ON THE KNOCKING OF GASOLINE ENGINES

By Ludwig Richter

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ON THE KNOCKING OF GASOLINE ENGINES.*

By Ludwig Richter.

Since Heller's report ("Zeitschrift des Vereines deutscher Ingenieure" 1923, Page 158) on the knocking of automobile engines, the results of extensive experiments by Ricardo and his assistants have been published (Ricardo, "The Internal Combustion Engine," Vol. II, High Speed Engines, London, 1923), which constitute a notable contribution to the knowledge and remedy of this trouble. It is of the greatest importance, not only for automobile engines, but also for every other kind of internal combustion engine, since it limits the degree of compression and the thermal efficiency and its investigation indicates ways for saving fuel.

Characteristics and Results of Knocking

If an ignitable, sufficiently compressed gaseous mixture is ignited in a closed space, the combustion is propagated at a certain velocity from the point of ignition and with an accompanying increase in pressure. If the heat, thus generated, exceeds a certain amount, there are produced, in and near the combustion places, temperature and pressure increases, which cause a sudden

combustion in the unburnt portion of the combustion chamber, thereby producing waves which strike violently against the walls and produce the well-known hard metallic "knocking."* This violent combustion or detonation increases the compression and temperature of the already burnt gas, as well as the temperature of the spark plugs and other poorly cooled parts and, if not remedied, allows the originally feeble knocks to become continually more violent and raises the temperature of the spark plugs, etc., until premature or self-ignitions take place during the compression and before ignition by the spark plugs, thus rendering operation impossible. These preignitions must not, however, be confused with the detonations. Self-ignition can even occur without previous detonation, when the final compression temperature exceeds the self-ignition temperature. Detonation can likewise occur without producing spontaneous and premature ignitions, provided the force of the detonation does not exceed a certain degree which depends on the cooling conditions of the given engine.

The force of the detonation varies. The weakest form is often very difficult to recognize, as there is no decided noise, but only a certain hard functioning of the engine. Since at the

*Berthelot measured the following velocities of explosion waves in tubes: Hydrogen and oxygen, 2820 m (9252 ft.)/sec. Acetylene and oxygen, 2450 " (8038 " )/ " Methane and oxygen, 2300 " (7546 " )/ " Chlorine detonating gas and oxygen, 1730 " (5676 " )/ " At 2500 m (8202 ft.) per second, the kinetic energy of a cubic centimeter of air, at 2500°C (4532°F) and 20 atm. (284 lb./sq.in.) is almost 8 m kg (58 ft.-lb.), which explains the force of the blow.
time of its occurrence, the highest practical compression under
the given conditions has been reached, the engine is then gener-
ally consuming the least fuel and generating the most power.

The endeavors were chiefly to determine to what extent the
power output and fuel consumption were affected by the detona-
tion, as well as the causes of its production and its relation
to the fundamental chemical and physical properties of ignitible
gas mixtures and to the functioning conditions and structural
forms of the engines and, lastly, to find means for its elimi-
nation.

The Experiments and Their Significance

1. The English experiments were performed in part on spe-
cial experimental engines*, namely, a vertical single-cylinder
engine with a very favorably shaped combustion chamber and ad-
justable compression during operation, and a single-cylinder en-
gine for overloading, and verified on numerous normal and mostly
four-cylinder engines; and also in part on a special compression-
ignition apparatus**(Fig. 1), which worked on a principle al-
ready utilized by Falk***. The latter's experiments were espec-
ially important for the knowledge of the connection between the

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*"Report of the Empire Motor Fuels Committee," published by the
Institution of Automobile Engineers," London, 1924, p.63. Ref-
ience will hereafter be made to this report simply by the word
"report."

**Tizard, "The Causes of Detonation in Internal Combustion En-
gines," Trans. N. E. Coast Institution of Engineers and Ship-
builders, May, 1921; "The Self-Ignition Temperature of Fuels," The
Automobile Engineer, 1923, p. 135.

***Falk, "The Ignition Temperatures of Gaseous Mixtures," Journal
of the American Chemical Society, 1907, p. 1936.
tendency of the gaseous mixture to detonate, on the one hand, and between the spontaneous ignition temperature and the combustion speed, on the other hand.

The working cylinder of 114.3 mm (4.5 in.) diameter and a maximum piston stroke of 203.2 mm (8 in.) can be shifted in a guide, so that the size of the compression chamber can be very accurately adjusted. The motion of a heavy flywheel, driven by an electric motor, is transmitted to the piston through a friction coupling, connecting rod and a bell crank. As soon as the piston reaches its highest position, the bell crank is automatically held firm in its extended position and the connecting rod is released. The compression pressure is recorded photographically by an optical indicator. From this record the exponent of the polytropic compression and also the final temperature, with known initial temperature, are calculated. First the heat communicated to the walls by compression below the self-ignition temperature and temperature measurement during cooling was calculated and it was found that the temperature loss was given quite accurately by \(- \frac{d\Delta t}{dz} = k\Delta t\), wherein \(z\) is the time in seconds; \(\Delta t\), the difference between the temperatures of the gas and walls; \(k\), the constant for air and carbon dioxide = 1.4 and for hydrogen 1.8. Fig. 2 is a diagram for hydrogen without ignition and Fig. 3 is a diagram for a mixture of 0.8 part heptane and 15 parts air with ignition. In this and in another diagram (Fig. 4) for the combustion of heptane in air with a small-
er time scale, 1) denotes the final compression pressure and the beginning of the combustion and 2) the beginning of a sudden rise in pressure and temperature, a point of time at which the heat developed by the combustion considerably exceeds the heat lost by cooling. The ignition temperature is given by the initial temperature and the final compression pressure, while the time interval 1) - 2), between the reaching of the final compression pressure, necessary for self-ignition, and the beginning of the sudden pressure increase caused by the rapid combustion, is a criterion for the combustion speed at the existing compression pressure and the corresponding temperature and can be quite large under certain conditions.

2. A small wind wheel was built into the apparatus, in order to determine the effect of the turbulence and of the consequent greater amount of heat communicated to the walls. Table I shows the effect on the ignition temperature.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Minimum ignition temperature without and with wind wheel</th>
<th>Temp. loss with or without wind wheel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heptane</td>
<td>280°C(536°F) 307°C(584.6°F)</td>
<td>2.90°C(5.23°F)</td>
</tr>
<tr>
<td>Ether</td>
<td>212°C(413.6°F) 235°C(455°F)</td>
<td>3.08°C(5.54°F)</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>253°C(487.4°F) 300°C(572°F)</td>
<td>3.40°C(6.12°F)</td>
</tr>
</tbody>
</table>

On the contrary, Ricardo's experiments with an engine having several valves, which he caused to operate all together and then
part at a time, showed no difference as regards the detonation, which was probably due to there being no essential difference in the strength of the turbulence.

The difference in the ignition temperatures is due, in my opinion, to the fact that, in the undisturbed gas, the portions adjacent to the walls form, to a certain extent, a heat insulator for the hotter interior portion from which the combustion proceeds. The mean ignition temperature of the disturbed gas would then closely approximate that of the given fuel and correspond to the temperature of the hotter interior in the undisturbed gas. In the latter case, the mean temperature of the combustion chamber is naturally lower than the temperature of the interior portion. Since the mean gas temperature is higher in the turbulent condition, the combustion speed would be greater and the ignition delay smaller, an assumption which appears to be confirmed by other diagrams published by Tizard ("Automotive Industries," 1922, p.130).

