

THE PHYSICAL PROPERTIES OF MOTOR FUELS.  
A DISCUSSION OF THEIR BEARING ON THE MOTOR INDUSTRY.

---

By W. R. ORMANDY, D.Sc., VICE-PRESIDENT, AND E. C. CRAVEN.

---

THE number of mixtures which have been proposed for use as motor fuels is enormous, though the essential constituents are in reality very few. A great many of these mixtures have been proposed without due regard to the physical characteristics necessary in a liquid which is to be suitable for the purposes of a motor spirit. The idea, however, that these mixtures should rather be used to conserve the supply of petrol spirit than as substitutes for petrol, gives another point of view of the matter. There are, of course, cases in which nothing but a thoroughly certain and dependable fuel can be used, for example, in aeroplanes where no chances can be taken, and in, say, racing, where the engine can be specially designed to get the utmost out of a given fuel.

In everyday commercial practice, however, a far more pertinent consideration is the cost, by which, of course, is meant not the cost per gallon but the cost of unit result. It is obvious that in order to ensure economical running, the fuel must have, to a certain degree, properties which it is proposed to discuss in this paper.

The main properties necessary to be considered in this connection include the following:—

- (1) Heat of combustion.
- (2) Freezing point.
- (3) Separation point.
- (4) Distillation range.
- (5) Latent heat of evaporation.
- (6) Flash-point.
- (7) Explosive range.
- (8) Corrosiveness.
- (9) Viscosity.
- (10) Toluene number.
- (11) Spontaneous ignition temperature.
- (12) Specific heat.

The authors propose to consider each of these sections in some detail.

## HEAT OF COMBUSTION.

As the energy derived from an internal combustion engine depends upon the pressure developed on the combustion of a fuel with the oxygen of the air, it is obvious that the total heat which can be given out on the burning of a given weight of fuel will be the most important factor in considering the value of that fuel. It is liable to be forgotten, however, that it is not nearly so much a question of the heat which is generated as of the availability of the heat generated for the purpose required. A pound of acetylene will give out more heat on its combustion than a pound of petrol, but it does not follow that acetylene is therefore a superior fuel even if its cost were sufficiently low. The fact that acetylene is liable to explode spontaneously when compressed rules it out as a motor fuel. As will be seen later, a pure paraffin hydrocarbon cannot be employed under such advantageous conditions in an internal combustion engine as can, for example, an aromatic hydrocarbon, benzene, and although the paraffin will have a slightly higher heat of combustion per lb. than the aromatic, nevertheless a greater percentage of the heat in the case of the aromatics can be converted into work than in the case of the paraffin. Nevertheless, of all materials which come within the range of practice as motor fuels, the heat value is the most important factor. It is customary in Tables of heat values to record results in such a form as that one pound of fuel when burnt has a calorific value of, say, 19,087 B.Th.U.s., and it is not always stated clearly whether such a figure represents the lower or the upper limit. In the first place, it is doubtful whether ordinary determinations of the heat value of a fuel are ever carried out under practical commercial conditions to an accuracy exceeding one-half of one per cent. Consequently it is no use giving any figures in the unit column, and doubtful whether figures in the second column are of any value.

As the exhaust products from an internal combustion engine pass away at a temperature far above that at which water condenses, it is clear that it is only the lower calorific value which is of interest to the internal-combustion engineer, but a statement as to the upper and lower calorific value enables the amount of hydrogen contained in the fuel to be calculated.

Table I., which is taken from Part I. of Ricardo's papers on "The Influence of Various Fuels on the Performance of Internal Combustion Engines,"\* shows us that the heat value of petrols varies from 18,700 to 19,100 B.Th.U.s. per lb., and from the Table we gather that the lighter, that is, the more volatile, the petrol, the higher its heat value, and further, that the aromatic hydrocarbons such as benzene and toluene have a lower heat value per lb., but in consequence of their high gravity have

\* See "The Automobile Engineer," February, 1921.

greater heat value per gallon. The hydrocarbons of the naphthene series are very similar in their heat value per lb., though they vary considerably among themselves in heat value per gallon, and they stand between the aromatics and the pure paraffins, though nearer to the latter as regards their calorific value. The alcohols generally are much lower in heat value even than the aromatics, but the variation among the alcohols is much greater; the variation, too, is more rapid as we pass from member to member of the series than is the case with the strict hydrocarbons. The variation between methyl alcohol and ethyl alcohol is very considerable, namely, in round numbers the difference between 9,000 and 12,000. As we rise in the alcohol series towards amyl alcohol the heat values approach those of the aromatics. The authors have preferred to quote figures from Ricardo's paper, as these determinations of heat values were exceedingly carefully carried out on a specially selected range of commercial petrols as well as on a large number of specially purified bodies contained in, or capable of being used as, motor fuels.

It is too frequently forgotten that combustion can be regarded, not from the everyday standpoint that the hydrocarbon is the fuel and that there is unlimited oxygen, as is the case in most industrial operations, but from the standpoint that the oxygen is the fuel and that the hydrocarbon is the body which consumes it, and this point of view is particularly important in the internal combustion engine, where the amount of air or oxygen is not unlimited but absolutely limited by the cylinder capacity and by the volumetric efficiency. It is interesting to note that a theoretical mixture of almost any hydrocarbon or alcohol with air gives out practically the same amount of heat per unit of volume, and hence, if the heat output per unit of volume were the only factor to be considered in considering the efficiency of an internal combustion engine, the work to be obtained would be practically equal in all fuels.

Another item to which consideration must be given is the intrinsic change of volume due to the chemical action taking place when the fuel is burnt. When coal-gas burns with air the volume of the resulting mixture is less than the original volume, due allowance being made for temperature, but in the case of the hydrocarbons there is a slight increase in volume, and in the case of the alcohols a still greater increase. The paraffin series increase in volume on combustion with the theoretical amount of air by about  $5\frac{1}{2}$  per cent, the aromatics by about 2 per cent, the naphthenes by 5 per cent, and the alcohols by just over 6 per cent, whereas in the case of carbon monoxide and hydrogen there is a diminution of about 15 per cent. These points have already been touched upon in a paper\* read before this Institution by

\* See Proc. I.A.E., Vol. VIII., p. 49.

TABLE I.

FUEL.	Sp. Gr. at 15° C.	Calorific Value, Exclusive of Latent Heat (Lower Values).	
		B.Th.U.s. per lb.	B.Th.U.s. per gal.
PETROLS.			
Aromatic free .....	0.718	19,080	137,000
"A" Petrol .....	0.782	18,450	144,300
"B" " .....	0.723	18,890	136,600
"C" " .....	0.727	19,000	138,100
"D" " .....	0.760	18,770	142,600
"E" " .....	0.719	18,970	136,400
"F" " .....	0.704	19,130	134,700
"G" " .....	0.750	—	—
"H" " .....	0.767	18,790	144,100
HEAVY FUELS.			
Heavy aromatic .....	0.885	17,900 (approx.)	158,500 (approx.)
Kerosene .....	0.813	19,000 (approx.)	154,400 (approx.)
PARAFFIN SERIES.			
Hexane (80 per cent) .....	0.685	19,250	131,900
Heptane (97 per cent) .....	0.691	19,300	132,800
AROMATIC SERIES.			
Benzene (pure) .....	0.884	{ 17,330 17,302	153,200 152,950
Toluene (99 per cent) .....	0.870	{ 17,580 17,522	153,000 152,300
Xylene (91 per cent) .....	0.862	17,800	153,500
NAPHTHENE SERIES.			
Cyclohexane (93 per cent) .....	0.766	18,800	147,800
Hexahydrotoluene (80 per cent) ....	0.780	18,760	146,200
Hexahydroxylene (60 per cent) ....	0.744	18,770 (approx.)	139,700 (approx.)
ALCOHOL GROUP.			
Ethyl Alcohol (98 per cent) .....	0.798	{ 11,450 11,480	91,400 91,600
Methyl Alcohol (purif. wood naphtha)	0.829	—	—
Acetone .....	0.798	12,350	98,440
Methylated Spirits .....	0.821	9,850	81,100
MISCELLANEOUS.			
Acetylene .....	—	21,010	—
CS <sub>2</sub> 50 per cent Aromatic free 50 per cent (by volume) .....	0.994	10,620	105,600
Ether (dilute) .....	0.735	13,350	98,000 (approx.)

one of the authors, and they have been studied in greater detail by Ricardo.

### FREEZING POINT.

Of the bodies likely to be used for fuels, the only ones having a high freezing point are benzene and paraxylene, which freeze at  $5.4^{\circ}\text{C}$ . and  $16^{\circ}\text{C}$ . respectively. The latter body is of little importance, as it only occurs to a limited extent in power hydrocarbons. It is thus only necessary to consider the freezing points of mixtures containing benzene. In Fig. 1 will be found the freezing-point curves of benzene with admixed liquids, from which it will be seen that the greatest effect is produced by toluene and xylol. The next curves given are for hexane and

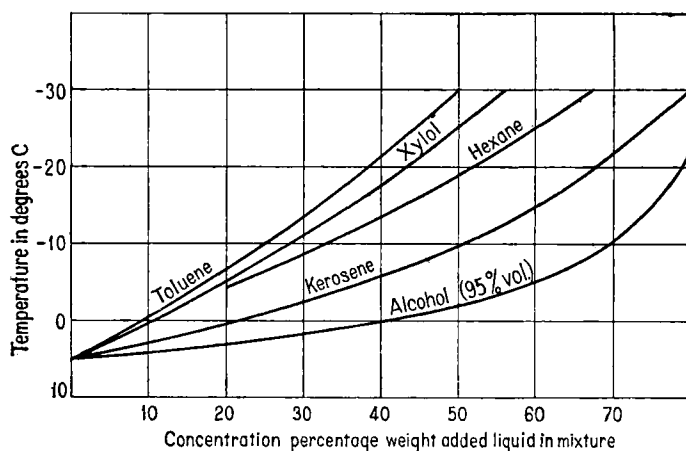


FIG. 1.—Freezing point curves of Benzene with added Liquids.

kerosene (White Rose). All the common light and heavy petrols and kerosenes fall between these two curves. The least effective liquid shown is alcohol. The depression of freezing point becomes less as the alcohol is reduced in strength, water having the curious effect of raising the freezing point of alcohol-benzene mixtures.

