DIE BESTIMMUNG DER PUMPFAHIGKEIT VON HEIZÖLEN

By H. R. Asbach and J. Tegethoff, February 1943 number
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DETERMINATION OF THE PUMPABILITY OF FUEL OILS

by H. R. Asbach and J. Tegethoff

The pour point of an oil is chiefly determined to characterize the behavior of the oil, in particular a fuel oil, at different temperatures. Although oil men know that the determination of the pour point is entirely empirical, and that the accuracy and reproducibility are far from satisfactory, this method of characterizing the behavior of fuel oils at low temperatures remains necessary as long as no other property, such as viscosity or density, can take its place. The pour point is conventionally known as the temperature at which an oil no longer moves, or begins to flow under the influence of gravity when the test container is inclined at an angle of $30°$. This involves the determination of two temperature limits, either the temperature at which the oil under investigation ceases to flow, or the temperature at which it just begins to flow again. Both temperatures are used to characterize the behavior of oils at low temperatures, but usually without specifying which of the two temperature limits is selected for the measurement. This results in considerable differences between the temperature data of various testing laboratories, but even when one of these temperature limits is agreed upon, the method still leaves a wide margin of $\pm 5°$ which is accepted as the permissible limit of error. This temperature margin of $\pm 5°$ might be tolerated if it were not causing trouble in practice. Complaints from various fuel oil consumers prove this conclusively. This is easy to understand if we consider the reasons for adopting a method of characterizing the behavior of oils at low temperatures. In most cases fuel oil is stored before use in either movable or stationary tanks from which it is conducted by means of pumps to the place of use, according to purpose. In addition to the heating quality of a fuel oil the consumer is also interested in its behavior at different

temperatures, in particular at temperatures at which it can no longer be conveyed
to or from the desired locality by ordinary means of transportation. A fuel oil
which under normally occurring temperatures requires excessive work for pumping
it with the customary pumping equipment may not always be accepted for practical use
despite its excellent combustion properties.

This illustrates clearly that the conventional determination of the pour point
is inadequate for establishing the temperature at which an oil is no longer convey-
able, since a limit of error of $\pm$ 5° is much too wide for such a purpose. Moreover,
the pour point only portrays the behavior of the oil at the temperature limit refer-
red to, but fails to give information on its behavior before it reaches this temp-
erature. In view of these facts, which often lead to complaints by fuel oil consumers,
Dr. Mueller suggested the development of a new testing method which would eliminate
the difficulties encountered at decreasing temperatures and allow an accurate deter-
mination of the temperature at which a fuel oil can no longer be satisfactorily pumped.
In the study of this problem a measuring instrument was developed which allows the
properties of fuel oil at low temperatures to be determined in advance with sufficient
accuracy for practical purposes -- a property which we have called "pumpability".

If we determine the work required by a pump to convey the oil to be tested
through a n accurately defined cross-section at variable oil temperatures, this
value allows drawing direct conclusions as to the temperature behavior, or the so-
called pumpability of/oil. Since due to the law of uniform distribution of pressure
                    the
in all directions the pressure of the piston on the oil in the pump cylinder is
uniform at every point, this pressure can be measured at any suitable place of the
cylinder. By multiplying this pressure with the surface area of the piston head,
which is known from the type of pump used, a figure is obtained for the total force
acting on the piston head. Further multiplication of this force by the length of
the piston stroke gives the desired figure for the work required. A pressure gage
fitted to the pump cylinder can be calibrated directly to read work units. In order
to obtain an accurate measurement with an ordinary pressure gage it is necessary to

take into account the time lag of the gage. This limits the number of piston strokes per minute. A value of 10 strokes per minute was found to be sufficient. This low number of strokes also has the advantage that the pressure indications dependent on temperature can easily be read.

Apparatus

Figure 1 shows diagrammatically an arrangement for determining pumpability. The piston pump 1 is connected through a suction line 2, and the pressure line 3 with the tank 4 containing the oil to be tested. A test nozzle 5 is placed in the pressure line 3, through which the pumpability can be determined at a variable cross-section of the pipe. The pump cylinder as well as the storage tank are both provided with cooling jackets 1' and 4', through which the coolant is passed after having been brought to a predetermined temperature in a thermostat. The temperature of the oil which is to be tested is measured in the lower portion of the pump cylinder by a thermometer 6 and the pressure in the pump cylinder with a gage 7. To prevent heat radiation, internally and externally, all parts through which the oil flows are covered with heavy insulation. The pump 1 is driven by the motor 9 through a gear 10 and the crank drive 11. In order to dampen jumpy indications caused by the motion of the pump, an air vessel 12 is inserted in the gage line. The means required for cooling the oil consist of a thermostat (manufactured by Gebr. Haake, Medingen) and a cold accumulator from the same manufacturer. Methanol is used as the thermostat liquid and dry ice as cooling agent. Figure 1 also shows the connection of the measuring apparatus to the cooling means.

Measurements

The oil to be tested for pumpability was first freed from fibrous and coarse, granular contaminations by filtration or settling. Of this prerefined oil about 400 cc was poured into the storage tank 8 (fig. 2). After connecting the cooling line to

the measuring apparatus the cooling means were put in operation and the cooling adjusted so that the temperature drop on the thermometer D was about 5° C in about 30 min. The temperatures and pressures indicated on the thermometer D and the gage E were plotted in curves on semi-logarithmic millimeter paper. The temperature was selected as abscissa and the corresponding pressure as ordinate. As will be seen from fig. 3, the curves are at first linear, then they bend to the left and, after reaching a maximum, drop again. This maximum, in addition to the temperature-dependent pressure reading, is a characteristic for the pumped oil. The temperature pertaining to this pressure maximum is the temperature limit at which the oil has a consistency such that it can no longer be conveyed by pumps under normal conditions. As indicated by a number of measurements, the temperature corresponding to the pressure maximum is independent of the diameter of the test nozzle used. A change in the cross-section by using nozzles of different size only increases or reduces the work required for pumping the oil, according to whether the cross-sections of the nozzles are increased or reduced. Fig. 3 to 6, which show the pumpability curves of different fuel oils, indicate that the deviation from the "critical" temperature for the first 3 oils is 0.5°, and for oil D not more than 1°. A striking fact in the pumpability curves of fuel oils C and D (figs. 5 and 6), is the very pointed shape of the curves. The reason for this behavior, in our opinion, is due to the fact that such oils suffer a sudden change in their consistency when they are undercooled and can no longer be considered to be homogeneous within this particular temperature range. On reaching this temperature threshold, all pressure indications on the gage begin to be irregular (when nozzles are used of less than 8 mm diameter). To indicate this state, the curves are shown in broken lines from that point on. The pressure maximum, however, is independent of these processes and can be definitely established.

In this connection it is of interest to compare the pour points (the temperatures in this case refer to the state at which the oil just begins to flow again) with the "critical" temperatures determined in the measuring apparatus. This

comparison is shown in table 1.

<div align="center">Table 1</div>

Fuel oil	Visc. in Cp at 20°C	Specific gravity at 20°C	Pourpoint °C	"Critical" temp. °C
A	76.83	1.036	- 13	+ 4
B	689.36	1.007	- 20	- 4.5
C	37.30	0.951	- 18.5	- 11
D	12.75	1.074	- 16	- 9.5

The table shows that no direct connection exists between the pour point temperature and the "critical temperature. Consider the rather unwelcome surprises the fuel oil consumer may experience if he believes that his fuel oil is still pumpable on the basis of pour point temperature data and then finds that at ± 0° the fuel pump no longer operates. To what results that may lead is not difficult to see, and it is understandable why complaints by fuel oil consumers are made for such reasons.

Illustrative in this series of tests was the inspection of two fuel oils having almost the same viscosity and burning properties, with respect to their fitness and behavior at low temperatures, as reported by one consumer. The results of this test are shown in figure 7. While the fuel oil U had a critical temperature of + 2.4°, this temperature was -1.5° for the fuel oil V. For this reason the oil V was better for practical purposes than the otherwise equivalent fuel oil U.

It is frequently necessary to blend a fuel oil having poor cold properties with another fuel oil having good properties in order to furnish a fuel oil blend meeting requirements. A requisite for making such a blend is naturally that the two oils are mutually miscible, in other words: they shall have no tendency to flocculate. This requirement applies to the blends listed in the following table. Table 2 gives interesting data on blends M to Q in this connection.

Figure 8 shows the corresponding pumpability curves in this series of tests and indicates that at least 40% of fuel oil Q must be added to fuel oil M to bring

the "critical" temperature within the desired limits, below -5°

In another case an oil for servicing a gasometer was inspected with respect to its cold properties.

As will be seen from table 3, "the critical" temperature of this oil was -10°, in contrast to the pour point temperature of -29°. We often found from experience gained during the last severe winter, that the pour point gives no satisfactory indication of the behavior of such gasometer-oils at low temperature.

Table 2

Mixture		Pourpoint °C	"Critical" temperature °C
Fuel Oil M	Fuel Oil Q		
100		+ 27	+ 15
80	20	+ 12	+ 5
50	50	- 9	- 13

Table 3

Characterization	Viscosity in Cp at 40°C	Pour point °C	Pumpability °C
Additive oil..........	11.68	- 67	- 19
Gasometer oil.........	55.30	- 29	- 10
30% Additive oil...... 70% Gasometer oil.....	31.66	- 36	- 13
50% Additive oil...... 50% Gasometer oil.....	25.25	- 49	- 16
70% Additive oil...... 30% Gasometer oil.....	17.13	- 58	- 17.5

The differences given in Table 3, resulting from a comparison of pour point and critical temperature, indicate clearly the dangers which are hidden in an absolute method of rating the quality of gasometer oils at low temperatures. Temperatures of -16° in the wells and, particularly at the walls of the container were measured by us. According to the value of the pour point no trouble should occur at these temperatures but, in practice, it was unfortunately not so. On the contrary, the gasometer oils when used at -16° had a consistency which made the immediate shut-down of the gasometers necessary. Attempts of blending these gasometer oils with some other, more cold-resistant oil resulted in a "critical" temperature of -16° first being reached for a blending ratio of 50:50, as shown in Table 3, so that this blend can only be used during extensive periods of frost when a temperature drop below -15° is prevented in the well and container by additional heating.

SUMMARY

A measuring apparatus is described which allows the determination of a factor comprising the behavior of fuel oils at low temperatures, in close agreement with practical conditions, and in a more satisfactory manner than by the usual pour point determination. This factor has been called "pumpability", as suggested by Dr. F. Mueller, and represents an expression for the work needed to pump an oil at a predetermined temperature. The temperature limit reached for the test oil on continuous cooling, at which the oil is no longer pumpable, is shown graphically and is called the "critical" temperature. This so-called "critical" temperature is, in our opinion, far better for rating the behavior of fuel oils at low temperatures than any heretofore applied factor.
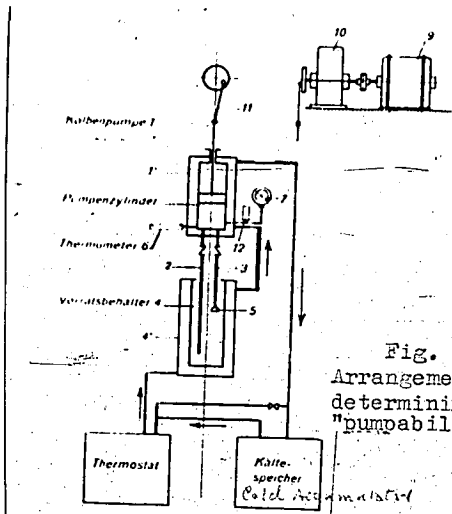
Fig. 1
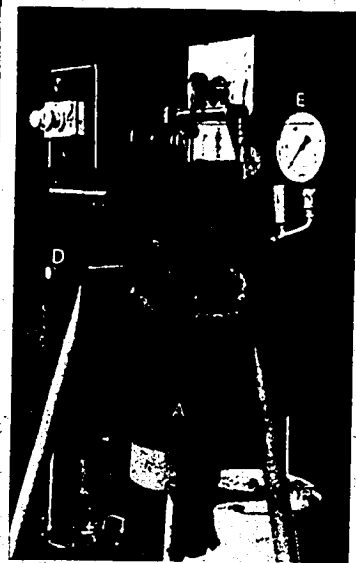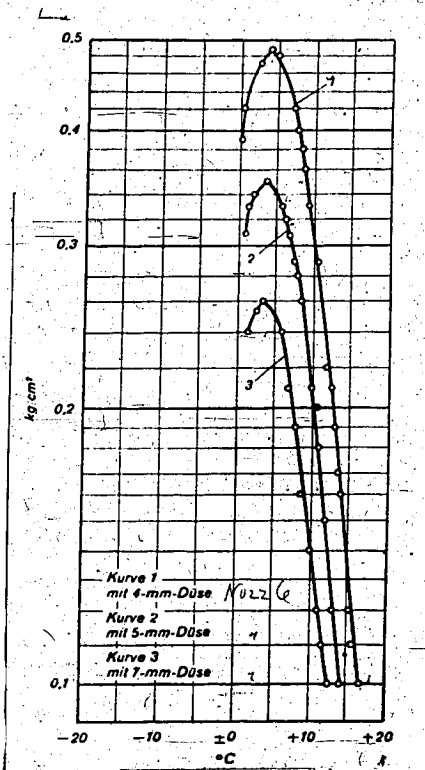Arrangement for
determining
"pumpability".