3. The well-known considerable effect of the shape and dimensions of the compression chamber, on the maximum allowable compression and the consequent power and efficiency, was again confirmed by numerous experiments on various engines and can be explained partly by the effect of the turbulence and partly by the differences in the ignition distances. The combustion chamber must be as compact as possible and the spark plugs near the
middle, in order to shorten the ignition distances. The well-known improvement in power and fuel consumption, through two opposite spark plugs in many engines, is due to the more rapid combustion of the whole mixture resulting from the shortening of the ignition distances. In order to lessen the knocking when the ignition is produced at only one end, the spark plug should be located at the hottest point, namely, near the exhaust valve, in order that the unused gases may lose some of their heat by being pressed against cold surfaces, so that the combustion speed will remain within the corresponding limits and no explosion waves will be generated. The more uniform the temperature throughout the whole combustion chamber and the more uniform the combustion of the mixture, just so much less is the danger that detached portions of the charge may detonate. From this viewpoint, the effects of the various arrangements, as shown in Fig. 5 (according to Ricardo), are easily understood.

4. The lessened tendency to knock, when the revolution speed is increased, is due partly to the increased turbulence, which eliminates the temperature differences in the combustion chamber and, through increased heat liberation, keeps the mean gas temperature lower, but the lessened charge probably has some effect also.

5. The final compression temperature not only determines the possibility of self-ignition, but also the combustion speed
from spark ignition. For judging fuels with regard to their
tendency to knock, the differences in the combustion speeds at
the same temperature, as also their increase with rise in tem-
perature, is just as important as the self-ignition temperature.
In Fig. 6 the ignition delay for various fuels is plotted
against the temperature. The differences between the curves
for heptane and carbon disulfide are especially manifest. The
latter has a very low self-ignition temperature and can never-
theless be very difficultly made to knock (if at all), while
heptane, with a 27°C (48.6°F) higher self-ignition temperature,
knocks very easily. This behavior can be explained by the dif-
ference in the combustion speeds, as indicated by the ignition
delay at temperatures above 300°C (572°F). According to Tizard,
at 300°C (572°F) heptane has the same; at 500°C (932°F), about
seven times; and at 1000°C (1832°F), about seventy times the com-
bustion speed of carbon disulfide. Hydrogen knocks very easily,
in spite of its higher self-ignition temperature. Its combustion
speed increases very rapidly with the temperature. Unfortunately
this does not show so clearly on the diagram, since the curve is
not crossed by any other.

Since the tests in the engines give just the same arrange-
ment of the fuels with regard to their tendency to knock, as the
experiments with the special compression-ignition apparatus, the
formula \( \frac{dw}{dt} \) (in which \( w \) denotes the combustion speed and \( t \) the gas temperature) seems, in fact, to be decisive. For
fuels with the same temperature coefficient (as Tizard calls $\frac{dw}{dt}$), the self-ignition temperature would, however, be decisive, as is the case for chemically pure hydrocarbons, alcohol, ether and acetone.

6. At the beginning of the combustion, the knocking seems to be affected more by the pressure than by the temperature. An increase of 0.1 in the compression ratio, between 4.8 and 5.2, requires, for equalization, a temperature reduction of the in-drawn hexane-air mixture of $10^\circ C$ ($50^\circ F$) in the region between 40 and 70$^\circ C$ ($104$-$158^\circ F$), corresponding to a temperature difference of about $17^\circ C$ ($30.6^\circ F$) at the end of the compression. In a few fuel mixtures the compression ratio which causes knocking can be determined with an accuracy of $\pm 5\%$ (Report, p. 248), i.e., at 4.8 : 1 there was only a very light knocking, while at 4.9 : 1 the knocking was already hard, this difference corresponding to a difference of only $\pm 1^\circ C$ ($\pm 1.8^\circ F$) in the compression temperature.

A relatively great effect of the pressure, in comparison with the temperature, leads to the conclusion that throttling the intake reduces the knocking, although at the same time (with the same proportionate weight of the exhaust gases and a smaller one of the fresh mixture) the mean temperature of the mixture during the compression is higher than in an unthrottled engine. This phenomenon was utilized in high-altitude aviation engines
and in an Austro-Fiat truck engine (Z.V.d.I. 1924, p.1199) to increase the compression, thereby reducing the fuel consumption. Although even here the greater dilution of the residual gases (in comparison with the unthrottled engine) has some effect, the pressure is certainly a very important factor. Experience has shown that the tendency to knock decreases in aviation engines at high altitudes (while the ratio of the residual gas to the fuel gas remains practically unchanged) and also when the intake temperature is kept constant by preliminary heating.

Unfortunately neither the experiments with the engines nor those with the compression-ignition apparatus sufficed to separate the effects of the temperature, pressure and mixture ratio. With the compression-ignition apparatus, sufficient temperature differences of the gases before compression could not be obtained, since the leather packing sleeve of the piston was damaged at temperatures of over 60\(^\circ\)C (140\(^\circ\)F) of the heating jacket, so that the final compression temperature could be raised only by increasing the compression ratio. The effect of the pressure could probably be determined by experiments with a previously compressed mixture, but I found no report on this subject. In the engine experiments, the changing of the compression ratio affected the quantity of the residual gases, which, as will be subsequently shown, has an important effect on the detonation.

7. Since everything indicates that the knocking depends
chiefly on the self-ignition temperatures and the combustion speed of the mixture, these experiments are specially important which render it possible to determine them both by themselves and, at times, in terms of only one of the independent variables (pressure, temperature, mixture ratio), for the largest possible number of fuels and their mixtures, as also with the use of catalysts. These are:

A. Experiments for determining the ignition point and pressure;

B. Experiments in a spherical combustion chamber for determining the combustion speed.

A. The experiments of Tauss and Schulte (Z.V.d.I. 1924, p.574) agree in giving about the same decrease in the self-ignition temperature with increasing pressure. Unfortunately the experimental results of only a few of the fuels utilizable in internal combustion engines were published (Fig. 7).

B. The establishment of the method of indication of the combustion speed is desirable before further discussion, since the speed at which a combustion surface advances can be measured:

*Nägel, "Versuche über die Zündgeschwindigkeit explosiver Gasgemische," Mitteilungen über Forschungsarbeiten, No.54, 1908.
a) Relatively to the unburned mixture (chemical, linear-combustion speed);

b) Relatively to the combustion products;

c) Relatively to the distance traversed by the combustion (direct combustion speed);

d) As mass combustion speed, i.e., by the weight or volume of the mixture (measured at the initial temperature and pressure) which burns per second in the unit area of the combustion surface.

Case a exists (for example) when a combustible mixture flows through a pipe and burns at its mouth and the rate of flow is so adjusted that the otherwise conical combustion surface changes to a flat one. The flow velocity of the unburned gas is then equal to the combustion speed as defined according to a. Since it must be assumed with Nusselt ("Die Zündgeschwindigkeit brennender Gasgemische," Z.V.d.I. 1915, p.872) that no sudden rise in temperature takes place in the combustion surface and that there is accordingly a gradual expansion of the inflowing gas and a simultaneous increase in the flow velocity before reaching the place of burning, it should be added that the velocity of the gas before reaching the burning place is meant. Nügeli, Neumann ("Untersuchung des Arbeitsprozesses im Fahrzeugmotor," Mitt. über Forschungsarb., No. 79, 1908) and Bucher ("Untersuchung über die Verbrennung methanhaltiger Gasgemische," Mitt. über
Forschungsarb., No. 117, 1912) ignited the mixture by an electric spark in the center of a spherical chamber having a radius \( r \) of 20 cm (7.87 in.), recorded the pressure continuously with an optical indicator, and determined from the elapsed time \( t \), the mean (spatial) combustion speed \( c = \frac{x}{t} \) from the ignition point \( a \) (Fig. 8) to the point of maximum pressure \( e \).

