then injected by means of the retractable injector nozzle, the time of ignition and of the subsequent explosion being recorded electrically on the paper strip, the time reading being estimated by means of the tuning-fork device. The temperature and the time-lag between injection and ignition are noted on the record, and a further test carried out at a lower temperature, the products of combustion being first drawn away by means of the vacuum pump.

CALORIMETRY.—As the work obtainable from any fuel is dependent on the amount of heat liberated by its combustion, the determination of the quantity of heat yielded by a unit weight of fuel is of fundamental importance. The measure of heat obtained from the combustion of a fuel is called the calorific power, or calorific value. This is an entirely different value from the calorific intensity, which is the maximum temperature obtainable by the combustion of a fuel.

The quantity of heat is expressed in terms of two units, the calorie and the British Thermal Unit. The calorie is the amount of heat required to raise 1 gm. of water 1° C. (though this quantity varies slightly at different temperatures, no standard temperature has been adopted). Callender determined the specific heat of water between 0° C. and 100° C. The specific heat (taken on a basis of 1·000 at 20° C.) was found to exceed 1·010 at 0° C., to fall to a minimum at 40° C., and to rise to 1·007 at 100° C. The Calorie (spelt with a capital C) is 1,000 cals.

The British Thermal Unit (B.Th.U.) is the amount of heat required to raise 1 lb. of water 1° F., from 60° to 61° F. When measuring the heat given by burning a fuel, either the number of calories given by the combustion of 1 gm. or the number of B.Th.U. given by 1 lb. of the fuel is employed. One kilogram is approximately 2·2 lbs., and 1° C. is $\frac{9}{5}$ of 1° F., therefore 1 Cal. is $\frac{9}{5} \times 2{\cdot}2 = 3{\cdot}96$ B.Th.U. One calorie is 0·003968 B.Th.U. One B.Th.U.=0·252 Cal., or 252 cals.

When the calorific power of a fuel is stated in calories, it is assumed that 1 gm. of fuel has been taken, whereas, when the value is stated in B.Th.U., it is understood that the heat is evolved by

1 lb. of fuel ; the relationship, therefore, between calories and British Thermal Units, when stating the calorific value of a fuel, is the relationship between the Fahrenheit and centigrade scales. Suppose that an oil has a calorific value of 10,000 cals., this means that the combustion of 1 gm. of oil will raise the temperature of 10,000 gm. of water 1° C. It is evident that the combustion of 1 lb. of this oil would raise 10,000 lbs. of water 1° C., and, as 1° C. is equal to 1·8° F., the heat yielded would be $1{\cdot}8 \times 10{,}000 = 18{,}000$ B.Th.U., or nine-fifths the number of calories. From this it will be seen that when referring to the calorific value of a fuel,

$$1 \text{ cal.} = 1{\cdot}8 \text{ B.Th.U.}$$
$$\text{and } 1 \text{ B.Th.U.} = \tfrac{5}{9} \text{ cal.}$$

The approximate calorific power of a fuel may be determined either by calculation from the ultimate analysis of the fuel or accurately by actual determination, *i.e.*, by combustion in a calorimeter. With certain types of fuel oils (American) a very close estimation can be obtained by means of a formula, such as :—

$$\text{British Thermal Units} = 40 \times (\text{degrees A.P.I.} - 10) + 18{,}320.$$

The Calculation of Calorific Power.—The elements found in appreciable quantities in fuels are carbon, hydrogen, sulphur ; oxygen and nitrogen are usually present but only in small quantities. Some fuels contain incombustible matter (*i.e.*, those yielding an ash content contain traces of other elements such as iron, vanadium, etc.), but it may be assumed that this will not affect the heat value of the fuel.

The combustible elements on burning undergo chemical changes. The final products, if the combustion be complete, are indicated by the following equations :—

$$\begin{aligned}
C + O_2 &= CO_2 && \text{(carbon dioxide)} \\
\text{or } 2C + O_2 &= 2CO && \text{(carbon monoxide),} \\
\text{and } 2CO + O_2 &= 2CO_2 && \text{(carbon dioxide),} \\
2H_2 + O_2 &= 2H_2O && \text{(water),} \\
S + O_2 &= SO_2 && \text{(sulphur dioxide),} \\
\text{and sometimes}\quad 2S + 3O_2 &= 2SO_3 && \text{(sulphur trioxide).}
\end{aligned}$$

Any oxygen and nitrogen present may be assumed to leave the combustion space without combining.

These chemical changes are accompanied by an evolution of heat, in the following amounts :—

1 gm. carbon burns to CO_2, evolving 8,137 cals.
1 gm. hydrogen burns to H_2O (in liquid form), evolving 34,500 cals.
1 gm. sulphur burns to SO_2, evolving 2,200 cals.
1 gm. sulphur burns to SO_3, evolving 3,300 cals.

As sulphur generally burns with the formation of both sulphur dioxide and sulphur trioxide, it is common to consider the calorific value of sulphur as 2,500 cals.

If only carbon, hydrogen, and sulphur were present, one should therefore use the formula :—

$$\text{Calorific power}=\frac{(C\times 8137)+(H\times 34500)+(S\times 2500)}{100},$$

where C, H, and S are the percentages of carbon, hydrogen and sulphur respectively in the fuel. When oxygen is present it is found that the heat value is lowered, and it is most satisfactory to assume that the oxygen is present in combination with the hydrogen (as water). Hydrogen combines with eight times its weight of oxygen to form water, therefore one-eighth of the oxygen content of the fuel must be deducted from the hydrogen content before the heat value is calculated. Thus :—

$$\text{Calorific power}=\frac{C\ 8137+\left(H-\frac{O}{8}\right)34500+S\ 2500}{100}.$$

In an internal-combustion engine the water leaves the engine in the form of steam, whereas the above formula is based on the assumption that the water is condensed. A deduction must therefore be made from the above formula as a correction for the latent heat taken away by the water formed during the reaction. The lower heat value obtained after this deduction is known as the net calorific value. The latent heat amounts to approximately 600 cals. per gm. of water, or 54 cals. for each per cent. of hydrogen present in the original fuel.

$$\text{Net Calorific Value}=\text{Gross Calorific Value}-54\ H.$$

The hydrogen content of light petroleum products (petrol) is about 14 per cent., therefore there is 54×14=756 cals. difference between the gross and net calorific values. Similarly, with heavy petroleum oil there is about 658 cals., but with tar oils only about 324 cals. difference between the gross and net calorific values.

It should be clearly understood that the foregoing formulæ make no allowance for the heat changes which have taken place in the formation of the compounds present in the fuel from their elements, and on this account the calculated calorific values are never very reliable; instances have been met where the error between calculated and actually determined calorific values amounted to 3 per cent.

The errors introduced in the combustion process (the ultimate analysis) are considerable, and are multiplied in the calculation of calorific value. The experimental determination of calorific value is more rapid, easier, and more accurate than the process of obtaining them from the ultimate analysis. For technical purposes it is not generally necessary to make an ultimate analysis, therefore the direct determination by means of a calorimeter is in all respects preferable. Calculations of calorific value are seldom made where a good calorimeter is available, but are frequently made to serve in laboratories which possess no calorimeter.

It is often considered desirable to make an allowance for the quantity of water contained in the original fuel, the adjusted calorific value thus being reported as calorific value (gross) dry basis.

This adjustment simply refers to the water present as such in the original oil, and has nothing to do with the water formed by the combustion of the fuel.

Experimental Determination of Calorific Value.—The experimental determination of calorific value is made by means of a calorimeter, which is an instrument in which a small quantity of the fuel is burnt, the heat evolved being measured. Calorimeters may be divided into three classes, depending upon the means which are employed for supplying to the fuel the oxygen necessary for combustion :—

1. Calorimeters employing oxygen at approximately atmospheric pressure.
2. Calorimeters in which a solid oxidising agent is employed (*e.g.*, sodium peroxide).
3. Calorimeters in which the combustion takes place in high-pressure oxygen (bomb calorimeters).

Gas calorimeters are not included in the above classes.

Bomb calorimeters are the only suitable type for use with liquid fuels. The original bomb calorimeter was devised by Berthelot, and has since undergone many modifications. There are several calorimeters at present on the market, and as the majority of these instruments only differ in detail, it will not be necessary to describe more than one example, the Mahler-Cook bomb, which the author uses for liquid-fuel determinations. For more detailed information on the subject, treatises on calorimetry should be consulted.[1]

The bomb calorimeter consists of a steel vessel, capable of withstanding 200-atmosphere pressure, lined either with platinum (which is the most satisfactory but most expensive lining) or with enamel. The vessel is provided with a cover, so attached as to make a perfectly tight joint when in use. The cover contains one or two passages leading to the inside of the bomb, each controlled by conical-seated valves. Two electric terminals (one insulated

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[1] Coste and Andrews, "Examination and Thermal Value of Fuels, Gaseous, Liquid, and Solid."

from the bomb) pass through the cover, both being so constructed as to withstand high pressures without leakage. These terminals conduct an electric current which serves to fuse inside the bomb a thin wire so that the oil is ignited when necessary. The bomb is enclosed in a light metal vessel of about 3-litre capacity, which, during the experiment, contains a weighed quantity of water. It is polished on the outer side to minimise radiation losses.