It is fortunate that toluene has such a pronounced effect on the freezing point, since it is therefore only necessary to arrange the "cut" in the distillation of benzol so that sufficient toluene passes over in order to reduce the freezing point to any reasonable required figure. The British Standard Specification called for the freezing point of motor benzol to be not higher than  $-14^{\circ}\text{C}$ ., corresponding to 30 per cent volume of toluene in a mixture of pure toluene and benzene. In practice, however, the presence of paraffins, xylenes

and sulphur-containing bodies lowers the freezing point also, so that such a high percentage of toluene is not required.

Further, in a mixed fuel containing only a proportion of benzol, the freezing point will be below that of the benzol employed, so that under the conditions prevailing in temperate countries no separation of solid need be feared.

Motor benzol, however, now appears to be on the market which has a higher freezing point ( $-8^{\circ}\text{C}.$ ), and no doubt the toluol

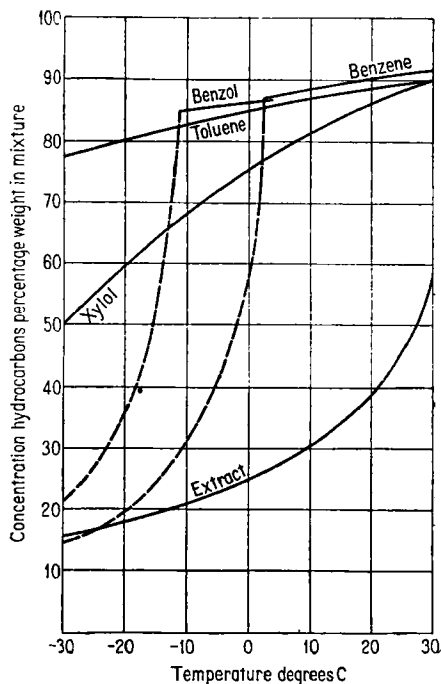


FIG. 2.—Solubility of Aromatic Hydrocarbons in Alcohol of 92 per cent Weight Strength.

content is liable to vary according to the relative prices which can be obtained for benzene and toluol elsewhere than in the fuel market.

#### SEPARATION POINT.

The commoner hydrocarbons, at least those likely to be used in motor fuels, are miscible in all proportions. When, however, we come to consider mixtures containing alcohol, it is found that, according to the strength of the alcohol and the temperature,

variations in the solubility occur. A large amount of work has been carried out for the Distillers' Co., Ltd., in relation to the solubility of aromatic hydrocarbons, paraffins and the like in alcohol of varying strength over a temperature range of  $30^{\circ}\text{C}$ . to  $-30^{\circ}\text{C}$ . In Figs. 2, 3 and 4 are given the solubility in 92 per cent weight (94.7 per cent volume) alcohol of aromatic hydrocarbons and paraffins and petroleum products.

Examining the curve for benzene, we find that it is highly soluble in alcohol of the commercial strength (95 per cent volume) down to the temperature of the triple point where a solid phase commences to separate. This triple point, in consequence of the small cryoscopic effect of alcohol, is only a few degrees below the freezing point of the hydrocarbon. For instance, with the pure benzene with a freezing point of  $5.2^{\circ}\text{C}$ ., the triple point is about  $2.5^{\circ}\text{C}$ ., a drop of  $2.7$  degrees  $\text{C}$ . In the curve marked "benzol" similar figures are given for a mixture of 3 volumes pure benzene + 1 volume pure toluene, roughly equivalent to a motor benzole. The freezing point of the original benzene-toluene mixture was  $-10^{\circ}\text{C}$ . and the triple point is about  $-11.5^{\circ}\text{C}$ ., a drop of  $1\frac{1}{2}$  degrees  $\text{C}$ . It is therefore of no avail to start with a hydrocarbon mixture of high freezing point in the hope that it will be considerably lowered by the addition of ethyl alcohol. At temperatures below the triple point, the solubility of the benzene or mixture falls enormously, as will be seen by the almost vertical slope of the solubility curve. The first point to be observed, therefore, in preparing a mixed fuel of this description is to avoid the separation of a solid phase by starting with a hydrocarbon mixture itself sufficiently stable against low temperatures.

Turning to the curve for toluene, it will be seen that the solubility is very little inferior to that of benzene, and as the melting point of this body is about  $-95^{\circ}\text{C}$ . there is no separation of solid phase down to  $-30^{\circ}\text{C}$ . With xylol a very much decreased solubility is observed. It will be noticed that with benzene, toluene, benzene-toluene and xylol mixtures the solubility curves are concave to the temperature scale. The curve marked "Extract" gives the solubility of the Edeleanu extract from a Borneo kerosene. This extract appears to consist mainly of high boiling-point aromatic hydrocarbons, and the curve differs from the others in that it is convex to the temperature scale. It will be noticed, too, that whilst it is easy to dissolve small quantities of any of these hydrocarbons in a large bulk of 95 volume alcohol, the converse is not true, and as, in certain cases, it would be of advantage to add, say, 5 per cent to 15 per cent of alcohol to a fuel, this matter is of some importance.

In Fig. 3 are given the solubilities in alcohol of a similar strength for various samples of reputed pure paraffins. Great differences will be noticed amongst the samples, for example, Lot I, pentane, shows a critical temperature of  $-17^{\circ}$  above which it is soluble in 95 volume per cent alcohol in all proportions,

whilst another sample, marked Lot II, shows no such critical temperature below  $30^{\circ}\text{C}$ . It will be noticed that with increase

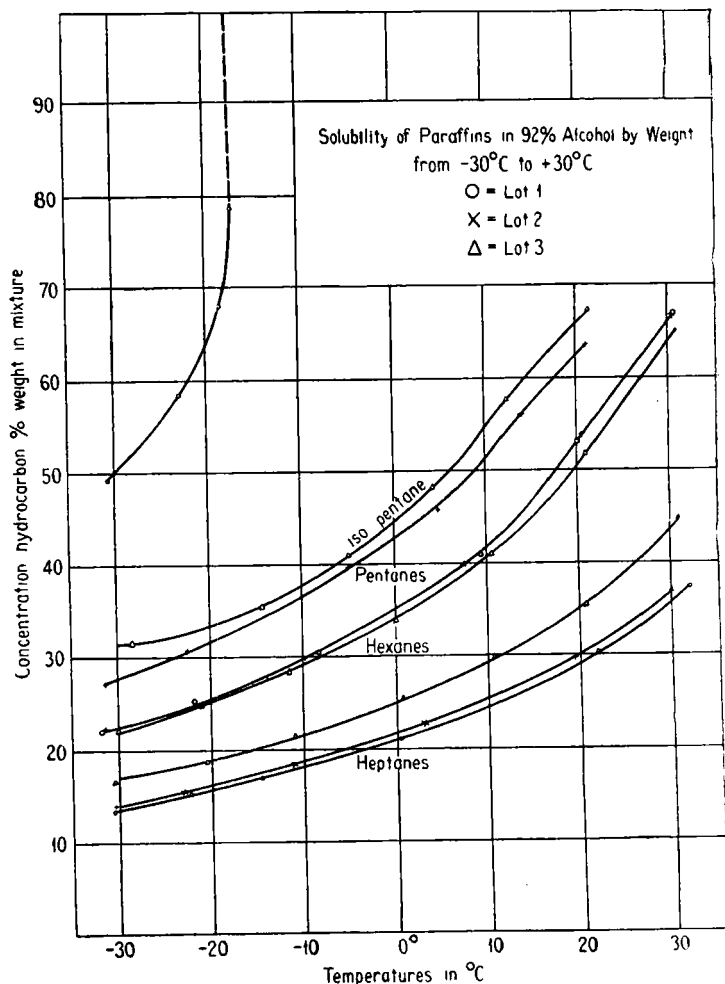


FIG. 3.

in molecular weight the solubility of the paraffins decreases rapidly. The temperature coefficients are also much greater than with benzene or toluene.



In Fig. 4 are given the solubility of various samples of petroleum spirits marked A, B, E, F and H in the 95 volume per cent alcohol. These petrols are those used by Mr. Ricardo in his recent work on the detonation compressions of various hydrocarbons.

