CHEMISTRY OF OTTO-CYCLE ENGINE COMBUSTION

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Chemical study of internal-combustion engines is amply justified from the theoretical as well as the practical point of view. Aside from their obvious economic importance, engines have provided a wealth of information regarding the nature of combustion, much of it unattainable with other conventional forms of laboratory equipment. In return, the interpretation of these results has been—and to a large extent still is—a complex problem which challenges those chemists who are interested in the general theory of the subject.

Nevertheless, it seems fair to say that, until recently, there has been in general a lack of effective coöperation between the chemists on one hand and the engineers on the other, and advances in the theory of engine combustion have been slow. This seems to have been due largely to a tendency, on both sides, to oversimplify the problem. Chemists have made numerous laboratory experiments under conditions not remotely resembling those of an engine, but the results were applied, without criticism, directly to engine combustion; at the same time no detailed analysis has been made of the chemical facts furnished by the engine itself. On the other hand, engineers have been largely occupied with the practical development and testing of engines and fuels, with little or no direct investigation of the chemical theory of the subject.

Recent years have seen considerable improvement in these respects. Chemical experimentation conducted directly with engines or closely related apparatus has given a series of facts to replace uncertain assumptions; simultaneously, the development of the chain reaction theory of the slow oxidation and explosion of gases has provided a reasonable basis for the explanation of the phenomena observed. As a result, it is now possible to advance a general outline of the nature of engine combustion which is in accord with the known facts and appears to be theoretically sound. At the same time, a great many details remain to be filled in and a number of major points are still in doubt.

It is the purpose of this paper to present, briefly, such an outline, to indicate some of the respects in which our knowledge is still deficient, and to emphasize further the relative complexity of engine combustion. It is hoped that this survey will to some degree promote better appreciation of the problem and encourage still more effective coöperation between the chemists and engineers who are concerned with it. We shall consider in our survey only the Otto-cycle engine, since the Diesel engine will be dealt with in other papers of this symposium. No attempt will be made to refer to the extensive literature on the subject, either in its entirety or specifically.[1] Only those data and conclusions which have been instrumental in establishing our present conception of the subject have been selected; their interpretation is the present author's personal one, but appears to be in general accord with the consensus of opinion.

NORMAL COMBUSTION

Normal combustion in an engine comprises the spark ignition and subsequent slow inflammation of the charge, followed by equilibrium changes in the burned gas. Owing to the method of operation, the hydrodynamic and thermodynamic aspects are highly complex, but the chemistry appears to be no more complicated than that of the similar inflammations which have been investigated by various laboratory methods.

First, the air–fuel mixture, containing the slight excess of fuel required for development of maximum power, is mixed with more or less exhaust gas, compressed to over 5 atm., and ignited by the spark. The mechanism of this ignition is a specific problem, and has been considered in foregoing papers in this symposium. In the engine there appears an ignition lag, which may be defined as the period, following the initial spark, during which no reaction is detected visibly or otherwise. The lag is about 1 millisecond or less, and does not seem to vary greatly with the fuel used. This subject has not been studied in any detail, and might well repay closer investigation. It is obvious that reactions of some kind are taking place during the lag, and information as to their nature might be obtained from correlation of lags with other combustion characteristics of the charge, such as normal flame speed and knocking tendency.

The flame front then travels through the charge, accelerating rapidly to a speed of the order of 100 ft. per second, then slowing down near the end of its passage; it is highly irregular in shape, owing to turbulence. For the type of air–fuel mixtures used in engines, there is as yet no exact solution of the problem of flame speed; we can only assume that the inflammation is a chain-reaction process in which the interaction between the chain carriers and the reactant molecules requires a considerable energy of

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[1] For recent selected bibliographies see the appropriate sections of *Science of Petroleum*, Oxford University Press (1937), *Proceedings of the Second World Petroleum Congress*, Paris, 1937, and this symposium; also references 1, 2, and 3.

activation, that is, the fuel molecules are relatively stable and slow to react. Thus, ahead of the flame front, the chains are broken until the resulting general temperature rise furnishes the surplus energy necessary for further chain extension. Then the flame velocity is a function of such variables as the number of chain carriers emitted, their available energy, and the surplus energy of activation required. These quantities, in turn, are dependent, in order of increasing importance, on the pressure, temperature, and composition of the unburned gas.