Kolbenpumpe 1
Pumpenzylinder
Thermometer 6
Vorratsbehälter 4

Thermostat

Kälte-
speicher
Cold Accumulator

Fig. 2

Kurve 1
mit 4-mm-Düse Nozzle
Kurve 2
mit 5-mm-Düse
Kurve 3
mit 7-mm-Düse

kg/cm²

−20   −10   ±0   +10   +20
°C

Fig.3. Fuel oil A.

Kurve 1
mit 5-mm-Düse Nozzle
Kurve 2
mit 7-mm-Düse
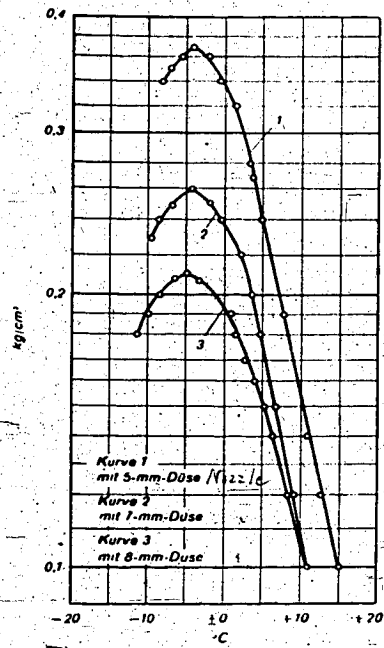Kurve 3
mit 8-mm-Düse

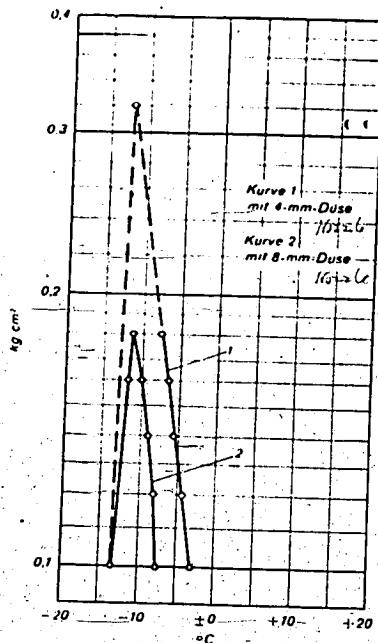kg/cm²

−20   −10   ±0   +10   +20
°C

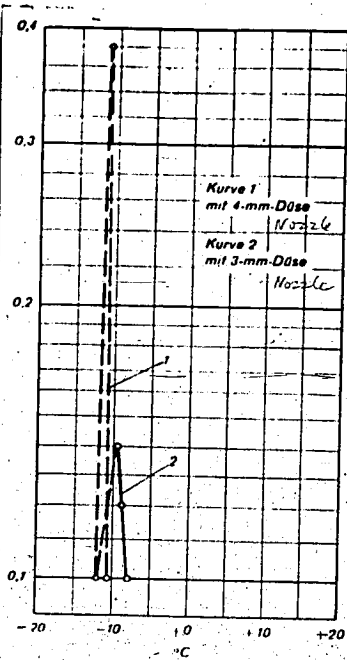Fig.4. Fuel oil B.

Fig.5. Fuel oil C.
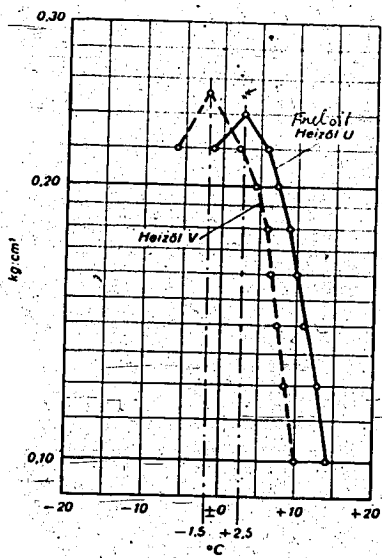

Fig.6. Fuel oil D.

Fig. 7
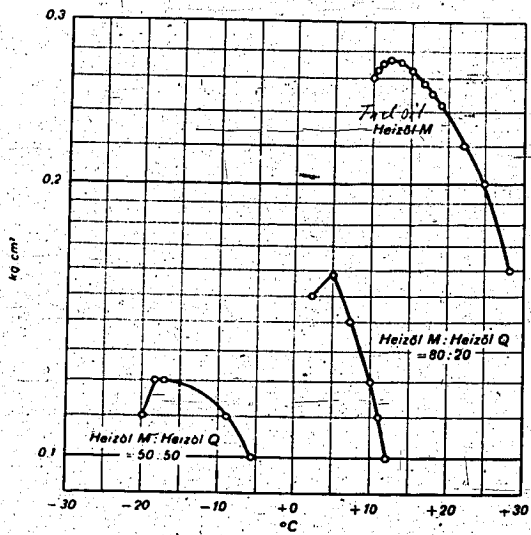

Fig. 8

SELBSTENTZÜNDUNGSEIGENSCHAFTEN UND CHEMISCHE KONSTITUTION

By Dr. Carl Zerbe und Dr. Franz Eckert
(Chemische Institute der Universität Kiel)

Self Ignition Qualities and Chemical Constitution

The definition of self ignition point, i.e. that lowest temperature at which a material is visibly ignited in an abundant current of oxygen without the presence of an outside source of fire, yields valuable aid in the evaluation of motor fuel and lubricating oils. Various apparatuses were proposed for its determination.

Placing the fault of the procedure on the processes going on in the combustion apparatus, the mistake which ruins most investigations, occured on account of apparatuses and starting materials. Thus the measurements were conducted with technical fuel oils and gave large deviations even in the experiments of one single investigator, since identical fuel oils could be very different chemically depending on their sources. The large variety of experimental equipments makes correlation even more difficult.

In the following experiments:

(1) the influence of the chemical constitution, (2) the "hydrogen concentration" i.e. the relative amount of carbon to hydrogen, (3) the oxygen content of the molecules of the self ignition process that are homogeneous hydrocarbons from the paraffinic, olefinic, naphthenic and aromatic groups will be treated.

An ideal and approved testing apparatus for the determination of the absolute self ignition point that would eliminate all possible sources of error of chemical and physical nature, will never be realized in practice. However, the Jentzsch ignition value tester is widely adopted for determining the dependence of self ignition on the two main outer factors, the temperature and the oxygen concentration of the atmosphere.

In order to ascertain the dependence of ignition on temperature and the oxygen content of the surroundings, which was first recognized by the Jentzsch,[1] the minimum amounts of oxygen needed for self ignition for various temperatures were graphed.

The curves start out with the "self ignition point" i.e. that lowest temperature at which one more ignition occurs in a copious current of oxygen (400 gas bubbless were destroyed every minute), and end in the "low ignition value", which is specified by the oxygen concentration of the atmosphere at the lowest temperature point, as well as in "high ignition value", i.e. that lowest temperature at which the oxygen supply, after being cut off, will support one more ignition. In between there is a necessary minimum oxygen concentration for each temperature to make the self ignition of the material at that temperature possible. The "low

[1] Jentzsch, Liquid Fuels, VDI Publication, 1926, p. 88

and "high ignition value" points can also be designated according to Schäfer[2] as the low and high "critical ignition temperature", since below it no self ignition is possible however large concentration of oxygen there is present, and because above it ignition always occurs even without any oxygen supply and in the greatly thinned atmospheric oxygen.

1. The Influence of Chemical Constitution.

Since every self ignition, according to undisputed views, is introduced by decomposition and cracking processes, the resistance of the material to decomposition, which is limited in the first place by chemical constitution, plays a decisive role in self ignition processes.

Till now it was recognized as a fact that the hydrogen-rich chain forming aliphatic hydrocarbons ignite easier, i.e. at a lower temperature and with lighter concentration of oxygen than the aromatic ring systems that are poor in hydrogen. The self ignition points of the napthenes, which are cyclic in structure, but in hydrogen content are similar to aliphatic hydrocarbons, lie between the aliphatic and the aromatic hydrocarbons. Thus the ratio of hydrogen to carbon was held responsible for these phenomena by many investigators without consideration for the chemical constitution of the material.

The self ignition points in Tables 1, 2 and 3 for aliphatic, naphthenic and aromatic hydrocarbons confirm the view on self ignition tendency, stated above, for certain definite representatives of these series.

Table I. Self Ignition Qualities of Aliphatic Hydrocarbons

No.	Material	Formula	C/H Ratio	Self Ignition pt. °C	High Ignition value °C	Ignition Range °C
1	Isoprene	C_5H_8	1:1.6	440	590	150
2	Diallyl	C_6H_{10}	1:1.66	330	500	170
3	Hexene	C_6H_{12}	1:2.0	325	540	215
4	Heptane	C_7H_{16}	1:2.28	300	560	260
5	Hexane	C_6H_{14}	1:2.34	296	560	264
6	Peatane	C_5H_{12}	1:2.4	300	580	280

Table 2. Self Ignition Qualities of Napthenes

No.	Material	Formula	C/H Ratio	Self Ignition pt. °C	High Ignition value °C	Ignition Range °C
1	Tetralin	$C_{10}H_{12}$	1:1.20	420	660	240
2	Octahydro-anthracene	$C_{14}H_{18}$	1:1.28	315	560	245
3	Cyclohexadiene	C_6H_8	1:1.33	360	460	100
4	Cyclohexene	C_6H_{10}	1:1.67	325	520	195
5	Decalene	$C_{10}H_{18}$	1:1.80	280	530	250
6	Cyclohexane	C_6H_{12}	1:2.0	325	520	195

[2] Schäfer, Annual Report of the Shipbuilding Technology Co. 1932, p.181

Table 3. Self Ignition Qualities of Aromatics

No.	Material	Formula	C/H	Self Ignition pt. °C	High Ignition value °C	Ignition Range °C
1	Anthracene	$C_{14}H_{10}$	1:0.71	580	770	190
2	Naphthalene	$C_{10}H_8$	1:0.8	630	700	70
3	Benzene	$C_6 H_6$	1:1	690	720	30
4	Toluene	$C_7 H_8$	1:1.14	640	730	90
5	Xylene	$C_8 H_{10}$	1:1.25	610	740	130
6	Hexamethyl-benzene	$C_{12}H_{18}$	1:1.15	375	640	265
7	Cyclopenta-diene	$C_5 H_6$	1:1.12	510	640	130
8	Dicyclopen-tadiene	$C_{10}H_{12}$	1:1.12	510	680	170

The tabulation, however, shows at the same time that the theory cannot be applied to all members of a single series, but that besides the carbon hydrogen ratio it also depends on the chemical constitution of the particular member of a single series. For example Table 3, No. 6 proves the aromatic structure of hexamethylbenzene, the aromatic ring system of which is packed with aliphatic side chains. This strong aliphatic load manifests itself in the greater decomposing tendency due to the aliphatic part, so that this clearly aromatic structure shows to a large degree a self ignition point ascribed to aliphatic structures. This is not surprising since by mixing aliphatic and aromatic materials, for example benzene and gasoline, a gradual change of the ignition curve characteristics can be followed depending on whether the aliphatic or aromatic components are allowed to predominate.

Just as in there are some aromatics with aliphatic ignition behavior, there are also clearly aliphatic structures whose self ignition points approach closely that of the aromatics, as for instance isoprene (Table 1, No. 1) shows.

Even more clearly is the influence of the chemical constitution demonstrated, if not the self ignition points alone but, as in Figures 1, 2, 3 and 4, self ignition curves constructed for the materials presented in the Tables.

The curves show that oxygen concentration necessary for self ignition with respect to temperature, is much smaller for most aliphatic than for aromatic hydrocarbons, for the aliphatics ignite without oxygen at a temperature where most aromatics do not tend to ignite even with the greatest oxygen supply. The naphthenes resemble the aliphatics. Furthermore the curves show that with increasing temperature a smaller amount of oxygen is sufficient for self ignition, and with increasing concentrations of oxygen lower temperatures will suffice. Thus the aliphatics and naphthenes show a partial deviation, which is clearly demonstrated in the "ignition gap" discovered by Jentzsch, on the ignition curve. The ignition gaps tell us that with certain aliphatics and naphthenes a temperature interval is possible above

the ignition temperature in which the rule, that with increasing temperature less oxygen is needed for self ignition, does not apply immediately. However, if this temperature range is passed the oxygen requirement decreases with increasing temperature even with the above named structures. This remarkable phenomenon has in the beginning aroused some doubts; it was thought to originate from a peculiarity of the vessel and was interpreted as its "Apparatus constant". The previous investigations show first of all the chemical structure and constitution of the material as their reason. If the ignition gap were an apparatus constant in the lower temperature range, then all structures should show a similar curve section in this temperature range. This however, is plainly contradicted by the ignition curve of 1,3-cyclohexadiene (Illustration 2), that shows no ignition gap in a temperature range in which usually aliphatics and naphthenes show such a gap. The same can be said about the ignition curve of hexamethylbenzene (Illustration 3), that reaches far into the ignition gap temperature range of the aliphatic hydrocarbons.

