

ON THE EFFECTS OF SURFACES UPON THE SPONTANEOUS IGNITION OF THE LIQUID FUELS.

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Prof. S. Horiba and his staff pupils in the laboratory have devoted themselves to find a new method to estimate the octane values of liquid fuels as simple as possible, and Yamakita¹⁾ reported the estimation method, which observes the spontaneous ignition time lag curves of the fuels using a Moore²⁾-type apparatus instead of measuring ordinary ignition temperature alone. The curves belonging to the same type and having the close composition measured in the current of O₂ stream, 20 cc/min., are arranged in the order of the octane value of the fuels.

According to Horiba-Goto's research³⁾, however, the main part of the thermal explosive reaction of a gas is not a homogeneous process throughout the gaseous phase, but it is the propagation of the flame caused by the momentary exothermic catalytic reaction on the wall of the vessel.

As it is probably inferred that the ignition of liquid fuels in the crucible may be caused from the wall, it is necessary to make full tests for the surface effects upon the spontaneous ignition in the crucible in order to complete the estimation method. This is the first object of this research.

And as the spontaneous ignition temperature time lag curves of fuels is considered to show the characteristics of the ignition of fuels, some knowledge for the mechanism of the ignition may be obtained by comparing the curves in various conditions (surface or oxygen concentration). This is the second object of this research.

Experimental Results and Considerations.

§1 Effects of crucible materials and oxygen concentration.

The effects of crucible materials upon the ignition were examined. The spontaneous ignition time lag curves obtained in the case of alumina, porcelain, quartz, terex glass, aluminium, or stainless steel almost agreed with one another. Differences of curves may be attributed mainly to those of the physical properties

1) I. Yamakita, *Rev. Phys. Chem. Japan*, 19, 69, 85, 98 (1945).

2) H. Moore, *J. Soc. Chem. Ind.*, 36, 109 (1917).

3) S. Horiba & R. Gotô, *Proc. Imp. Acad. Tokyo*, 16, 218 (1940); R. Gotô, *Rev. Phys. Chem. Japan*, 16, 101, 141, 152 (1942).

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of crucibles. Among the above materials, porcelain or alumina was selected as the representative. On the contrary, in the case of platinum, copper or nickel, the curves obtained were entirely different from each other.

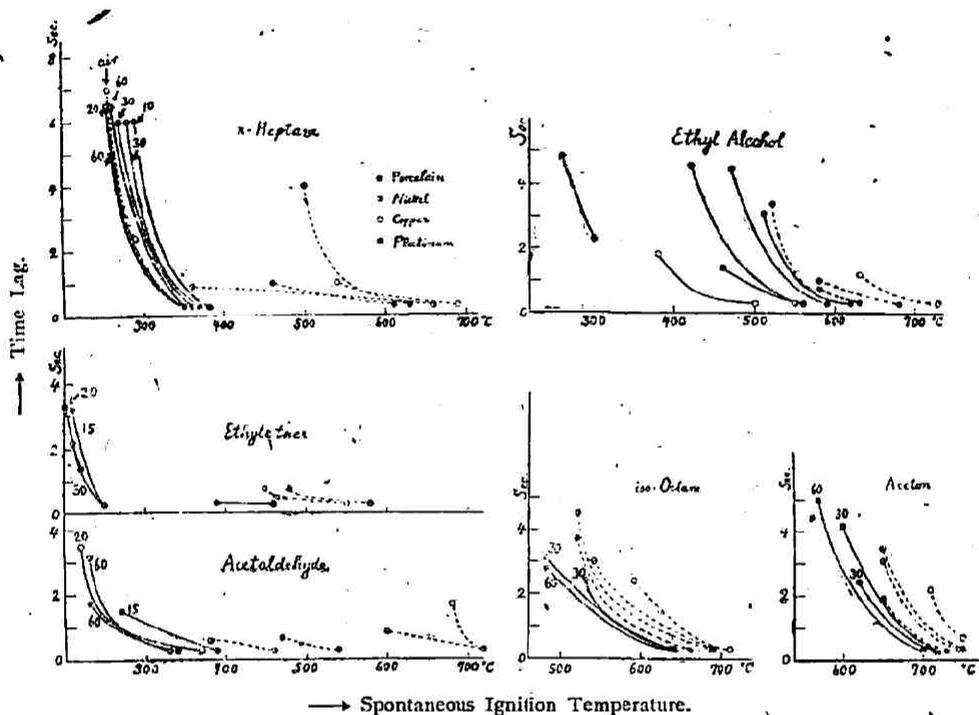


Fig. 1. Effect of Surfaces and oxygen concentration.