The effect of the temperature on the mean combustion speed can only be determined qualitatively from two of Nägele's experimental groups with mixtures of illuminating gas and air, and generator gas and air. Fig. 9 shows a somewhat higher velocity at an initial temperature of 750°C (1670°F) than at 150°C (59°F). No further conclusions can be drawn from this fact, however.

Bucher's experiments were all performed with mixtures of methane and air, and methane, hydrogen and air, at 150°C (59°F), while most of Neumann's were made at the initial temperature of 400°C (104°F).

The effect of the initial pressure is not the same in the individual mixtures. While with mixtures of hydrogen and air, the mean combustion speed increases perceptibly with increasing pressure above a certain proportion of hydrogen and increases very rapidly with rich mixtures (Fig. 10), there is an increase in speed in poor mixtures only between 0.5 and 1 kg/cm² (7.1 - 14.2 lb./sq.in.) absolute pressure and not any speed increase at all in the very poorest mixtures (0.1% of hydrogen), and there is even a decrease in speed at higher pressures. A similar
behavior is exhibited by mixtures of methane and air; methane, hydrogen and air; and gasoline vapor and air (Figs. 11-13). The mean combustion speed gives, however, only a crude picture of the actual behavior of the mixture since, in nearly all cases, the first (the gradual ascent) of the pressure line is decisive. The more or less rapid increase of pressure and combustion speed (dependent on Tizard's temperature coefficients) in the last part of the combustion period appears only very much diminished.

A clearly perceptible bend in the gasoline-air pressure lines at high initial pressures is characteristic. This bend separates the line of gradual pressure increase from that of sudden increase and is probably connected with a combustion wave and therefore probably shows the effect of the pressure more plainly than the mean combustion speed. Under such circumstances, it is very gratifying that Flamm and Maché succeeded in developing an analytical method (already suggested by Nägel) for calculating the chemical (a) and mass (d) combustion speed from the time-pressure lines, at each instant of the combustion period, and their relation to the spatial combustion speed (c).

Since a measured pressure and a computable ignition temperature can be coordinated for every instant of the combustion period, it is possible, according to Maché, to plot the combustion speed against the pressure and temperature. Figs. 14-15 give Maché's computed values of the chemical and mass combustion speed $w$ for a hydrogen-air mixture with about 21.3% of hydrogen.
The mass combustion speed increases in this case beyond 100°C (212°F) with the temperature, but then remains almost constant. Its dependence on the pressure $p$ can be well represented by $w = w_0 p^n$ with an exponent gradually decreasing from 1.36 to 1.30, so that Mache suspects that for very high pressures, it will be proportional to the pressure, as in the case of solid, completely vaporizable fuels (colloid powders). The chemical (linear) combustion speed increases with the temperature, but the increase is smaller in the mass than the density of the mixture decreases with increasing temperature. It increases with the pressure, but the rate of increase gradually diminishes as the pressure increases and finally becomes constant at very high pressures (when $w$ is proportional to the pressure).

Since this method of determining the combustion speed is probably the only one capable of yielding information concerning its magnitude at high pressures and temperatures, further searches in this direction would be very desirable. In judging the values given here, it should not be forgotten that for making the computation, certain simplifications are desirable (momentary pressure equalization in the combustion chamber at every instant, and therefore no flow, and no heat transmission to the walls), the admissibility of which should be verified by new computations or experiments. It may perhaps be possible to make the computations more closely approximate the actual processes.

The laws of chemical dynamics make the effects of pressure
and temperature on the ignition temperature and combustion front, and consequently on the tendency to knock, seem reasonable and even necessary, since the mean speed is increased by the temperature; since the number of molecules per unit volume is increased by the pressure; and since, in any case, the capacity of the mixture for chemical reaction is increased.

8. The effect of the mixture ratio and its content in oxygen and fuel is explained by the change in the number of active molecules per unit volume. Ricardo burned a fuel mixture, enriched with oxygen and diluted with nitrogen, carbon dioxide and water vapor, in an engine with variable compression ratio. In the first case the compression ratio had to be considerably reduced, in order to stop the knocking, with 3.1-4.12 : 1 unit volumes of additional oxygen against 4.5 : 1 when operated with air, gasoline free from aromatic hydrocarbons being used. Considerably higher compression ratios were permissible in the diluted mixtures, as shown by Fig. 16. Thereby the final combustion pressure was naturally higher, but the difference between the final compression pressure and the combustion pressure for all the combustion gases and all the mixture ratios, was only slight in comparison with the normal fuel mixture of gasoline and air. The maximum combustion temperature, however, was higher for the mixture enriched with oxygen and lower for the mixtures diluted with inert gases than for the normal mixture of gasoline and air,
because less heat was generated with approximately the same charges. In like manner the combustion speeds also differed from the normal. The effect of the lower density of the charge in reducing the combustion speed was therefore still further increased by the lower combustion temperature. A similar elevation of the allowable compression pressure and an improvement in the fuel consumption was also effected by the addition of cooled exhaust gases (Fig. 17). The increase in the fuel consumption at a compression ratio greater than 6:1 is due to incomplete combustion in the then too poor mixture. By using gasoline free from aromatic hydrocarbons, the compression ratio could be raised from 4.85 (at which the normal mixture detonated) to 7.5.

The employment of mixtures poor in oxygen accordingly appears as a means for increasing the compression ratio and reducing the fuel consumption, but even here, unfortunately, narrow limits are set to the dilution of the mixture. These limits are given approximately for single-cylinder engines of the best type, by the largest volume percentages shown in Fig. 16. Further dilution causes retarded combustion and misfires. The dilution cannot be carried so far in multicylinder engines on account of the uneven distribution. The mixture ratio seems to affect both the self-ignition temperature and the combustion speed.

Moore (Z.V.d.I. 1921, p. 1280) and Tauss (Z.V.d.I. 1924, p. 576) both found in the engine experiments a considerable lowering
of the self-ignition temperature as a result of increasing the oxygen content. I could not find, however, any experimental data on the combustion speed of fuel mixtures over-rich in oxygen.

From what has been said, it seems to follow that in mixtures of fuel and air, deviations from the chemical mixture ratio lessen the tendency to knock. This is at least approximately true, although according to Neumann, a mixture of gasoline vapor and air has the maximum combustion speed when there is about a 25% shortage in the air supply (Fig. 13). Since a much greater enrichment than impoverishment is possible, without danger of retarded combustion it follows that the custom of burning easily knocking fuels only in rich mixtures is justified. Not over 20% excess of air can be used with most liquid fuels in a well-built, one-cylinder engine and 10% in multicylinder engines, while the air-shortage limit is much greater (up to 75%).

The effect of fuel enrichment on the attainable compression pressure seems to depend just as much on the elevation of the specific heat of the mixture (perhaps also on the increase in the heat-conduction capacity), as on the elevation of the ignition temperature and the retardation of the combustion through deviation from the exact chemical ratio of the fuel mixture.*

*Schüle (Technische Thermodynamik," 3d edition, Vol. II, p.329) plotted the results of the experiments on the effect of the mixture ratio against the ignition temperature (Fig. 20). Falk (Z.V.d.I. 1915, p.875) gave an empirical formula for the effect of the nitrogen content on the ignition temperature of combustible mixtures.
For a mixture of heptane and air, the compression pressure necessary for self-ignition increases, according to Tizard's experiments with the combustion-ignition apparatus (The Automobile Engineer, 1923, p. 137) approximately as the proportion of heptane in the mixture (Fig. 18), while the exponent of the polytropic compression curve \( k = \frac{c_p}{c_v} \) rapidly decreases.

