DISCUSSION

(pps. 71 - 77)

Zeise.   E. Schmidt's results show a clear dependence on mixture strength and pressure. This may be explained by assuming that a formation and spontaneous dissociation of intermediate compounds, e.g. of a peroxide, take place. Thus there would always be an equilibrium between formation and dissociation; and the higher the pressure, the more the dissociation is counteracted. The curve should consequently move to the right in proportion, and its maximum corresponds to this equilibrium. The shifting of the curves to the right as the compression ratio mounts would then correspond to a repression of a reaction, namely the reverse reaction. The spontaneous decline could be interpreted as follows: in the maxima previously occurring, the critical concentration possibly leading to ignition was not yet reached; it is reached in this case, with the result that knocking appears and a corresponding temperature drop would occur.

Kamm.   In the highly ignitable RCH Diesel fuel the ignition lag measured with a perfectly clean quartz window was found to be smaller at the start than later on. The evaluation of the measured ignition lag limits gave thus a cetane number range of about 90 to 78.

If the quartz window is not quite clean but the flame is still clearly visible, cetane number for RCH fuel is found to be 78 from the start. This gave rise to the hypothesis that the ignition lag-measurements are affected by chemical pre-reactions.

In the Luftfahrtforschungsanstalt Hermann Göring in Braunschweig it was actually found that with RCH diesel fuel chemical reactions occur in the engine before the self-ignition proper. A clear blue flame could even be observed through the quartz window. Presumably this blue flame is detected by the photoelectric cell only with a thoroughly clean window; it is absorbed by small soot particles, thus augmenting the measured ignition lag. Once the blue flame is fully absorbed, the measured ignition lag remains the same.

These chemical dissociations appearing before the flame proper are connected with a small pressure rise. If the photoelectric cell does not detect the chemical pre-reactions, (and these are coupled with a pressure variation,) the pressure lag (time between injection start and pressure start) is distinct from the flame lag (time between injection start and flame start).

Photos show that in the course of tests with the oscillograph the pressure appears before the flame, the pressure and the flame together, and the flame before the pressure.

Fig. 1 shows the pressure and radiation curves of RCH Diesel fuel of cetane number 78; it appears that the radiation lags behind the pressure, which could be explained with the above-mentioned chemical pre-reactions.

Fig. 2 shows the pressure and radiation curve of Abadan gas oil with cetane number 61. Here the pressure start coincides with the flame onset.

Finally a mixture of 40 vol. cetane and 60 vol. methyl naphthalene (i.e. cetane number 40) showed that the pressure lagged behind the radiation. In this case the chemical dissociations occurring before the self-ignition would be coupled with a radiation without pressure.

The above tests show that the chemical pre-reaction depends on the fuel composition. A quantitative analysis of the reaction products is desirable.

Damköhler. We should not try and interpret these pressure effects before making analyses, which are exceptionally difficult. We know this quite well and at Braunschweig we ventured the analysis only in one of Schmidt and Mühlner's engine tests, together with my co-worker Eggersglüss, obtaining quite interesting results. The measured temperature increase can give an indication of the oxygen consumption, which in turn can be compared with the reaction products. We found mainly aldehydes, peroxides in very small quantity, probably as a result of the high temperature (the exit temperature was about 200°C) and finally also small quantities of acids. The aldehyde yield is the main point under discussion. Formaldehyde was found in preponderance, smaller quantities of acetaldehyde and even traces of higher aldehydes. How did these aldehydes originate? The chart developed by Pope, Dykstra and Edgar (1) seems to indicate that aldehydes result from the gradual dissociation of the hydrocarbon chain. If we compare this dissociation with the oxygen consumption obtained, we find that this would be quite sufficient to explain the acetaldehyde yield. If however we assume that the formaldehyde is similarly produced by the oxidative dissociation of acetaldehyde, then the oxygen consumption is by far insufficient. Most likely the formaldehyde yield originated quite differently from the higher aldehydes. This can be concluded from these measurements, i.e. from the analysis, compared with the temperature increase for the oxygen consumption and finally also from the water content of the exhaust gases (i.e. humidity of intake air + reaction H_2O). Now we can try and find how the formaldehyde was produced. There are various possibilities and we reached the theory that it was probably formed in radical chains, something like: CH_3-radicals + O_2CH_2O + OH-radical, or alkyl radical + O_2 - CH_2O + alkoxy-radical or something similar. If we study how the formaldehyde can be produced, we must set out a whole list of reaction possibilities, among which are some of particularly high energy. We can choose between three main possibilities: 1. Formaldehyde is the result of more or less saturated molecules, such as peroxides etc. ; 2. Formaldehyde results via radical chains; 3. Formaldehyde is formed by the recombination of radicals, in my opinion from two CH_3 radicals and an oxygen molecule. This third mechanism delivers such high energies, as afford an explanation for the cold flames observed in these pre-reactions, containing exactly the formaldehyde spectrum. It seems now that radical chains are present in the pre-reactions, as indicated by the formaldehyde proportion as well as by the cold flame. Indeed if there are radicals, not only do they go on reacting in chains, but also they can be destroyed by recombination. It is therefore not quite surprising that the pre-reaction onset coincides with the appearance of the blue cold flame.