The water container rests on insulating supports, and is separated from the outer jacket by an air space. The outer jacket is either made of insulating material, or better, it may be a metal jacket filled with water and covered with insulating matter on the outside. The upper portion of the apparatus is provided with a cover through which passes a stirring gear, used to agitate gently the water in the container during experiments. Through this cover are passed the electric leads and a Beckmann thermometer which registers the temperature of the water in contact with the bomb.

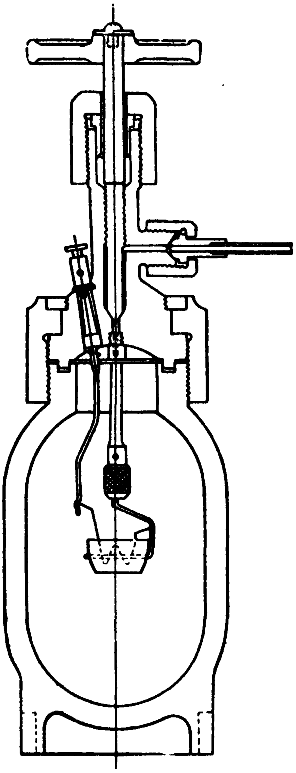


FIG. 63.—Section through Bomb of Cook-Mahler Bomb Calorimeter.

In the accompanying diagram (Fig. 63) is shown a section of the Mahler-Cook bomb. Fig. 64 shows a section of container and jacket with bomb in position.

Water Equivalent of the Calorimeter.—For the calculation of results of a calorimeter determination, it is necessary to know the water equivalent of the instrument, since the total heat evolved is distributed through the apparatus as well as through the water. This amount of heat, which is known as the " water equivalent," is the amount of heat necessary to raise the apparatus 1° C. This value may be obtained either by weighing the various parts of the apparatus which undergo a change of temperature during the determination and calculating their water equivalent from the specific heats of the metals of which these parts are made, or preferably by means of a calorimeter determination, using a standard material of known calorific value. The standard used may comprise a pure chemical compound having recognised calorific value, such as benzoic acid, 6,330 cals. per gm.

It is recommended that the use of naphthalene for this purpose should be discontinued because of the possibility of sublimation, with subsequent loss of heat units due to incomplete combustion.

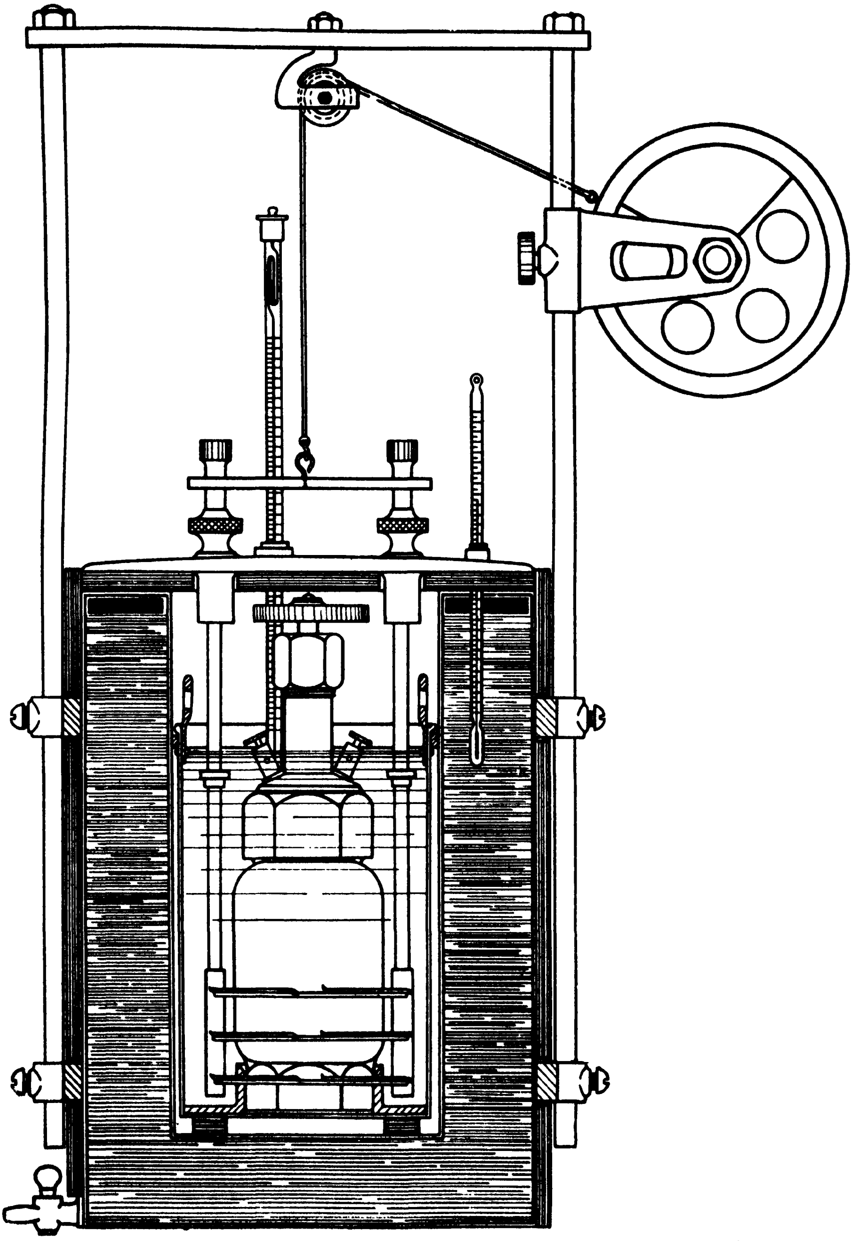


FIG. 64.—Section through Jacket and Container of Cook-Mahler Bomb, showing Bomb and Stirring Gear in Position.

The use of cane sugar for this purpose should also be discontinued.

It is now possible to purchase samples of specially prepared medicinal paraffin with a guaranteed calorific value, for example, from Kahlbaum & Co., Germany. The use of this material as a means for determination of water equivalents and as a check of the accuracy of calorimeters is gradually becoming general practice. A liquid standard such as this is certainly an improvement over the solid standards ; it is easier to handle, and there is greater assurance of its complete combustion.

The practical details of the method of determination of water equivalent are the same as for the determination of calorific value of a fuel oil, the difference in procedure being in the calculations. In the former determination the calorific value of material burnt is known, whereas in the latter experiment the calorific value is being sought. An example of an actual determination of a water equivalent, using a specimen of Kahlbaum paraffin with guaranteed calorific value of 10,992 cals. per gm., is as follows :—

Quantity of standard taken (Kahlbaum paraffin) = 0·8181 gm.
Quantity of water in calorimeter = 2,500·0 „
Quantity of filter paper taken to assist combustion } = 0·0092 „
Filter paper = 4,190 cals. per gm. }
Corrected rise in temperature of water in calorimeter = 2·831

Therefore, from the oil one has 10,992 × 0·8181 = 8,997·0 cals.
And from the paper one has 4,190 × 0·0092 = 38·5 „

9,035·5 „

The heat absorbed by the water = 2,500 × 2·831 = 7,078·0 „
The heat absorbed by apparatus = 9,035 × 7,078 = 1,957·0 „

And therefore the water equivalent of apparatus $= \frac{1{,}957\cdot0}{2\cdot831} = 691.$

Calorific Value (Gross), I.P.T., Serial Designation F.O. 6.—The calorific value shall be determined in a suitable type of bomb calorimeter, permitting the use of oxygen at filling pressures up to 30 atmospheres by the gauge.

The centigrade thermometer employed must be clearly graduated either in one-hundredth of a degree or to every one-fiftieth of a degree, with the graduations sufficiently spaced to allow of estimating the readings to one-hundredth of a degree.

A suitable thermometer would have a range of from 12° to 30° C., graduated in one-fiftieth of a degree and readable by estimation to one-hundredth of a degree, with the lowest graduation 75 to 80 mm. above the top of the bulb, the total length being about 65 cm. The thermometer shall be graduated for approximately 12 cm. immersion. It is desirable that calorimeter thermometers shall be specially tested at the National Physical Laboratory, and certificates, with the corrections as necessary, are issued.

The ignition wire should be of fine platinum, a suitable diameter being 0·15 mm., but if iron wire has to be employed, its weight must be known and allowance must be made for the heat of combustion.

Ten millilitres of distilled water shall be measured into the bomb before the water equivalent is determined, and in all subsequent estimations a like quantity of distilled water shall be employed in the bomb. The use of this water in the bomb is not absolutely necessary in determining the calorific value, but since the determination of the sulphur in a sample involves the " bomb washings " which can be available after determining the calorific value, if the 10 ml. of water have been added in order to absorb the sulphur trioxide formed, hence it is always advisable to standardise with this quantity of water in the bomb and make all determinations under like conditions.