Likewise an experiment of Ricardo's (Report, p.334) on an engine with variable compression ratio with gasoline free from aromatic constituents (Fig. 19), shows that an increase in the compression ratio is possible in a deviation from the mixture ratio for perfect combustion, but only to a relatively small degree. The attempt to work with very poor mixtures through stratified charging (with a rich layer at the ignition point and the rest of the combustion chamber filled with as poor a mixture as possible) gave very fine results in the experimental engines, which are impossible, however, in practice, due to structural and technical difficulties. The experimental points marked by crosses (Fig. 19) indicate how high the compression can be carried in this manner.

Gaseous fuels allow considerably greater dilutions and compression ratios and thus enable a regulation of the mixture within wide limits, which is naturally much more economical than the simple throttling of engines using liquid fuels. The dilution of hydrogen can be carried especially far, Ricardo attaining in this way an air excess of 100\% and a compression ratio
of 7, with a thermal efficiency of 43%. With hydrogen, however, any shortage of air causes preignition and violent explosions (Fig. 19).

9. Before considering the individual fuels more in detail, we will explain the method employed by Ricardo for classifying the fuels according to their tendency to knock. Toluene was chosen as the characteristic liquid which, in an engine with variable compression, stands a compression ratio of over 7.8, and which was given an index value (the "toluene value") of 100. On the other hand, an index value of 0 was given to gasoline free from aromatic hydrocarbons, which allows a compression ratio of 4.85. The toluene values 0-100 were coordinated with the compression ratios 4.85-7.8 and a fuel, which admitted of a definite intermediate compression ratio, was given the corresponding toluene value. Since it was found that the compression ratio at which the detonation begins is, in general, directly proportional to the ratio of mixture (by weight) with aromatic hydrocarbons (Report, p.82), it would also be possible to determine the toluene values in other engines with variable compression than the ones employed by Ricardo. It would only be necessary to determine the allowable compression ratio for the given fuel and the mixture of toluene and normal gasoline which has the same compression ratio.

As shown by Table II, the gasoline used by Ricardo as the basis of comparison (line 1), which contains 1.7% aromatic hydro-
carbons, is by no means the fuel with the lowest allowable compression ratio, so that negative toluene values are also possible. Moreover, toluene is surpassed, in its preventive effect against detonation, by other liquid fuels (e.g., ethyl alcohol) but, for Ricardo, the easy availability, in large quantities, and the mixability of the fuels compared were the determining factors. For standardization purposes, only chemically or practically pure fuels were considered as permanent bases of comparison. The investigation could be carried on with small quantities with the compression-ignition machine and the necessary degree of purity of the standard fuels had to be established by comparison with chemically pure fuels. Ricardo also determined, in his engine for overloading, the toluene values of various fuels, which agreed very well with the results obtained in the engine with variable compression.

In determining the toluene values of the fuels, the elimination of influences which, aside from the chemical composition, can affect the detonation, is naturally of great importance, but can be only partially accomplished, and hence calculations are often necessary on the basis of experiments with the same fuel under different operating conditions. Above all, the fuels must be tested under the same accurately defined ratios of mixture.

10. Ricardo tested a large number of fuels (chemically or technically pure, both in natural and artificial mixtures) with
reference to their tendency to knock, the results being given in Table II (end of report).

The tendency of the hydrocarbons to knock increases with the relative content of hydrogen, as shown in

<table>
<thead>
<tr>
<th>Formula</th>
<th>Toluene value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_n H_{2n-6} )</td>
<td>100</td>
</tr>
<tr>
<td>( C_n H_{2n} )</td>
<td>30 (about)</td>
</tr>
<tr>
<td>( C_n H_{2n+2} )</td>
<td>-20</td>
</tr>
</tbody>
</table>

Table III.

Among the aromatic hydrocarbons, benzene (benzol) \( (C_6H_6) \) detonates the easiest, followed by xylene \( (C_8H_{10}) \) and toluene \( (C_7H_8) \) which, with the exception of methyl alcohol, is the most difficult to detonate of all the fuels tested. In fact, it could hardly be made to detonate and was accordingly chosen as the basis of comparison. Its effect in fuel mixtures is correspondingly great, though considerably smaller than that of benzene.

The aromatic hydrocarbons cannot be made to detonate in the variable-compression engine, but self-ignition occurs at a compression ratio of 7:1. The addition of a small quantity of the paraffines caused detonation at high compressions. In this group the specific weight and boiling point furnish no basis for judging the tendency to knock.

In the naphthenes and paraffines the tendency to knock increases with the size of the molecules and the corresponding in-
crease in the specific gravity and boiling point. The alcohols have but little tendency to detonate, ethyl alcohol being the best anti-knock substance for fuel mixtures. Unfortunately, only absolute alcohol will mix in all proportions with the paraffines, naphthenes and aromatic hydrocarbons and the water content of alcohol cannot be reduced below 5% by the customary process of distillation. Ormandy and Craven (Report, p.313) thoroughly investigated the solubility of the hydrocarbons in water and found that it generally increases in 92% alcohol with the toluene value, but that there are numerous exceptions (Fig. 22).

Ether had the smallest toluene value of all the fuels tested. Pure carbon disulfide ignited spontaneously, even at very low compression ratios and cooling-water temperatures, so that it cannot be used pure in engines. It does not detonate, however, and serves as a remedy for fuels which knock too easily. In like manner the aromatic hydrocarbons and ethyl alcohol ignite spontaneously without detonation at correspondingly high temperatures.

All numerical data must, however, be regarded as only approximate, since the so-desirable investigation of fuels in the perfectly pure state was impossible, because sufficient quantities were not available.

11. The mixture law applies approximately to mixtures of hydrocarbons, as already mentioned. The aromatic components naturally have the greatest effect on the tendency of the fuel to
detonate, so that the value of a fuel can be measured directly according to the amount of them it contains. As regards the knocking and consequently, the general evaluation of the fuels, the boiling curves are of as little value as the specific gravities and, since the value of a fuel depends chiefly on its capacity for compression, the endeavors to use mean boiling points, or boiling curves standardized in any way for judging liquid fuels, is just as unpractical as the still common method of judging a fuel by its specific gravity.

The possibility of obtaining a certain uniformity of fuels as regards their tendency to knock, by the addition of aromatic hydrocarbons, is of great importance for the user and manufacturer of gasoline engines because, with a uniform behavior of the fuels, the compression ratio of the engine can be made high, and lower fuel-consumption rates and higher engine powers can be attained, while now consideration must be taken of the fuels with the lowest toluene value in the choice of the compression ratio, or the knocking must be prevented by adjusting the carburetor so as to deliver a richer mixture with a smaller spark advance, whereby the economy of operation suffers. On account of such considerations, the Shell Marketing Company (Report, p.90) decided to keep their fuel at a constant predetermined toluene value. It would certainly be a great advantage if this important step toward fuel standardization were emulated.

Mixtures of 99.4% pure alcohol with ether and gasoline show
(Report, p.247) that the allowable compression ratio increases faster than the proportion of alcohol (Fig. 23), so that the toluene value can be taken at 130 for mixtures containing about 30% of alcohol, and 160 for 40% of alcohol.