E. Schmidt. Naturally we have also thought of these theories. I did not want to discuss them now, but wait and see how the problem appears with the further development of our analysis methods. It should be avoided to issue a premature statement, before it can be really proved right in its details. Imaginative but hasty statements have very often been made on the question of knocking and allied chemical processes. It is better to wait until real evidence is available. We observed blue flames only once with a very ignitable diesel fuel, but perhaps the window was smeared with oil. In future tests we shall see to it that it is possible to observe the blue flames which probably appear in other tests as well.

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(1) I.C. Pope, F.I. Dykstra and H. Edgar: Journ.Amer.chem.Soc. 51 (1929), 1875, 2203, 2213.

v. Weber. The indicator diagram produced by E. Schmidt shows that an alternation of the pre-reaction occurs each seven or eight periods, so that a period with pre-reaction was regularly followed by one without it. We might conclude that the residual gases of a period with pre-reaction prevent the pre-reaction of the following period; this would agree with the hypothesis that the pre-reaction dies down as a result of the collection of inhibiting reaction products. I should ask, was this alternation observed accidentally or regularly?

E. Schmidt. - The alternation was regular and we have explained it with the effect of the residual gases.

Penzig. The influence of pre-reactions can be observed also in supercharge tests. If we determine at various excess air coefficients the boost pressure at which knocking appears, we obtain the well known knock limit curves; they reach a maximum of the boost pressure or of the M.E.P. with air deficiency and a minimum with air excess. Similar tests carried out on an engine working with an 80° valve overlap, show that a knock region of elliptical shape lies below the knock limit curve.

At very low boost pressures the mixture begins to knock, then it knocks no more at a rather higher pressure and it ends by knocking steadily above the known knock limit curve. We have found that this lower knock area occurs at pressures below atmospheric pressure and deduced the following conclusion:

If the boost pressure is below atmospheric pressure, with a wide valve overlap a proportion of the exhaust gases are pushed from the exhaust into the inlet pipe; they remain there and are again admitted into the cylinder at the next admission stroke. We must assume that these residual gases do not hinder but rather favour knocking, which points to rather stable reaction nuclei. Tests on the Hesselman engine show that this delayed injection gasoline engine demands a fuel of lower anti-knock value than the conventional aspirated gasoline engine. Undoubtedly this is due to the shorter pre-reaction time during the compression stroke. On the other hand the above knocking can be explained by hot exhaust gases reaching the cylinder during the admission and accelarating the pre-reaction of the fuel injected in the inlet stroke.

Lindner. It seems that we must likewise expect an acceleration of the pre-reactions due to the presence in the cylinder of residual products of the preceding cycles. Tests carried out in England by W. Th. David (Proc.Inst. Mech. Eng. Paper No.4916 of 19.12.33) mention the appearance of luminous phenomena when residual gases are compressed again immediately after the combustion; this justifies the hypothesis that an excited state may be reached after several cycles. In the case of tests in the engine cylinder, the influences of the activated molecules from the preceding cycles are superimposed; it is therefore difficult to exclude these influences in the engine or on the other hand to produce them by an artificial addition of active combustion products. Thorough investigations on the fading velocity of activation state would therefore be highly interesting. It is thus possible that these tests lead to considerably different results on the pre-reactions as compared with the ignition engine, because no ignition and no residual products of a complete reaction were involved in our tests.

Jost. Naturally it is possible that radicals survive from one cycle to the next and we have considered these tests.

Zeise. I should mention again W. Th. David's tests; mainly on the ignition of $CO-O_2$ mixtures in a spherical bomb, from the calculated and measured temperature and from pressure measurements, he inferred that there are great energies in the gases, which remain latent for a

long time and under subsequent compression produce a luminous effect. This is connected first with dissociation products and second with the formation of excited molecules. The latter can remain stable for a relatively long time, before they are deactivated by collision and produce the luminosity. The times - lifetimes - involved are so great that in normal engine operation they would amply last from one cycle to the next.

v. Philippovich. The action of residual gases varies greatly with the fuel-air ratio. Reaction inducing elements are probably absent from the residual gases of lean mixtures; the temperature effect of the residual gases will then be decisively noticeable. On the other hand it is possible that radicals remain in rich mixtures. The effect of residual gases varies considerably with the excess air; it also manifests itself differently in different engines according to their scavenging efficiency.

E. Schmidt. In future tests we shall provide for an additional intermediate scavenging. This will allow us to determine with certainty the difference in the effect of residual gases with and without it.

Fig. 1 - Pressure and radiation curves with RCH fuel.

Fig. 2 - Pressure and radiation curves with Abadan gas oil.

Fig. 3 - Pressure and radiation curves in a mixture of 40 vol. cetane and 60 vol. α methyl naphthalene.

Fig. 4 - Knock Boundary Curves of Engines with Large Valve Overlap.