Typical examples are shown in Fig. 1. In the figure the dotted lines are obtained in the air and the real lines in the current of oxygen stream, and numerical values suffixed to the curves means the streaming velocity of oxygen poured into the crucible (cc/min.). By comparing these curves, the effects of surface materials and oxygen concentration upon the ignition of fuels, and also differences in the nature of ignition of various fuels can be easily understood.

For example, the ignition characteristics of n-heptane is as follows.

(1) In the air, the ignition is remarkably influenced by the surface. Compare the porcelain curve with the platinum, the nickel or the copper curve.

(2) In the stream of oxygen (20 cc~60 cc/min.), the surface effects are very small.

(3) In the porcelain crucible, the ignition is markedly accelerated by the increase in the oxygen concentration. Difference between the ignition in the air and that in the slow oxygen stream (10 cc/min.) are the most remarkable.

These six kinds of fuels being compared with one another in respect of the three points cited above, the following table is obtained.

Table. Effect of surfaces and oxygen concentration.

	n-Heptane	Acet-aldehyde	Ethyl-ether	Ethyl-alcohol	iso-Octane	Aceton
1) Effect of surface in lower concentration of O_2 (=in the air)	much	much	little	much	little	little
2) Effect of surface in higher concentration of O_2 ($=O_2$ 20 cc~60 cc/min.)	little	little	little	much	little	little
3) Effect of O_2 conc. in the porcelain crucible	much	much	much	little	little	little

§2 Effects of surface coatings.

(a) Compounds.

(i) KCl. The effects of KCl coating on the terex glass or platinum crucible upon the ignition of fuels were observed as seen in Fig. 2. From the figure it is clear that KCl exerts the inhibiting influence upon the ignition in the case of ethyl alcohol, but almost no effect upon the ignition of iso-octane.

(ii) Other several compounds. Using as the test fuels n-heptane, iso-octane, ethyl alcohol, decaline, turpentine oil, and 69 gasoline, the effects of coatings of various compounds (i. e. potassium carbonate, sodium carbonate, potassium nitrate, ammonium sulphate, borax, and orthophosphoric acid) were examined. For example, in the case of ethyl alcohol, the result is as shown in Fig. 3. From the figure it is clear that potassium salts and carbonates have the inhibiting influence upon the ignition. Such an inhibiting influence was also seen in the case of other fuels

tested except iso-octane, the ignition of which was not influenced by the above salts.

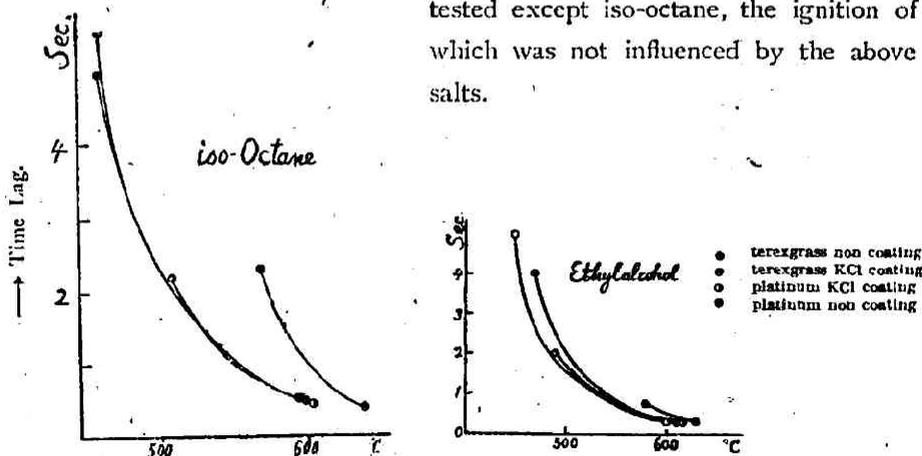


Fig. 2. Effect of coating upon the ignition in the air.