The ignition curves of the aliphatic hydrocarbons (Illustration 1) all show a more or less large ignition gap outside of isoprene. Pentane and its homologues (hexane, heptane) show, for instance, the large ignition gaps typical of aliphatics, with unsaturated aliphatics, for example hexene and diallyl, the ignition gaps are smaller. Accordingly through the double bond the molecule possesses a greater resistance in ignition characteristics. This stabilizing effect of the structural relation appears in a special form in the case of isoprene.

This differs fundamentally from the other aliphatic hydrocarbons that its ignition curve lies in the high temperature ranges, but particularly, as was already mentioned, by its lack of ignition gap. In its self ignition characteristics it lies closer to the aromatic than the aliphatic hydrocarbons. The presence of the conjugated double bond apparently gives even open aliphatic chains a tenacity in their ignition conduct that brings them close to aromatic ring systems.

Now it would be interesting to determine whether this resistance of the aromatics could be traced back to the presence of the conjugated double bonds in the ring system, which by systematic saturation of the double bonds in the benzene nucleus through partial hydrogenation should be easily demonstrable.

If the conjugated double bond is made responsible for the resisting strength against self ignition process dihydrobenzene should show a high self ignition point and should not show none of the characteristic course of aliphatic and naphthenic curves and no ignition gaps. If the conjugated double bond of dihydrobenzol is saturated by further hydrogenation, tetrahydrobenzol (Cyclohexene) is obtained, a naphthene with one double bond which now must show a typical ignition gap. The ignition curves of these materials, that are drawn in Illustration 2, bear out fully this prediction. Dihydrobenzene, like isoprene with its self ignition

characteristics, stands without ignition gap close to aromatics, tetrahydrobenzene, on the other hand, and naturally hexahydrobenzene also show typical aliphatic self ignition characteristics with definite ignition gaps.

Cyclopentadiene and its polymer dicyclopentadiene must behave in self ignition processes like an aromatic structure as long as they have conjugated double bonds; this is confirmed by the ignition curves. The same thing applies to tetralin, which still has an intact benzene ring.

Octahydroanthracene shows in spite of the intact benzene nucleus, an ignition gap (Illustration 2). This could be traced back to the fact that strong loading with hydrogen is not sufficient for the still present double bonds, so that the ignition quality will be shifted just as much to the aliphatic as to the naphthenic side, as it is noticeable in loading with aliphatic side chains. This tendency is clearly noticeable from the ignition curves of benzene, toluene, xylene, hexamethylbenzene.

On the basis of the above experimental data it can well be stated with the greatest certainty that the stability of a molecule in its ignition characteristics depends mostly on its structural setup and is limited primarily by the presence of a conjugated double bond.

As to how different the stability of a molecule as compared to the decomposition processes releasing self ignition, can be, is particularly indicated by the large ignition range between self ignition point and high ignition value. Aliphatic open chains with simple structure possess an ignition range that are multiples of aromatics. For example the ignition range of benzene is within 30°, while to octadecanol 310° and to stearic acids as much as 410° is attributed, as the oxygen content of an aliphatic when self ignition tendency diminishes must be considered (see below). The ignition range of the naphthenes lies between that of the aromatics and aliphatics. Naturally the consolidating influence of the double bond is typically expressed in the ignition range.

The influence of chemical constitution, discussed in connection with self ignition point, applies also to the high ignition values, i.e. also to the self ignition points in preheated atmospheric air.

2. The Influence of Hydrogen Number

The influence of the hydrogen-carbon ratio, the so-called "hydrogen number", on the behavior of a hydrocarbon in self ignition is undisputable.

In Table 4 widely different hydrocarbons are arranged in order of increasing hydrogen concentration without regard to their chemical constitution.

The tabulation shows that there is no absolute relationship, applicable to all series, between self ignition point and hydrogen number. The same applies to high ignition value and to the range between self ignition point and high ignition value. The picture is entirely different, however, if hydrogen number is considered in connection with chemical constitution.

Table 4.

No.	Material	C:H Ratio	Self Ignition pt. °C	High Ignition value °C	Ignition Range °C
1	Anthracene	1:0.71	580	770	190
2	Naphthalene	1:0.80	630	700	70
3	Benzene	1:1	690	720	30
4	Toluene	1:1.14	640	730	90
5	Tatralin	1:1.2	420	660	240
6	Cyclopentadiene	1:1.2	510	640	130
7	Xylene	1:1.25	610	740	130
8	Octahydroanthracene	1:1.28	315	560	240
9	Cyclohexadiene	1:1.33	360	460	100
10	Hexamethylbenzene	1:1.5	375	640	265
11	Isoprene	1:1.6	440	590	150
12	Diallyl	1:1.66	330	500	170
13	Cyclohexene	1:1.67	325	520	195
14	Decalin	1:1.8	280	530	250
15	Cyclohexane	1:2.00	325	520	195
16	Hexene	1:2.0	325	540	215
17	Heptane	1:2.28	300	560	260
18	Hexane	1:2.34	296	560	264
19	Pentane	1:2.40	300	580	280

In Tables 1, 2, and 3 the compounds of Table 4 are arranged according to single series, namely aliphatics, naphthenics and aromatics, and even in order of ascending hydrogen concentration. This way the figures of Table 1 for aliphatics show that in the case of compounds with similar structure, particularly for homologous series (Exp. 4, 5, 6) the self ignition pt. decreases with increasing hydrogen number, the high ignition value, on the other hand, increases. Isoprene (Exp. 1) with one conjugated double bond is, as previously stated, an exception.

Nothing can be said about the influence of the hydrogen concentration for naphthenes, since the compounds tabulated in Table 2 do not permit any comparison on account of their different chemical structures.

The above stated relationship for aliphatics, the dependence on hydrogen ratio, is applicable to homologous series of aromatics (Table 3, Exp. 3, 4, 5). However, it must be made clear that an enrichment of hydrogen content with the retention of the aromatic ring system is always connected with the introduction of side chains. Thus an inseparable relation is displayed by the two quantities, so

that in place of "hydrogen number" "aliphatic side chains" could be used.

However, if the molecule displays several structural relationships, as in the case of naphthalene and anthracene (Exp. 1, and 2), or if the decomposing tendency of the molecule is considerably increased by introducing a number of aliphatic side chains, the relationship as regards to hydrogen number ceases.

Since the experimental results indicate that no "generally" applicable rule can be deducted from the hydrogen number for the occurrence of an ignition gap or the oxygen demand of self ignition, without regard to chemical constitution, therefore the terms "hydrogen number" and "chemical constitution" are inseparably linked together in the explanation of the self ignition processes of hydrocarbons.

3. The Influence of the Oxygen Content.

It is known that aliphatics when self ignition point is raised through their oxygen content, for example aliphatic alcohols, show characteristics that we associate with aromatics.

Table 5. Self Igniton Properties of Alcohols.

No.	Material	Formula	C:H:O Ratio	Self Ignition pt. °C	High Ignition value °C	Ignition Range °C
1	Methyl	CH_4O	1:4:1	500	535	35
2	Glycol	$C_2H_6O_2$	1:3:1	500	570	70
3	Ethyl	C_2H_6O	1:3:0.5	375	670	295
4	Propyl	C_3H_8O	1:2.7:0.33	370	590	220
5	Cyclohexyl	$C_6H_{12}O$	1:2:0.17	350	640	290
6	Octadecyl	$C_{18}H_{38}O$	1:2.1:0.056	270	580	310

In Table 5 and in Graph 5 the self ignition properties of different alcohols are illustrated.

The tabulation indicates that the self ignition properties of alcohol depend primarily on the ratio of carbon to oxygen in the molecule, and that with increase in oxygen content the temperature of self igniton point and the oxygen requirement for ignition increase. This increase is so considerable that oxygen rich aliphatic alcohols (Exp. 1 and 2) approach normal aromatics very closely in their self ignition properties. A very small oxygen content, as, for example, octadecanol (Exp. 6) is naturally hardly noticeable. The same is true of cyclo-hexanol (Exp. 5) that, on account of its relatively small oxygen content, possesses a definite ignition gap, too. The influence of the oxygen content, however, is clearly indicated when compared to the diminished ignition tendency of cyclo-hexane.

From the data of Table 6 and Graph 6 is shown that the effect of oxygen exists, and that it is equally valid in the form where the oxygen radical is bound; the same observations can be made in the cases of aliphatic carboxylic acids (Exp.1 to 3); ethyl ether (Exp. 4) and naphthenic ketones (Exp. 5 and 6) as with aliphatic alcohols.'

Oxygen acts directly opposite with aromatics, as Table 7 and Graph 7 for phenols indicated, where with increase in oxygen content the self ignition point decreases, i.e. the ignition tendency decreases. The resistance of the aromatic nucleus to self ignition processes in thus lowered by oxygen substituted into the nucleus. This is equally valid to aromatics when oxygen radical is introduced in the molecule, as Exp. 4 (Benzoic acid) and 5 (quinone)of Table 7 show.

Table 6. Self Ignition Properties of Oxygen Containing Aliphatics

No.	Material	Formula	C:H:O Ratio	Self ig-nition pt. °C	High ig-nition value °C	Igni-tion Range °C
1	Acetic acid	$C_2H_4O_2$	1:2:1	570	730	160
2	Oxalic acid	$C_2H_2O_4$	1:1:2	640	680	40
3	Stearic acid	$C_{18}H_{36}O_2$	1:2:0.011	250	660	410
4	Ethyl ether	$C_4H_{10}O$	1:2.5:0.25	200	500	300
5	Cyclopentanone	C_5H_8O	1:1.6:0.2	540	600	60
6	Cyclohexanone	$C_6H_{10}O$	1:1.67:0.17	550	680	130

The loading of an oxygen containing molecule, such as phenol, with alkyl groups, as could be expected, would cause the previously mentioned changes on the aliphatic side (Exp. 6 (Anisol) and 7 (Xy-lenol)).

The investigations are carried on. The practical consequences and evaluations which present themselves from the previous observations, especially the ones that contribute to motor ignition processes, to clarify the interrelation between knock resistance of fuels and chemical structure will be reported later.

The previous investigation results show that the relationships in ignition qualities hold only within the same series and even there only to a certain extent. The last decision on the self ignition characteristics of all technical mixtures can only be made by the determination of the self ignition curve.

Experimental Part

The ignition value tester of Jentzsch consist of an electri-
cally heated combustion crucible made of V-2A steel with four
equally large symmetrically arranged bores, each of 15 mm. dia-
meter and 40 mm. deep, out of which one serves as thermometer
hole and the three others as combustion chambers. Through a
central bore, 6 mm. in diameter and three radial bores, each 3
mm. in diameter, each one of the combustion chambers can be
equally supplied with oxygen, which is measured in every minute
with a calibrated jet. The nozzle is installed in such a way
that 60 oxygen bubbles amount to 5 cc. every minute. The addition
of the liquid material was done with a pipette with a 1 mm. dis-
charge and in drops of approximately 0.01g. The solids were in-
troduced into the middle chamber with a small ladle in equal amount.
The vapor regulators in the combustion chambers are exchanged after
each material addition to remove possible residuum and to rinse
the chambers.

Summary

Self ignition point determinations with pure hydrocarbons and
oxygen containing compounds from the aromatic, aliphatic and nap-
hthenic series were performed, and the oxygen requirement for self
ignition at each temperature was determined. It appeared that:

1. Self ignition is dependent on temperature and the oxygen
concentration of the surroundings.

2. To each self igniton temperature there belongs a minimum
oxygen concentration and to each oxygen concentration a minimum
temperature.

3. For increasing temperatures a smaller quantity of oxygen
and for higher concentrations of oxygen lower temperatures are
necessary. In the case of aliphatics and naphthenes that have
no conjugated double bonds there are temperature intervals above
the self ignition point where this rule does not apply, and which
is indicated on the ignition curves by an ignition gap.

4. The magnitude of the self ignition point, the necessary
amount of oxygen therefor, as well as the occurence of an igni-
tion gap are primarily dependent on the decomposing tendency of a
material which, in turn, depends on the chemical constitution.
It can be confirmed that the conjugated double bond decreases
self ignition tendency, and is of significance in the stability
of aromatics regarding their ignition tendency.

5. The influence of the hydrogen number on the ignition be-
havior is significant only when considered simultaneously with
chemical constitution.