Method.—Not more than 1 gm. of oil shall be employed. The requisite quantity of water (in grams) for the calorimeter shall be weighed out. The water should be at room temperature. A sufficient quantity of water, for duplicate determinations at least, shall be left in the laboratory near the instrument, so that it shall be at room temperature when the determinations are to be made.

Ten millilitres of distilled water shall be measured into the bomb. A small strip of filter paper or blotting paper 4 to 5 mm. wide shall be employed for the ignition. It should be sufficiently long, so that when folded in both ends shall dip into the oil when the strip of paper is laid over the firing wire. The weight of this paper shall be accurately determined. The bomb shall be charged with oxygen to a pressure of not less than 25 atmospheres. After firing, readings of the thermometer shall be taken every half-minute from the time of firing until not less than twelve half-minute readings from the time of reading the maximum temperature have been taken. The rate of loss by radiation during the experiment shall be deduced from the average of the last ten of these readings.

Calculation and Expression of Calorific Value.—Corrections shall be applied for :—

(*a*) Losses by radiation.
(*b*) The heat due to ignition paper.
(*c*) The heat of combustion of the iron firing wire, if used.

No correction is to be made for nitric acid or sulphuric acid formed.

(*a*) Loss by radiation. To the observed rise in temperature add : For each half-minute period during the rise when the mean temperature for the period does not differ by more than 0·5° C. from the maximum temperature, apply the full half-minute radiation correction as determined during the cooling period. When the mean temperature for a given half-minute is lower by more than 0·5° C. than the maximum, then for each such half-minute period the radiation loss shall be calculated as directly proportional to the mean difference of temperature, *e.g.*, the rate of loss per half-minute when the water in the calorimeter is 2·8° C. above the initial temperature—*i.e.*, is at its maximum—was found to be 0·005° C. The mean temperature of the first half-minute was 1·4° C. below the final temperature. The correction for this first half-minute will be :—

$$\frac{1{\cdot}4}{2{\cdot}8} \times 0{\cdot}005 = 0{\cdot}0025.$$

The total radiation correction to be added to the observed rise will be the sum of the individual half-minute corrections up to the time for the maximum reading of the thermometer. From the weight of water in the calorimeter, plus the water equivalent, and from the corrected rise of temperature, the total calories shall be calculated.

(*b*) From this value deduct the calories due to the ignition paper, the calorific value for which is to be taken as 4,190 cals. per gram.

(*c*) If iron firing wire is used, a further deduction for its heat of combustion as 1,600 cals. per gram shall be made. The calories due to the oil alone shall then be calculated and expressed as calories per gram.

Results should also be expressed as British Thermal Units per pound (B.Th.U.), this value being 1·8 times the calories per gram.

APPENDIX

GRAPHS, CHARTS, AND TABLES

TEN YEARS' IMPORTS AND THEIR TOTAL VALUE

	Motor Spirit.	Kerosene.	Lubricating Oil.	Gas Oil.	Fuel Oil.	Crude Oil.	Total (including " Other Sorts ").	Value Sterling.
	Gals.	Gals.	Gals.	Gals.	Gals.	Gals.	Gals.	£
1924 . .	422,310,541	124,678,042	101,746,917	67,084,264	385,581,996	465,184,604	1,570,910,891	41,424,417
1925 . .	404,834,226	141,649,425	84,361,784	72,652,528	334,489,850	569,082,169	1,613,301,365	39,512,451
1926 . .	562,092,941	210,950,966	91,816,039	117,832,968	398,693,254	537,444,340	1,913,102,805	46,799,910
1927 . .	538,306,590	214,276,347	91,592,581	96,003,390	439,421,056	664,799,827	2,051,130,323	43,314,953
1928 . .	734,737,509	189,763,214	105,429,311	117,976,698	450,876,134	498,001,683	2,112,760,672	39,253,603
1929 . .	810,084,428	255,032,820	98,018,113	113,941,234	405,610,933	487,348,477	2,195,348,366	43,392,774
1930 . .	954,609,176	245,792,441	101,937,815	130,822,853	491,089,111	460,968,094	2,403,752,045	46,446,831
1931 . .	905,205,452	270,946,490	97,531,280	85,041,138	485,814,062	344,370,004	2,207,226,948	28,996,606
1932 . .	971,154,877	216,720,695	86,308,444	97,116,670	493,438,269	368,502,111	2,248,813,515	31,201,405
1933 . .	1,076,601,565	185,340,654	103,138,456	114,886,956	570,232,175	391,563,021	2,457,370,421	30,343,084

POUNDS PER GALLON AND SPECIFIC GRAVITIES CORRESPONDING TO DEGREES A.P.I.

Degrees A.P.I.	TENTHS OF DEGREES									
	0	1	2	3	4	5	6	7	8	9
10	8.328	8.322	8.317	8.311	8.305	8.299	8.293	8.287	8.282	8.276
	1.0000	.9993	.9986	.9979	.9972	.9965	.9958	.9951	.9944	.9937
11	8.270	8.264	8.258	8.252	8.246	8.241	8.235	8.229	8.223	8.218
	.9930	.9923	.9916	.9909	.9902	.9895	.9888	.9881	.9874	.9868
12	8.212	8.206	8.201	8.195	8.189	8.183	8.178	8.172	8.166	8.161
	.9861	.9854	.9847	.9840	.9833	.9826	.9820	.9813	.9806	.9799
13	8.155	8.150	8.144	8.138	8.132	8.127	8.122	8.116	8.110	8.105
	.9792	.9786	.9779	.9772	.9765	.9759	.9752	.9745	.9738	.9732
14	8.099	8.093	8.088	8.082	8.076	8.071	8.066	8.061	8.055	8.049
	.9725	.9718	.9712	.9705	.9698	.9692	.9685	.9679	.9672	.9665
15	8.044	8.038	8.033	8.027	8.021	8.016	8.011	8.006	8.000	7.995
	.9659	.9652	.9646	.9639	.9632	.9626	.9619	.9613	.9606	.9600
16	7.989	7.984	7.978	7.973	7.967	7.962	7.956	7.951	7.946	7.940
	.9593	.9587	.9580	.9574	.9567	.9561	.9554	.9548	.9541	.9535
17	7.935	7.930	7.925	7.919	7.914	7.909	7.903	7.898	7.893	7.887
	.9529	.9522	.9516	.9509	.9503	.9497	.9490	.9484	.9478	.9471
18	7.882	7.877	7.871	7.866	7.861	7.856	7.851	7.846	7.841	7.835
	.9465	.9459	.9452	.9446	.9440	.9433	.9427	.9421	.9415	.9408
19	7.830	7.825	7.820	7.814	7.809	7.804	7.799	7.793	7.788	7.783
	.9402	.9396	.9390	.9383	.9377	.9371	.9365	.9358	.9352	.9346
20	7.778	7.773	7.768	7.762	7.757	7.752	7.747	7.742	7.737	7.732
	.9340	.9334	.9328	.9321	.9315	.9309	.9303	.9297	.9291	.9285
21	7.727	7.722	7.717	7.711	7.706	7.701	7.696	7.691	7.686	7.681
	.9279	.9273	.9267	.9260	.9254	.9248	.9242	.9236	.9230	.9224
22	7.676	7.671	7.666	7.661	7.656	7.651	7.646	7.641	7.636	7.632
	.9218	.9212	.9206	.9200	.9194	.9188	.9182	.9176	.9170	.9165
23	7.627	7.622	7.617	7.612	7.607	7.602	7.597	7.592	7.587	7.583
	.9159	.9153	.9147	.9141	.9135	.9129	.9123	.9117	.9111	.9106
24	7.578	7.573	7.568	7.563	7.558	7.554	7.549	7.544	7.539	7.534
	.9100	.9094	.9088	.9082	.9076	.9071	.9065	.9059	.9053	.9047
25	7.529	7.524	7.519	7.514	7.509	7.505	7.500	7.495	7.491	7.486
	.9042	.9036	.9030	.9024	.9018	.9013	.9007	.9001	.8996	.8990
26	7.481	7.476	7.472	7.467	7.462	7.458	7.453	7.448	7.443	7.438
	.8984	.8978	.8973	.8967	.8961	.8956	.8950	.8944	.8939	.8933
27	7.434	7.429	7.424	7.420	7.415	7.410	7.406	7.401	7.397	7.392
	.8927	.8922	.8916	.8911	.8905	.8899	.8894	.8888	.8883	.8877
28	7.387	7.383	7.378	7.373	7.368	7.364	7.360	7.355	7.351	7.346
	.8871	.8866	.8860	.8855	.8849	.8844	.8838	.8833	.8827	.8822
29	7.341	7.337	7.332	7.328	7.323	7.318	7.314	7.309	7.305	7.300
	.8816	.8811	.8805	.8800	.8794	.8789	.8783	.8778	.8772	.8767
30	7.296	7.291	7.287	7.282	7.278	7.273	7.268	7.264	7.259	7.255
	.8762	.8756	.8751	.8745	.8740	.8735	.8729	.8724	.8718	.8713
31	7.251	7.246	7.242	7.238	7.233	7.228	7.224	7.219	7.215	7.211
	.8708	.8702	.8697	.8692	.8686	.8681	.8676	.8670	.8665	.8660
32	7.206	7.202	7.198	7.193	7.188	7.184	7.180	7.176	7.171	7.167
	.8654	.8649	.8644	.8639	.8633	.8628	.8623	.8618	.8612	.8607
33	7.163	7.158	7.153	7.149	7.145	7.141	7.137	7.132	7.128	7.123
	.8602	.8597	.8591	.8586	.8581	.8576	.8571	.8565	.8560	.8555
34	7.119	7.115	7.111	7.106	7.102	7.098	7.093	7.089	7.085	7.081
	.8550	.8545	.8540	.8534	.8529	.8524	.8519	.8514	.8509	.8504
35	7.076	7.072	7.068	7.063	7.059	7.055	7.051	7.047	7.042	7.038
	.8498	.8493	.8488	.8483	.8478	.8473	.8468	.8463	.8458	.8453