The petrols marked A and B are of Borneo or Sumatra origin and have a high aromatic content. Those marked E and F are of American origin. Petrol H is rather unique in character in that it consists mainly of naphthenes. It is found only in one

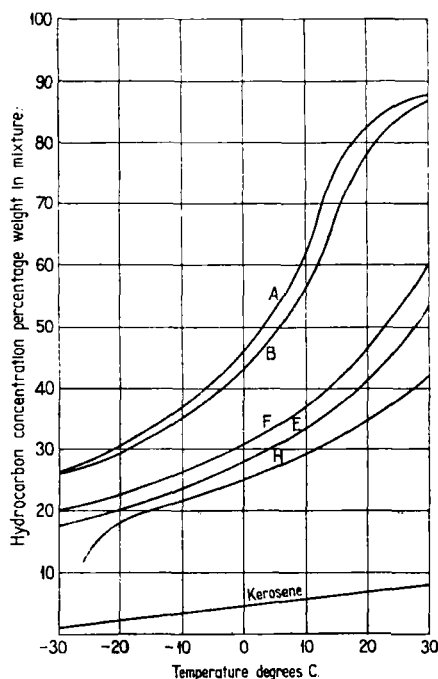


FIG. 4.—Solubility of Petrols in Alcohol of 92 per cent Weight Strength.

well in the Miri field of Borneo. The aromatic-containing petrols are obviously much more soluble in the 95 volume per cent alcohol than the other three. This arises from the superior solubility of the aromatic hydrocarbons over the paraffin hydrocarbons of the same boiling-point. The authors are not able to say from the petrol H that the naphthenes are of low solubility as the distilling range of this particular sample is very high.

The lowest curve of all is for an American kerosene. The low solubility and the high temperature coefficient will be noted, the solubility increasing about eight times in passing from  $-30^{\circ}\text{C}$ . to  $+30^{\circ}\text{C}$ .

It has already been mentioned that it might be desirable to dissolve small quantities of alcohol in petrol spirit. The reason for this will be referred to later in connection with Ricardo's work on toluene numbers. For the present, however, the authors give in Table II. the necessary strength in weight per cent which alcohol must have in order to dissolve to given extents.

TABLE II.

*Collected Figures for Solubility of Alcohol in Petrols. The Figures give the Strength of Alcohol necessary to Dissolve to the Extent stated.*

Wt. Concen- tration A.	No. 1, Pratt's.	A.	B.	E.	F.	H.	Hexane.	Heptane.
30° C.	2	95.4	96.2	96.3	96.1	96.4	95.0	96.0
	4	95.2	96.2	96.2	96.0	95.8	95.2	96.2
	6	94.7	96.0	95.7	95.8	95.4	95.4	96.4
	8	94.3	95.0	95.4	95.4	95.2	95.3	96.3
	10	94.1	94.4	95.2	95.2	95.1	95.0	96.1
	12	93.9	94.1	95.0	95.0	94.9	94.6	95.8
-30° C.	2	98.1	97.6	98.3	97.7	97.6	98.5	98.0
	4	98.1	98.2	98.7	98.0	98.9	98.1	98.5
	6	97.9	98.3	98.7	98.2	99.0	97.8	98.8
	8	97.6	97.8	98.5	98.2	98.8	97.5	98.9
	10	97.3	97.2	98.1	98.1	98.7	97.1	98.9
	12	97.0	96.6	97.7	98.0	98.7	96.8	98.7

The alcohol strengths are in all cases very high, which means in practice that the alcohol would have to be specially dehydrated, the strongest alcohol produced in regular practice being about 92½ weight per cent. Various patents have been taken out from time to time in which it is proposed by the addition of a third body to increase the miscibility of petrol with the lower strength alcohol. Fig. 5 shows the effect of the addition of 5 per cent of amyl alcohol to a Pratt's No. 1 petrol. It will be seen that in order to add 10 per cent of alcohol before the addition of the amyl alcohol the ethyl alcohol must be of 95.8 weight per cent strength. After the addition of the amyl alcohol the necessary strength is reduced to 93.2, the temperature in both cases being

15° C. In Fig. 6 the decrease in solubility of the same petrol of the same temperature on removal of the aromatic hydrocarbon content is shown. The actual percentage of aromatics as shown by the aniline point method was 5·8.

#### DISTILLATION RANGE.

If it were customary to use chemical individuals such as pure benzene or pure alcohol for motor fuels, the question of distillation range would not arise, but the fact is that all the fuels

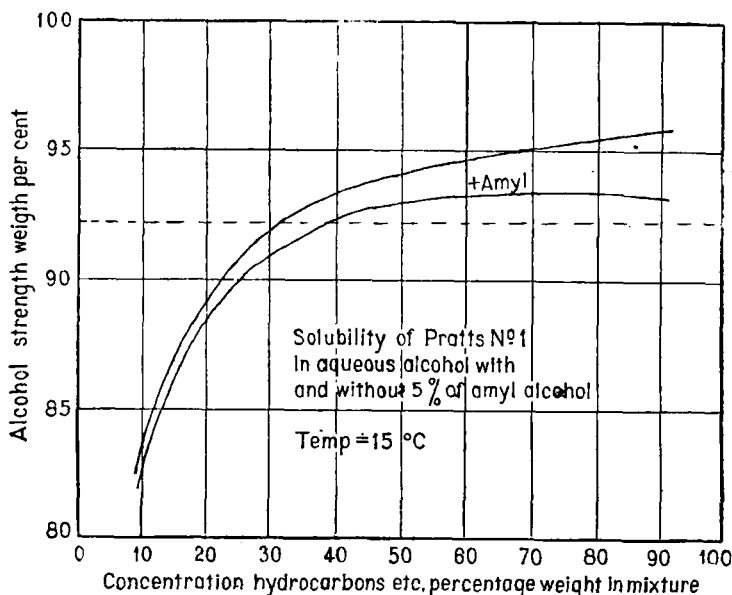


FIG. 5.

used industrially in internal combustion engines are complex mixtures, portions of which begin to come over at a low temperature, the thermometer rising during the whole period of distillation.

Table III. gives the Engler distillation figures of a number of fuels, named and unnamed varieties, and for the better discussion of the results Fig. 7 has been made from these figures.

In the first place it is interesting to compare the curves of the Shell spirit and the Pratt's No. 1. It will be seen from Figs. 7 and 8 that the Pratt's begins to give off a condensable vapour at

8 degrees lower temperature than Shell, and that 5 per cent of Pratt's comes over at 10 degrees lower than 5 per cent of Shell, and at 10 per cent the difference is 12 degrees in favour of Pratt's. Other things being equal, this implies that Pratt's spirit in cold weather will give easier starting. In the section on flash-points further reference will be made to the relationship existing between the first-drop temperature and the flash-point. The next point of interest in connection with the distillation curves is the position at the half-way distillation point. It will be seen that 50 per cent of Shell has passed over at 115° C. and 50 per cent of Pratt's at

TABLE III.

*Engler Distillation Table.*

	No. 1 Grade.	No. 3 Grade.	Shell.	Pratt's No. 1.
Per cent.	°C.	°C.	°C.	°C.
Drop Point	54	62	63	55
1	64	76	—	—
2	68	79·5	—	—
5	73·5	86·5	83	73
10	78	93·5	90	78
20	87·5	105·5	—	—
30	95·5	115·3	104	95
40	102	125	—	—
50	109·5	135·5	115	110
60	117·5	146	—	—
70	125·5	157	131	130
80	142	170	—	—
90	163	189	156	164
95	189	208	169	188
Dry Point	200	224	180	193
Residue	1·5 per cent	1·5 per cent	2 per cent	2 per cent
Loss	1·5 per cent	0·5 per cent	2 per cent	2 per cent
S.G. 60/60° F.	0·7285	0·747	0·7555	0·722

110°. Ricardo has pointed out in his work with the variable-compression engine that the temperature at which half the fuel has passed over in an Engler distillation is a good guide to the behaviour of the fuel in the engine. It is clear that the evaporation of a fuel in the induction pipe will reduce the temperature of the in-going air, and the amount of this reduction will be a function of the latent heat of evaporation of the fuel and the amount which is evaporated in any one unit-volume of air. Ricardo found that the reduction in temperature of the air-fuel mixture was more nearly proportionate to the temperature at the 50 per

cent distillation point than to any other constant of the fuel. It must, however, be realised that this is very empirical, and is only applicable to the average type of fuel on the market to-day. It is easy to conceive of mixtures where this ruling would not hold.

The last item of importance in the examination of a distillation curve is the reference to the finishing temperatures. It will be seen that the 95 per cent temperature for Shell is  $169^{\circ}$  and for Pratt's  $188^{\circ}$ , and the dry points  $180^{\circ}$  and  $193^{\circ}$  respectively. This means in other words that the Pratt's spirit contains a larger quantity of the kerosene-like higher boiling-point fractions.

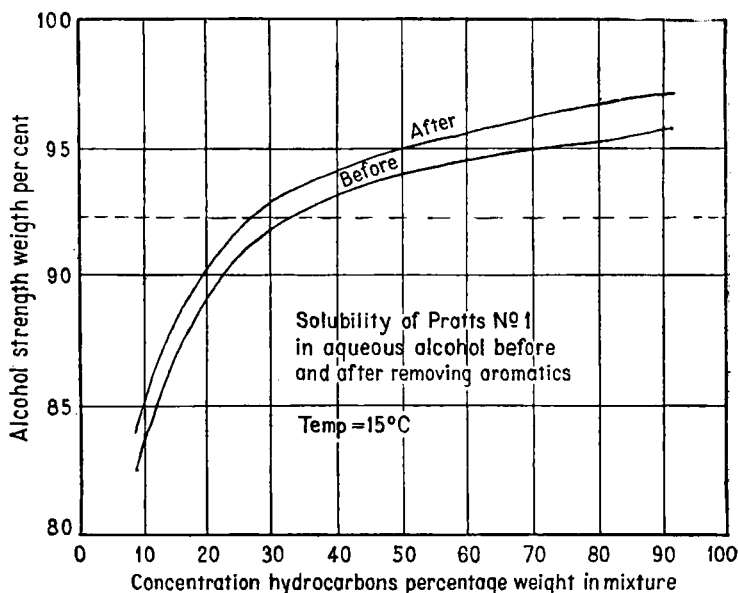


FIG. 6.