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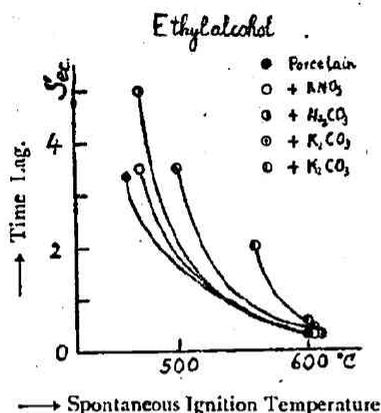


Fig. 3. Effect of coating upon the ignition in the air.

(b) Carbons.

After the ignition of some fuels (for example ethyl alcohol or turpentine oil) in the air, a deposit like carbon often appeared in the bottom of the crucible. This deposit exerted a remarkable influence upon the next ignition. And it may be inferred that in the case of ignition in the engine, carbon produced by the ignition may deposit on the inner surface of the engine cylinder and exert an influence upon the following ignitions. In connection with this view, it is necessary to examine the effect of carbon upon the ignition in the crucible

experiment. Using a porcelain crucible, the effect of graphite or lampblack upon the ignition of such fuels as n-heptane, 69 gasoline, iso-octane, ethyl alcohol or etc. in the air. Typical examples are seen in Fig. 4.

Some natural graphite powders exert an inhibiting influence upon the ignition of n-heptane or 69 gasoline. In the case of ethyl alcohol, on the contrary, the graphite powders could not change the lowest ignition temperature and only shortened the time lag.

Lampblack produced by firing a mixture of benzene and soy-bean oil was heavily coated on the inner wall of the porcelain crucible. In the case of n-heptane or 69 gasoline, the ignition happened at markedly lower temperature in the presence of lampblack than in the absence. Though the values of the time lags were at random, they fell into the hatched range as seen in Fig. 4. The heavier the lampblack was the longer the time lag became, and also the shorter of preheating

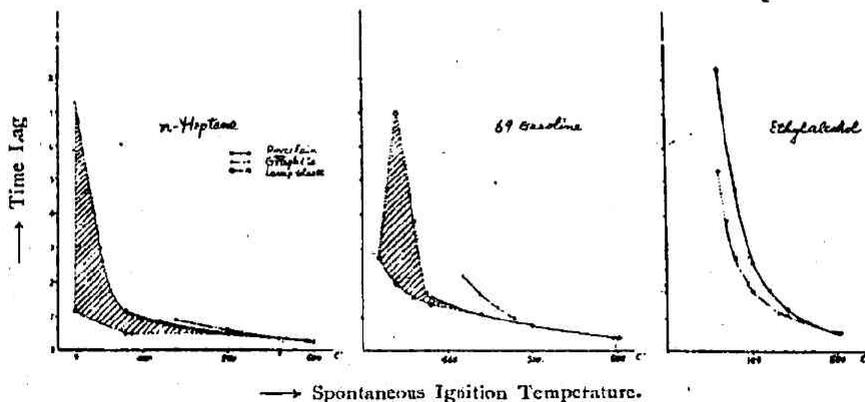


Fig. 4. Effect of coating upon the ignition in the air.

of the lampblack at 500°C the longer the time lag did. In the case of ethyl alcohol, the time lag was shortened by the presence of lampblack as in the case of graphite. Contrary to the above results, the ignition of iso-octane was not influenced by the presence of graphite or lampblack.

§3 Effects of deposits on the bottom of crucible.

From the test experiments it has been found that the most important parts of a crucible concerned to the ignition are the bottom and the side wall quite near the bottom.