Degrees A.P.I.	TENTHS OF DEGREES									
	0	1	2	3	4	5	6	7	8	9
36	7.034 .8448	7.030 .8443	7.026 .8438	7.022 .8433	7.018 .8428	7.013 .8423	7.009 .8418	7.005 .8413	7.001 .8408	6.997 .8403
37	6.993 .8398	6.989 .8393	6.985 .8388	6.980 .8383	6.976 .8378	6.972 .8373	6.968 .8368	6.964 .8363	6.960 .8358	6.955 .8353
38	6.951 .8348	6.947 .8343	6.943 .8338	6.939 .8333	6.935 .8328	6.930 .8324	6.926 .8319	6.922 .8314	6.918 .8309	6.914 .8304
39	6.910 .8299	6.906 .8294	6.902 .8289	6.898 .8285	6.894 .8280	6.890 .8275	6.886 .8270	6.882 .8265	6.878 .8260	6.874 .8256
40	6.870 .8251	6.866 .8246	6.862 .8241	6.858 .8236	6.854 .8232	6.850 .8227	6.846 .8222	6.842 .8217	6.838 .8212	6.834 .8208
41	6.830 .8203	6.826 .8198	6.822 .8193	6.818 .8189	6.814 .8184	6.810 .8179	6.806 .8174	6.802 .8170	6.798 .8165	6.794 .8160
42	6.790 .8155	6.786 .8151	6.782 .8146	6.779 .8142	6.775 .8137	6.771 .8132	6.767 .8128	6.763 .8123	6.759 .8118	6.756 .8114
43	6.752 .8109	6.748 .8104	6.744 .8100	6.740 .8095	6.736 .8090	6.732 .8086	6.728 .8081	6.724 .8076	6.720 .8072	6.716 .8067
44	6.713 .8063	6.709 .8058	6.705 .8054	6.701 .8049	6.697 .8044	6.694 .8040	6.690 .8035	6.686 .8031	6.682 .8026	6.679 .8022
45	6.675 .8017	6.671 .8012	6.667 .8008	6.663 .8003	6.660 .7999	6.656 .7994	6.652 .7990	6.648 .7985	6.645 .7981	6.641 .7976
46	6.637 .7972	6.633 .7967	6.630 .7963	6.626 .7958	6.622 .7954	6.618 .7949	6.615 .7945	6.611 .7941	6.607 .7936	6.604 .7932
47	6.600 .7927	6.596 .7923	6.592 .7918	6.589 .7914	6.585 .7909	6.582 .7905	6.578 .7901	6.574 .7896	6.571 .7892	6.567 .7887
48	6.563 .7883	6.560 .7879	6.556 .7874	6.552 .7870	6.548 .7865	6.545 .7861	6.541 .7857	6.537 .7852	6.534 .7848	6.530 .7844
49	6.526 .7839	6.523 .7835	6.520 .7831	6.516 .7826	6.512 .7822	6.509 .7818	6.505 .7813	6.501 .7809	6.498 .7805	6.494 .7800
50	6.490 .7796	6.487 .7792	6.484 .7788	6.480 .7783	6.476 .7779	6.473 .7775	6.469 .7770	6.466 .7766	6.462 .7762	6.459 .7758
51	6.455 .7753	6.451 .7749	6.448 .7745	6.445 .7741	6.441 .7736	6.437 .7732	6.434 .7728	6.430 .7724	6.427 .7720	6.423 .7715
52	6.420 .7711	6.416 .7707	6.413 .7703	6.410 .7699	6.406 .7694	6.402 .7690	6.399 .7686	6.396 .7682	6.392 .7678	6.389 .7674
53	6.385 .7669	6.381 .7665	6.378 .7661	6.375 .7657	6.371 .7653	6.368 .7649	6.365 .7645	6.361 .7640	6.357 .7636	6.354 .7632
54	6.350 .7628	6.347 .7624	6.344 .7620	6.340 .7616	6.337 .7612	6.334 .7608	6.330 .7603	6.326 .7599	6.323 .7595	6.320 .7591
55	6.316 .7587	6.313 .7583	6.310 .7579	6.306 .7575	6.303 .7571	6.300 .7567	6.296 .7563	6.293 .7559	6.290 .7555	6.287 .7551
56	6.283 .7547	6.280 .7543	6.276 .7539	6.273 .7535	6.270 .7531	6.266 .7527	6.263 .7523	6.259 .7519	6.256 .7515	6.253 .7511
57	6.249 .7507	6.246 .7503	6.243 .7499	6.240 .7495	6.236 .7491	6.233 .7487	6.229 .7483	6.226 .7479	6.223 .7475	6.219 .7471
58	6.216 .7467	6.213 .7463	6.209 .7459	6.206 .7455	6.203 .7451	6.199 .7447	6.196 .7443	6.193 .7440	6.190 .7436	6.187 .7432
59	6.184 .7428	6.180 .7424	6.177 .7420	6.174 .7416	6.170 .7412	6.167 .7408	6.164 .7405	6.161 .7401	6.158 .7397	6.154 .7393
60	6 151 .7389	6.148 .7385	6.144 .7381	6.141 .7377	6.138 .7374	6.135 .7370	6.132 .7366	6.129 .7362	6.125 .7358	6.122 .7354

Degrees A. P. I.	TENTHS OF DEGREES									
	0	1	2	3	4	5	6	7	8	9
61	6.119 .7351	6.116 .7347	6.113 .7343	6.109 .7339	6.106 .7335	6.103 .7332	6.100 .7328	6.097 .7324	6.094 .7320	6.090 .7316
62	6.087 .7313	6.084 .7309	6.081 .7305	6.078 .7301	6.075 .7298	6.072 .7294	6.068 .7290	6.065 .7286	6.062 .7283	6.059 .7279
63	6.056 .7275	6.053 .7271	6.050 .7268	6.047 .7264	6.044 .7260	6.040 .7256	6.037 .7253	6.034 .7249	6.031 .7245	6.028 .7242
64	6.025 .7238	6.022 .7234	6.019 .7230	6.016 .7227	6.013 .7223	6.010 .7219	6.007 .7216	6.004 .7212	6.000 .7208	5.997 .7205
65	5.994 .7201	5.991 .7197	5.988 .7194	5.985 .7190	5.982 .7186	5.979 .7183	5.976 .7179	5.973 .7175	5.970 .7172	5.967 .7168
66	5.964 .7165	5.961 .7161	5.958 .7157	5.955 .7154	5.952 .7150	5.949 .7146	5.946 .7143	5.943 .7139	5.940 .7136	5.937 .7132
67	5.934 .7128	5.931 .7125	5.928 .7121	5.925 .7118	5.922 .7114	5.919 .7111	5.916 .7107	5.913 .7103	5.910 .7100	5.907 .7096
68	5.904 .7093	5.901 .7089	5.898 .7086	5.895 .7082	5.892 .7079	5.889 .7075	5.886 .7071	5.883 .7068	5.880 .7064	5.877 .7061
69	5.874 .7057	5.871 .7054	5.868 .7050	5.866 .7047	5.863 .7043	5.860 .7040	5.857 .7036	5.854 .7033	5.851 .7029	5.848 .7026
70	5.845 .7022	5.842 .7019	5.839 .7015	5.836 .7012	5.833 .7008	5.831 .7005	5.828 .7001	5.825 .6998	5.823 .6995	5.820 .6991
71	5.817 .6988	5.814 .6984	5.811 .6981	5.808 .6977	5.805 .6974	5.802 .6970	5.799 .6967	5.796 .6964	5.793 .6960	5.791 .6957
72	5.788 .6953	5.785 .6950	5.782 .6946	5.779 .6943	5.776 .6940	5.773 .6936	5.771 .6933	5.768 .6929	5.765 .6926	5.762 6923
73	5.759 .6919	5.757 .6916	5.754 .6913	5.751 .6909	5.748 .6906	5.745 .6902	5.743 .6899	5.740 .6896	5.737 .6892	5.734 .6889
74	5.731 .6886	5.728 .6882	5.726 .6879	5.723 .6876	5.720 .6872	5.718 .6869	5.715 .6866	5.712 .6862	5.709 .6859	5.706 .6856
75	5.703 .6852	5.701 .6849	5.698 .6846	5.695 .6842	5.693 .6839	5.690 .6836	5.687 .6832	5.685 .6829	5.682 .6826	5.679 .6823
76	5.676 .6819	5.673 .6816	5.671 .6813	5.668 .6809	5.665 .6806	5.662 .6803	5.660 .6800	5.657 .6796	5.654 .6793	5.652 .6790
77	5.649 .6787	5.646 .6783	5.643 .6780	5.641 .6777	5.638 .6774	5.635 .6770	5.632 .6767	5.630 .6764	5.627 .6761	5.624 .6757
78	5.622 .6754	5.619 .6751	5.617 .6748	5.614 .6745	5.611 .6741	5.608 .6738	5.606 .6735	5.603 .6732	5.600 .6728	5.598 .6725
79	5.595 .6722	5.592 .6719	5.590 .6716	5.587 .6713	5.584 .6709	5.582 .6706	5.579 .6703	5.577 .6700	5.574 .6697	5.571 .6693
80	5.568 .6690	5.566 .6687	5.563 .6684	5.561 .6681	5.558 .6678	5.556 .6675	5.553 .6671	5.550 .6668	5.548 .6665	5.545 .6662
81	5.542 .6659	5.540 .6656	5.537 .6653	5.534 .6649	5.532 .6646	5.529 .6643	5.526 .6640	5.524 .6637	5.522 .6634	5.519 .6631
82	5.516 .6628	5.514 .6625	5.511 .6621	5.508 .6618	5.506 .6615	5.503 .6612	5.501 .6609	5.498 .6606	5.496 .6603	5.493 .6600
83	5.491 .6597	5.489 .6594	5.486 .6591	5.483 .6588	5.480 .6584	5.477 .6581	5.475 .6578	5.472 .6575	5.470 .6572	5.467 .6569
84	5.465 .6566	5.462 .6563	5.460 .6560	5.458 .6557	5.455 .6554	5.453 .6551	5.450 .6548	5.448 .6545	5.445 .6542	5.443 .6539
85	5.440 .6536	5.437 .6533	5.435 .6530	5.432 .6527	5.430 .6524	5.427 .6521	5.425 .6518	5.422 .6515	5.420 .6512	5.417 .6509