6. The self ignition point in the case of aromatics is low-
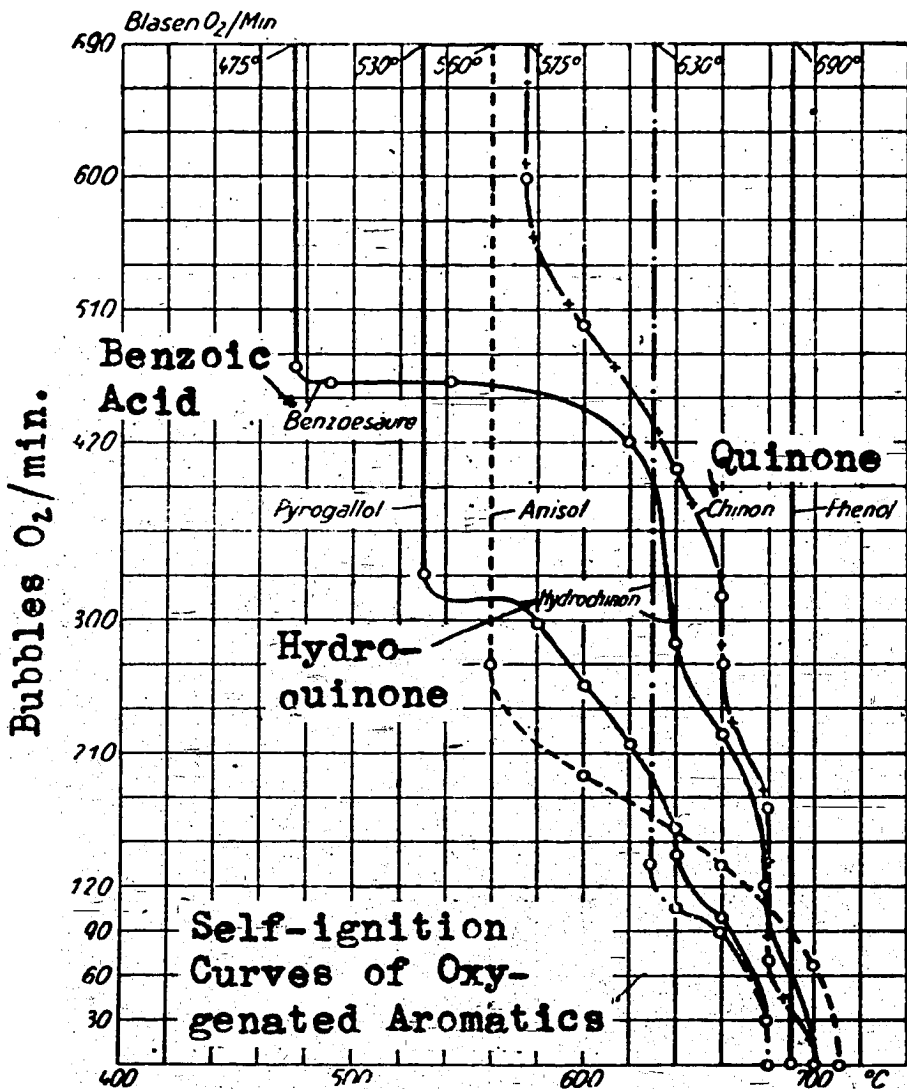ered by oxygen content, and increased for aliphatics.

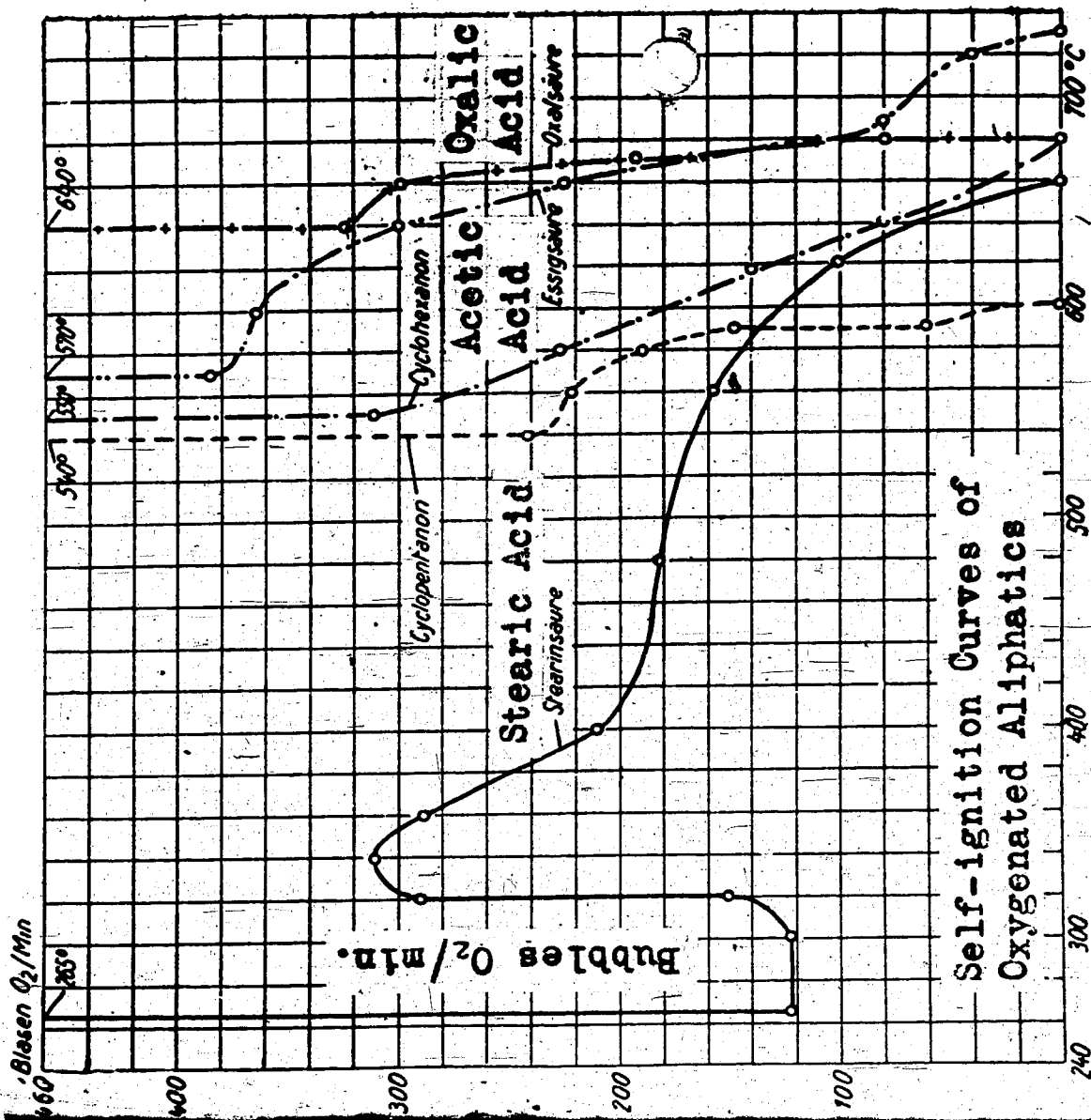Fig. 7. Self-ignition Curves of Oxygenated Aromatics.

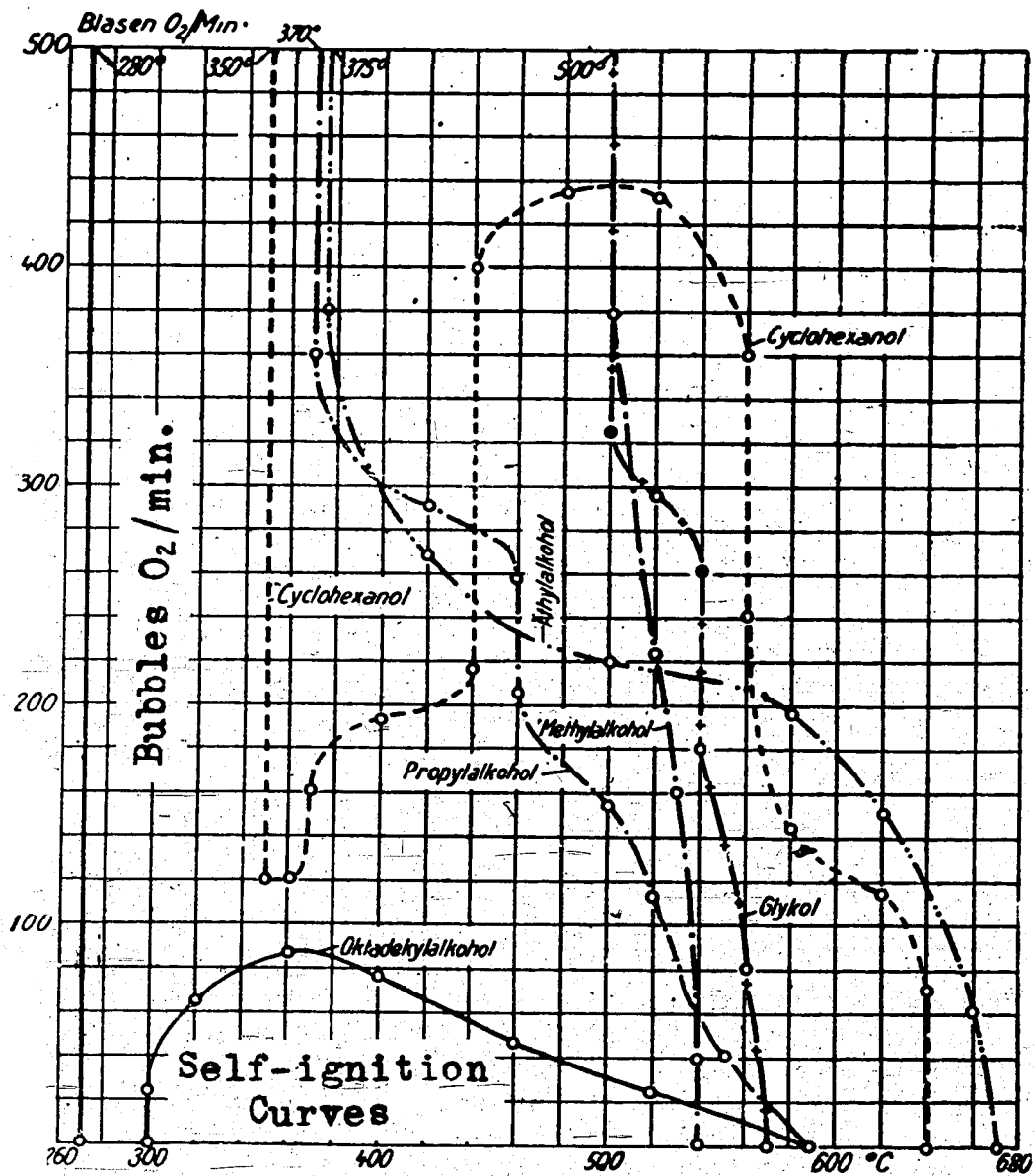Fig. 6. Self-ignition Curves of Oxygenated Aliphatics.

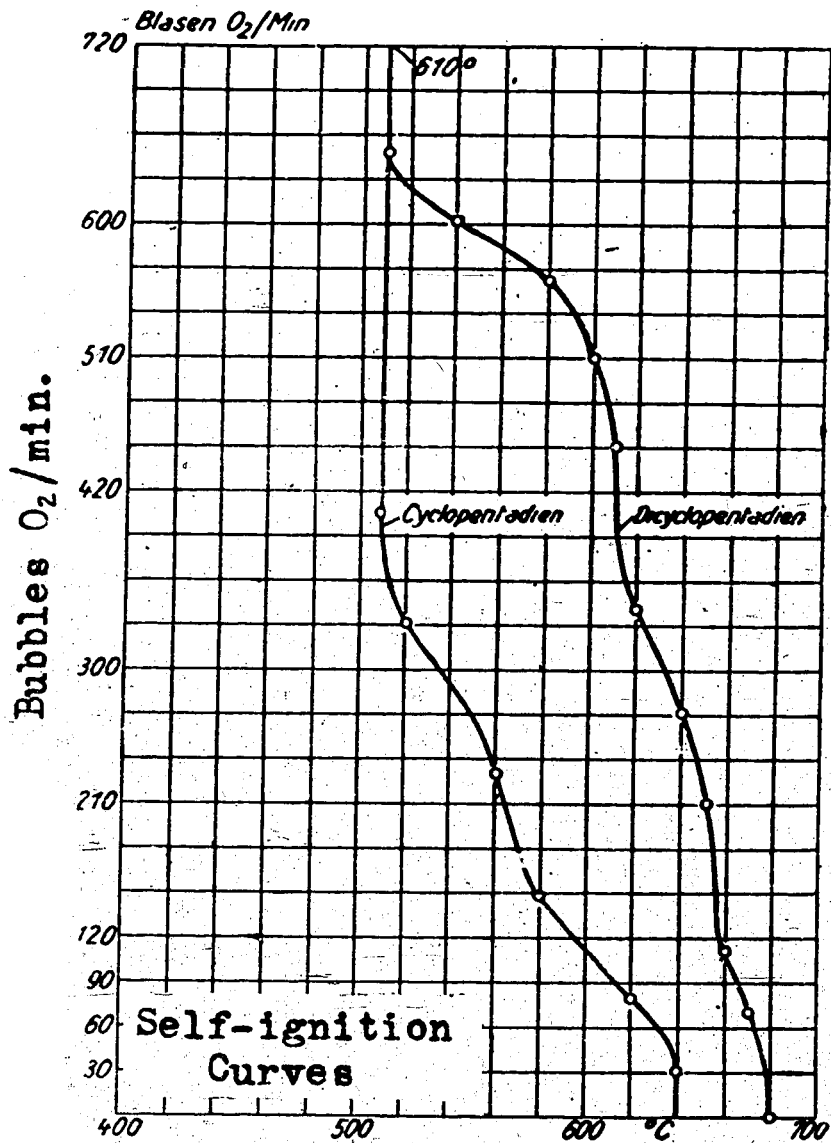Fig. 5. Self-ignition Curves of Alcohols.