These portions of the fuel are the most difficult to volatilise, and they tend, probably more than any other portion of the fuel, to get through into the crankcase and to reduce the viscosity of the lubricating oil. It cannot be said, however, that any of the leading motor spirits sold in this country are bad in respect of the amount of high boiling-point fraction. A dry point of  $190^{\circ}$  compares more than favourably with the dry point of  $240^{\circ}$  which is not uncommon in the gasoline of America. As supplies of volatile fuel get shorter, the tendency will be to bring more and more of the kerosene fraction into motor spirit, and when this country has to use a petrol more like that which obtains on the

average in America, much greater attention will have to be paid to induction pipes and induction manifolds.

#### LATENT HEAT OF EVAPORATION.

It has, of course, long been recognised that the latent heat of evaporation of fuel is important from the point of view of car-

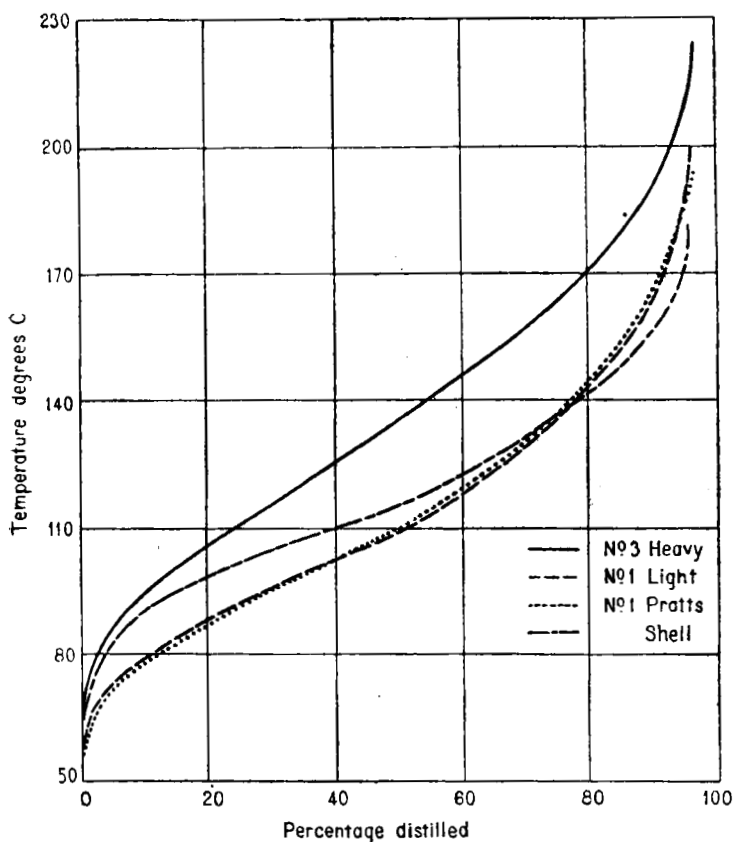


FIG. 7.

buration. Put quite simply, the latent heat of evaporation involves that when the fuel evaporates, the temperature of the air-fuel mixture will be reduced unless heat is found from somewhere to make up for that absorbed in the change of state of the fuel from a liquid to a gas. The heat of evaporation of the petrols

is fairly constant in the neighbourhood of 135 B.Th.U.s. per lb., that of ordinary motor benzol is about 164 B.Th.U.s. and that of ethyl alcohol about 400 B.Th.U.s. These figures are a measure of the amount of heat that has to be supplied either to the in-going air to the carburettor or to the carburetted mixture on its way to the cylinder if the cylinder is to be provided with a truly gaseous mixture.

Any attempts, however, to supply sufficient heat in the in-going air to evaporate the whole of a commercial petrol would be a mistake, since the time available with the temperature that it

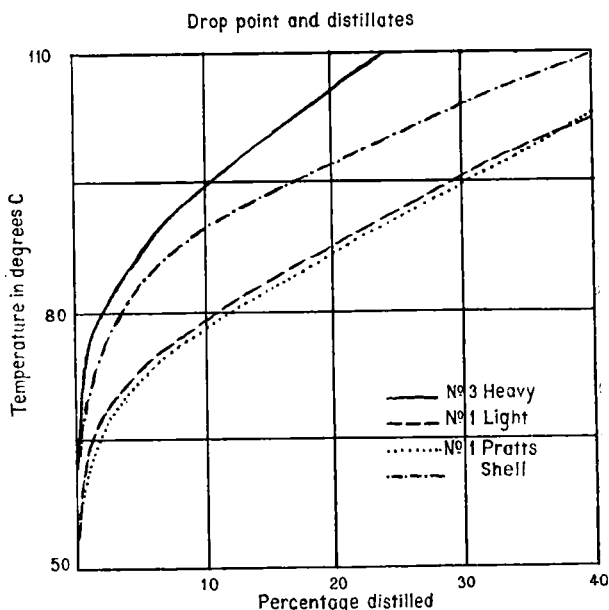


FIG. 8.

would be possible to give the air in practice would not suffice to transfer the heat from the air to the fuel; the end result would be that the fuel-air mixture would enter the cylinder with a lot of the fuel unevaporated and the air so far heated that the volumetric efficiency would be reduced owing to the temperature of the air expanding the gas and giving less weight in unit-volume. In practice it is probably better to rely on bringing the fuel itself in contact with a highly heated surface, the so-called hot spot manifold, rather than to attempt volatilisation by heat carried through the air itself. It is when we consider carburation that

the question of the amount of high boiling-point constituents in a motor fuel becomes of such importance. The problems of carburation would be greatly simplified if we had to deal with such fuels as benzol or alcohol, which have a constant boiling-point. The high latent heat of evaporation of alcohol necessitates the provision of more heat during carburation, and this is the more necessary since if this heat is not provided the alcohol-air mixture enters the cylinder at a very low temperature, and under these conditions air saturated with alcohol vapour will hardly ignite at ordinary temperatures. Considered from another point of view, the high latent heat of evaporation of a fuel is a great advantage, since if the fuel can be brought into the cylinder in a sufficiently fine state of division its evaporation in the cylinder reduces the temperature of the air-fuel mixture at the expense of heat taken from the cylinder walls or from the exhaust gases present, with a consequent proportional increase in the weight of charge which can be taken into the cylinder. Not only is heat which would otherwise be wasted, caused to do useful work but the thermal efficiency of the cycle is improved. Ricardo in his before-mentioned papers has pointed out that the latent heat of evaporation should be added to the lower calorific value of the fuel in order to get a proper picture of the real relative value of the fuel for use in internal combustion engines.

#### FLASH-POINT.

Probably the most important factor in determining the easy-starting qualities of a fuel is the amount of readily volatile hydrocarbons which it contains. The authors have shown recently\* that by determining the flash-point in a suitably proportioned instrument a very good idea of the amount of these volatile hydrocarbons can be obtained. In general, they have found that the flash-points of the common petrols are of the order  $-25^{\circ}\text{C.}$  to  $-30^{\circ}\text{C.}$ , of motor benzol  $-11^{\circ}$ , and of 95 volume per cent alcohol  $16^{\circ}\text{C.}$  It is well-known that in cold weather it is much more difficult to start up on benzol than on, say, a No. 1 petrol. It would, therefore, be still more difficult with a straight 95 volume per cent alcohol, and no doubt when the temperature of the air is below  $16^{\circ}\text{C.}$  unless liquid alcohol entered the cylinder it would be impossible for an explosive mixture ever to be formed. It is thus necessary to liven up the alcohol by the addition of a suitable quantity of a low flash-point material such, for example, as benzol or ether (flash-point  $-41^{\circ}\text{C.}$ ). It does not, of course, follow that all fuels having the same flash-point will be equally easy in starting or equally efficient in running, but taken in conjunction with other factors a fairly good idea of the character of a fuel in this direction may be obtained from the flash-point.

In a paper recently read before the Institution of Petroleum

\* Inst. Pet. Tech. Journal.



Technologists the authors give the results of a long research into the question of the flash-points of hydrocarbons and other liquids, in which both the lower flash-point and the upper flash-point have been determined for a large number of liquids. The flash-point most generally considered is the lower, corresponding to the mixture with the minimum amount of combustible vapour present which will propagate flame. It must not be forgotten, however, that there is an upper limit beyond which the mixture becomes too rich for a flame to be propagated. This mixture corresponds to, and can be calculated from, the vapour pressure of the liquid in question at the upper flash-point which the authors have determined. It was found that for all hydrocarbons tested an interesting relationship exists between the two flash-points and the initial boiling-point of the liquid. In the case of mixed liquids the temperature of the first drop from the condenser in an Engler distillation is taken as the initial boiling-point. It is shown in the paper that there is a fair amount of justification for taking this figure and not any other for the initial boiling-point. The relationship referred to can be expressed in two equations:—

$$\text{Lower flash-point } ^\circ\text{K}^* = \text{initial boiling-point } ^\circ\text{K} \times 0.736$$

$$\text{Upper flash-point } ^\circ\text{K} = \text{initial boiling-point } ^\circ\text{K} \times 0.800$$

There are some disturbing factors which slightly change the values of the above constants such, for example, as the presence of dissolved inflammable gases and an undue steepness of the beginning of the distillation curve. With a reasonable degree of accuracy, however, the relations hold for all the common hydrocarbon motor fuels, and in order, therefore, to determine the flash-points of a petrol it is only necessary to determine the first-drop temperature of an Engler distillation and to use the above relations. In the case of one or two pure hydrocarbons, for example benzene and cyclohexane, the lower flash-point is below the freezing-point.