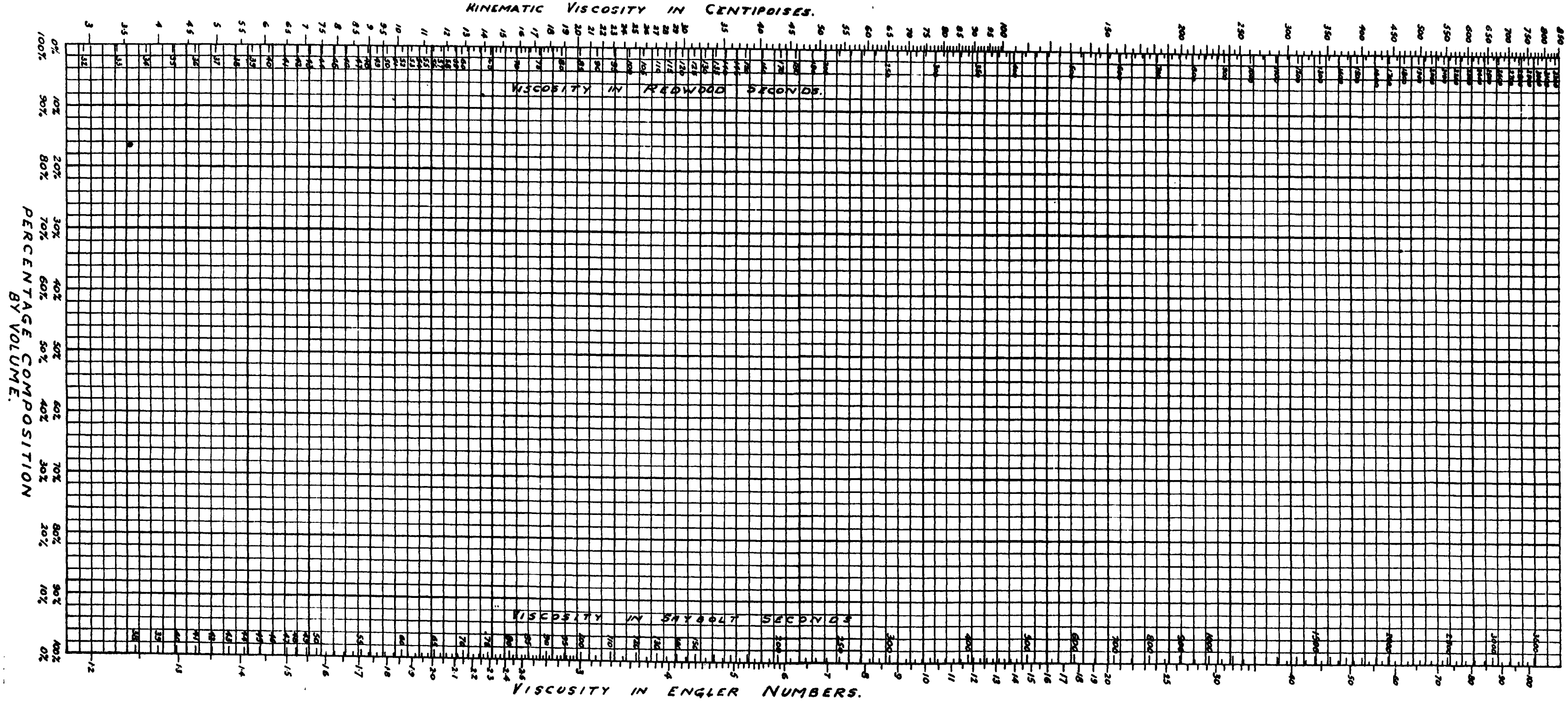
Degrees A. P. I.	TENTHS OF DEGREES									
	0	1	2	3	4	5	6	7	8	9
86	5.415	5.412	5.410	5.407	5.405	5.402	5.400	5.397	5.395	5.392
	.6506	.6503	.6500	.6497	.6494	.6491	.6488	.6485	.6482	.6479
87	5.390	5.387	5.385	5.382	5.380	5.377	5.375	5.372	5.370	5.367
	.6476	.6473	.6470	.6467	.6464	.6461	.6458	.6455	.6452	.6449
88	5.365	5.363	5.361	5.358	5.356	5.353	5.351	5.348	5.346	5.343
	.6446	.6444	.6441	.6438	.6435	.6432	.6429	.6426	.6423	.6420
89	5.341	5.338	5.336	5.334	5.331	5.329	5.326	5.324	5.321	5.319
	.6417	.6414	.6411	.6409	.6406	.6403	.6400	.6397	.6394	.6391
90	5.316	5.314	5.312	5.310	5.307	5.305	5.302	5.300	5.297	5.295
	.6388	.6385	.6382	.6380	.6377	.6374	.6371	.6368	.6365	.6362
91	5.293	5.291	5.288	5.286	5.283	5.281	5.278	5.276	5.274	5.271
	.6360	.6357	.6354	.6351	.6348	.6345	.6342	.6340	.6337	.6334
92	5.269	5.266	5.264	5.262	5.260	5.257	5.254	5.252	5.250	5.248
	.6331	.6328	.6325	.6323	.6320	.6317	.6314	.6311	.6309	.6306
93	5.246	5.243	5.240	5.238	5.236	5.234	5.232	5.229	5.227	5.225
	.6303	.6300	.6297	.6294	.6292	.6289	.6286	.6283	.6281	.6278
94	5.222	5.220	5.217	5.215	5.213	5.210	5.208	5.206	5.204	5.201
	.6275	.6272	.6269	.6267	.6264	.6261	.6258	.6256	.6253	.6250
95	5.199	5.196	5.194	5.192	5.190	5.187	5.185	5.183	5.180	5.179
	.6247	.6244	.6242	.6239	.6236	.6233	.6231	.6228	.6225	.6223
96	5.176	5.174	5.172	5.170	5.167	5.164	5.162	5.160	5.158	5.156
	.6220	.6217	.6214	.6212	.6209	.6206	.6203	.6201	.6198	.6195
97	5.154	5.151	5.149	5.146	5.144	5.142	5.140	5.138	5.136	5.133
	.6193	.6190	.6187	.6184	.6182	.6179	.6176	.6174	.6171	.6168
98	5.131	5.129	5.126	5.124	5.122	5.120	5.118	5.116	5.113	5.111
	.6166	.6163	.6160	.6158	.6155	.6152	.6150	.6147	.6144	.6141
99	5.109	5.107	5.105	5.102	5.100	5.098	5.096	5.093	5.091	5.089
	.6139	.6136	.6134	.6131	.6128	.6126	.6123	.6120	.6118	.6115
100	5.086									
	.6112									

VISCOSITY CONVERSION TABLE FOR REDWOOD, ENGLER, SAYBOLT, AND ABSOLUTE.