12. Of very great importance is the knowledge that there are certain substances which, on being added in relatively small quantities, considerably lesson the tendency to knock. Lubricating oil and sulphur were previously known to soften the detonation (Tizard, "The Causes of Detonation," p.52). Carbon disulphide acts as a remedy, as already mentioned. Amyl nitrite and amyl nitrate (Report, p.324) work in the same way. Midgley and Boyd (Report, p.305) found a series of other substances, some of which increase the knocking and some prevent it, as given in

<table>
<thead>
<tr>
<th>Element</th>
<th>Form</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iodine</td>
<td>Element</td>
<td>Preventive</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Aniline</td>
<td>&quot;</td>
</tr>
<tr>
<td>Selenium</td>
<td>Diethyl compound</td>
<td>&quot;</td>
</tr>
<tr>
<td>Tellurium</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Zinc</td>
<td>Tetraethyl</td>
<td>&quot;</td>
</tr>
<tr>
<td>Lead</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Bromium</td>
<td>Element</td>
<td>Promotive</td>
</tr>
<tr>
<td>Oxygen</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Ethyl nitrite or nitrate</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
Midgley employed a special method for determining the strength of the detonation; cere sine, as the basic fuel for judging the admixtures; xylidine, which has a strong anti-knock effect, as the admixture for comparison. Fig. 24 shows its effect in comparison with admixtures of alcohol, xylene, toluene and benzene. Five per cent of xylidine by volume in the mixture with cere sine produced the same effect as 45% of benzene. Moreover, in these experiments (differing from those of Ricardo), xylene was more effectual than toluene in preventing detonation, which may have been due to a difference in the purity of the xylene used.

Midgley also found other substances which, when added in extremely small quantities to cere sine, produced the same effect as 25% of benzene, as shown in

<table>
<thead>
<tr>
<th>Element</th>
<th>Form</th>
<th>Percentage by volume</th>
<th>No. of mol. in mixt. to 1 mol. anti-knock sub.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td></td>
<td>25.0</td>
<td>150</td>
</tr>
<tr>
<td>Iodine</td>
<td>Ethyl iodide</td>
<td>1.6</td>
<td>2150</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Xylidine</td>
<td>2.0</td>
<td>2600</td>
</tr>
<tr>
<td>Zinc</td>
<td>Tetra-ethyl-</td>
<td>1.2</td>
<td>7100</td>
</tr>
<tr>
<td></td>
<td>zinc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Selenium</td>
<td>Diethyl selenide</td>
<td>0.4</td>
<td>11750</td>
</tr>
<tr>
<td>Tellurium</td>
<td>Diethyl telluride</td>
<td>0.1</td>
<td>50000</td>
</tr>
<tr>
<td>Lead</td>
<td>Tetra-ethyl-</td>
<td>0.04</td>
<td>215000</td>
</tr>
<tr>
<td></td>
<td>lead</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Moreover, the effect of the anti-knock substance does not increase in proportion to the quantity added to the fuel, but attains its maximum value at a certain relatively high concentration. Midgley does not ascribe the effect to the compound as such, but to the particular active element, as shown for two different combinations in Table VI.

Table VI

<table>
<thead>
<tr>
<th>Element</th>
<th>Ethyl compound</th>
<th>Phenyl compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iodine</td>
<td>1.09</td>
<td>0.88</td>
</tr>
<tr>
<td>Selenium</td>
<td>6.9</td>
<td>5.2</td>
</tr>
<tr>
<td>Tellurium</td>
<td>26.8</td>
<td>22.0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.036 (knock-promoting)</td>
<td>0.122</td>
</tr>
</tbody>
</table>

There were at first some objections to the use of the most active substance, tetra-ethyl-lead, which has a toluene value of about 40,000. The originally very high price was reduced by quantity production and, in the small quantities required, did not greatly increase the cost of the fuel. The combustion products corroded the spark plug electrodes, but this was overcome by the addition of carbon tetrachloride and ethyl dibromide to the fuel. Lastly, tetra-ethyl itself or its disintegration products, affected the lubricating oil and caused gray deposits on the cylinder walls. This, however, did not harm the functioning. Its poisonous nature seems to offer no serious obsta-
cle to its use in America, since "ethylizers" are kept at the service stations with which the required quantity of tetra-ethyl-lead and ethylene dibromide is added to the gasoline while filling.

13. It has not been satisfactorily explained as to just what the really active properties of knock-influencing substances are and on what properties of the fuels they act. The aromatic hydrocarbons and the alcohols seem, at least when they form the principal part of the mixture, chiefly to raise the self-ignition temperature. (In my opinion, this seems to be confirmed by the direct proportionality between the allowable final compression pressure and the percentage of toluene.) Moreover, with alcohols, the high heat of vaporization seems to have the effect of lowering the temperature of the mixture in the cylinders. On the contrary, an admixture of carbon disulfide seems rather to affect the combustion speed and the same seems to be the case in the anti-knock substances tested by Midgley. At least the admixture of tetra-ethyl-lead to heptane lowered the self-ignition temperature only about 14°C (25.2°F).

* Report, p.312. The general public sale of tetra-ethyl-lead was recently stopped, on the basis of an investigation (not yet published) by the Columbia University, in spite of the fact that the Bureau of Mines had previously published its opinion on the harmlessness of the admixtures. Their further sale now depends on a conference under the control of the chief medical authority of the Union.
Fig. 25 shows that the tendency to knock can be lessened without affecting the self-ignition temperature. Up to an admixture of about 65% of benzene to a fuel mixture of heptane and air (with the same proportion of air and but a very slight change in the specific heat of the mixture), its self-ignition temperature remains constant, as is demonstrated by the constancy of the compression ratio at which self-ignition occurred in the compression-ignition apparatus, while in Ricardo's engine with variable compression and increasing benzene content, the allowable compression gradually increased (dashed line).

In any event, practically valuable results, as well as further light on the physics of combustion phenomena, are still to be expected and it is to be hoped that German investigators will again enter this field of research.

The effect of solid bodies, especially the walls of combustion chambers, on the process of combustion should also be explained, since its existence has long been demonstrated (Le Chatelier, "Le chauffage industriel," p.105, Paris, 1912).

The use of such expressions as "anti-catalytic effect" denotes no progress, but only the substitution of one unknown quantity for another.

14. While the above-mentioned works give considerable information as to what influences favor or hinder knocking, especially regarding the self-ignition temperature and the combustion speed as characteristic for the tendency of a gaseous mixture to
detonate and thus furnish important bases for engine designers and further research, our knowledge of the production and properties of explosion waves has not been essentially increased since Nernst's report on the work of Berthelot, Mallard, Le Chatelier, Dixon, Jonguet and himself.*

Only one article by Nusselt can be mentioned, which computes the linear (chemical) combustion speed of a gas, flowing from a tube and burning at its mouth, from the chemical and physical properties of the mixture.** His results not only agree well with the results of other investigators, but lead also to further knowledge on the effect of the mixture ratio, of the initial temperature (preliminary heating) and of the compression, which agrees qualitatively with what we know regarding combustion in closed vessels.