So, in such a case as the surface coating of any substance to be tested is difficult, it is a nearly satisfactory condition for the test that the substance is deposited in a thin layer on the bottom of the porcelain crucible. For example, γ alumina powder* deposited on the bottom of the crucible generally accelerated the ignition of alcohols (ethyl, methyl or many kinds of alcohol) and retarded the ignition of iso-propyl alcohol as seen in Fig. 5. Details about the influence of γ alumina will be reported later.

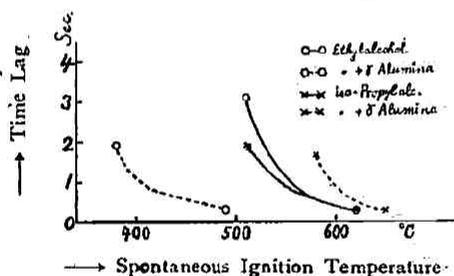


Fig. 5. Effect of γ alumina,
O₂ 20 cc/min.

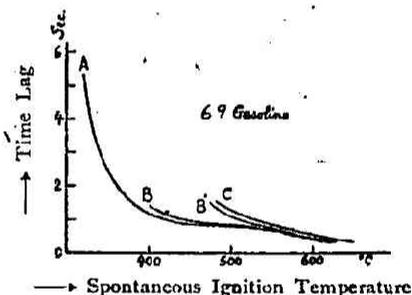


Fig. 6. Effect of tetra ethyl lead,
O₂ 20 cc/min.

§4 Action of tetra ethyl lead.

In the case of a fuel, whose octane value is increased by the addition of tetra ethyl lead, the spontaneous ignition temperature time lag curve of the fuel is shifted towards higher temperature side by the addition of tetra ethyl lead. For example, 69 gasoline (curve A) is retarded by the addition of 0.1% tetra ethyl lead (curve C) as seen in Fig. 6.

In the case of ethyl alcohol, on the contrary, its octane value is hardly increased by the addition of tetra ethyl lead. In the crucible experiment, however, the ignition of ethyl alcohol (curve A) is accelerated somewhat by the addition of 0.1% tetra ethyl lead (curve C) as seen in Fig. 7.

* G. Manabe's patent. (Pat. No. 157245)

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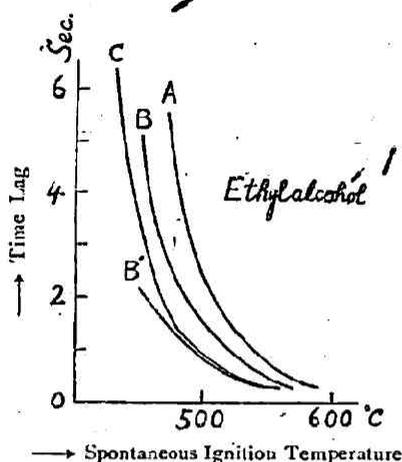


Fig. 7. Effect of tetra ethyl lead,
O₂ 20 cc/min.

The following experiments were carried out to elucidate the mechanism of actions of tetra ethyl lead upon the ignition of fuels. Now two kinds of crucibles were prepared as follows: fuels with tetra ethyl lead in one of the two similar porcelain crucibles and fuels without tetra ethyl lead in the other crucible were examined in the oxygen stream (20-cc/min.). When ethyl alcohol was examined in the former crucible (crucible B), curve B in Fig. 7. was obtained, and when the same alcohol was examined in the latter crucible (crucible A) curve A was obtained. In the bottom of the crucible B there was some part slightly yellowish or brownish in color. From these results it is quite probable that on the wall of the crucible B in which fuels containing tetra ethyl lead have been examined, there remain some lead compounds (perhaps some oxide) and these may accelerate the ignition of ethyl alcohol by the direct oxidation or surface catalytic reaction.

As the deposits (in the crucible B) which exert the accelerating influence may be considered to be some of lead oxides, the influences of various oxides upon the ignition of ethyl alcohol were examined. Pb₂O, PbO, Pb₃O₄ or PbO₂ was deposited in a thin layer on the bottom of the separate crucible. As the curves obtained almost agreed with one another, the curve obtained in the case of PbO is shown in Fig. 7 (curve B') as the representative.