Redwood Seconds.	Saybolt Universal Seconds.	Engler Units.	Absolute Centipoises (assuming Specific Gravity 0·900).	Redwood Seconds.	Saybolt Universal Seconds.	Engler Units.	Absolute Centipoises (assuming Specific Gravity 0·900).
30	33·6	1·13	1·87	375	442·5	12·94	87·34
32	36·0	1·20	2·66	400	472·0	13·80	93·22
34	38·4	1·26	3·42	425	501·5	14·66	99·09
36	40·8	1·33	4·14	450	531·0	15·52	104·9
38	43·3	1·40	4·83	475	560·5	16·39	110·8
40	45·6	1·47	5·50	500	590·0	17·25	116·7
42	48·2	1·54	6·15	525	619·5	18·11	122·6
44	50·6	1·61	6·79	550	649·0	18·97	128·4
46	53·0	1·67	7·41	575	678·5	19·84	134·3
48	55·4	1·74	8·02	600	708·0	20·70	140·1
50	57·8	1·81	8·61	625	737·5	21·56	146·0
52	60·2	1·88	9·20	650	767·0	22·42	151·9
54	62·6	1·95	9·78	675	796·5	23·29	157·7
56	65·0	2·01	10·34	700	826·0	24·15	163·6
58	67·3	2·08	10·91	725	855·5	25·01	169·4
60	69·6	2·14	11·47	750	885·0	25·87	175·3
62	71·9	2·21	12·02	775	914·5	26·74	181·1
64	74·5	2·28	12·57	800	944·0	27·60	187·0
66	77·1	2·34	13·10	825	973·5	28·46	192·9
68	79·6	2·41	13·64	850	1003·0	29·32	198·7
70	81·9	2·48	14·17	875	1032·5	30·19	204·6
72	84·2	2·55	14·70	900	1062·0	31·05	210·4
74	86·6	2·62	15·24	925	1091·5	31·91	216·3
76	88·9	2·68	15·75	950	1121·0	32·77	223·1
78	91·3	2·75	16·27	975	1150·5	33·64	228·0
80	93·6	2·82	16·79	1,000	1180·0	34·50	233·8
82	95·9	2·89	17·31	1,025	1209·5	35·36	239·7
84	98·3	2·96	17·83	1,050	1239·0	36·22	245·5
86	100·6	3·02	18·33	1,075	1268·5	37·09	251·4
88	103·0	3·09	18·84	1,100	1298·0	37·95	257·2
90	105·3	3·15	19·35	1,125	1327·5	38·81	263·1
92	107·6	3·22	19·85	1,150	1357·0	39·67	269·0
94	110·0	3·29	20·35	1,175	1386·5	40·54	274·8
96	112·3	3·36	20·85	1,200	1416·0	41·40	280·7
98	114·7	3·43	21·36	1,225	1445·5	42·26	286·5
100	117·0	3·50	21·86	1,250	1475·0	43·12	292·4
105	123·4	3·67	23·11	1,275	1504·5	43·99	298·2
110	129·8	3·84	24·35	1,300	1534·0	44·85	304·1
115	135·7	4·01	25·58	1,325	1563·5	45·71	309·9
120	141·6	4·18	26·80	1,350	1593·0	46·57	315·8
125	147·5	4·34	28·02	1,375	1622·5	47·44	321·6
130	153·4	4·51	29·24	1,400	1652·0	48·30	327·5
135	159·3	4·68	30·46	1,425	1681·5	49·16	333·3
140	165·2	4·86	31·67	1,450	1711·0	50·02	339·2
145	171·1	5·03	32·87	1,475	1740·5	50·89	345·0
150	177·0	5·20	34·08	1,500	1770·0	51·75	350·9
155	182·9	5·38	35·28	1,525	1799·5	52·61	356·7
160	188·8	5·55	36·49	1,550	1829·0	53·47	362·6
165	194·7	5·75	37·68	1,575	1858·5	54·34	368·5
170	200·6	5·90	38·88	1,600	1888·0	55·20	374·3
175	206·5	6·07	40·07	1,625	1917·5	56·06	380·2
180	212·4	6·25	41·27	1,650	1947·0	56·92	386·0
185	218·3	6·42	42·46	1,675	1976·5	57·79	391·9
190	224·2	6·59	43·65	1,700	2006·0	58·67	397·7
195	230·1	6·76	44·84	1,725	2035·5	59·51	403·6
200	236·0	6·94	46·03	1,750	2065·0	60·37	409·4
205	241·9	7·11	47·22	1,775	2094·5	61·24	415·3
210	247·8	7·28	48·41	1,800	2124·0	62·10	421·1
215	253·7	7·45	49·60	1,825	2153·5	62·96	427·0
220	259·6	7·62	50·78	1,850	2183·0	63·82	432·8
240	283·2	8·29	55·52	1,875	2212·5	64·69	438·7
260	306·8	8·97	60·25	1,900	2242·0	65·55	444·5
280	330·4	9·66	64·97	1,925	2271·5	66·41	450·4
300	354·0	10·35	69·69	1,950	2301·0	67·27	456·2
325	383·5	11·21	75·58	1,975	2330·5	68·14	462·1
350	413·0	12·07	81·66	2,000	2360·0	69·00	467·9

Fig. 65

BLENDING CHART Nº 1.



INSTRUCTIONS FOR USE

The main Chart No. 1 is divided into viscosity readings in different scales, Redwood in seconds, Saybolt in seconds, and Engler in numbers.

The kinematic viscosity scale is also given. If it is desirous to know the absolute viscosity, the latter value can be obtained by multiplying the kinematic viscosity by the specific gravity of the oil at the temperature at which the viscosity has been determined. The standard gravity constants per degree difference in temperature are given below.

The chart is based on the assumption that the viscosity of a blend is an additive function of the logarithm of the absolute viscosities of the components. In computing a blend, take the viscosity of the two components on any instrument at the same temperature. The scales apply to both sides of the chart. Set off these viscosities at opposite sides of the chart. Then draw a straight line (which can be done by holding a thread or straight-edge across the chart) when the viscosity of the blends of various composition can be read on any instrument on either side of the chart, the composition of the blend being given by the percentages of the components reading horizontally across the chart. One must bear in mind that the composition containing the larger proportion of the more viscous component will be at the higher end of the graph. By employing this system it will be found possible either to determine the viscosity of a blend of given composition or to find the composition necessary to give a required viscosity from two given components. It is also possible to determine the viscosity required by one component of which a given quantity is to be employed, given the viscosity of the other component and the viscosity desired in the finished blend.

[*To face page* 252.

EXAMPLES OF CALORIFIC VALUES (GROSS) DETERMINED IN THE MAHLER-COOK BOMB CALORIMETER.

Type of Oil.	British Thermal Units per Lb.
South American fuel oil (Aruba) . .	18,500
Russian fuel oil (Baku)	19,250
Texas fuel oil	18,900
Roumanian fuel oil	18,950
Mexican fuel oil	18,600
South American fuel oil (Curaçao) . .	18,600
Russian fuel oil (Grozny)	19,220
Trinidad fuel oil	18,300
Diesel fuel oil	19,580
Creosote	17,200

TEMPERATURES OF SPONTANEOUS IGNITION.[1]

Description.	Specific Gravity.	Spontaneous Ignition Temp. in Oxygen.	Spontaneous Ignition Temp. in Air.
Petroleum Distillates.		° C.	° C.
Pratt's perfection spirit, No. 1	0·710	272	383
Petrol (Mex.)	0·718	279	361
Pratt's spirit, No. 2	0·724	270	371
Taxibus spirit (A.A.O. Co. Ltd.)	0·729	272	390
Paraffin oil from A.A.O. Co.	0·807	251	...
Petrolite kerosene	0·814	251·5	432
Empire paraffin	0·782	253	395
Petrol from Anglo-American	0·735	...	392
Lamp oil from Anglo-American	0·787	...	367
Gas oil (A.A.O. Co. Ltd.)	...	254	358
Petroleum (crude and residue).			
Crude petroleum (Egypt)	0·851	260	...
Digboi oil (Assam)	0·890	261	384
Anglo-Persian Oil Co.'s Oil	0·894	254	408
Crude petroleum (Texas)	0·895	256	387
Anglo-American fuel oil	0·900	269	430
Anglo-Mexican oil	0·908	259·5	417
Crude petroleum (Texas)	0·936	268·5	416
„ „ (Borneo)	0·939	269	380
Mexican fuel oil	0·948	259·5	424
Crude petroleum (Mexico)	0·949	258	425
„ „ (Trinidad)	0·950	274	424
„ „ (California)	0·952	264	...
Venezuelan petroleum	0·955	275	429
Crude petroleum (California)	0·961	262	420
Shale Oils.			
Oil engine oil (Broxburn Oil Co. Ltd.)	0·768	253	333

