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Recent experiments on self-ignition of fuels under adiabatic compression.

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I

The theory we have advocated for years, i.e. that knocking is nothing but a self-ignition of the last residues of unburnt charge in the engine, can to-day be considered as almost generally accepted. Naturally our theory is based on the assumption that no portion of the cylinder wall is incandescent in the proximity of the last burning fuel-air mixture. In other words we consider only rationally built and operated engines, neglecting any cylinder wall reaction (apart from heat exchange, which lasts longer than the self-ignition process). The purpose of further research is now:

1. More thoroughly to study the features of the knock process.
2. To find out what contribution self-ignition tests offer to the problem of engine development.

In this report I shall deal with the first question, leaving Mr. Rögener to discuss the second one in the next report.

I should mention a trivial cause of the difficulty of self-ignition tests as compared to practical detonation tests: each detonation measurement on the engine represents the average of many, possibly thousands of single cycles; in spite of marked variations between them the final result is quite accurate. In self-ignition tests the final result must be obtained from very few single measurements, which must therefore be highly accurate. Moreover some of the operations, such as producing and checking the mixture, are much more difficult in the case of isolated tests than with periodical operations.

The experiments described below constitute only a makeshift; owing to war conditions a new equipment planned two and a half years ago could not be produced. We had therefore to choose the problems according to the available equipment. Self-ignition tests at induction times of some 10^{-3} to a maximum of 10^{-1} seconds are possible with the present equipment; longer induction times, which however are outside the range of practical operations, are not covered because the errors due to cooling become too great. Should another test method be applied, such as a flow into a pre-heated container, instead of cooling errors there would always be cylinder wall effects. For shorter induction times the measuring range is restricted by the finite duration of the compression, in the course of which a pre-flame ignition occurs; this however will be overcome with a new equipment now in the course of construction, which will go up to a few 1/10,000 sec. Another fundamental difficulty in the measurement of very short induction times should also be mentioned. The dimensions of the equipment are too large, with the result that high piston velocities are soon reached, which produce in the compressed gas shock waves of considerable amplitude; these cause unfavourable test conditions. (Naturally the same could also occur in the engine). Moreover the investigation of high anti-knock fuels is difficult, because the actual compression ratio at the requisite high initial temperature (80° to 120°C) is not completely obtainable. In the new equipment planned by us with a piston design by Tizard and Pye this difficulty too will be overcome.

II

First of all we have continued our systematic tests on n-heptane after it had appeared that the attempt to measure the susceptibility to lead of higher anti-knock fuels is impracticable, owing to the disturbances caused by the lubricant in the present equipment.

1. Mr. Teichmann had found that the mixture strength, when the true final temperature is considered, has very little effect on the self-ignition process. In Fig. 1 the obtained induction times are plotted (logarithmically) as a function of the mixture strength (air-excess factor λ) at constant initial temperature and compression ratio. τ appears to vary considerably as a function of λ . The same variables are plotted again in Fig. 2, with the difference that 1/T is plotted as abscissae, T being the terminal temperature calculated from the initial temperature and ε , taking into account κ ($= C_p/C_v$) which varies rather markedly with λ . Within the limits of accuracy the line obtained (log τ against 1/T) agrees with that resulting from measurements at varying compression ratios or varying initial temperatures. Within the limits of accuracy τ does not depend on λ , as long as we compare tests at equal terminal temperatures; or else at constant initial temperature and compression ratio, λ varies and so too the terminal temperature varies with λ .

2. Tizard and Pye and subsequently Teichmann had already found that τ varies but little with the pressure p (in fact it is approximately inversely proportional to it). In both cases p was varied (within narrow limits) in such a manner that the same terminal temperature was obtained by simultaneous variation of initial temperature and compression ratio; Teichmann, moreover used mixture pre-compression. In our present experiments the initial pressure was varied by as much as 40%. The results are collected in Fig. 3. Initially there seems to be a slight, but noticeable pressure effect (Deviating from the straight line in Fig. 3, which reproduces tests at normal pressure). For rich mixtures however this disappears at the longest induction times. This is explained by the following: at higher back pressures the compression lasts longer, with the result that the pre-reaction before total compression plays a bigger part; this is most apparent at the shortest induction times. Altogether these tests are most consistent, if it is assumed that τ is independent of p. At the end we shall deal with the significance of this result for the kinetics of the reaction.

3. Subsequently we have investigated the self-ignition of n-heptane-air mixtures, with additions of H_2, CO_2 and CH_4. This was done in view of the possible effects of residual gases.

If a pure n-heptane-air mixture at the given conditions had $\tau = 0.014$ sec, a mixture with 2.6% H_2 gave $\tau = 0.016$ sec., one with 4.5% CO_2 $\tau = 0.025$ sec. Whether it is that hydrogen has a certain inhibiting action or that the variation is purely accidental cannot be decided owing to possible experimental errors. In the case of CO_2 the reduction of κ slows down the process and the same can be said of CH_4.

Further it had been planned to replace the air nitrogen with argon, but these tests could not be carried out because our argon cylinder was lost in transit.

4. Finally mention should be made of some tests on isomeric Xylenes, at the request of Mr. v. Philippovich.

The critical compression ratio (KKV) 1) varies quite considerably. According to Boyd it is:

	o-	m-	p- Xylene
KKV	9.6	13.6	14.2

First of all we measured the thermal dissociation velocity of the pure compounds, finding the following relative values at 616°C:

10.7 2.47 1

The thermal process runs parallel to the anti-knock value. Therefore the slow oxidation velocity measured by Mr. Sieg runs parallel again; the temperature of "initial" oxidation measured in a flow arrangement is as follows:

500° 588° 598°C

See Fig. 4. Recently measurements of induction times for self-ignition could be made at $T = 578°C$; the following preliminary values were found:

0.003 0.013 0.010 sec.