In an engine these variables are continuously changing in the gas ahead of the flame front, and the flame velocity might be expected to show a regular increase as combustion proceeds. But these effects are not noticed, since the true mass or transition velocity is much less than the actually observed space velocity, owing to the turbulence of the charge. Hence, in engines, the visible flame speed is determined almost wholly by engine speed and the corresponding turbulence. Changes in composition of the charge, including dilution by exhaust gas, have some effect, variations in charge temperature and pressure have little or no effect, and the presence of small amounts of antiknock compounds is not noticeable.

Combustion of the fuel is practically complete within the narrow flame front; behind the flame front, as the temperature falls, shifts occur in the equilibria between the reaction products. The corresponding pressures and temperatures at different points in the burned gas have been experimentally determined, and are in accord with this mode of combustion. The pressure rise is smooth and noiseless; its maximum rate is of the order of 1000 lb. per in.^{2} × msec. The flame spectrum is normal, and shows the C—C and C—H bands.

ABNORMAL COMBUSTION

As the "severity" of engine conditions—the pressure, temperature, and heating time of the charge—is increased, the fuel no longer remains entirely inactive, but instead tends to react spontaneously in one way or another, leading to an abnormal type of combustion. The type obtained depends both on the particular engine conditions and on the chemical nature of the fuel. We distinguish, roughly, three different types: preignition, after-firing, and knock.

In preignition the charge, on coming in contact with some hot spot, such as the exhaust valve, ignites prior to passage of the spark, and if this occurs early enough in the cycle, there is back-firing into the carburetor. Some fuels, notably benzene and methanol, tend to preignite under the same conditions under which other fuels tend to knock. This distinction is not only of practical importance but has obvious significance in the theory of combustion. As might be expected, the addition of antiknock compounds such as tetraethyllead has but a slight effect, often detrimental, on the preigniting fuels; the organic antiknock compounds have not been tested extensively. In this connection laboratory tests of ease of ignition by a hot wire or the like might prove valuable; the time of heating should be very short.

In after-firing the spark may be cut out and the charge continue to ignite by compression. It is not clear to what extent this phenomenon is a form of preignition or is a form of knock. It can be regarded as a sort of delayed preignition, but there may be some effect on adding an antiknock agent, depending on the type of fuel used; this might well be investigated in machines of the adiabatic-compression type where the operating variables, especially the temperature, can be better controlled.

Knock is a form of spontaneous ignition, starting at one or more points in the "end gas" or unburned charge ahead of the flame front. The amount of charge entering into knocking combustion may vary from an indistinguishably small portion to at least three-quarters of the whole; also, apparently, the intensity or rate of knock may vary considerably. The knock flame seems to sweep through the remaining unburned charge, with a velocity in the neighborhood of 1000 ft. per second,—a value far greater than that of the normal flame, but much less than would be calculated for a true detonation wave in similar air-fuel mixtures. Correspondingly, the rate of pressure rise is high, the maximum value being of the order of 10,000 lb. per $\text{ft.}^2 \times \text{msec.}$, and the change in the rate of pressure rise is sufficiently abrupt to set up pressure waves, which induce the emission of sound waves from the engine. The spectral emission of the knocking flame resembles that of the normal flame, but it has a greater extent and intensity and the characteristic hydrocarbon C—C and C—H bands are weak or disappear. The normal flame prior to knock is indistinguishable from that observed in the entire absence of knock.

In non-knocking operation no indication is found of any extensive chemical change in the end gas. As conditions are changed in the direction to produce knock, formaldehyde appears in the end gas in increasing amounts, which may vary for fuels of equal knock intensity. Compounds of the peroxide type are also present, but the amount of oxygen consumed is small. Suppression of knock by addition of aniline eliminates the formaldehyde, but with tetraethyllead, it is stated, this effect is not obtained in the engine. Both antiknock agents suppress the formation of those unidentified compounds which, under conditions of incipient knock, give a continuous absorption in the spectrum of the end gas.

FACTORS IN KNOCK

By and large, any changes which increase the temperature, pressure, or heating time of the charge, or modify its chemical composition in the direction of readier ignition, tend to promote abnormal combustion of one type or another. In the case of knock, any variations which would be expected to favor preflame oxidation of the end gas are found to promote knock. Because of its greater interest, subsequent remarks will be confined to the phenomenon of knock.