Fig. 4. Self-ignition Curves of Cyclopentadiene and Dicyclopentadiene.
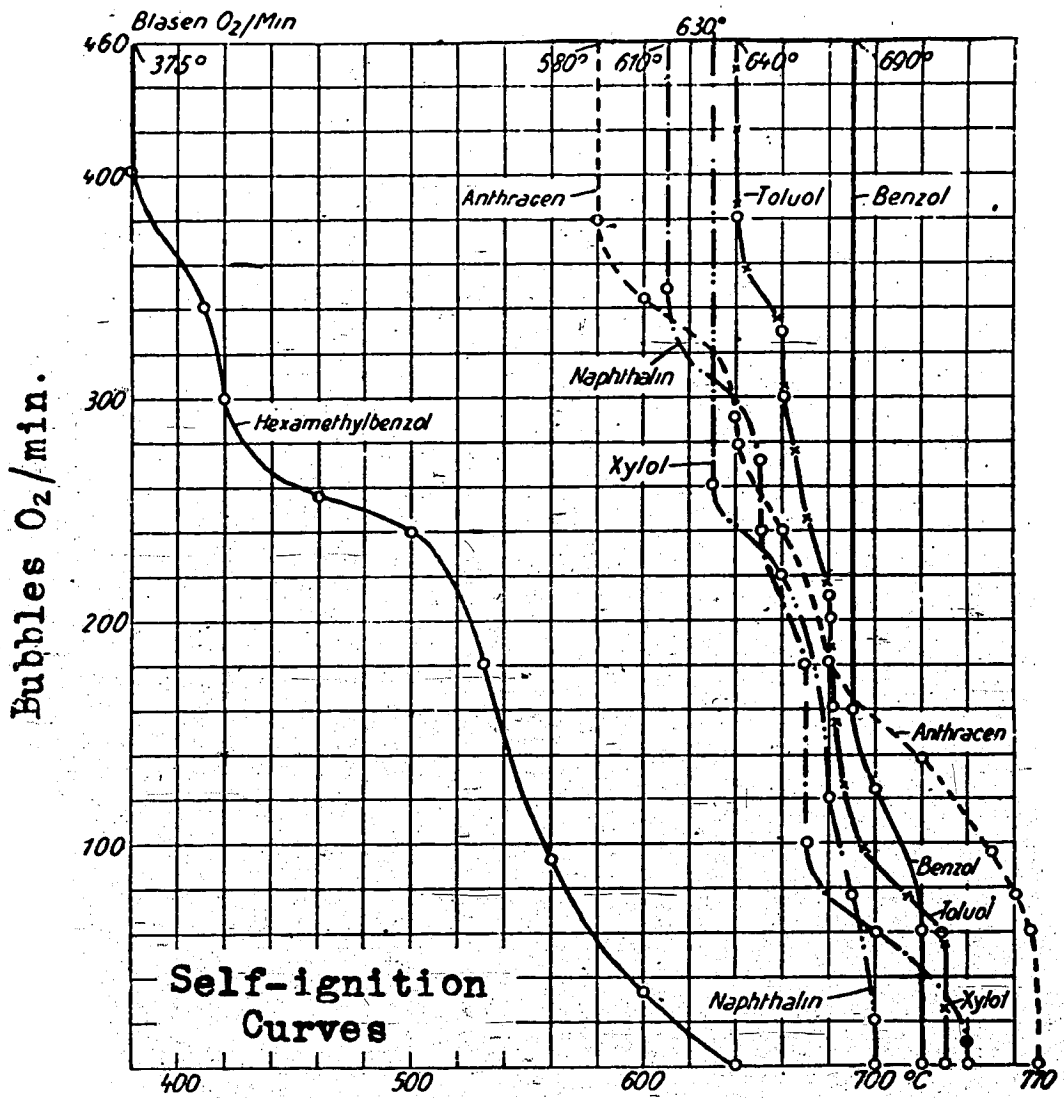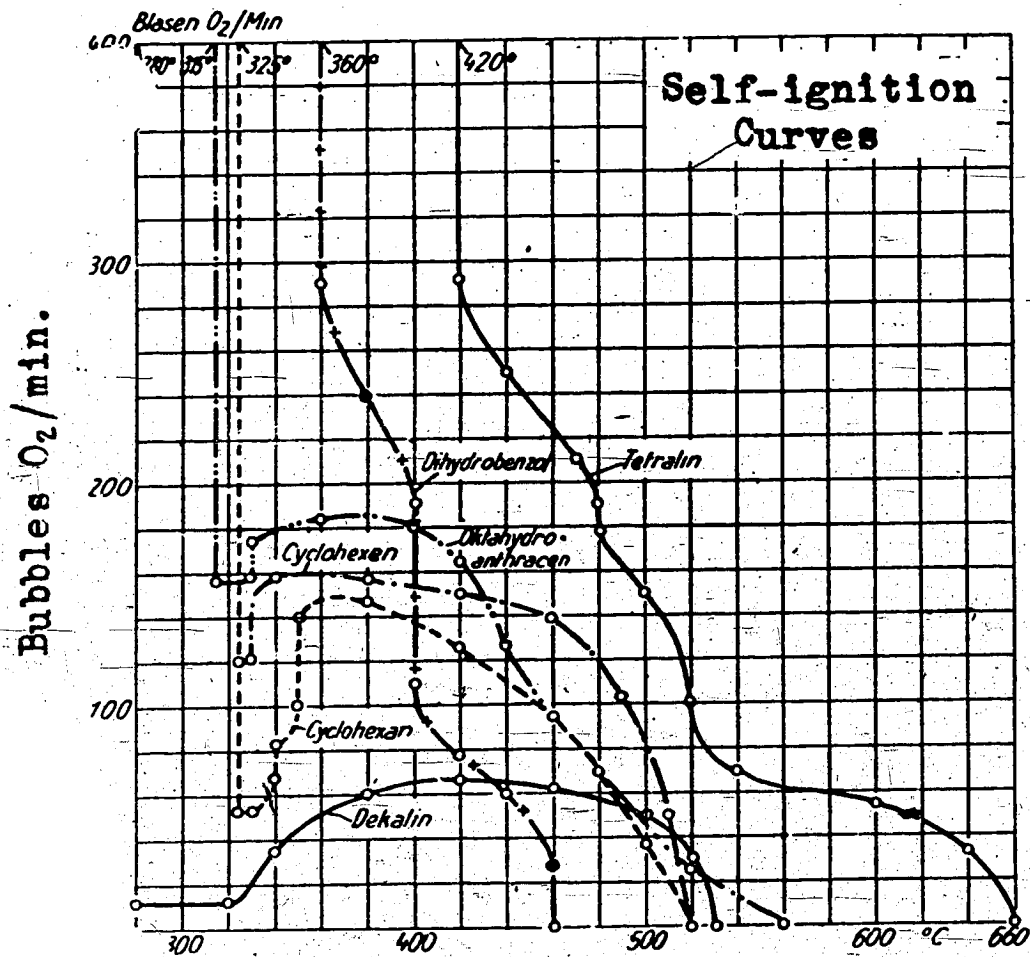
Fig. 3. Self-ignition Curves of Aromatics.

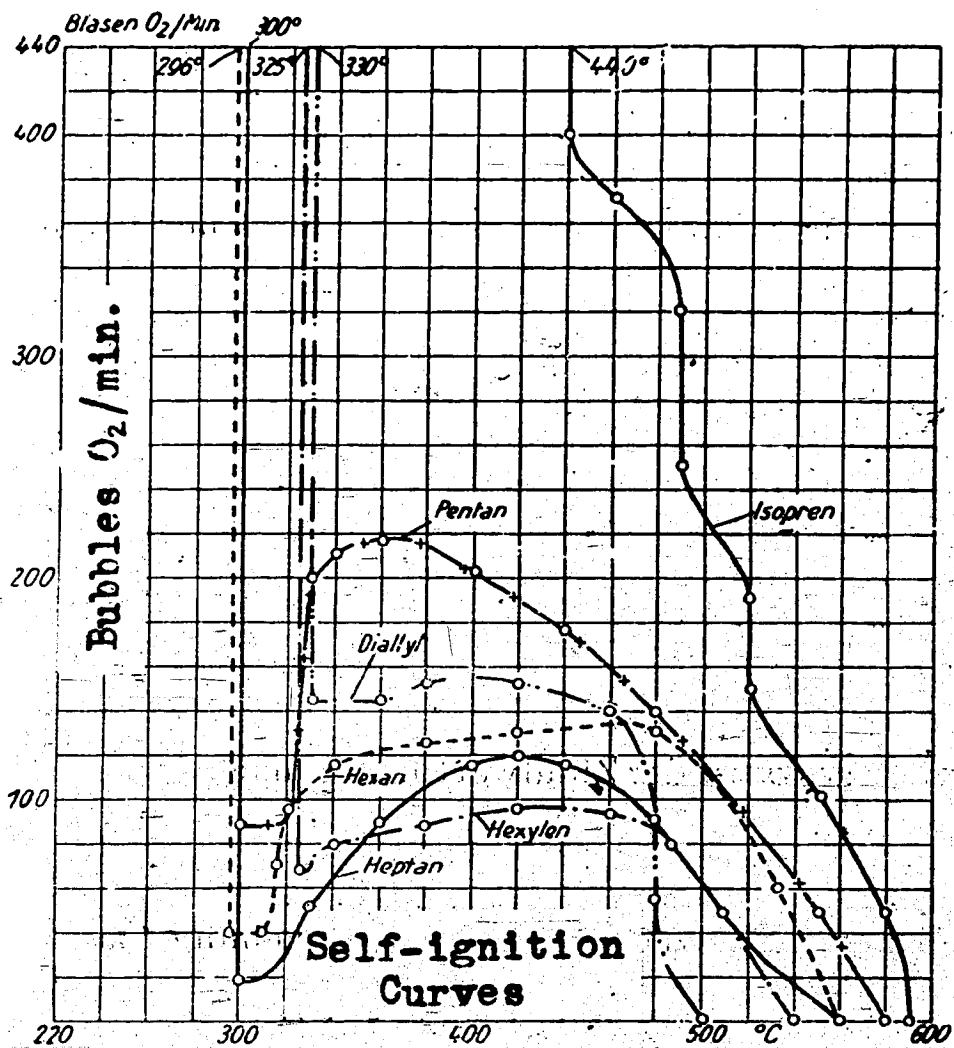Fig. 2. Self-ignition Curves of Naphthenes.

Fig. 1. Self-ignition Curves of Aliphatics.

ÜBER DIE ZUSAMMENHÄNGE ZWISCHEN SELBSTZÜNDUNGS-
UND MOTORISCHEN VERBRENNUNGSVORGÄNGEN

By Dr. Carl Zerbe and Franz Eckert
   (Chemische Institute der Universität Kiel)

The Relationship between Self-Ignition and Motor Combustion Processes.

By Dr. Carl Zerbe and Franz Eckert
(From the Chemical Institute of the Univ. of Kiel)

. Part I.

(Self Ignition Characteristics
and Knock Processes.

Up till now we have not formed a uniform conception of the nature of Knocking processes. Numerous works point out the self ignition temperature of the fuel as the most reliable indication of Knocking tendency, so that knocking could be regarded as a process related to self ignition in the engine. Consequently the opinion, that the self-ignition qualities of an engine fuel are of extraordinary importance for its suitability in motors, is more and more prominent.

We have already reported[1] on the factors which affect the self-ignition of fuels; we have established the fact that self-ignition is principally dependent on temperature, the oxygen concentration of the surroundings, as well as on the chemical constitution of the fuel, and is indicated in the following.

1. Inasmuch as these factors can be transferred to the processes in the cylinder, as observed by Jentzsch on an ignition value tester, and

2. Inasmuch as it seems possible to evaluate different fuels with the above apparatus.

The ignition value tester of Jentzsch consists of an electrically heated oven with a number of V_2A steel chambers in which the self-ignition of the particular fuel is determined. Through a regulator valve pure oxygen in the required proportion can be admitted from a pressure container. The oxygen mixture is controlled by a calibrated flow meter.

By self-ignition pt. (Szp) is meant that lowest temperature (t_u) at which, in a copious oxygen current, (usually 300 to 400 bubbles per minute) self-ignition still occurs.

The temperature at which, without direct oxygen addition, ignition still occurs is called the high ignition value (Z_o).

The low ignition value is obtained by dividing the lowest self-ignition temperature by the oxygen addition rate/min., necessary for its determination, plus one.

Characteristic ignition value (Z_k) means the ratio of the $(t_o - t_u)$ to the oxygen bubbling rate of the low ignition value (b_u) plus one.

$$Z_k = (t_o - t_u)/(b_u + 1).$$

[1] Zeitschrift der Angewandte chemie ▪ 45, 594 (1932)

The cracking process which precedes every self-ignition, depends on the cracking tendency of a material, and this, in turn, depends on the chemical constitution. The overall dimensions of this cracking tendency can be expressed by means of the temperature required for self-ignition and the oxygen concentration of the surroundings, and can be determined by means of or self-ignition curves for the whole ignition range (Fig. 1).