From physico-chemical considerations the authors have shown also that at the flash-points, all hydrocarbons possess, within the limits of experimental error, the same vapour tension. At the lower flash-point this is about 12 mm. mercury pressure. It thus follows that at the lower limit of flame-propagation all hydrocarbon-air mixtures possess the appropriate composition  $1\frac{1}{2}$  per cent by volume combustible vapour,  $98\frac{1}{2}$  per cent volume air. From the theoretical standpoint this opens up some interesting speculations as to the nature of combustion and flame-propagation. It follows from this equality of vapour-pressure law that at this lower limit the mean distance between the molecules of the combustible substance is the same whatever the nature of the hydrocarbon. It would thus appear that for flame-propagation to take place, the molecules must be within a certain distance of each other, and that when a flame is started in such a mixture the molecules receive an increase of translational energy sufficient

\*  $^\circ\text{K} = ^\circ\text{Kelvin or } ^\circ\text{C abs.}$

to affect the neighbouring molecules. The propagation of the flame would therefore appear to be dependent upon a critical energy-increment arising from the heat of combustion of the molecules, but allowance has to be made for the molecular specific heats. As a deduction from this it again follows that with a substance having a low heat of combustion closer packing of the molecules will be necessary in order to carry on the explosion. This is borne out by experiment, and it is found, for example, that with methyl alcohol the vapour pressure necessary is 2.3 times as high as with a hydrocarbon. With ethyl, propyl, and butyl alcohols the corresponding figures are 2.1, 1.6 and 1.4. With ether the figure is in the neighbourhood of 1.5. The relative distance apart of these molecules can, of course, be calculated, making assumptions as to the form of distribution in the gas.

If inert buffer-substances be introduced into the explosive mixture it is probable that they will prevent the free collision of the burning molecules, and thus we should expect that addition of substances like air,  $\text{CO}_2$ , water vapour, nitrogen or the like would raise the flash-point, and this is found experimentally to be the case. Conversely, the removal of some or all of the nitrogen molecules from air should lower the flash-point. This, again, is found experimentally to be the case, for instance, a petrol spirit which in air flashed at  $-10\frac{1}{2}^\circ$  in oxygen flashed at  $-30^\circ$ .

Some work has also been carried out on the influence of pressure changes on the flash-point. It has been found that over small increases of pressure the boiling-point-flash-point rule holds. Thus, if for the boiling-point we know the value of  $dt/dp$ , by multiplying this by the appropriate factor for the lower or upper flash-point we can determine the change in flash-point for a given change in pressure. Some work on flash-points at high pressures is being considered, but in the meantime extrapolating from the known results, i.e., assuming the flash-point-boiling-point law holds, we are able to calculate at what temperature of carburation with a given fuel an engine of given compression will cease to ignite. This temperature depends to a large extent on the speed of rotation of the engine leading to a change in the value of the exponential constant in the adiabatic equation. The higher the compression of the engine the narrower is the range of the exponential constant within which ignition can take place.

#### EXPLOSION RANGE.

From the work we have just been considering on flash-points and vapour tensions derived from the flash-point temperatures, we can calculate the composition of the fuel vapour-air mixture which is just too weak or just too strong to ignite. The results of course refer to a mixture at atmospheric pressure. The work has not been extended sufficiently far to state, except in an approximate manner, what the corresponding compositions would

be under given increased pressures such as obtain in an engine. At atmospheric pressure, however, Table IV. gives the calculated figures for the limits between which the fuel vapour-air mixture is combustible.

An examination of these figures will show that with practically all the pure hydrocarbons, and, therefore, presumably with hydrocarbon motor fuels, the explosive limit compositions are in the neighbourhood of  $1\frac{1}{2}$  per cent volume combustible vapour at the minimum and about  $4\frac{1}{2}$  per cent volume at the maximum. It will be noticed moreover that the range on the weak mixture side below the optimum composition is less than that on the maximum side. Taking the mean of the figures for hydrocarbons given, we find the following compositions:—Minimum 1·5 per cent volume,

TABLE IV.

Substance.	Percentage by volume of combustible vapour in mixture.		
	Minimum.	Optimum (calculated).	Maximum.
Methyl Alcohol.....	3·6	10·8	21·1
Ethyl „ .....	3·4	6·2	10·6
Propyl „ .....	2·6	4·4	8·2
Butyl „ .....	2·2	3·4	—
Amyl „ .....	1·8	2·7	—
Benzene .....	1·6	2·6	5·8
Toluene .....	1·7	2·2	4·9
Xylol .....	1·4	1·9	4·2
Naphthalene .....	1·4	1·7	—
Hexane .....	1·3	2·1	6·3
Heptane.....	1·5	1·8	4·0
Ether .....	2·4	3·4	6·0

optimum 2·1 per cent volume and maximum 4·2 per cent volume. This shows that at atmospheric pressure combustion will take place on the average when a mixture is about 28 per cent weak and 100 per cent rich below and above the optimum respectively. Mr. Ricardo in his work on “The Influence of Various Fuels on the Performance of Internal Combustion Engines” gives the figures on his standard aromatic free petrol from 25 per cent weak to 75 per cent strong, and it can be gathered from the text of his papers that at strengths below or above this the running became unstable.

Turning to the figures for the alcohols, we see that in point of absolute magnitude the range of explosibility, particularly for methyl alcohol, is greater than that for the hydrocarbons. As a

ratio, however, we see that from ethyl alcohol downwards the maximum concentration divided by the minimum is of the same order as for the hydrocarbons, namely, about 3 to 1. In the case of the alcohols, the work done by Ricardo is not such as to allow of an easy comparison, but in any case it is desirable that the flash-point work should first be extended to pressures up to about, say, 5 atmospheres. When this has been done the authors will be in a better position to bring these various researches into line.

It may be interesting to give the results of an approximate calculation of the explosion temperatures of the mixtures at their lower flash-points, see Table V.

On the right are given similar figures as calculated by Eitner.\* A reference may be made here to the theoretical researches of Messrs. Tizzard & Pye, who have calculated the explosion temperatures for various liquids, particularly benzene, heptane and

TABLE V.

		Eitner.
	° C.	° C.
Methyl Alcohol .....	800	—
Ethyl „ .....	1400	1290
Ether .....	1600	960
Benzene .....	1500	1310
Toluene .....	1900	—
Xylol .....	1850	—
Naphthalene .....	2700	—
Hexane .....	1550	1450
Heptane .....	2050	(benzene)

alcohol at various degrees of dilution with air. Figures of about the same order are given for these temperatures.

#### CORROSIVENESS.

The modern hydrocarbon fuels, particularly since limits have been placed upon the amount of sulphur compounds in them, are quite without action upon most metals. In some cases a surface film of sulphide may be produced, but the action extends to an infinitesimal depth only. It may be that the presence of this sulphide film, in the absence of moisture, inhibits any active corrosion which might otherwise take place. When, however, we come to fuels which may contain 1 per cent, 2 per cent or more of water the possibility of corrosion must be considered seriously. It is well known that alcohol, unless specially treated, always

\* Explosionsgrenze Brennbaren Gase, 1902.

possesses a slight acidity owing, no doubt, to its oxidation through aldehyde to acetic acid. A certain degree of ionization is thus produced in any fuel in which aqueous alcohol is one of the ingredients. This will lead, in the case of commercial metals immersed in the fuel, to local pitting and corrosion owing to the presence of impurities in the metal setting up a large number of electrolytic couples over its surface. Again, in the construction of an engine and its accessories it is common to use a large number of metals in more or less good electric contact. For instance, we may have an aluminium carburettor chamber containing a sheet-brass float. The latter will probably be jointed by soldering. The aluminium carburettor may be connected to the feed tank by tinned or nickelled copper pipe with a brass cone union. This copper pipe may be in turn connected to a sheet-iron tank. In this manner a large number of metal couples immersed in the liquid are produced in any arrangement. A potential difference is set up between each of the two metals, and the one which forms the cathode is liable to be corroded away.

It is well known from experiments made by the London General Omnibus Company that alcohol or mixtures of alcohol with benzol have a corrosive action on iron and on other metals. Work is proceeding in order to elucidate the nature of this corrosion and if possible to discover some means of preventing it.

The London General Omnibus Company found that alcohol-benzol mixtures corroded the iron tanks in which the fuel was carried. This difficulty was overcome by using terne plates, that is, sheet iron coated with an alloy of lead and tin containing a comparatively small amount of tin. The authors have since found that the addition of a very small amount of alkali tends to prevent this corrosive action of alcohol-benzol on iron, and the pyridine which is now insisted upon by the Government as one ingredient of the denaturant used in power alcohol, and which is a powerful base, serves this purpose. They have further found that the corrosion of brass is increased in the neighbourhood of a soldered joint, but that if the solder employed contain two parts of tin to one of lead this action of the solder appears to be inhibited. It is hoped at a later date to make public the results of a considerable amount of work which is being done on this aspect of the question.