Knocking, Engine Power, and Efficiency

Tizard and Pye have demonstrated by computation (Report, pp. 4 and 10) and Ricardo (Report, pp. 54 and 100. See also Table II), by numerous experiments that, with like compression

* PHYSIKALISCH CHEMISCHER BETRACHTUNGEN ÜBER DEN VERBRENNUNGS-PROZESS IN DER GASMASCHINE," Z.V.d.I. 1905, p.1426. Morgan's article, "Some Experiments on Gas Explosions in Closed Tubes, with Particular Reference to 'Pinking'" (The Automobile Engineer, Vol. XV, 1925, p.27), describes interesting methods of research, without giving any new information, however, on the nature of the explosion wave or its connection with the phenomenon of knocking.

and chemical-mixture ratios (or with the practically employed ratios which do not differ greatly from the chemical ratios as regards high efficiency), as likewise with equal preliminary heating of all the hydrocarbons and alcohols, the same thermal efficiency (with differences of not over 1%) and, for hydrocarbons, also the same maximum mean indicated pressure (with differences of not over 0.3%) will be obtained. The alcohols yield higher mean indicated pressures, since their greater heat of vaporization allows greater charges. If these are kept equal, the maximum engine powers also remain within the same limits as for the hydrocarbons. Also the heating power of the mixture per unit volume shows, with the chemical mixture ratio, a maximum difference of only 2%. The compression ratio, at which the various fuels are compared, must, of course, be so chosen that no knocking will occur. The attainable maximum engine powers and thermal efficiencies can therefore be regarded as independent of the otherwise individual properties of the fuels and as dependent only on the compression ratio, whose maximum value is determined by the tendency of the given fuel to knock.

Fig. 26 shows the maximum thermal efficiencies in the variable-compression engine. Moreover, according to Tizard and Pye, the thermal efficiencies for cyclic processes with adiabatic compression and expansion of the initial volume and thermal gain and loss (combustion and exhaust) at constant volume, are given.
a) For an ideal gas, without dissociation and with constant specific heats:

b) For mixtures of benzene and air containing 50 and 20% excess of air and having a chemical mixture ratio with allowance for the dissociation and the changeableness of the specific heat.*

In all cases the thermal efficiency is \( \eta = 1 - r^{-n} \), in which \( r \) is the compression ratio and \( n \) is to be taken from Table VII.

<table>
<thead>
<tr>
<th>Air excess %</th>
<th>0</th>
<th>20</th>
<th>50</th>
<th>( \infty )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )</td>
<td>0.26</td>
<td>0.30</td>
<td>0.33</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Fig. 27 shows the effect of the mixture ratio on the thermal efficiency for the compression ratio of 5:1.

In Fig. 28, the maximum mean indicated pressure is plotted against the compression ratio, according to the results of Ricardo's experiments with the variable-compression engine and computed according to Tizard and Pye for the chemical-mixture ratio.

The fact that, according to the experiments, an increase in the mean pressure with the compression does not occur in the same ratio as in the computations, while the experimental and computed thermal efficiencies agree very well, is due to the decrease in the volumetric efficiency with increasing compres--

*Report, p.1. H. Nusselt ("Entropievormehrung in der Gasmaschine," Zeitschrift für das gesamte Turbinenwesen, 1917, Nos. 1-3) also makes allowance for the energy lost in mixing the gases. For earlier computations with the same goal, see Nernst, already referred to.
The fact that the toluene value of a fuel can be regarded to a certain degree as the criterion of the fuel, follows, in conjunction with the above, from Fig. 29, in which the maximum power and the thermal efficiency are plotted against the toluene value according to the experiments with the variable-compression engine.

Fig. 30 shows how the knocking affects engine power and efficiency with a fuel for which the detonation begins at a compression ratio of 5:1. With a further increase in the compression ratio, there is at first a gradual and then a more rapid decrease in power and efficiency.

If, therefore, I have demonstrated that "knocking" is decisive for the evaluation of fuels for gasoline engines, this will excuse the length of my article, in which I have endeavored to make the scattered and, in part, difficultly obtainable but extremely valuable information more easily available for German technicists, without concealing the gaps and deficiencies, and to stimulate engineers to the application of and scientists to further additions to our present knowledge.

*Perhaps an accurate determination of the heat content of the residual gas, together with an approximate computation of the heat absorbed from the indrawn mixture by the cylinder walls would explain it.
Supplementary

A new theory of the action of anti-detonating agents (Automotive Industries, Vol. 52, April 9, 1925, p. 650) was propounded in a recent paper by Prof. G. L. Wendt of the Pennsylvania State College and V. F. Grimm of the Standard Oil Company of Indiana, read before the American Chemical Society. The theory is explained as follows.

"It is well known that all flames are highly ionized, that is, they are excellent carriers of an electric current. This means that the energy released in the burning of the gas mixture serves in part to liberate electrons from the reacting molecules. The advance of electrons propelled at high velocity from the flame front undoubtedly ionize the molecules in the gaseous region just ahead of the flame.

"This ionization is tentatively regarded as the factor directly responsible for the increased acceleration of the flame. At high temperatures and high pressures, such as always obtain when detonation is excessive, the velocity of the liberated electrons is high and their energy is readily absorbed by the combustible gas.

"The rate of flame propagation therefore becomes extremely high. It is, then, the function of the anti-knock molecules or, more particularly, the lead atoms present in the commonest example of anti-knock, tetra-ethyl-lead, to attract these electrons,
thus forming highly charged lead ions and preventing the former ready ionization of the unburned gas."

A communication from Prof. Kutzbach which, with his permission, I shall utilize extensively in the following paragraphs, and several remarks in the technical journals have influenced me to suggest standard terms for the combustion processes in engines, in order, by the coordination of the terms and ideas to facilitate their explanation, without deviating more than necessary from current terminology.

1. First of all, the idea of ignition must be distinguished from that of combustion and I suggest that the term "ignition" be applied only to the beginning of the combustion and that, in its continuation, we speak only of "combustion," that is, "propagation of the combustion," not of the ignition; "combustion speed," not ignition speed, etc. In the narrower sense, combustion is the combining of any substance with oxygen gas to form oxides as combustion products, with the evolution of heat. In a broader sense, combustion may denote the combining of any substance with oxygen compounds or even with other substances, with the evolution of heat.

2. In gasoline engines the combustion is started by the "igniter" (generally a spark plug), whereby, according to the time of the ignition with reference to the position of the piston.
dead center, which may be adjustable by hand or automatically, we speak of "advanced" or "retarded" ignition.

3. "After-burning" (or retarded combustion) occurs when, at the time the exhaust valve opens, the combustion is still in progress, as the result of too slow combustion or too late ignition.

4. "Premature ignition" is the term I apply to the unintentional starting of the combustion from highly heated parts in the combustion chamber (e.g., valves and spark plugs), before the passage of the spark, which is usually due to fouling and incrustation.

5. By "self-ignition," on the other hand, I mean:
   a) When the chemical reaction takes place without any external agency, as, for example, with explosives and carbon under certain conditions, but also with gases, usually with the simultaneous action of catalyzers;

   b) When the fuel ignites from its environment, e.g., highly heated and highly compressed air in internal combustion engines and in testing devices for determining self-ignition temperatures.*

**Self-ignition temperature" (also often called "ignition temperature") seems clearer to me than the expression "ignition point," which would more properly denote the location in the combustion chamber from which the combustion spreads. It is the lowest temperature at which, under the given conditions, combustion can be started.
6. The starting of the combustion entirely or principally by compression may be termed "pressure ignition" and can be produced:

a) By reducing the volume of the ignitable mixture inclosed in a chamber (compression-ignition chamber) in such a way that the combustion proceeds from the center of the chamber, which can the least readily impart heat to the chamber walls.

b) By the propagation of a correspondingly high pressure from a source of pressure and at a velocity which correspondingly diminishes the liberation of heat and consequently makes the compression nearly adiabatic. In most cases, the latter process should be termed "pressure combustion," since the pressure increase almost always comes from a combustion process which has already been started in some other way.