The relative importance of the time, temperature, and pressure factors is difficult to estimate, since they are not readily susceptible of independent variation in an engine and the functions relating these variables to the occurrence of spontaneous ignition remain entirely unknown for time periods as short as those in an engine. Recent work on spontaneous ignition indicates that the pressure as well as the temperature is an important factor, and it is to be hoped that further information will be obtained for shorter time lags. In the engine the pressure and heating time for the end gas can be quite accurately measured; the time is of the order of 1 to 10 msec. The temperature ahead of the flame has only been estimated approximately, but probably exceeds 500°C.; it will doubtless be desirable, later, to determine this more accurately.

Equally important in determining the onset of knock is the chemical composition of the charge, including the nature of the fuel, the air–fuel ratio, dilution with exhaust gas, and the presence of pro- or anti-knock compounds. The pronounced effect of the molecular structure of the fuel is well known, but the explanation of this effect is still far from complete. As to air–fuel ratio and charge dilution, it is difficult to determine to what extent these factors have a direct, chemical influence on the oxidation and ignition of the end gas, and to what extent they act indirectly by virtue of their effects on the velocity and temperature of the normal flame.

The influence of pro- and anti-knock compounds is conspicuous: as little as one molecule of tetraethyllead in over 200,000 molecules of hydrocarbon may be sufficient to give a noticeable decrease in knock. Proknock compounds usually either contain active oxygen or else react readily with air to yield it; some other compounds, such as certain bromides, are also effective. Antiknock agents are mostly metals or organometallic compounds, and a series of aniline derivatives. On a molecular basis the former are of the order of one hundred times as effective as the latter, the distinction being so marked as to suggest a fundamental difference in their modes of action. The relative and the absolute effectiveness of an antiknock agent may vary considerably, both for different fuels and for different operating conditions; for a given fuel the effectiveness is not directly proportional to the amount added, but tends to approach a limiting value.

In general, the characteristics of the knocking flame, particularly its spectrum, are the same, regardless of which factor—increase in time–temperature-pressure, or change in chemical composition of the fuel, or decrease in the amount of antiknock agent—is responsible for its occurrence, and we conclude that all these factors are concerned with the initiation rather than the propagation of the flame.

The physical and chemical factors are often interrelated; thus the effect of a specific change in engine conditions is by no means necessarily the same for two different fuels, or for a given fuel with and without an antiknock agent added.

In addition there may be other factors, such as the effect of radiation or ionization from the flame front, the turbulence of the end gas, or the nature of the engine walls in contact with the end gas. These do not appear to be important; however, little is known about them, and it is quite possible that turbulence, in particular, may be a significant factor. There is as yet no particular evidence for the existence in the engine of surface effects of the chain-reaction type. The fact that such effects may be controlling factors in many slow oxidation reactions which have been studied by laboratory methods is no *a priori* reason for their importance in an engine, where conditions are widely different. The strictly thermal effect of surface, particularly of hot spots, is of course conspicuous.

THEORY

The foregoing facts readily suggest their own general explanation, and the hypothesis that knock results from a spontaneous ignition of the unburned charge was advanced at least thirty years ago. However, the lack of correlation between the knocking tendency and the spontaneous ignition temperatures of different fuels, alone or with antiknock compounds present, casts doubt on the correctness of the hypothesis. This doubt disappears when the meaning of the term "spontaneous ignition" is analyzed, and it is realized that relative values measured under one set of conditions, as in some specific laboratory method, cannot be applied to widely different engine conditions; any attempt to extrapolate such values to reach engine conditions is insecure, owing to the chain-reaction nature of the processes involved.