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[1] "Spontaneous Ignition Temperatures of Liquid Fuels for Internal Combustion Engines." H. Moore, *Jour. Soc. Chem. Ind.*

TEMPERATURES OF SPONTANEOUS IGNITION—*continued.*

Description.	Specific Gravity.	Spontaneous Ignition Temp. in Oxygen.	Spontaneous Ignition Temp. in Air.
Shale Oils.		° C.	° C.
Lighthouse oil (Broxburn Oil Co. Ltd.)	0·803	251	322
Tar Distillates.			
Xylol commercial	0·860	484	...
Toluol 90 per cent.	0·863	516	...
Benzol 100 per cent.	0·875	566	...
Premier tarless tar oil	0·992	349	...
Creosote oil (Hardman & Holden)	1·010	415	...
Water gas tar creosote (Stainsby & Lyons)	1·036	473	...
Coke oven tar oil (Simon Carvès)	1·046	478	...
Tars.			
Tar (product of low temp. carbonisation)	0·987	307	508
C.W.G. tar (Stockport Gas Works)	1·074	464	...
Oil gas tar (Beckton)	1·077	415	...
Horizontal retort tar (Heywood Gas Works)	1·114	445	...
„ „ „ (Stockport Gas Works)	1·123	454	...
Coke oven tar (Simon Carvès)	1·132	494	...
„ „ (Coppée Co.)	1·140	488	...
„ „ (Koppers Type Ovens)	1·145	495	...
Blast furnace tar (Carlton Iron Works)	1·172	498	...
„ „ „ (Wm. Baird & Co.)	...	410	...
Miscellaneous.			
Alcohol	0·817	395	518
Turpentine	0·842	275	275
"Mirrlees-Diesel" compressor lubricating oil	0·875	265·5	405
"Mirrlees-Diesel" engine lubricating oil	0·894	265·5	401·0
Whale oil	0·921	273	470
Ether	0·730	190	347
Paraffin wax	...	245	...
Naphthalene	...	402	...
Free carbon from tar	...	348	...
Asphaltum from oil	...	260	...

LOWER LIMITS FOR DOWNWARD PROPAGATION OF FLAME IN A TUBE (AIR AND FUEL MIXTURE).

Obtained by Le Chatelier and Boudouard (*Comp. Rend.*, 1898, 126, 1510).

	Per Cent.		Per Cent.
Hydrogen	10·0	Turpentine	0·73
Carbon monoxide	16·0	Acetone	2·9
Carbon disulphide	1·94	Methyl alcohol	6·0
Illuminating gas	8·1	Ethyl „	3·07
Methane	6·0	*n*-Propyl „	2·55
Pentane	1·1	*i*-Propyl „	2·65
Hexane	1·3	*i*-Butyl „	1·68
Heptane	1·1	Allyl „	3·04
Octane	1·0	Amyl „	1·19
Nonane	0·83	Acetic acid	4·05
Acetylene	2·8	Ether	1·9
Amylene	1·6	Ethyl acetate	2·3
Benzene	1·5	Ethyl nitrate	3·8
Toluene	1·3		

LIMITS FOR DOWNWARD PROPAGATION OF FLAME (AIR AND FUEL MIXTURE).

(*As given by Eitner; obtained in a Bunte burette.*)

	Lower Limit.	Upper Limit.
	Per Cent.	Per Cent.
Hydrogen	9·45	66.4
Carbon monoxide	16·5	74·95
Water gas	12·4	66·8
Methane	6·1	12·8
Ethylene	4·1	14·6
Coal gas	7·9	19·1
Acetylene	3·45	52·2 (75 °/o in large vessel)
Alcohol	3·95	13·65
Ether	2·75	7·7
Benzene	2·65	6·5
Pentane	2·4	4·9
Benzine	2·4	4·9

CONVERSION OF DEGREES CENTIGRADE, FAHRENHEIT, AND REAMUR.

The three thermometric scales are: Celsius, or Centigrade (C.); Fahrenheit (F.); and Reamur (R.), used in Russia. The formulæ for converting one to another are:—

To convert °C. to °F. - - - $(°C. \times \frac{9}{5}) + 32 = °F.$
„ °F. „ °C. - - - $(°F. - 32) \times \frac{5}{9} = °C.$
„ °C. „ °R. - - - $(°C. \times \frac{4}{5}) = °R.$
„ °R. „ °C. - - - $(°R. \times \frac{5}{4}) = °C.$
„ °F. „ °R. - - - $(°F. - 32) \times \frac{4}{9} = °R.$
„ °R. „ °F. - - - $(°R. \times \frac{9}{4}) + 32 = °F.$

CONVERSION TABLE FOR DEGREES BAUMÉ (LIGHTER THAN WATER) TO SPECIFIC GRAVITY AND LBS. PER GALLON.

Degrees Baumé.	Specific Gravity.	Lbs. in 1 Gallon (American).	Degrees Baumé.	Specific Gravity.	Lbs. in 1 Gallon (American)
10	1·0000	8·33	43	·8092	6·74
11	·9929	8·27	44	·8045	6·70
12	·9859	8·21	45	·8000	6·66
13	·9790	8·16	46	·7954	6·63
14	·9722	8·10	47	·7909	6·59
15	·9655	8·04	48	·7865	6·55
16	·9589	7·99	49	·7831	6·52
17	·9523	7·93	50	·7777	6·48
18	·9459	7·88	51	·7734	6·44
19	·9395	7·83	52	·7692	6·41
20	·9333	7·78	53	·7650	6·37
21	·9271	7·72	54	·7608	6·34
22	·9210	7·67	55	·7567	6·30
23	·9150	7·62	56	·7526	6·27
24	·9090	7·57	57	·7486	6·21
25	·9032	7·53	58	·7446	6·20
26	·8974	7·48	59	·7407	6·17
27	·8917	7·43	60	·7368	6·14
28	·8860	7·38	61	·7329	6·11
29	·8805	7·34	62	·7290	6·07
30	·8750	7·29	63	·7253	6·04
31	·8695	7·24	64	·7216	6·01
32	·8641	7·20	65	·7179	5·98
33	·8588	7·15	66	·7142	5·95
34	·8536	7·11	67	·7106	5·92
35	·8484	7·07	68	·7070	5·89
36	·8433	7·03	69	·7035	5·86
37	·8383	6·98	70	·7000	5·83
38	·8333	6·94	75	·6829	5·69
39	·8284	6·90	80	·6666	5·55
40	·8235	6·86	85	·6511	5·42
41	·8187	6·82	90	·6363	5·30
42	·8139	6·78	95	·6222	5·18

The specific gravity multiplied by 10 = weight in pounds per imperial gallon.

Table of Conversions of Various Measures.

[1] 1 metre = 39·370113 inches.
[1] 1 gallon = 4·5459631 litres.
[1] 1 kilogram = 15432·3564 grains.
1 metre = 3·28084 feet.
,, = 1·09361 yards.
1 foot = ·304799 metre.
1 litre = 61·0239 cubic inches.
,, = ·219975 gallon.
1 cubic metre = 35·3147 cubic feet.
,, ,, = 1·30975 cubic yards.
,, foot = 28·3167 litres.
1 kilogram = 2·20462 pounds.
1 pound = ·453592 kilogram.
1 metric ton = 1,000 kilograms.
,, ,, = ·984206 ton English.
,, ,, = 2204·62 pounds.
1 ton English = 1016·04 kilograms.
,, ,, = 1·01604 metric tons.
1 gram per square millimetre = 1·42233 pounds per square inch.
,, ,, centimetre = ·014223 ,, ,, ,, ,,
1 pound per square inch = ·703071 grams per square millimetre.
,, ,, ,, = 5·17006 centimetres mercury.
1 atmosphere = 14·7 pounds per square inch.
,, = 1·03351 kilograms per square centimetre
1 British thermal unit = 778 foot-pounds.
1 foot-pound = ·138254 kilogrammetre.
1 kilogrammetre = 7·23301 foot-pounds.
1 British thermal unit = 107·562 kilogrammetres.
1 large calorie (k) = 1,000 small calories (c).
1 British thermal unit = ·251995 calorie (k).
1 calorie (k) = 426·841 kilogrammetres.
,, = 3087·35 foot-pounds.
1 horse power = 33,000 foot-pounds per minute.
,, = 550 foot-pounds per second.
1 force de cheval = 75 kilogrammetres per second.
1 cheval = ·986319 horse power.
1 horse power = 1·01387 chevaux.
1 pound per horse power = ·447386 kilogram per cheval.
1 kilogram per cheval = 2·23520 pounds per horse power.
1 cubic foot per horse power = ·027929 cubic metre per cheval.
1 square ,, ,, ,, = ·091631 square ,, ,, ,,
1 ,, metre per cheval = 10·9132 ,, feet per horse power
1 cubic ,, ,, ,, = 35·8045 cubic ,, ,, ,,
1 B.Th.U. per square foot = 2·71246 calories per square metre.