Theoretical Relationship.

1.   Chemical Structure.

Among the liquid fuels of the paraffin, naphthenic and aromatic series the chain forming hydrogen-rich aliphatics ignite easier, i.e., at a lower temperature and lower oxygen concentration, than the aromatics which are poor in hydrogen content. The self ignition points of the naphthenics; which are cyclic in structure, but resemble the aliphatics in hydrogen content, are between those of the two other hydrocarbon series. We showed that the "hydrogen number," regarded as the only significant factor in these phenomena, can be a guiding principle only if the chemical structure is considered at the same time. Thus the double bond lowers the self-ignition temperature of every compound, and is responsible for the easy ignition tendency of the aromatics. A definite chain branching of the molecule has a similar effect, as the ignition curves of n-octane and isooctane (2,2,4-trimethylpentane) show (Fig. 1).

The following tabulation indicates how well the characteristic ignition value shows the relationship between structure and thermal cracking tendency, which best identify the knocking tendency of light fuel oils.

Characteristic Ignition Value

Benzene	0.19
Toluene	0.24
Xylene	0.38
Hexamethylbenzene	0.68
Pentane	3.14
Hexane	5.35
Heptane	23.0

The aromatics have the lowest (below 1) the aliphatics, on the other hand, the highest characteristic value. Even the greater cracking tendency of aromatics with long side chains and aliphatics with long chains is clearly brought out in the characteristic ignition value. If, for example, in the case of aromatics the double bond is lost through hydrogenation, the characteristic ignition value takes on an aliphatic character.

Characteristic Ignition Value

Hexane	5.35
Hexene	3.1 (1 double bond)
Diallyl	1.17 (2 double bonds)
Isoprene	0.39 (1 conjugated double bond)

The influence of stereoisomerism is also shown by the characteristic ignition value (for example: c. i. v. of n-octane = 56, that of iso-octane = 0.45.

The relationship between chemical constitution and self-ignition is responsible for the results on the knocking tendency of light fuel oils in engines; since it is known that the light self-igniting paraffinic hydrocarbons with straight chains and even with increasing molecular weight, behave very favorably; compounds with great ignition tendency, on the other hand, such as aromatics, aliphatics alcohols, as well as paraffins with conjugated double bonds [2] or with branched chains (isooctane) show great knocking tendency corresponding to their easy ignition characteristics. Naphthenes stand, as a result of their partly aliphatic partly aromatic character, as in self-ignition, between the two groups regarding their knocking tendencies. Ignition and knocking tendency are thus closely bound to each other on a structural basis.

2.   Temperature and Oxygen Concentration

The oxygen demand for self-ignition of a material decreases measurably with increasing temperature; to be sure, there are some temperature intervals above the self ignition points of the easily cracked aliphatics and naphthenes where the rule fails; this is indicated on the ignition curve by an ignition lag (Fig. 1). These ignition lags indicate that in their temperature range a maximum amount of thermal cracking is obtained so that the added oxygen mixture is too weak to be able to produce an ignitable mixture with the suddenly liberated rich cracking product mixture. Thus a non-ignitable mixture is produced in the ignition chamber, to which the motor expert refers as "too rich".

Since the temperature and the oxygen concentration increases with compression in the cylinder space also, the fact, that the knocking tendency of the fuel increases with compression, is proved by the interdependence of temperature and oxygen concentration which was already observed in the ignition value tester. The observation, however, is not clear, since during compression, besides oxygen concentration, temperature and pressure change, too.

We, therefore, conducted experiments in an engine in which we varied the oxygen concentration alone by the addition of oxygen through the suction tube of the engine at constant pressure and temperature, and then we varied the temperature at constant pressure and oxygen concentration by varying cooling. The results, which were fully explained later, were briefly as follows:

If, at constant pressure, temperature and other working conditions,

[2] Fritz Hoffmann and coworkers. Brennstoffchemie 14, 326 (1933)

the oxygen concentration is varied, then with increasing concentration the knock resistance of every fuel is lowered to a certain extent, so that even the knock resistant benzene develops signs of knocking that can lead to a complete stop of the engine. With increasing oxygen addition an increase in capacity is also developed under the increased ignition pressure. Past a certain magnitude of oxygen concentration capacity is again decreasing in spite of rising ignition pressure, since the temperature increase, connected with rise in compression and favoring performance, is lacking. Thus the capacity reached by addition of oxygen is not quite as great as that obtained when this same oxygen concentration is brought about through compression rise.

" If the experiment is conducted with increasing cooling water temperature then the capacity can indeed be raised and yet knocking develops correspondingly easier. Even though these experiments do not wholly reproduce the conditions of a practical operation (since there the oxygen molecules are imbedded to a certain degree in a padding of nitrogen, while the nitrogen cushioning is lacking in our experiments), yet they show that the oxygen concentration and temperature basically influence the knock processes in the motor just as much as the self-ignition does in the tester. The figures obtained from ignition value tester thus justify us, even though pressure is neglected, to draw definite conclusions as to knocking tendency.

The great influence of oxygen concentration on knock resistance is revealed also in practice in the fact that by increased fuel supply and the consequent oxygen content decrease of the explosion mixture a not too strong knocking can, as a rule, be eliminated.

In a treatise on the influence of catalysts [3] we could show that, even in the presence of contact materials, self-ignition depends primarily on temperature and oxygen concentration, and that the individual contact catalysts show a contact effect in two ways, which are similar and characteristic even though varying in magnitude: with plenty of oxygen the contact catalyst speeds up self ignition, i.e., the self ignition point sinks. If, however, only as much oxygen is supplied as would be sufficient for ignition without a catalyst, then, as a rule, no ignition occurs, i.e, the speeding up action of the contact catalyst is not only missing, but the reaction is retarded, as we know the case is with anti-knock compounds. Indeed, depending on the oxygen mixture on hand, the contact catalyst acts either as a "whip" or as a "brake." The observation is readily evaluated in practical engine work [4] and states very definitely the close relationship between self-ignition and combustion in the engine.

Practical Evaluation.
The knock resistance of a material is determined nowadays by comparison tests on a machine and is expressed by the so called "octane number" [5],

[3] Zeitschrifte f. angewandte Chemie 46, 659 (1933)

[4] "Glückauf" 965/82 (1932) Pamphlet 43

[5] The octane number gives the percentage of isooctane mixed with n-heptane till the mixture reaches the knock resistance of the material tested.

- 4 -

since all other tests, such as distillation, aniline point, fire point, etc. fail to work. To the following determinations, as to how the individual values denoting (self-ignition of engine fuels:

1. Self-ignition point
2. Low ignition value
3. High ignition value
4. Characteristic ignition value
5. Ignition delay

are related to octane number and how they can be used in the knock resistance values of light engine fuels, there will be included as comparison materials:

1. Engine fuels whose octane number was determined under various test conditions[6]).

2. Engine fuels whose octane numbers were determined by the CFR test method.[7]).

Since the octane number is not an absolute quantity and is strongly dependent on working methods and test motors, both lines of investigation should be discussed separately.

Engine fuels of D.V.M.[6]).

Commercial engine fuels of various compositions were used in the D.V.M. tests. The knock value determinations for the engines, expressed in octane numbers, indicated that in engines of equal construction differences amounting to as much as 12 octane number units occurred. The impossibility of developing a uniformly agreed upon method for test engines of different construction in order to obtain uniform knock values illustrates the difficulty of obtaining values of all, which would indicate the working qualities of all fuels in all types of engines.[8]).

If in the D.V.M. tests the calculated mean value is taken as the basis, as the one nearest to actual conditions, then the order of magnitude of Table 2. on basis of mean values is obtained.

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[6] Comparative engine fuel testing conducted on the suggestion of the German Society of Material Testing for procedure (D.V.M.) see Report.

[6] Kf 40/13 III The Material Division of the German Research Bureau of Air Travel (D.V.L.), 7-19, 1932.

[7] The engine fuel samples were made available to us by Rhenania-Ossag and Derop, for which we herewith express our appreciation.

[8] Even in the combustion space of motors made knock resistant by a fixed division.

The deviations for low ignition values in the ignition value determinations of Berlin and Kiel are so slight (within 0.4) that a good reproducibility of the ignition value method cannot be doubted.

Self-Ignition Point.

The self-ignition point can be used in discussing knock resistances of engine fuels of uniform chemical composition only, because the components of a mixture can essentially raise the knock resistance without noticeably changing the self ignition point (see Table 1.)

Low Ignition Value.

The influence of the mixture components on the self-ignition can be comprehended numerically better by the low ignition value, because through it the oxygen, needed for all materials in ignition, is expressed.

TABLE 1.

Material	Self-Ignition pt. in oC	Oxygen need in bubbles/min.	Low ignition value
Gasoline A	295	28	10.2
Gasoline A + 20% Benzol	295	38	7.55
Gasoline A + 40% Benzol	295	46	6.25
Gasoline B	300	42	7.0
Gasoline B + 20% Benzol	305	54	5.55
Gasoline B + 40% Benzol	310	72	4.3
Gasoline C	300	54	5.45
Gasoline C + 20% Benzol	315	68	4.57
Gasoline C + 40% Benzol	320	78	4.05

It is also admitted that addition of benzene effects distinctly the individual gasolines.

If in the case of D.V.M. gasolines the average octane numbers are compared with the low ignition values, the decreases in the low ignition values do not correspond perfectly to the increase of the octane number (see Table 2), which must be accounted for by the fact that through the low ignition value the factors, important to ignition tendency (temperature and oxygen demand), are obtained, but not the decomposing quality important to knocking tendency.

Characteristic Ignition Value.

These three factors are best expressed quantitatively through the characteristic ignition value. Consequently the characteristic ignition values with the average octane numbers in order of rating agree well with the engine tests.

If the characteristic ignition values are plotted against definite iso-octane heptane mixtures in a coordinate system (Fig. 2), then at times the octane number corresponding to the characteristic ignition value can be read. Considering the large differences in the test values, from which the engine mean values were calculated, the octane numbers calculated from the characteristic ignition values agree satisfactorily with the engine tests till engine fuel 7. Where this disagreement originates from, will be discussed below later.

In Fig. 3 the characteristic ignition values of D.V.M. engine fuels are plotted against their aromatic, naphthenic, and paraffinic contents. Similarly to knocking tendency, the characteristic ignition value decreases at high proportions of aromatics and naphthenes; at higher paraffinic contents, however, it increases.

TABLE 2.

Engine Fuel No.	Mean octane No. by engine test	Low Ignition Value	Characteristic Ignition value	Octane No. Calculated from Ch. I.V.	Ignition delay in sec. at 320°C & 120 bubbles of O_2/min.
7	68	6.4	4.9	58	4.6
10	68.6	5.3	4.4	63.5	5.4
9	74.1	5.5	3.8	70	6.0
6	81.0	3.6	2.8	81.0	5.2
5	84.2	3.1	2.3	85	6.6
3	84.5	3.5	2.5	83.5	8.8
4	86.1	4.6	2.6	83.0	11.0 with 19% Alcohol
7 + 20% Benzene	74	---	2.9	78	
9 + 20% Benzene	75	---	3.0	79.5	
10 + 30%	78	---	2.8	81	

Benzene addition, too, is indicated in the octane number, calculated from the characteristic ignition values corresponding to the sequence of the engine tests (Table 2).

The Ignition Delay.

Besides ignition temperature, the delay between the introduction of the fuel and its consequent ignition is also a factor in the cylinder. In the case of engines with spark ignition the self-ignition and with it the knocking tendency of a fuel can noticeably be lowered through ignition delay.

Table 2 also shows within what limits the ignition delay can fluctuate for D.V.M. engine fuels.

The great ignition delay of engine fuel 4 is due to its alcohol content (19%), since with increase in alcohol addition the ignition delay of an

engine fuel also increases (Fig.4) Thus it can be concluded with good probability that the effect of alcohol addition to repress knocking clearly depends on the igniting delay caused by it. Investigations are in progress in order to correlate ignition delay with octane ratings obtained from the characteristic ignition values.

Comparison Tests with C.F.R. Test Procedures.

The gasoline samples whose octane numbers were determined by the C.F.R. method, as well as the secondary standards for engine tests were made available to us by Derop and Rhenania-Ossag. On the basis of Fig. 2 we made out a calibration curve with the secondary standards and derived from it the octane number corresponding to the obtained ignition value of the fuel.

Derop Gasoline.

With six gasoline samples the Derop showed the relationship between C.F.R. and the octane numbers calculated from ignition values as tabulated in Table 3.

TABLE 3.

Number	C.F.R. Octane No.	Octane No. Calculated from Ch. I.V.
1	74	72
2	72	68.5
3	71	60
4	55	51.5
5	47.5	42
6	60.5	54

The numerical agreements correspond to the results obtained with D.V.M. fuels.

Rhenania-Ossag Gasolines.