The general theory is, then, about as follows: Before the arrival of the flame front, slow oxidation occurs in the end gas by a chain-reaction mechanism. In normal combustion the amount of such oxidation is slight, and the products formed have no important effect on the subsequent inflammation. Doubtless the rate of such oxidation is not constant and increases with time, but before the ignition point is reached the arrival of the flame completes the combustion. When the conditions are such that knock will occur, then the rate of oxidation is greater, probably owing to greater efficiency of chain extension, and it increases until the critical point is reached where the coefficient of chain branching becomes unity. There is then a sudden very considerable increase in the concentration of activated partial oxidation products in the end gas. It may be that this reaction itself is the actual ignition, and that the completion of the combustion and the appearance of flame take place in conjunction with it, throughout the charge. Or, as seems more likely, it may be that the partial oxidation reaction merely gives a mixture which is far more inflammable than the original mixture. Its combustion may then be abruptly completed, as another step, by a flame which starts from one or more favorable points and is able to spread at a rate far greater than normal; that is, the combustion may be regarded as a kind of two-stage process. Thermodynamically, these alternative modes of ignition—by local action or by a moving flame—are practically identical, and there is no essential chemical distinction between them; the important point is that in either case the ignition is a result of a sudden change in the chemical composition of the gas, and not of a final critical increment in temperature alone. If we grant the presence of a moving flame of knock, it seems reasonable to expect this to start from the normal flame front, where the available energy is greatest, and the photographs suggest that this does occur in many cases. But it need not do so, since the development of the preliminary branched-chain reaction is probably not uniform throughout the end gas, and as a result that part of the gas which first attains the condition of extra-inflammability and ignites, may be well removed from the normal flame front.

The occurrence of a moving flame having a velocity intermediate between that of the normal flame and that of a detonation wave is not an unreasonable hypothesis. Although the inflammability of the mixture through which the flame of knock passes has become much greater than normal, there is no particular reason to suppose that it attains the degree of inflammability necessary for the propagation of a detonation wave. Such intermediate flame velocities are not usually observed in combustion experiments in tubes, etc., for the obvious reason that no chemical changes take place in the unburned charge in those cases; however, abnormal flame velocities or quasi-detonations have been observed when the ignition source provides a high surplus of energy.

Any attempt to make the foregoing description of knock more specific by defining the exact nature of the chain reactions involved and the products obtained possesses considerable uncertainty. Specific reactions have been proposed to describe the results obtained in slow oxidation and ignition of gases carried out under conventional laboratory conditions, but the actual chemical analysis of these reactions is far from complete. For the more drastic engine conditions practically no actual facts are available, other than the afore-mentioned presence of formaldehyde and other unidentified oxygenated compounds and the disappearance of the C—C and C—H bands in the subsequent inflammation. Correspondingly, any attempt to correlate the knock resistance of specific hydrocarbons with the mechanism of their slow oxidation is uncertain to the same degree, and there is as yet no sound reason for believing that the results obtained for these hydrocarbons under laboratory conditions can be applied to engine conditions without modification. The extent, if any, to which straightforward thermal decomposition of the fuel molecules influences the oxidation reactions preceding knock is unknown. It seems possible that differences in thermal stability may account for the variation in knocking tendency of some structurally similar hydrocarbons which would appear to be of approximately equal susceptibility to attack by oxygen. Investigations along this line are desirable.

The action of pro- and anti-knock compounds is, of course, readily explainable on the basis of this theory of slow oxidation by chain reactions in the end gas. But here again, the specific mechanism of their action remains almost entirely unknown. The organic antiknock agents are presumably destroyed in the act of chain-breaking. If this can be confirmed, it is possible that valuable information as to the number and length of the chains can be obtained from a quantitative study of the effects of these agents. There is a strong suggestion that the metallic atoms are able to break chains repeatedly, probably by virtue of alternate oxidation and reduction; it is reported that the absorption spectrum of the end gas shows atomic lead but no lead monoxide when knock is eliminated by the addition of tetraethyllead.

COMPLEXITY

The foregoing summary of the observed facts and general theory of engine combustion has failed to fulfil its purpose, if it has not sufficiently indicated the complexity of such combustion and given some indication of the chemical and mechanical problems which remain to be solved before a more detailed theory can be developed.

Actually, in engine studies, the principal variables under direct control are the speed, spark timing, and jacket temperature of the engine, and the pressure, temperature, and composition of the charge. As regards the end gas, any attempt to change one variable alone inevitably causes one or more of the others to change also, either directly, or indirectly by affecting the speed or temperature of the normal flame. Other factors, such as the turbulence and the nature of the combustion chamber surfaces, cannot be closely controlled during the progress of a run. The effect of such uncontrollable factors, or of slight variations in the controlled variables, leads to considerable irregularity in the combustion from one explosion to the next. This is clearly shown, photographically and otherwise, even by engines operated under rigidly specified conditions; the flame speeds and temperatures, for example, may vary by as much as 5 or 10 per cent. This complexity makes both the correlation and the analysis of results very difficult.