The inversion of the figures for p and o-Xylene may be considered within the limits of accuracy.

The replacement of air nitrogen with argon in the scientific investigation of self-ignition may give valuable results: namely it allows the testing of extremely high anti-knock fuels in average conditions (of compression ratio and initial temperature), which simplifies considerably the necessary equipment; naturally it must first of all be checked whether the presence of argon has the same effect as nitrogen.

To avoid misunderstandings, it should be mentioned that the use of A instead of N_2 in the engine would affect the knock behaviour in a manner difficult to appreciate at a glance; beside $\varkappa$, also the heat transfer and to a high degree the flame propagation velocity are affected.

III

The parallel found between:

1. Knock behaviour (KKV)
2. Self-ignition behaviour
3. Behaviour under slow oxidation
4. Behaviour at the thermal dissociation

in Xylenes is so remarkable, that it hints at the possibility of the same primary process applying in all cases. This could only be established by a complete explanation of the kinetics of the reaction.

The results on n-heptane can be summed up as follows: if we vary λ , p or $\varkappa$, within the limits of accuracy the variations of the knock-behaviour observed at constant ε are due to the variations occurrring in temperatures. Naturally a slight influence of λ and p will manifest itself.

I should like to stress that this result is satisfactory, especially as regards the λ effect. In the case of slow oxidation and low pressure self-ignition, often mixture enriching produces an

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1) The critical compression ratio being the compression ratio at which knocking starts in a test engine, in conditions similar to CFR research method.

extremely steep increase of the ignitability. If at high pressure a noticeable mixture effect were apparent, this could not be reconciled with practical experience. Taking into account all heat effects, an extremely small variation with alteration in the excess air ratio λ affords the natural explanation for similar variation found in the engine; I shall mention this point again and Mr. Rögener will discuss it in his paper.

The following points should be noted to avoid misunderstandings: the fact that the induction time is independent of the pressure in no way means that the reaction velocity is independent of the pressure, but rather that this is proportional to the first power of the pressure; in other words the reaction velocity must be doubled, to convert a double fuel quantity in the same time. The same would apply to the dependence on the hydrocarbon concentration. The results can be expressed in the following formula for the reaction velocity:

$$v \approx kp^{1 \pm 1} \approx K' [O_2]^{0 \pm 1} [KW]^{1 \pm 1} \quad (KW = \text{hydrocarbon})^{1)}$$

In the formula we have assumed a relatively wide limit of accuracy in the order of magnitude, corresponding to $\tau = p^{0 \pm 1}$. We should mention for the purpose of comparison that Bodenstein finds for the slow oxidation of acetaldehyde at low pressure

$$v = \frac{k_1 [A]^2}{k_2 + k_3 [O_2]}$$

which at high pressures (k_2 negligible against $k_3 [O_2]$) and constant strengths ($[A]$ and $[O_2]$ proportional to p) leads to the same pressure effect. Our result is therefore not anomalous. Perhaps in the presence of anti-knock additives or in the case of unsaturated compounds a stronger concentration effect may be expected. Even if the kinetics of the knock reaction were thoroughly investigated as regards their bearing on engine operations, it would still be difficult to follow the actual process in the engine. The following consideration, which is already implied in our earlier observations though not explicitely presented, illustrates how a ~~hasty~~ evaluation of operational observation can lead to wrong inferences.

It is assumed that:

1. In the knock process τ is not dependent on pressure and mixture strength; the reaction varies as an exponential function of T with higher activation energies.

2. No heat transfer occurs in the engine (Mr. Rögener will point to its great importance for the interpretation of knock observations on the engine); in spite of this the same variation of the knock behaviour as a function of λ , p and T is not found in the engine, as assumed for τ .

Knocking is determined by obtaining the same knock intensity more or less accurately under varying condition with any indicator (it can be the ear). Without going into the question of the objective recording of knocking, which has not been quite satisfactorily solved even in practice, we wish to make the simplest assumption: equivalent knocking in the same engine means equivalent liberated energy 2) in

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1) in which the chemical symbols or abbreviations in square brackets mean the concentrations of the elements, which are in turn proportional to partial pressures.

2) or more accurately equal ΔF or ΔG.

the detonating portion. This is in any case a plausible assumption, which cannot be very far from the truth 1).

If I have an engine that just starts knocking, according to the above assumptions doubling the pressure would double the knock rate. To return to the original intensity of knock I must alter another variable, perhaps the compression ratio, and a quantitative ~~study would~~ show that the variation would be considerable. This gives the wrong inference of a considerable pressure effect on the knock reaction.

Conversely: If I raise the initial temperature, e.g. by 25% of its value in Kelvin degrees, knocking will naturally increase. But as this implies a 25% lowering of the volumetric efficiency, this knock increase falls off considerably, as compared with what could be expected according to the temperature dependence of the self-ignition reaction. This gives the wrong impression of a very small temperature effect on the knock reaction.

The experiments were carried out with the support of the D.V.L. We owe thanks to Mr. v. Philippovich for several suggestions.

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1) If we could record the knocking with a pressure indicator of infinitely small dimensions, fitted at the point where there is an infinitely small residue, the smaller the knocking residue, the more intensive would be the knock obtained. This case may however be ignored because: 1, such a recording is exceptionally improbable, 2, the results thus obtained would contrast with the otherwise determined knock behaviour.

Fig. 1 - Self-ignition of Heptane-air mixture at variable air excess.

Fig. 2 - Self-ignition of Heptane-air mixture. Induction time as a function of the temperature.

Fig. 3 - Self-ignition of Heptane-air mixture. Supercharge effect.

Fig. 4 - Slow oxidation of I. o-Xylene
II. m-Xylene
III. p-Xylene.