In cooperation with Rhenania-Ossag 31 comparison tests were so far conducted with all types of engine fuels applicable to carburetor type engines. The investigations indicated that the fuel can be classified similar to earlier tests with respect to the C.F.R. octane rating; in Group 2, however, differences amounting to more than 20 octane numbers are noted. In the case of these fuels the question is whether cracked gasoline or mixtures with large cracked gasoline or alcohol content are present.

TABLE 4.

Test Results of Rhenania - Ossag A.G.
with C.F.R. Engine
Group I

Sequence No.	Mark	C.F.R. octane No.	Jentzsch octane No.	Difference	
1	A	31	37	+6	
2	B	45.5	48	+2.5	
3	C	52	48.5	-3	
4	D	57	57	0	)same
5	E-	57	60	+3	)sample
6	E	62.5	58	-4.5	
7	7*)	67.7	61.5	-6.2	
8	10*)	68.3	66	-2	
9	Q	68.5	60	-8.5	
10	9*)	73.6	74	+0.6	
11	J	74.5	77	+1.5	)similar
12	C-	74.5	66	-8.5	)samples
13	K	75.5	72.5	-3	
14	L-	75.5	70	-5.5	
15	5*)	86.6	88.5	+1.9	
16	N-	93	97	+4	
17	O	95	90	-5	)similar
18	O	96	86.5	-9.5	)sample
19	G-	73	65.5	-8.5	

Group II

Sequence No.	Mark	C.F.R. octane No.	Jentzsch octane No.	Difference	
20	F-	65	53	-12	
21	B-	67.5	53	-15	
22	P	67.5	57.5	-10	
23	F-)	67	47	-20	)same
24	A-)	67.5	52	-15.5	)sample
25	F)	67.5	47	-20.5	)
26	G	69.5	55	-14.5	
27	H-)	70.5	58	-12.5	)same
28	H)	72	46	-26	)sample
29	D-)	72	47	-24.5	)
30	L	75.5	59	-16.5	
31	M	83	69	-14	

*) D.V.M. Engine Fuels (see Report KF 40/3 Material Div. D.V.L. Sept. 1932)

Investigations conducted at the present readily indicate that these disagreements are due to the fact that the chemical structure of these materials deviate from normal engine fuels and that they are strongly unsaturated. Some individual components of such a gasoline are probably subject to self ignition at a lower temperature and oxygen concentration than the mixture. These premature component ignitions are indicated perhaps by nothing more than an occasional knock which cannot be noticed in the C.F.R. tests, because the C.F.R. test is based on strong knocking causing a failure of performance. Since it is very important for airplane engines to discern a light occasional knocking of the engine fuel, the strobophonometer was developed whose measuring range is greater than the knock pin employed by the C.F.R. method. With this instrument the difference between C.F.R. and ignition value octane number of group 2 will be further adjustable.

The difficulty of knock determinations in test engines, due to unsaturated constituents, is characteristic of the D.V.M. testing, too; without gasoline from lignite and synthetic gasoline, both of which contain a lot of cracking products, show the most widely differing results.[9] Even with equally constructed engines (Delcomotor of D.A.P.G. and of I.G.) lignite gasoline showed 10 octane number differences (iodine no. 46.7) which made the observer [10] recommend "that it would be fitting to investigate these deviations still closer".

Recently Philippovich pointed out that the investigations conducted in Germany indicated that a certain agreement between test engine octane numbers and the practical behavior of the engine fuel exists only in the case of natural gasoline. Cracked gasoline and its mixture therefore must have an essentially higher octane number to give an acceptable performance and combustion. With alcohol and anilin containing engine fuels also the agreement is bad.

H. K. Cummings [11] stated the same about the knocking properties of aviation gasolines, and points out that the C.F.R. values and actual behavior of aviation gasolines agree only for a certain group. In America, [12] therefore, the C.F.R. Committee should approve of the C.F.R. test method for aviation fuel testing only under the condition that cracked gasoline and mixtures of considerable benzene content should be excluded. It seems therefore proper, in evaluating the relationship between ignition value and engine octane numbers, to consider the engine fuels of Group 2 only when it is ascertained how valid the C.F.R. values are in practice for unsaturated cracked gasolines and alcohol containing engine fuels.
The investigations show that the complicated knock process can be clarified partially if we go back to the basic phenomena of self ignition and transfer these to the process.

9) see Report Kf. 40/13 III D.V.L. p.5 Par. 1 and 3.

10) of D.V.L.

11) Reports of the World Petroleum Session, London (1933).

12) Private communications of the Secretary of the Cooperative Fuel Research Steering Committee.

Summary.

1.   The theoretical relationship between self-ignition and knock processes
were discussed and evaluated from the practical viewpoint.

2.   The octane numbers calculated from self-ignition characteristics are
closely related to engine octane ratings in the case of natural gasoline
(Fig. 5).   With gasolines that contain a large percentage of unsaturated
components or alcohols, a large deviation can occur; these deviations will
probably be equalized when it will be possible to note readily the knocking
start and intermittent knocking.   Such engine fuels can be referred to
ignition value methods for evaluation, only if it is determined how well
the test engine octane number agrees with actual behavior in engines.

Jentzsch ignition delay (s)	Jentzsch Comparison No.	Difference Comp. No. - C.F.R. Octane No.
2.7	38	+7
2.9	54	+8.5
3.4	57	+5
4.1	66	+9
3.5	64	+7
3.9	65	+2.5
4.6	70	+2.3
5.4	75	+6.7
3.9	69	+0.5
6.0	82	+8.4
4.5	81	+6.5
3.0	71	-3.5
5.1	80	+4.5
4.8	72	-3.5
6.5	92	+5.4
10	98	+5
10	90	-5
10	92	-4
3.2	71	-2
3.2	61.5	-3.5
5.2	66	-1.5
4.1	66	-1.5
6.5	60	-7
4.5	63	-4.5
6.6	60	-7.5
4.8	66	-3.5
3.6	67	-3.5
6.2	60.5	-11.5
7.2	62.5	-9.5
7.2	72	-3.5
6.0	79	-4

The incorporation of ignition delay in the determination of the comparison numbers (construction of nomograph) gave these values. Particularly with Group 2 a far reaching approximation to engine octane numbers results.
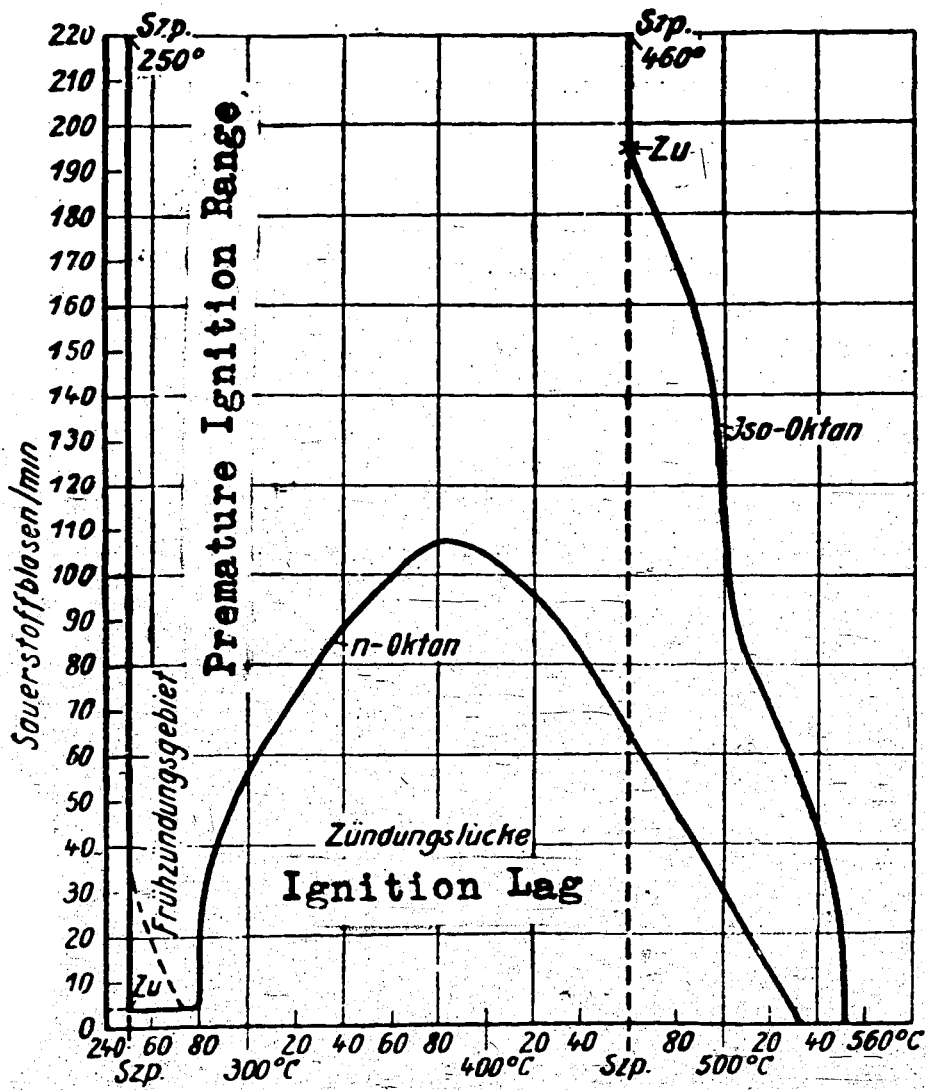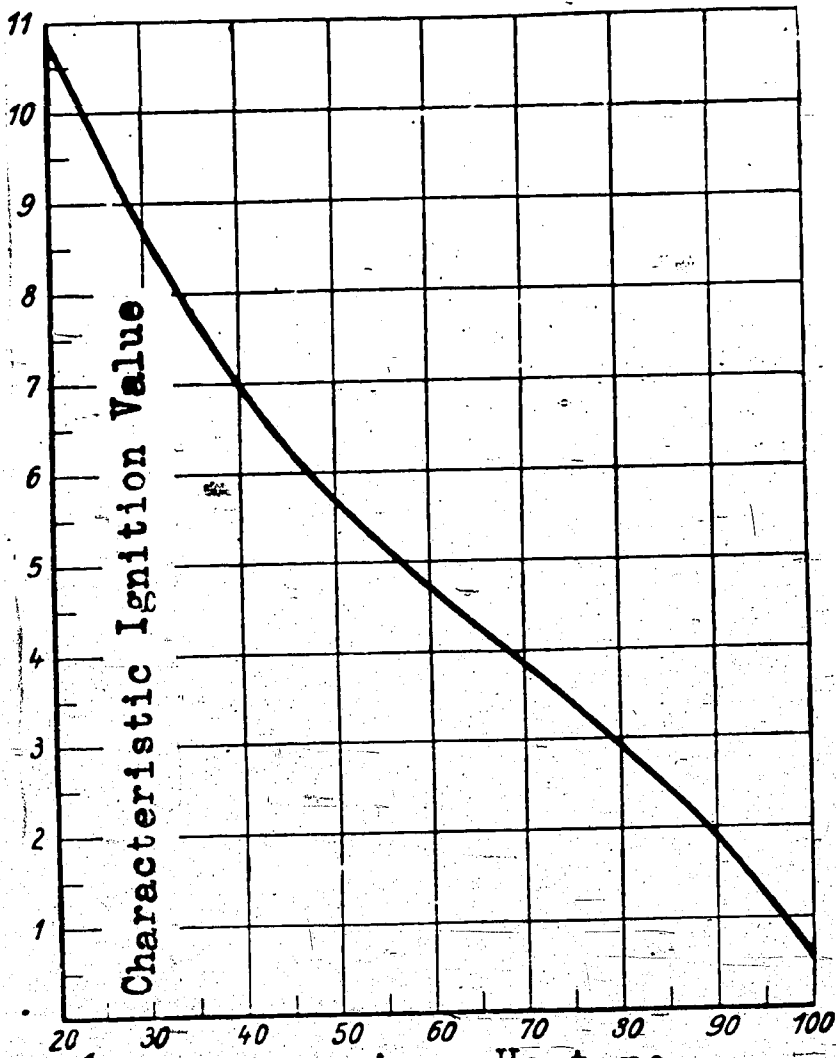
Fig. 1 Self-Ignition Curves for Octane
and Isooctane