On the other hand, laboratory experiments conducted in special equipment and under carefully controlled conditions so far have failed to come anywhere near duplicating engine conditions, and, as previously pointed out, the relations between the different conditions are uncertain to a high degree. For example, ignition temperatures may be measured in the conventional manner, with a time lag of one second to one hour or more, during which time it is supposed that a certain necessary amount of slow oxidation takes place, and relations may be established between the pressure, temperature, etc., and the time lags. But this slow oxidation during the time lag may itself also have an induction period (probably largely conditioned by the combustion chamber surfaces) of the order of, say, one millisecond. Then the effect of the pressure, temperature, etc., on this short time lag will be entirely overlooked in the laboratory experiment, but may be the paramount factor in the engine.

An analogous case occurs in Diesel combustion, where it can be shown that the flame starts in the vapor envelope surrounding the fuel spray, after a time lag whose origin is largely chemical and is not merely the time of evaporation and heating of the vapor. The dependence of this time lag on the pressure and temperature is by no means a linear or simple function.

An even worse situation arises when we have the possibility of simultaneous reactions, with different pressure or temperature coefficients, and this probably is the case in the slow oxidation of the higher hydrocarbons. A further complication is that under certain conditions such reactions have a negative temperature coefficient over a certain temperature range. To what extent this effect applies under engine conditions is uncertain, but there is evidence that under some conditions an increase in temperature may reduce the possibility of knock, while increasing that of after-firing.

Examples

The result of this engine complexity is well illustrated by the ambiguity which arises in determination of the absolute or relative knock ratings of different fuels or pure hydrocarbons. An example of the magnitude of the variations which can be obtained for two pure structurally similar hydrocarbons is furnished by the following data from the recent results of S. D. Heron and F. Gillig of this Laboratory (1). The data give the effects of engine speed and jacket temperature on the *ratio* of the maximum power output obtained from diisobutylene to that from isoöctane (2,2,4-trimethylpentane), when run in a supercharged test engine, with the inlet pressure increased until the fuel fails by giving abnormal combustion. At 900 R.P.M. this power ratio falls from 1.64 at a jacket temperature of 212°F. to 1.01 at 350°F.; at 1800 R.P.M. the corresponding ratios are 0.90 and 0.82. Thus these moderate changes in engine conditions can effect a twofold change in the ratio of the power outputs. Many other similar examples are available, but have received little or no attention from the chemical point of view.

On the other hand, as is well known, chemical information of a comparative nature, which is relatively free from the effects of changing engine conditions, is provided by the ratings of fuels of different structures and by their response to antiknock compounds. Such results need not be confined to hydrocarbons of the gasoline type, but may be extended to other compounds, with possible added significance for combustion theory. An example is furnished, through the courtesy of S. D. Heron and F. Gillig, by their unpublished results for a series of propyl derivatives tested as above, at 900 R.P.M. and 212°F., alone or with 3 cc. of tetraethyllead per U. S. gallon. The respective power output ratios, relative in each case to unleaded isoöctane, are as follows: *n*-propyl alcohol, 1.29 and 1.23; isopropyl alcohol, 1.54 and 1.56; 91 per cent isopropyl alcohol, 1.63 and 1.64; propylene oxide, 0.82 and 0.88; acetone, 1.72 and 1.78; diisopropyl ether, 0.92 and 1.05. The marked lead response of the ether, and the slight response, if any, of the other substances appears chemically significant.

This brief survey shows what type of knowledge has so far been obtained regarding the mechanism of combustion in an engine. It also indicates how the complexity of the problem accounts for the scantiness of definite information. Decided inroads are being made by the groups of investigators attacking the problem from various angles. Their realization of the difficulties encountered and of the necessary slowness of progress, coupled with their caution in drawing conclusions after each advance is made, bids fair for definite achievements and possibly for an ultimate solution of this extremely delicate and important chemical problem.

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