#### VISCOSITY.

Since motor spirits are as a rule very mobile liquids, the subject of viscosity is liable to be overlooked. Viscosity is in reality a property which is dependent upon the internal friction of the material. It is true that viscosities do not vary very greatly among the petroleum spirits usually employed, but there is a very considerable difference between the viscosity of a petrol, benzol motor spirit and an alcohol, and, what is even more important, the effect of temperature in causing a variation of internal friction

varies greatly among these classes of fuel. The relative value of the viscosities at ordinary temperature may be taken as petrols 5, motor benzol 6, and alcohol 11. The question of viscosity has to be considered in its relation to the jet carburettor. It is frequently desirable that fuel shall issue from a jet with a comparatively small pressure-difference of air between the choke tube and the outside atmosphere, and the more viscous a liquid is the greater the pressure-difference that will be necessary to get fuel to issue, and, incidentally, the more difficult will it be to get the fuel into a fine state of division. If a carburettor has been adjusted to give a certain amount of fuel under specified conditions of reduced pressure in the induction system when the fuel is at, say, 15° C., it is obvious that with the fuel supplied at 30° C. or 40° C. the amount issuing from the jet, under otherwise the same conditions, will increase considerably simply on account of the reduced viscosity. Some figures as regards the effect of viscosity, quoted by Brewer, will be found in the Proceedings of this Institution\* and in Brewer's book on carburation. The whole subject is treated very fully from its scientific standpoint in Dunstan & Thole's well-known volume on "Viscosity." So long as the jet carburettor is employed, so long will it be theoretically desirable that the fuel should pass through the jet as nearly as possible at constant temperature, that is, that in carburation the problem is theoretically more easily solved by warming the air supply or by heating the fuel-air mixture rather than by warming the fuel on its way to the jet.

#### TOLUENE NUMBERS.

The use of the words "toluene number" as having a pertinent significance in relation to fuels and internal combustion engines originated quite recently from the researches of Ricardo. The toluene number is an empirical method of denoting in a more or less quantitative degree the tendency which a fuel has to detonate, that is, to cause pinking, at a certain compression. Experiments carried out on a variable-compression engine designed so that quantitative measurements could be accurately made in a very short space of time led to the discovery that for every fuel there is a compression-pressure at which pinking or pre-ignition becomes evident. It was found that, as a rule, pinking or detonation took place before pre-ignition commenced, but with a few fuels capable of withstanding an unusually high compression, pre-ignition started before detonation, due probably to the very high temperature bringing about local overheating of the sparking-plug points or from some similar cause. Working with this specially designed engine, Ricardo found that the safe compression-pressure was highest with pure toluol and lowest with a special sample of petrol from which practically all the aromatics had been removed. This aromatic-free hydrocarbon was taken as the zero material,

\* See Proc. I.A.E., Vol. VIII., p. 83.

and the toluene as 100, and the other fuels investigated fell between these limits. Generally, it may be said that among the paraffins the higher the boiling-point the lower the compression which can be employed, that is, the lower the toluene number. This is borne out, of course, by common experience, as paraffin engines have to be run at a lower compression-pressure than that which can safely be used in petrol engines. The naphthenic constituents of the paraffin motor spirits were found to withstand a higher compression than the true paraffin bodies. The aromatics resisted a much higher compression than any of the paraffins, and of the aromatics, toluol was found to withstand the highest compression. From the previous remarks in the section on freezing points, it will be remembered that motor benzol had to contain 30 per cent, or thereabouts, of toluol to prevent the possibility of the benzene freezing and separating in the solid state. From the point of view of its practical application it is a fortunate circumstance that the toluol thus added for one purpose should prove to be so admirable from an entirely different standpoint. Experiments carried out by Ricardo for the Empire Motor Fuels Committee since the publication of his work in the "Automobile Engineer" have led to the discovery that ordinary ethyl alcohol will withstand with safety much higher compressions than those which can be employed even with toluol, and that if toluol be classed as having an efficiency of 100, ethyl alcohol would be of the order of 165.

It must be borne in mind that the toluene numbers are a measure of the compression which can safely be employed in a specially designed engine, having as nearly as possible an ideally-shaped combustion chamber with very efficient cooling, with aluminium piston and with unusually large valves. It does not follow that the compressions which could be used with the variable-compression engine could be safely employed in any engine, for there are still engines on the market so badly designed as regards combustion space, cooling and position of sparking plug that they would almost pre-ignite if fed with a mixture of alcohol and water. These questions of the effect of design do not, however, alter in any degree the relative orders of the various fuels as expressed by the toluene number.

In view of the present tendency to design small-bore engines of high efficiency, these questions as to the influence of the chemical nature of a fuel on its physical properties and behaviour become increasingly important. To escape taxation, designers endeavour to get the maximum horse-power out of an engine designed with the smallest possible cylinder diameter. In order to do this they increase the compression to an extent which often places the owner in a difficult position in that he finds that he cannot run with comfort on some fuels and that unless he can get benzol to mix with certain of the fuels otherwise available the added horse-power of which his engine should be capable cannot be realised,

and when running on these unsuitable fuels he is not only deprived of the extra potential horse-power, but has to run with partly-closed throttle and retarded spark when hill-climbing, conditions which make for a hot engine and burnt and pitted valves. It will gradually become realised by the purchasing public that the super-efficient engine is only super-efficient when supplied with certain fuels, and that with unsuitable fuels it can become a "super-nuisance."

It is only by a study of the physical properties of fuels in relation to their chemical properties that we can hope to get out of the present difficulties. There is not enough benzol available to make all the existing motor spirit capable of withstanding, what we may call generally, super-efficient conditions, but it is by no means improbable that other means may be found of overcoming these difficulties.

#### SPONTANEOUS IGNITION TEMPERATURES.

Closely related to toluene numbers is the subject of spontaneous ignition temperature. It is known that if a mixture of fuel and air in the right proportion to form an explosive mixture be rapidly compressed there comes a point when the mixture spontaneously ignites, due partly to the heat produced by the compression and partly to the compression bringing oxygen and fuel particles within closer range of each other. Experiments have also been made by heating fuel vapour and air separately and bringing them together in order to find out the lowest temperature at which the hot fuel will ignite in coming in contact with the hot air. Generally, the figures obtained by either method of work agree in the main, but very considerable variations are found between the results of different workers in the same field. It is difficult to disentangle the various causes at work, and, particularly when the fuel and air are heated separately, to entirely remove the effect of surface of material in bringing about increased combustion at lower temperatures. Although these figures are of the greatest importance, experiments have as yet yielded no very concordant results, and the experimental methods are slow and expensive. The spontaneous ignition meter has opened out the way to obtaining with rapidity and at low cost figures which, though as yet uninterpreted, are concordant and of considerable value. The principle of the meter consists in letting a single drop of the fuel in the liquid state fall into a crucible heated to the required temperature and full of oxygen at that temperature. A great deal of work has been done by Moore with this instrument, and he has found that the paraffins ignite at a very much lower temperature than the aromatics and that of the paraffins the ignition temperature falls with increase in the molecular weight. In the case of the aromatics the same law obtains; thus, toluol has a lower ignition temperature than benzol, and, finally, the



alcohols have higher ignition temperatures than even benzol. In general, it may be said that spontaneous ignition measurements as made by Moore agree qualitatively with Ricardo's results.

All attempts up-to-date to correlate chemical and analytical results of examinations of liquid fuels with the toluene number or with the spontaneous ignition meter have failed. It is possible to gather an idea as to the probable behaviour in an engine of any fuel from its chemical examination, but, like the weather forecasts, though they are correct on the average they are wildly wrong at intervals. A great deal of work remains to be done on underlying principles regarding the propagation of flame.

It will be obvious that very many physical properties which have a bearing on the use of volatile fuels in internal combustion engines have not been touched upon, but some of these, such as dissociation, have recently been dealt with at considerable length by Tizzard & Pye, and it was felt that they were not of a nature which could readily be dealt with in conjunction with the matter here included. It could truly be said that a great deal of this paper consists in a re-statement of known results, but the authors doubt very much whether, in the first place, the work is as widely known as it should be, and, in the second place, whether the full implication of the work is actually realised.

They wish to place on record their appreciation of the financial help that has been rendered by the Distillers' Company, Ltd., and by the Fuel Research Board of the Department of Scientific and Industrial Research.

#### SPECIFIC HEAT.

Dr. Lanchester has suggested that reference might be made to the specific heat of liquid fuels. Comparatively little exact work appears to have been done as regards the determinations of the specific heats of liquid fuels, and it is desirable that the matter should be investigated, as although the heat involved in automobile practice is not considerable, it is of importance in many industrial operations. The specific heat of petroleum ether at 0° C. is given as 0.42, and of heavy petrol at 100° C. as 0.48, the specific heat of the naphtha fraction of American petroleum is stated by Graefe to be 0.487, but no limits of temperature are given. The kerosenes are stated to have a specific heat varying from 0.45 to 0.6 as the temperature rises from 0° C. to 400° C. Benzol may be taken to have a specific heat at ordinary temperatures of about 0.45, and alcohol 0.61. It will be seen that assuming that a motor fuel has to be heated from 60° F. to 140° F., and assuming an average specific heat of 0.5 only 40 B.Th.U.s. are involved, that is approximately one-third of the latent heat of evaporation.