Fig. 2 Std. Curve for Determination
of Octane Numbers from
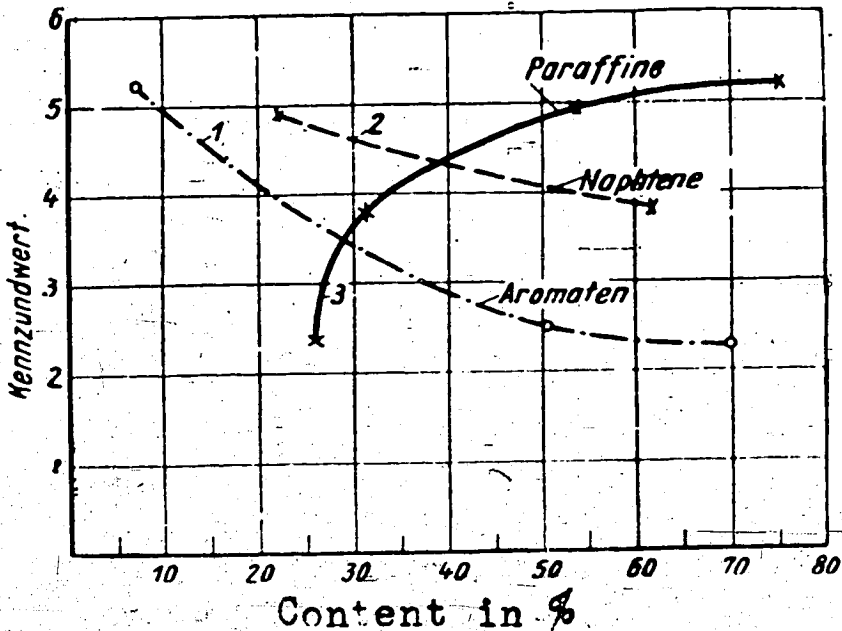the Characteristic Ignition
Values of Motor Fuels

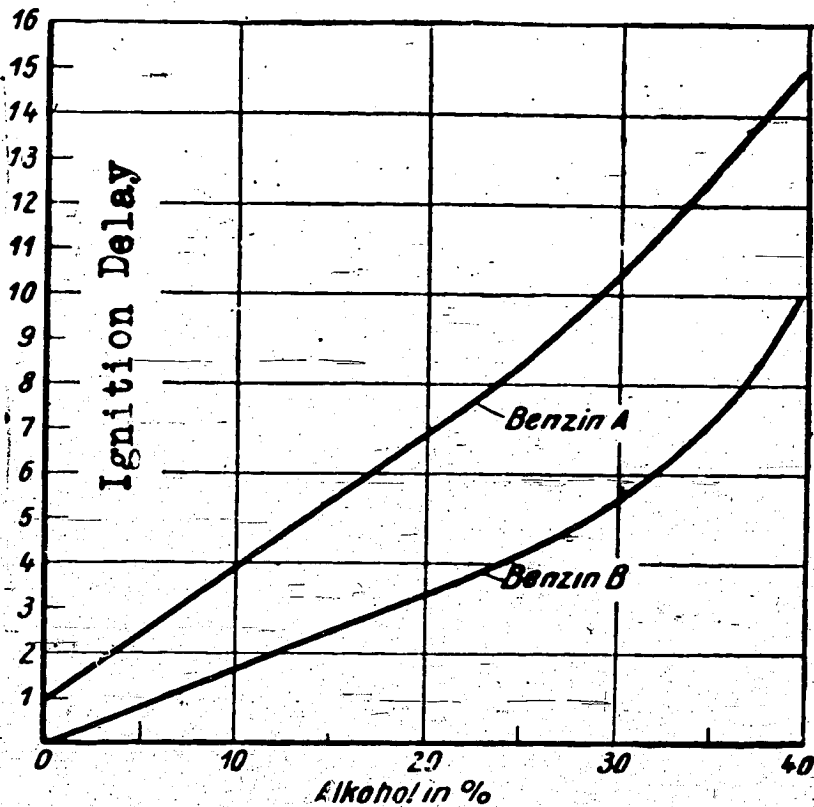Fig. 3 Characteristic Ignition
Value as a Function of Admixed
Component in the D.V.M. Fuel

Fig. 4 Dependence of Ignition Delay
on Alcohol Added
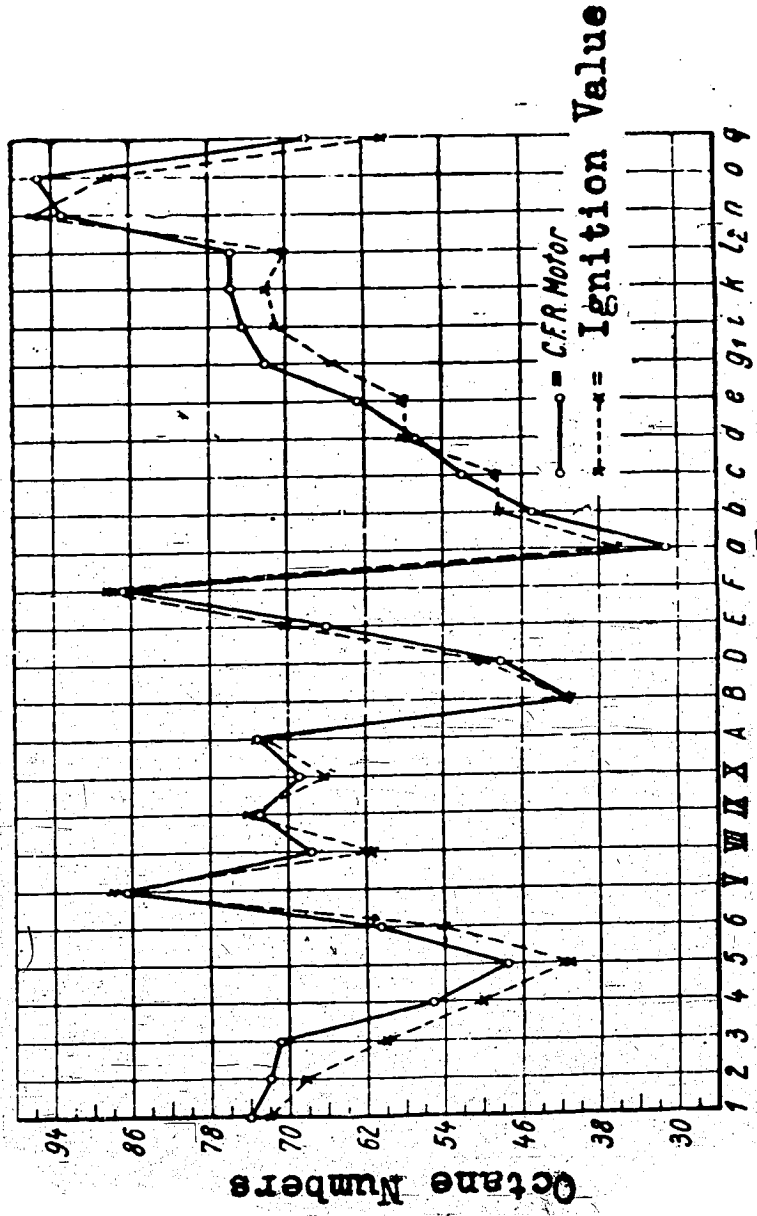
Fig. 5 CFR Octane Numbers and Ignition Value
Octane Numbers of 27 Commercial Gasolines

SPECIFICATIONS FOR GERMAN NAVAL FUEL

Translation of a document photographed on Frames
70566 through 70568 of TOM Reel No. 175 (Navy Reel No.5895-1)
and comprising Item (L) of the TOM 175 index.

Navy Department
Bureau of Ships
30 October 1946

Translation by
Mayer Schwartz, S2/c,USN

Quality Requirements for Marine Fuel Oil.

	Fuel Oil from Petroleum Hydrogenation Syntheses	Fuel Oil from Bituminous Coal
Appearance		Clear
Mechanical Impurities	—	must be absent
Sp. gr. at 20° C.	Not over 0.88	not-over 0.90

Submarines need fuel oil of sp. gr. between 0.84 and 0.87. The bulletins of the Central Bureau on Mineral Oil use this range throughout. In case a fuel oil is delivered with irregular sp. gr. which is very easy to avoid it is imperative to call special attention to it.

	Fuel Oil from Petroleum Hydrogenation Syntheses	Fuel Oil from Bituminous Coal
Viscosity at 20° C		Not over 2.6E Not below 1.2E
Flash point (P M)		Not below 55° C
Flash point (D V M)		Not below 70° C
Boiling Range		At least 60% should distill over below 350°C
Water Content		Not over 0.5%
Ash Content		Not over 0.05%
Sulphur Content	Not over 1.0%	Not over 1.3%
Neutralization No.		Not over 1.5
Mineral Acids		Must be absent
Cold Behavior		Must flow and be free from precipitate at ±0° C
Low Heat Value		Not below 9900 Kcal/kg
Conradson Carbon Residue	Not over 0.8 %	Not over 1% Not below .32

When agitated with water at room temperature (10 cc. of fuel oil and 10 cc. of distilled water are vigorously shaken for 1/2 min. in a DIN shaking cylinder) no stable emulsion should form. The separation of water should begin within one minute after the conclusion of the agitation; or standing for one half hour, water and oil must be so well separated that a possible layer of emulsion would not be wider than one graduation mark (i.e., 1 cc.) of the cylinder; high foam is permissible. On addition of 1 cc of n/10 NaOH, and on 1/2 min. vigorous shaking the water may turn faintly pink within 24 hours at most. The effect of fuel oil in sea water is noticeably smaller, as it is less distinctly colored in some cases. Therefore, in cases where in the preliminary NaOH test a strong coloring appears, a similar test with sea water (without the addition of NaOH) should be performed. Sea water will upon request be sent from the Naval Dock, Nachschub Division (23) in Achin and Bremen respectively.

The fuel oil must show an Ostwald color of, at least 4-5. Naturally lighter fuel oils are brought to this color tone with Sulan Brown R and black varnish. Colorless oils attain this color by addition of

$$
\left.\begin{array}{ll}
13 \text{ mg.} & \text{Sulan Brown R} \\
3 \text{ "} & \text{Black Varnish}
\end{array}\right) \text{ To 1 kg of fuel oil}
$$

The coloring material can be obtained from:

Marine Service Stations: I.G. Farbenindustric A.G. Agency
W. Berlin NW. 7, Unter den Linden 78

Firms: I.G. Farbenindustric A. G. Frankfurt
Am Main

A fuel oil, which does not meet these specifications, namely, emulsion strength, coloring of water and color depth, can only be employed for surface craft or by land customers, not for submarines.

Quality Requirements For Special Diesel Oil 2.

The specifications of marine fuel oils apply SDK 2 (Special Diesel Oil 2.) with the following exceptions:

Flash point	Not below 21. C
Viscosity at 20°C	Not below 1.1 E

The specifications of emulsion behavior coloring of water and color depth do not apply to SDK 2.

Storage of SDK 2.

SDK 2 falls into Danger Category A2 of the Police Ordnance on the trade of inflammable liquids.   Permission is herewith given for marine districts to store SDK 2 in containers provided for Danger Category 3. If in some special cases SDK2 is mixed with marine fuel oil (which is permissible), the mixture is handled as SDK2.

A Guide on the Application of SDK 2.

(1)   SDK 2 differs in its physico-chemical properties from regular Diesel
oil only as far as sp.gr. and flash point are concerned. The lower
sp. gr. causes a lower heat content per unit volume (heat value per
liter) which means that the performance of Diesel Motors when using
SDK 2 is less efficient (about 5 %) than by employing normal Diesel
oil. This decrease in performance is so slight that it can hardly be
noticed in practical work, and in practice, at least it can be neglected.
There is no noticeable effect on the injection pump or any other part
of the Diesel Motor or conversion from Normal Diesel oil to SDK 2.

(2)   The flash point, which lies between 21 and 55° C, necessitates the greatest cleanliness in the operation of the engine room, especially at the tanks, when starting the motor and during operation. Before the new fuel is taken aboard, the complete setup of the vessel should be most scrupulously examined for tightness and existing defects should be done away with. The entering fuel must definitely evaporate at leaks that develop during operation. The evaporated fuel should be removed from the engine room.

(3)   Fuel must be kept out of the bilges.

(4)   The discharge pipe of the fuel container should be securely attached, and lead up to the deck, in order that the fuel that runs over will not be able to get into the engine room. The vacuum pipes must similarly lead to the deck and their openings should be protected with a flame filter safety device or a Davy type wire screen.

(5)   The engine rooms and the compartments, in which the fuel oil containers are, as well as the bilges should be evacuated as effectively as possible with the natural and artificial vacuum apparatuses on hand (the fuel vapors concentrate in the lowest parts of the compartments). This is all important when the motor is turned on and when, during operation, leaks are noticed, that develop at fuel outlets or on the motor.

(6)   Combustion materials that are lighted with more open flames should be applied with special caution. Kindling paper holders should be taken out only after 5 minutes in starting failures.

(7)   In engine rooms and in compartments where fuel oil containers are stored, as well as in the adjoining compartments, smoking, the use of open fire, flame or other sources of fire, are prohibited. During operation the steam boilers and furnaces in the engine room serve to prevent any pointed flame or glowing coal or ashes from being blown or thrown against the Diesel engine or the fuel oil ducts.

(8)   The electrical equipment in the engine room, particularly the generators motors and the switch boards must be so maintained that sparks will be avoided as much as possible.

(9)   While fueling, the Diesel motors should stand still and all fires must be extinguished. Besides this, smoking and the use of open fire and flame aboard is also prohibited while fueling.

(10)   Warships are excluded from the use of SDK. Ships and boats, in the engine room of which steam boilers or furnaces are operated, as well as boats with ignition type motors are excluded, if the natural or artificial air circulating equipment is not capable of sufficiently removing benzene vapor and air mixture. The decision, as to which ships and boats should be excluded on these grounds, lies with the MOK who is entrusted with the command of the vessel. The commander of the ship makes out a certificate on this account.