Such arrangements, however, as are described in "Zeitschrift des Vereines deutscher Ingenieure 1906," p. 437 (Fig. 1) in which the combustion, starting from the point of ignition Z, by explosive overlapping from the chamber A, demolished the chamber B, while the combustion, on the removal of the intervening partition, proceeded without disturbance and hence without generating a higher pressure, represent, on the contrary (if B is regarded as the real combustion chamber and A as the ignition chamber) arrangements for flow ignition, as they were proposed also for the ignition places of engines (spark plugs with igni-
tion chamber), for accelerating the combustion.

In these cases, the Berthelot pressure wave (onde explosive) is generated, beside which the heat conduction and the turbulence play only a subordinate role in propagation of the combustion. For this phenomenon I have proposed the word "Verpuffung" as the logical translation of the English "detonation," a word which was introduced by Guldner for the combustion process in gasoline engines, but which, with the substitution of the clearer expression "Zündermotor" (internal combustion engine or gasoline engine) for "Verpuffungsmotor" (detonation or explosion engine), could again be reserved for explosive combustion.

7. The word "combustion" may denote any one of three forms of chemical reaction, which differ greatly in their propagation velocity (see paragraph 1):

a) The combustion of outflowing gases in the spherical combustion-chamber experiments of Nägel and his followers, with velocities of an order of magnitude up to a little over 5 m (16 ft.) per sec.

b) The combustion in the experiments of Berthelot, Dixon and others, with velocities corresponding to the velocity of sound in the combustion gases used.

c) Engine combustion with velocities about ten times as great as the ones measured by Nägel, as demonstrated directly by the pressure diagrams and indirectly by the fact that almost
complete combustion is attainable in combustion engines at the highest attainable piston speeds.

Unfortunately these very combustion processes, in which the turbulence or propagation by connection probably plays a decisive role, have hitherto been comparatively little investigated.

In the form a, the heat was probably transmitted by conduction and in the form b, by the pressure wave. All three forms of combustion, according to the circumstances, may change more or less constantly into one another and the very first stages, or the increase in the combustion speed during the same, may be important.

For testing fuels for internal combustion engines, one of the pressure-ignition engines similar to Tizard's into whose cylinders, on reaching the dead point, small portions of fuel were injected in the liquid form, the same as in solid-injection Diesel engines, would perhaps be valuable. The combustion process could be judged from the pressure curve.

8. According to the prevailing conception, which I adopted as the basis of my report, knocking (English "pinking") is due to combustion waves of high velocity. Pure mechanical noises, such as the striking of piston pins and connecting rod and crankshaft bearings, can usually be distinguished without difficulty, although the sounds may be similar under certain circumstances, since they also occur, when anti-knock measures (such as retard-
cd ignition and enrichment of the mixture) are adopted.

The ignition waves can be produced both in normal ignition and in premature ignition (Section 4). The latter case was observed in gas engines, where abnormal and sudden pressure increases were established, by means of indicator diagrams, as the cause of the knocks and shocks, which frequently occurred with rapidly diminishing strength during the exhaust stroke. This evil was eliminated by cleaning the cylinders, but began again as the cylinders gradually became foul. Cooling the exhaust valves lessened and the residues of poor oil increased the knocking, which also decreased with increasing revolution speed. That knocking occurs in such cases of preignition, even with fuels otherwise exhibiting but little tendency thereto, may be due to the fact that the preignition during the compression stroke takes place some time before the dead center, so that the increase in the combustion speed is greater.

Translation by Dwight M. Miner,
National Advisory Committee for Aeronautics.
### Table II: Properties of Liquid Fuels (according to Ricardo).

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Specific gravity at 15°C</th>
<th>Vapour pressure at 20°C (C.S.I. units)</th>
<th>Maximum recommendation</th>
<th>Approx. specific gravity</th>
<th>Evaporated at 60°C 100°C 140°C 180°C</th>
<th>degree centigrade</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>60° 100° 140° 180°</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gasoline</td>
<td>0.728</td>
<td>0.934</td>
<td>0.942</td>
<td>0.958</td>
<td>0.790</td>
<td>0.880</td>
</tr>
<tr>
<td></td>
<td>0.792</td>
<td>0.980</td>
<td>1.000</td>
<td>1.020</td>
<td>0.920</td>
<td>0.960</td>
</tr>
<tr>
<td></td>
<td>0.772</td>
<td>0.940</td>
<td>0.960</td>
<td>0.980</td>
<td>0.870</td>
<td>0.900</td>
</tr>
<tr>
<td>Heavy oil</td>
<td>0.680</td>
<td>0.920</td>
<td>0.940</td>
<td>0.960</td>
<td>0.870</td>
<td>0.900</td>
</tr>
<tr>
<td>Corrosion</td>
<td>0.811</td>
<td>0.820</td>
<td>0.830</td>
<td>0.840</td>
<td>0.770</td>
<td>0.800</td>
</tr>
<tr>
<td>Pentane</td>
<td>0.624</td>
<td>0.630</td>
<td>0.630</td>
<td>0.630</td>
<td>0.620</td>
<td>0.620</td>
</tr>
<tr>
<td>Hexane(80%)</td>
<td>0.658</td>
<td>0.660</td>
<td>0.660</td>
<td>0.660</td>
<td>0.650</td>
<td>0.650</td>
</tr>
<tr>
<td>Heptane(95%)</td>
<td>0.691</td>
<td>0.700</td>
<td>0.700</td>
<td>0.700</td>
<td>0.690</td>
<td>0.690</td>
</tr>
<tr>
<td>Arom. Hydrocarbons</td>
<td>0.864</td>
<td>0.880</td>
<td>0.880</td>
<td>0.880</td>
<td>0.870</td>
<td>0.870</td>
</tr>
<tr>
<td>Benzene(pure)</td>
<td>0.870</td>
<td>0.870</td>
<td>0.870</td>
<td>0.870</td>
<td>0.860</td>
<td>0.860</td>
</tr>
<tr>
<td>Tolene(99%)</td>
<td>0.870</td>
<td>0.870</td>
<td>0.870</td>
<td>0.870</td>
<td>0.860</td>
<td>0.860</td>
</tr>
<tr>
<td>Xylene(91%)</td>
<td>0.870</td>
<td>0.870</td>
<td>0.870</td>
<td>0.870</td>
<td>0.860</td>
<td>0.860</td>
</tr>
<tr>
<td>Naphthenes</td>
<td>0.790</td>
<td>0.800</td>
<td>0.800</td>
<td>0.800</td>
<td>0.790</td>
<td>0.790</td>
</tr>
<tr>
<td>Zyklohexan (9) v. H1</td>
<td>0.790</td>
<td>0.800</td>
<td>0.800</td>
<td>0.800</td>
<td>0.790</td>
<td>0.790</td>
</tr>
<tr>
<td>Hexahydrotoluol (9 G H 1),</td>
<td>0.744</td>
<td>0.750</td>
<td>0.750</td>
<td>0.750</td>
<td>0.740</td>
<td>0.740</td>
</tr>
<tr>
<td>Odstoffe, Alkohole u. Verschiedene</td>
<td>0.737</td>
<td>0.750</td>
<td>0.750</td>
<td>0.750</td>
<td>0.740</td>
<td>0.740</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.737</td>
<td>0.750</td>
<td>0.750</td>
<td>0.750</td>
<td>0.740</td>
<td>0.740</td>
</tr>
<tr>
<td>Äthyalkohol (95 v. H1)</td>
<td>0.790</td>
<td>0.800</td>
<td>0.800</td>
<td>0.800</td>
<td>0.790</td>
<td>0.790</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.790</td>
<td>0.800</td>
<td>0.800</td>
<td>0.800</td>
<td>0.790</td>
<td>0.790</td>
</tr>
<tr>
<td>Butanol</td>
<td>0.727</td>
<td>0.750</td>
<td>0.750</td>
<td>0.750</td>
<td>0.740</td>
<td>0.740</td>
</tr>
<tr>
<td>Ethanol (50%)</td>
<td>0.727</td>
<td>0.750</td>
<td>0.750</td>
<td>0.750</td>
<td>0.740</td>
<td>0.740</td>
</tr>
<tr>
<td>3. Methyl alcohol</td>
<td>0.710</td>
<td>0.730</td>
<td>0.730</td>
<td>0.730</td>
<td>0.720</td>
<td>0.720</td>
</tr>
<tr>
<td>4. Chloroform</td>
<td>0.810</td>
<td>0.830</td>
<td>0.830</td>
<td>0.830</td>
<td>0.820</td>
<td>0.820</td>
</tr>
<tr>
<td>5. Naphthalin</td>
<td>0.810</td>
<td>0.830</td>
<td>0.830</td>
<td>0.830</td>
<td>0.820</td>
<td>0.820</td>
</tr>
<tr>
<td>6. Ackerons</td>
<td>0.810</td>
<td>0.830</td>
<td>0.830</td>
<td>0.830</td>
<td>0.820</td>
<td>0.820</td>
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<tr>
<td>7. Schwefelkohlenstoff</td>
<td>0.810</td>
<td>0.830</td>
<td>0.830</td>
<td>0.830</td>
<td>0.820</td>
<td>0.820</td>
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</table>