## THE DISCUSSION.

Mr. R. H. PEARSALL, in opening the discussion, said: In the course of some recent experiments, I wanted clearer information in regard to the petrol that I was using, and taking the figures of the aromatic and the "A" to "H" petrols in Table I., I plotted as ordinates the B.Th.U.s. per gallon, and as abscissæ the specific gravity, and drew a straight line through them with a very small amount of error. I should like to ask the author if he thinks that was a justifiable proceeding, and if I can assume from that that, at any rate with approximate accuracy, the specific gravity does indicate the B.Th.U.s. per gallon. If so, does that apply to the Shell spirits, does it apply to petrol in general, or what are the limitations, because a straight-line law between specific gravity and B.Th.U.s. per gallon gives such a simple diagram; whatever the flow-meter measures, it can be translated into the B.Th.U.s. that are being put into the engine with such accuracy that the errors do not matter at all. The author has referred to flame-propagation; at the Motor Show this last year, the Sphinx Plug Co. had four glass tubes, with a little coal gas jet coming up from the bottom, with Sphinx plugs at the top, and as the mixture rose up the tubes the plugs ignited it, and the flame travelled down the tube again and blew out. The flame appeared to me to travel much faster down the outer surface of the column of gas than down the centre. I can imagine that this was due to the residual temperature of the glass walls heating the part of the gas in contact with them, and making it more inflammable, so that the rate of propagation was faster at this point. I shall be glad if the author can instruct me on that point, because it may have an influence directly on the engine.

Mr. D. S. HEATHER: I notice that both in Mr. Ricardo's paper and in the present paper the range of fuels dealt with goes up, as far as Shell or Pratt's No. 1, but there is on the market so-called aviation spirit, sold by Shell and Pratt's, and I should like to ask the author to tell us in what way that differs from the ordinary No. 1 petrol of commerce at present, so that we may have some idea of whether the extra 5d. or so per gallon is really justified, and if, in practice, any advantages are obtained from it.

Mr. H. S. KIPLING: I should like to ask the author if he has gone to the trouble of fractionating petrol and ascertaining the spontaneous ignition temperatures of the various fractions, because I did some a little while since, and they gave some rather interesting results. The first 10 per cent ignited at a temperature of 284° C., and the residual 10 per cent at 254°. I also made mixtures of benzol and petrol, and it was very interesting to see

that it was necessary to add at least 30 per cent of benzol to affect the spontaneous ignition temperature by 5 degrees C. After the addition of 40 per cent of benzol it goes up with a rush, and, of course, with 50 per cent it is well known how it affects the actual working of the engine. The real difficulty is that the results obtained by different investigators are liable to considerable variations though I can get very concordant results with the same petrol on different days, and results which agree with engine tests.

Dr. ORMANDY: Do you get the 20 seconds wait with oxygen?

Mr. KIPLING: Yes, but not to the same extent as yourself. I should say that I tested the fuel in the reverse way to yourself, that is, on a falling temperature. It is quite easy to tell when the temperature has fallen to about 15 degrees or 10 degrees above ignition, because then the delay commences, and increases until the true point is reached, when the delay may be as much as 40 seconds.

Dr. ORMANDY: That is extraordinary.

Mr. KIPLING: And there is a big difference in the sound, which again cannot be put on paper. It seems to me that this is a most valuable test, and I should like to suggest that if the author can "make" this test in the sense of making it a popular one it would be exceedingly valuable, because in the meantime it is very little used indeed, and the makers tell me that the apparatus is rarely called for now.

Mr. J. NASMITH: The author and others have carried out valuable experiments on motor fuels which should be of great assistance to the designers of motor car engines. With the information now at their disposal designers should be able to evolve an engine of maximum efficiency when using a grade of fuel of known qualities. The difficulty seems to be, however, that there is no certainty that the quality of the fuel will remain constant. It is well known that the fuel we buy to-day is quite different from that which we purchased ten years ago. I would like to ask the author if any standard of quality has been laid down, and, if so, would it be possible to get the petrol companies to work to it?

Mr. J. BURTON: I should like to ask the author if he can say what is the effect of pre-heating the spirit before it enters the carburettor. I have heard that if the spirit is heated beforehand it causes pinking to be worse.

Mr. W. D. SHURROCK: With regard to the question of spontaneous ignition, I should like to have the author's opinion as to the possibility of the surface tension of the liquid causing the phenomena observed.

Mr. D. S. HEATHER: The figures given by Mr. Ricardo and the author lead us to suppose that we are, in general, right in using some form of benzol, or, at any rate, toluene-containing fuel. Is it a fact that such a fuel, particularly commercial benzol as we know it, gives a higher exhaust temperature, because it has been

(Mr. D. S. Heather.)

found by many people who are using such a fuel that it has a bad effect on the exhaust valves?

Mr. C. H. Cox: Some little time ago I came across an engine which would only give the best results so far as power is concerned if the fuel was not too finely atomised. I have noticed with other engines that if the fuel is atomised so finely as to give perfect combustion they do not develop their maximum power with that finely atomised mixture, and it is necessary, in order to get the best results, to use a lumpy mixture, the petrol being put in in great bubbles, so to speak.

The CHAIRMAN: I have been particularly interested in the latter part of the paper in which the author deals with the spontaneous ignition temperature. Apparently there is some similarity between the results that are obtained with these fuels and the results that are obtained with metal specimens stressed in a Wöhler testing machine. In a Wöhler test the nearer the stress approaches to the ultimate strength of the material, the sooner the specimen breaks off, and it is found that the curve showing the relationship between the number of revolutions required to break the specimen and the stress is approximately a hyperbola. It appears from the figures quoted that the author's curve plotted as temperature against time may also be a hyperbola, thus producing a very interesting similarity, possibly however for totally different reasons. With regard to the much higher spontaneous ignition temperature for gas as compared to liquid, although I have never made any accurate tests, I have always assumed from experience that spontaneous ignition in a cylinder does not take place unless some portion of the interior—I am talking about petrol now—of that cylinder has reached a temperature of about 700° C., which roughly corresponds to the figure given by the author for tests in the apparatus.

Dr. ORMANDY, in replying on the discussion, said: Mr. Pearsall suggested that the relationship between specific gravity and B.Th.U.s. lies approximately on a straight line. He is correct for the hydrocarbon fuels, that is, the benzenes, the aromatics, and the naphthenes, but utterly wrong so far as alcohols, the ethers, the ketones and other classes of bodies are concerned. Without seeing the actual arrangement, it would be difficult to say the reason for the formation of the cone in the travel of the explosion down the tube in the Sphinx plug experiment; it may be due to the fact that the gas mixture is more concentrated in the centre owing to the manner in which the test is made. The effect of cooling or heating a surface is extraordinary, and in this matter of the propagation of flame, it is very difficult to say what is going to happen. It is possible to have ether burning on a surface which is a little hotter than the temperature of boiling water, but it gives a blue flame, in which part of the ether only is burning, and it is hardly hot enough to light a match. The main

difference between aviation spirit and ordinary No. 1, as shown by the usual fractionating curve by the so-called Engler distillation test, is that it begins to come off at a lower temperature, and a much higher percentage comes over. There is less rise in temperature in the portion of the first 10 per cent of the spirit, and consequently an engine would start more easily, but so long as a fuel will allow the engine to start easily it is foolish to pay 5*d.* a gallon extra for the lighter spirit, because it gives less B.Th.U.s. per gallon, and the best value for money in reality is obtained with that portion of the petrol which distils between 80° and 180°. It must be borne in mind, too, that every gallon of lighter spirit that is used robs the world of several gallons of motor spirit, because every gallon of aviation spirit contains enough highly volatile liquid to enable two or three gallons of heavier mixture to be made into No. 1 spirit, and we in this country do not realise that we are getting a spirit which is far better than anything they get in America. We grumble if our spirit, which starts distilling at 60°, finishes at 190° or 200°, but in America their so-called gasolene finishes distilling at 240°. In other words, it contains more of the kerosene fraction than our English petrol, and the reason why the Americans send their best quality spirit to this country is because they get more money for it. The effect of benzol on the exhaust valve is due to the fact that benzol requires more air. When running an engine on a mixture rich in benzol, either the jet or the weight of the float must be altered, and a common-sense use must be made of the auxiliary air inlet valve. It is worth repeating that the fuel in a motor car cylinder is oxygen. The cylinder cannot be more than filled with air, and the oxygen of the air is burnt by means of fuel, and it does not matter what fuel is used, the same amount of heat is got out of it. It is a fact that nearly all fuels give practically the same amount of heat if the ideal amount of fuel is supplied to burn so many cu. in. of air in the cylinder. If one lot of fuel allows the use of a higher compression than another, more work is obtained, but that is another matter altogether. The spontaneous ignition temperatures of a very wide range of bodies have been obtained by Mr. Moore, and these he gives in his book on "Fuel Oils for Diesel Engines." Mr. Kipling pointed out that 30 per cent of benzol must be mixed with petrol before it begins to affect the spontaneous ignition temperature appreciably. Mr. Craven and myself published in the Journal of the Institution of Petroleum Technologists a short research into the boiling points, flash-points and spontaneous ignition temperatures of mixtures of benzene and petrol, and alcohol and benzene, and so on, in order to find out what connection existed between the various physical properties of these mixtures, and possibly that might interest Mr. Kipling. I should also like to say to Mr. Kipling that if 20 per cent benzol is added to petrol, it increases the vapour pressure nearly as much as if 30, 40 or 50

(Dr. Ormandy.)