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[1] Legalised fundamental equivalents.

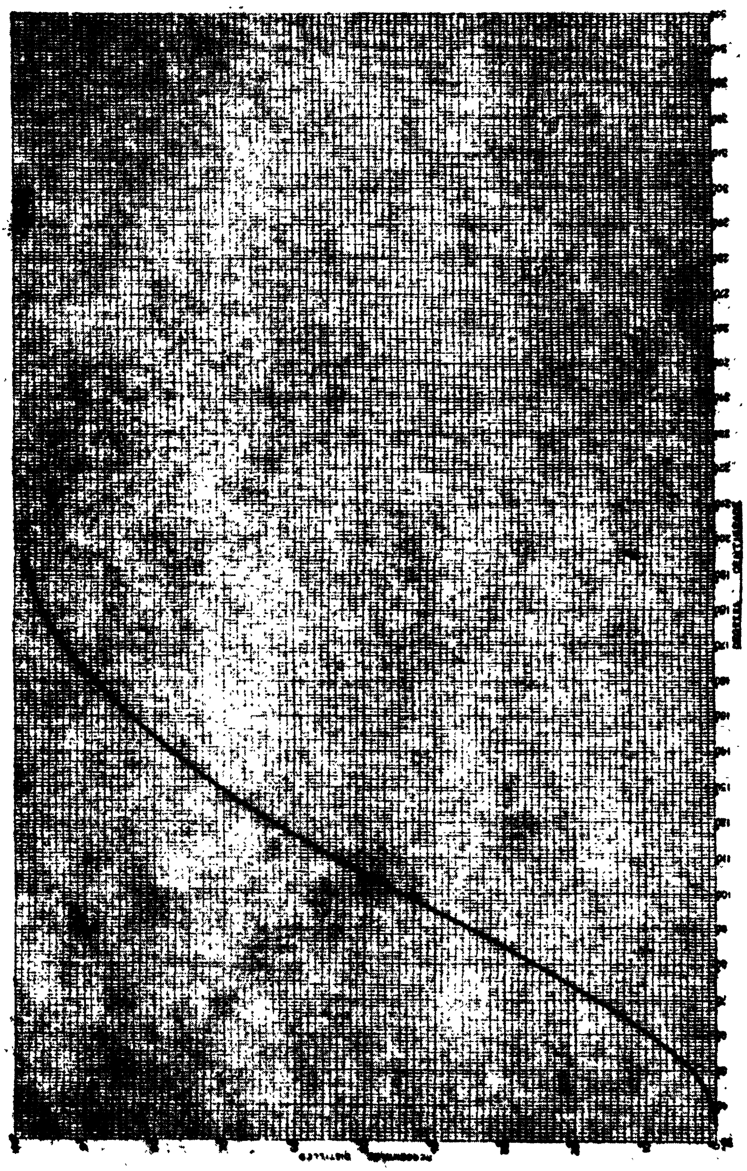

FIG. 66.—Distillation Curve. Shell No. 1.

[FIGS. 66, 67, 68 (*following page* 258).

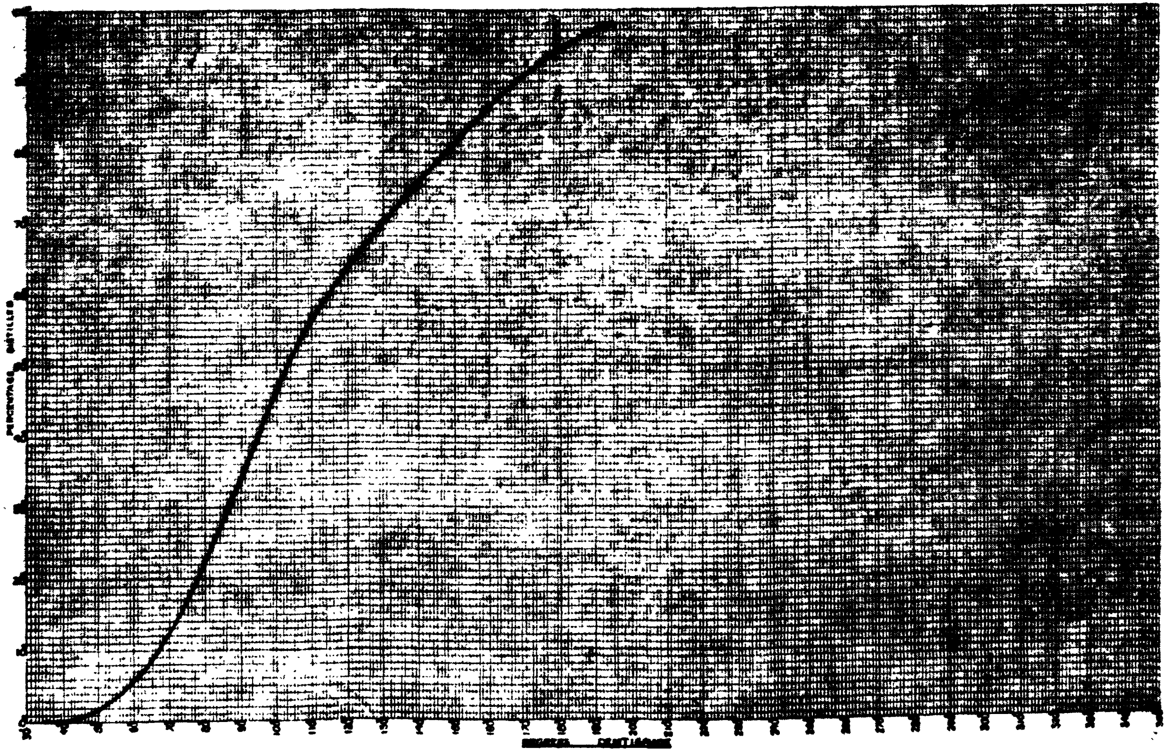

FIG. 67.—Distillation Curve. Pratt's Benzole Mixture.

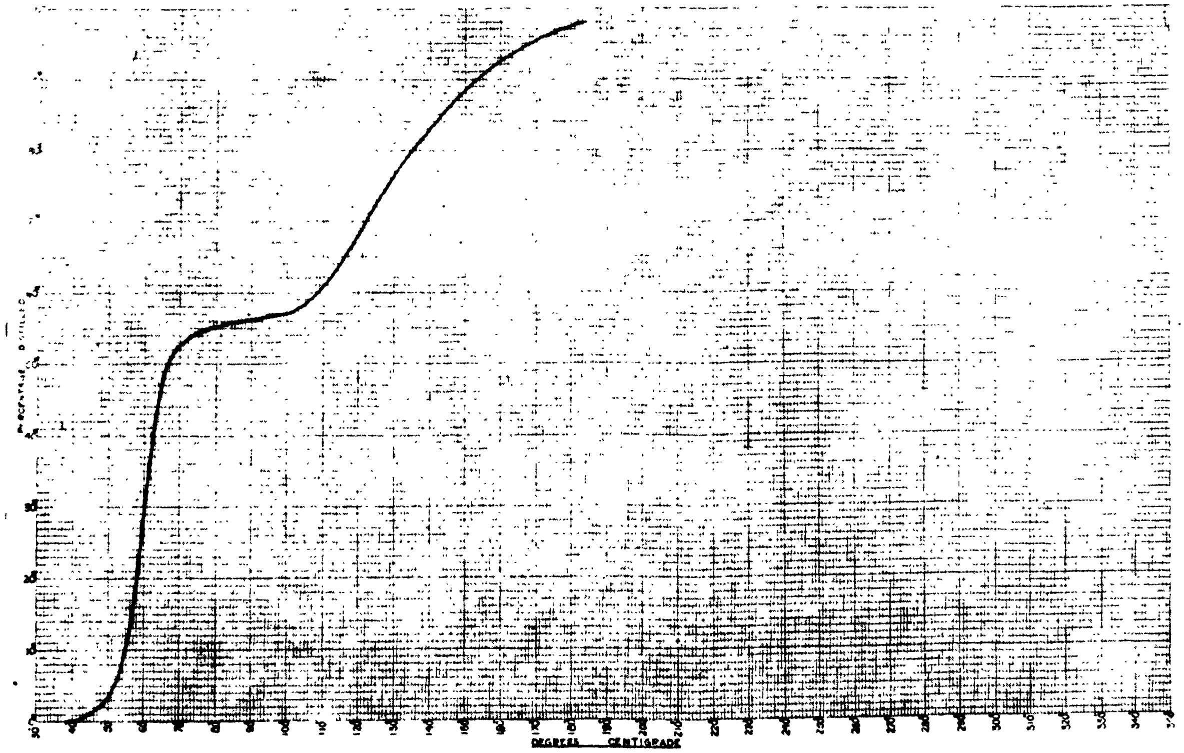

FIG. 68.—Distillation Curve. Citex "Koolmotor."

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AUTHOR INDEX

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