- Approximately
- Self-ignition, before audible detonation occurs.
- Computed values, since the fuels detonate at a lower compression ratio than 5:1.
- The fuel could not be made to knock in the engine for overloading.
Fig. 1

Compression-ignition apparatus.
k = \frac{c_p}{c_v} = 1.29

1) Final compr. press. 29.5 atm.
2) Final pressure after cooling.
3) Atmospheric line.

Fig. 2 Pressure diagram of Tizard's compression ignition apparatus. Compression of hydrogen without ignition. Initial temperature 60°C (140°F); compression ratio 13.8:1.

1) Compression pressure 9.34 atm. (computed temperature 292°C (557.6°F)).
2) Ignition after about 0.25 seconds delay.
3) Atmospheric line.

Fig. 3 Pressure diagram of Tizard's compression ignition apparatus. Heptane 0.8 part in 15 parts air. Initial temperature 59°C (138°F); comp. ratio, 5.5:1.
Fig.4 Time-pressure diagram of Tizard's compression-ignition apparatus. Heptane-air mixture. Final compression temperature 282°C (539.6°F), wind vanes at rest. Ignition delay 0.58 sec.

<table>
<thead>
<tr>
<th>No.</th>
<th>Shape &amp; spark-plug</th>
<th>Compression chamber</th>
<th>Bore/stroke</th>
<th>Remarks</th>
<th>Compr. ratio</th>
<th>Relative efficiency</th>
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<tr>
<td>1</td>
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<td>2 2</td>
<td>Roof-shaped</td>
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<td>100</td>
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<td>2</td>
<td>2 3</td>
<td>1/2</td>
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<td>100</td>
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<td>3</td>
<td>2 3</td>
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<td>High spec. turb. accor. to Ricardo</td>
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<td>4.6:1</td>
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<td>Spark-plug over intake valve</td>
<td>4.2:1</td>
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Fig.5 Evaluation of various cylinder-head shapes according to Ricardo (1923).
Fig. 6. Ignition delay at various compression temperatures as measured in Tizard's compression ignition apparatus.

1. Paraffine
2. Kerosine
3. Gas oil
4. Machine oil
5. Gasoline
6. Cylinder oil
7. Benzene

Fig. 7. Effect of pressure on self-ignition temperature.

$\tau \leftarrow 1\text{ sec.} \sim 3030\text{ mm}$

Experiment 3. $P_1 = 1.5$ absolute atm., $u = 0.0935$ sec.
$z = 70\text{ mm} \gamma = 8.62 \text{ m/sec.}$

Fig. 8. Time-pressure diagram from Nagel's spherical chamber exp.
Fig. 9 Experiments with illuminating gas and generator gas mixed with air. Combustion speed $\gamma$ plotted against the initial pressure.

Fig. 10 Experiments with hydrogen-air mixtures combustion speed $\gamma$ plotted against initial pressure, with same hydrogen content.
**Fig. 11** Combustion speed of mixture, with 5% methane and increasing hydrogen content, plotted against various initial pressures of the charge.

**Fig. 12** Combustion speed of methane-air mixtures with unchanged heating value and various initial pressures of the charge.

**Fig. 13** Combustion speed of mixtures of gasoline and air at various mixture ratios and various initial pressures of the charge.
Fig. 14

Linear combustion speed in the spherical chamber. Hydrogen-air mixtures.

Initial temperature 288° C, abs. = 150°C (according to Mach).
Mass combustion speed of a hydrogen-air mixture (21.4% H by Vol.) in the spherical chamber diameter 400 mm (15.75 in.). Initial temperature 150°F (65°C) (according to Mache).
Fig. 16 Effect of admixtures of inert gases on the compression ratio at which knocking occurs.

Fig. 17 Mean indicated pressure and fuel consumption on the admixture of cooled exhaust gases. Mean indicated pressure and fuel consumption with a fuel, which can also stand normal compression ratios.
Fig. 18 Effect of mixture ratio on compression ratio at which self-ignition occurs (according to Tizard).

Fig. 19 Comp. ratio at which knocking occurs plotted against mixt. ratio. Experiments with stratified charges (gasoline without aromatic hydrocarbons).

Fig. 20 Effect of mixture ratio plotted against ignition temperature.

A (Mixture of oxygen or detonating gas with H₂ or CO).
Fig. 21  Toluene value plotted against compression ratio according to experiments in engine with variable compression.

Fig. 22  Self-ignition temperature plotted against solubility in 92% alcohol (according to Ormandy).

○ = gasoline-benzene mixtures
× = gasoline-xylene mixtures
Fig. 23  Toluene values of mixtures. A, benzene in heptane, B, toluene in heptane, C, alcohol in Mexican fuel, D, alcohol in Pratt's fuel.

Fig. 24  Comparison of the knock-preventing effect of alcohol, benzene, toluene and xylene with xylidine (according to Midgley).
A Cyclic process with an ideal gas.
B 50% excess air
C 20% air excess.
D Chemical mixture ratio
E Maximum observed values (Ricardo)

Fig. 25 Effect of benzene content of a heptane-benzene mixture on the compression ratio necessary for self ignition and detonation.

Fig. 26 Thermal efficiency plotted against the compression ratio. Computed by Tizard & Rye.

Fig. 27 Maximum thermal efficiency (calculated) for a compression ratio of 5.1 and various mixture ratios of benzene and air.

Parts by weight of benzene to 13.2 parts of air.

A Cyclic process with an ideal gas.
Fig. 28  A. Effect of compression ratio on the mean indicated pressure for the chemical mixture ratio and a cyclic process according to Tizard & Rye as also for a volumetric efficiency of 77%.

B. Effect of compression ratio on the mean indicated pressure according to experiments in the variable-compression engine. C. Volumetric efficiency plotted against compression ratio.
Fig. 29  Effect of toluene value on the mean indicated pressure and on the thermal efficiency (engine with variable compression).

Fig. 30  Mean indicated pressure and thermal efficiency at various compression ratios for a fuel which begins to knock at a compression ratio of 5:1.