per cent is added, so that from the point of view of easy running and easy starting the full benefit is obtained from the benzol if only 20 per cent is added, and that was found out, strangely enough, purely empirically, without any theory, by the men who drove racing motor cars in France, and who ran invariably on petrol containing 20 per cent of benzol. Mr. Nasmith referred to the fact that fuels vary very greatly as between one maker and another. The only firm I know who are turning out systematically a spirit with a standard detonation value is the Shell Company, and they do it because they have at their command these natural aromatic-containing petrols from Borneo, and they mix these with their other petrols, and they have them regularly tested by Mr. Ricardo, because there is no means of calculating it by any method of analysis, and they regulate their mixtures so that all the spirit that they send out will spontaneously ignite or detonate in an engine at the same compression. No other companies do that. We are faced with this position, that either we have got to make our engines with a lower compression to suit the fuel, or we have got to tell the fuel makers that they must give us a fuel that will suit our engines. There is not only benzol, which will make the ordinary American petrol equal to Shell, but the figures given in Table II. indicate that there is a great possibility that we can get over the difficulty by adding a very small amount of very strong alcohol to ordinary American petrol. Mr. Ricardo finds that, whereas toluol has an anti-detonating effect, which he calls 100, ordinary ethyl-alcohol has a figure of nearly 210, and ordinary motor benzol has an anti-detonating effect of 60, but if 30 per cent of motor benzol is added to the American petrol, that makes it equal to a No. 1 Shell, and instead of adding 30 per cent of a material which has a toluene number of 60, only about 8 per cent of a material which has a toluene number of 200 need be added. I think it will be found that if somewhere between 5 and 10 per cent of strong alcohol is added to an American petrol or a Russian petrol, its pinking propensity will be reduced to about the same as that of an ordinary American petrol to which 30 per cent of benzol has been added. There will be no difficulty in supplying the world with 5 to 10 per cent of alcohol to mix with this petrol, and if we can only get a standard petrol, and if the motor designer knew that with a standard engine he had fuels which would detonate at the same compression, he would know exactly how high he might go with his compression from the point of view of the fuel. Mr. Morgan referred to the formation of ice in the induction pipe; when a fuel evaporates from a liquid to a gas, heat is absorbed in the gas to the extent of about 135 B.Th.U.s. per lb. of petrol evaporated. In the case of benzol the figure is 165 B.Th.U.s. per lb., and in the case of alcohol it is 400 B.Th.U.s. If the fuel evaporates into the air, as it has to take its heat from somewhere, it takes it from the air and reduces the temperature. If the temperature

of the mixture is reduced, the moisture in the air separates out in the form of ice, so that if a very good vaporising or atomising carburettor jet is used the incoming air must be warmed, and the necessary heat supplied to a corresponding degree or water will inevitably be produced in the induction pipe. With benzol the tendency to get ice in the induction pipe is very much greater, owing to its higher latent heat of evaporation, and as stated in the paper, Ricardo has proved that this latent heat of evaporation is a positive asset. The fuel is injected into the cylinder as a liquid, and if that liquid has a high latent heat of evaporation it picks up heat from the cylinder walls and from the piston top, and it cools down the gases in the cylinder and gives a higher volumetric efficiency, and in reality the latent heat of evaporation ought to be added to the heat of combustion to get an appropriate picture of the value of any fuel.

In reference to the use of "spots," Mr. L. S. Palmer in his paper\* read before this Institution showed that if 30 per cent of naphthalene is added to petrol, the value of the fuel is increased by 3 per cent. Now, if 30 per cent of naphthalene gives 3 per cent increase, 10 per cent gives 1 per cent, and as a "spot" is about a hundredth part of one per cent, what will that give? Mr. James, the head of the Fuel Department of the Bureau of Standards in America, referred me to the label on a box containing one of the American "spots" which read as follows: "Before using the spots, take down the cylinder and scrape the engine and cylinder walls, clean the head of the piston, grind in the valves, put in a smaller jet, see that the choke tube is not too small, and use an auxiliary air inlet, and then add one spot and fuel consumption will be reduced." Mr. James explained to me that the price the public paid to the makers of "spots" was repaid to the nation a hundred times in the economy that it brought about in the use of petrol through keeping the engines in better condition. Mr. Burton referred to the possibility of preheating the fuel, but in the paper it was pointed out that owing to the alteration in the viscosity of the fuel it is bad in principle. Let me put it this way: it is a very difficult problem indeed to arrange the jet of a carburettor which will deliver fuel proportionately to the throttle opening if the temperature of the petrol is constantly varying, because a jet which will permit under a given suction a certain amount of fuel to pass when the fuel is, say, at 15° C., may allow nearly twice as much to pass if the fuel is heated almost to the boiling point. It is much wiser in principle to apply the heat to the air going into the carburettor, and then, by means of the hot-spot manifold, or some modification thereof, to heat the mixture of fuel and air on its way to the cylinder.

I would like to refer to the experiments carried out by the London General Omnibus Co. in the use of a mixture of 70 per

\* See Proc. I.A.E., Vol. XV., p. 195.



(Dr. Ormandy.)

cent alcohol and 30 per cent benzol on a standard engine with a compression of 90 lb. per sq. in. They got a bad consumption in the ordinary way, and they altered the compression of a number of engines to 126 lb., and ran them on this mixture. They then got about the same fuel consumption, or very little more than when running with the standard 90 lb. engine on a standard petrol. They then replaced 5 per cent of the alcohol with ether, the mixture then being 30 per cent benzol, 5 per cent ether, and 65 per cent alcohol, and they got a lower consumption on their 90 lb. compression engines with that mixture than with petrol, or a mixture without ether at 126 lb. compression. Thus, it is quite obvious, from that experiment alone, which was carried out, not on one motor 'bus running for 100 miles, but on six 'buses running 6,000 miles each in actual London usage, that some of these fuels, like ether, which have extraordinarily low ignition temperatures and a very low detonation pressure and very low spontaneous ignition temperature, can have the effect of causing the mass of fuel with which they are mixed to burn much more completely. I am glad to say that the Empire Motor Fuels Committee has now got some funds, and Mr. Ricardo is carrying out some work with his variable-compression engine, his super-charging engine, and others, on mixtures of alcohol and ether, and alcohol, petrol and ether, in order to get some fundamental facts which will be of use when the time comes that we have to make use of these fuels. Mr. Shurrock referred to surface tension and its effect on spontaneous ignition temperatures. I do not see why surface tension should have much to do with it, but there is this possibility; it is well known that whenever one drop of liquid falls on to a plate it splits up into a number of smaller particles. There is, in other words, a vast increase of surface, a great electrification of the particles, and what is called an electrical double layer is broken up, and electrical charges are produced, and it is possible that these electrical charges in some way bring about ionisation of the fuel, which puts it into a state in which it is easily capable of combining with the oxygen of the air. Whether that is an explanation or not I do not know, but it is a line of attack which is worth consideration. Mr. Cox referred to the fact that it pays, possibly, in some engines to allow the fuel to get into the cylinder, so to speak, in lumps. In a certain engine, running at a compression of nearly 7 to 1, alcohol is injected into the cylinder; in consequence of the high temperature of explosion due to the high compression the piston gets very hot indeed, but by injecting the alcohol in lumps, as it were, on to the top of the piston, the waste heat of the piston is used to evaporate the fuel, which has a very high latent heat of evaporation, to cool the charge in the cylinder, and a mean brake effective pressure of 160 lb. per sq. in. is obtained. The Chairman referred to the ignition temperature and time relationship possibly being a hyperbola. Mr. Moore, who has hitherto been the



only one who has done work on this apparatus to any extent, did not plot his times, nor did he record them sufficiently accurately to enable this to be done. A modification of Moore's apparatus is, however, being constructed for work under a normal pressure, and up to 5 or 6 atmospheres, and we hope to carry out these determinations, not only as to the influence of time and temperature, but also as to the influence of varying amounts of dilution gases, i.e., the presence of  $\text{CO}_2$  and water, which are always present in the residual gases left in the cylinder. Ricardo has found that it is possible, by adding a small percentage of exhaust gases to the air going into the carburettor along with the air going through the induction system, to run the engine with wide open throttle with so little fuel going through that the power generated by the engine was only sufficient to just drive the flywheel round. The mixture could be weakened down and down and steady combustion yet maintained, of course at the expense of fuel. But there is something extraordinary about the effect that  $\text{CO}_2$  and water, i.e., the products of combustion, have on the nature of the propagation of flame that requires investigation. I hope that other people are working on it, but at any rate, Mr. Craven and I decided that this is a line of attack which is worthy of consideration.

## COMMUNICATION.

Mr. R. H. PEARSALL wrote: Table I. indicates that we may express the heating value (lower) of motor fuels, petrol and benzol in B.Th.U.s. per gallon in terms of the specific gravity. Writing specific gravity  $G$ ,

$$\text{B.Th.U.s. per gallon} = 38000 + 137500 G.$$

Petrol "C" in Table I. is given by Shell Mex, Ltd., as having an ideal combustion ratio of 14.7 to 1 by weight.

And Shell No. 1, in recent samples, has specific gravity = 0.755.

Hence the ideal mean effective pressure becomes 504 E, and the efficiency  $\eta = 0.1445/C$ , or 0.1445/pints per horse-power per hour.

It is therefore of close and sufficient accuracy to draw the  $E = 0.2$  Ray from the origin to the point 100  $\eta p/100$  per cent charge, and to erect the efficiency scale on the 100 per cent ordinate for Shell No. 1, S.G. = 0.755.

The above approximate relation of B.Th.U.s. per gallon to specific gravity appears to be within two-thirds of one per cent, and Dr. Ormandy considers that it is applicable generally as stated, and not only to the list A—H given in his paper.