In the case of 69 gasoline, on the contrary, lead compounds retard the ignition. The curve obtained in the crucible A is curve A and that in the crucible B is curve B in Fig. 6. And curve B' in the same figure shows the effect of PbO deposit on the bottom of the porcelain crucible upon the ignition.

From the above experiments, it is quite probable that some part of tetra ethyl lead added to a fuel may remain as some of lead oxides on the crucible wall after the ignition and exert an influence upon the following ignitions.

Accordingly, in order to estimate the octane values of the fuels from the ignition temperature time lag curves, fuels with tetra ethyl lead and fuels without ethyl lead must be examined in the separate crucibles.

Many investigations have been carried out to elucidate the mechanism of the action of tetra ethyl lead upon the ignition, but any satisfactory interpretation has

not yet been obtained.

From the present investigation, it is not unreasonable to suggest that in the ignition of the fuel containing tetra ethyl lead, tetra ethyl lead or some lead compound produced from tetra ethyl lead may exert influences upon the surface reaction and also the ignition thereby.

In the case of fuels containing iron penta carbonyl and also in the case of fuels which separate some deposits on the wall of the crucible after ignition, the estimation must be carried out with similar cares in the case of tetra ethyl lead addition.

§5 Considerations.

The table in §1 summarises not only the effects of surfaces or oxygen concentration as shown in Fig. 1, but also includes the effects of surface coatings (§2) and deposits (§3).

The ignition of iso-octane or acetone which has high octane value is slightly influenced by the surfaces or oxygen concentration in the porcelain crucible. The ignition of n-heptane, ethyl ether or acetaldehyde which has low octane value, is also slightly influenced by the surface in higher concentration of oxygen, but is influenced very much by the oxygen concentration in the porcelain crucible. The ignition of ethyl alcohol is influenced slightly by the oxygen concentration in the porcelain crucible, but influenced very much by surfaces in any concentration of oxygen. So ethyl alcohol resembles iso-octane in respect of the effect of oxygen concentration, and does not resemble iso-octane in respect of the effect of surface.

As already cited, the octane value of any fuel can be estimated by the measurement of the spontaneous ignition temperature time lag curve, so it is probable that between the ignition in the engine and that in the crucible a fair parallelism may exist.

The ignition of ethyl alcohol in the crucible, however, is remarkably accelerated by the presence of metals, carbons or lead oxides. It is, therefore, not unreasonable to consider that the ignition of ethyl alcohol in the engine may be accelerated by the discharge plug surface, carbons produced by ignitions or lead oxides produced from tetra ethyl lead. And ethyl alcohol has some unfavourable properties, such as causes the temperature rise of the engine cylinder. It is also not unreasonable to infer that this fact may be attributed to the high sensitivity of this fuel to the surface effects.

Next, let us consider a catalytic action of surface. Platinum, copper, and nickel are known as the catalysts for the dehydrogenation reaction and de-

composition reaction. In the presence of the above surface, however, an ignition of a fuel is not always accelerated, but often retarded as in the case of ignition in the air as seen in Fig. 1 or as in the case of the ignition of iso-propyl alcohol in the current of O_2 stream in the presence of γ alumina as seen in Fig. 5. It is not unreasonable to consider that such a fact may be attributed to the poisoning phenomena caused by the reaction products which have been produced from the surface reaction catalysed by the above surface and is more difficult to be ignited than the original fuel. It is clear, therefore, that the researches on the relation between the ignition and the catalytic activity of surface may be of great importance to elucidate the mechanism of the ignition. Further researches on this point will be continued.

§6 Conclusions.

I. Some contributions were made to complete the method which estimate the octane values of fuels from the observation of the spontaneous ignition temperature time lag curve.

II. From the remarkable effect of surface upon the ignition, it was pointed out that the surface reaction may be of great importance in the ignition.

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