

MOLECULAR STRUCTURE OF HYDROCARBONS AND ENGINE KNOCK

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During the past ten years considerable progress has been made in the development of a knowledge of the relationship between molecular structure and knocking characteristics of hydrocarbons when used as fuels in internal-combustion engines (1 to 22). This knowledge is of considerable significance both from the engineering standpoint, where power output or thermal efficiency is a primary consideration, and also from a more theoretical standpoint, where it is desired to extend our present understanding of fuels and combustion reactions.

From the engineering standpoint, it will suffice here to point out that the efficiency of the conventional internal-combustion engine is largely dependent upon compression ratio,—increasing compression ratio making possible higher efficiency and greater power output per unit of engine displacement. Thus, within certain limits, it is desirable to use a high compression ratio, but the limit to which it is possible to go is determined by the tendency of the fuel to knock. This is a very real limitation, and that it is intimately related to the subject of molecular structure is shown by the fact that the maximum power output obtainable without knock from an engine of given piston displacement may vary by as much as 50 per cent with different isomeric paraffin hydrocarbons. Needless to say, the further development of knowledge in this direction is almost certain to have an important and far-reaching influence in the engineering progress of the automobile, aviation, and petroleum-refining industries.

The unique feature of this general situation is that the still largely unknown phenomena of gaseous combustion in an engine are controlled by slight differences in the molecular structure of fuels to an extent of tremendous economic importance. We know that the structures now predominant in most commercial fuels are relatively very poor as compared with those that we would have, had we better control of chemical reactions such as those of isomerization. This situation represents a common meeting ground of molecular physics, gaseous combustion, organic chemistry, and economics of considerable social importance.

For the purposes of this symposium we are mainly concerned with what might be termed the theoretical standpoint. Certainly the observations which have thus far been made in connection with this subject provide material which can be woven into the theory of many branches of science to give, eventually, a clearer conception of the mechanisms involved. It will be a purpose of this paper to review some of the consistent relationships between molecular structure and knock which have been found.

It now appears that chemical constitution, as revealed by molecular structure, is related to knock, and hence the ultimate utility of a fuel, in two distinct ways: first, by direct influence on knock, and second, by influencing the effectiveness of antiknock compounds when used in the fuels.

In order to evaluate the relationship between the structure of hydrocarbons and their tendency to knock, various methods have been used, all of them depending upon direct measurements in an engine. The use of an engine is essential, since we do not have precise enough information as to the conditions in an engine cylinder to enable them to be duplicated satisfactorily or conveniently outside of an engine. However, it happens that an engine under the proper conditions offers an extraordinarily sensitive, convenient, and rapid method of measurement. The development of the concept of the octane number of a fuel, and of the standardized method of its measurement, discussed in detail elsewhere in this symposium, is a specific application of this principle to the testing of commercial gasolines. This commercial testing method, because of the restricted engine conditions employed in it, is not ideally adapted to the broad study of the knocking characteristics of hydrocarbons. Consequently, in the work described herein, wide deviations from the commercial test procedure have been utilized.

One method of measurement which has been used with hydrocarbons is to burn the hydrocarbon in question as a fuel in an engine in the pure state and to determine the maximum compression ratio at which it will operate without knock. This method is quite simple and direct, although the values must, of necessity, relate to the particular engine and operating conditions used in the experiments. For some purposes this method is not entirely suitable, because the materials under test may not have physical properties adapted for use in a carburetor. It also has another disadvantage in that the use of that method of measurement requires considerable amounts of material for test, and such amounts may not always be available in the case of compounds whose laboratory preparation is difficult.

For these and other reasons measurements have often been made in solution in a reference or standard fuel, measuring the change in knock of

the fuel upon the addition to the fuel of a definite amount of the material under test. The change in knocking behavior may be conveniently expressed as the change in the equivalent octane number of the fuel or, as was done before this method came into use, it may be measured and expressed in terms of the amount of an antiknock compound such as aniline or lead tetraethyl which will produce a similar change in knocking tendency. Other modifications of these most widely used methods have been used; for a complete discussion of them and the precise methods of test and computation, reference may be made to the original papers.

As previously mentioned, all methods involve the use of an engine, and it is true that the precise values obtained will depend to an extent upon the engine used and the conditions under which it is operated. In other words, the knocking characteristics of a fuel are not entirely a property of the fuel alone. From the limited amount of data thus far made available, it appears that, with few exceptions, the changes in the values of different hydrocarbons observed under different engine conditions are relatively small as compared with some of the differences between different hydrocarbons under comparable engine conditions. Again, for detailed expositions of these phenomena reference must be made to separate papers covering these various aspects of the subject (5, 7, 15).

It is of considerable significance, however, that under given engine conditions the knocking characteristics of hydrocarbons fall into a very consistent pattern, according to their molecular structure. The significance of this may be twofold. This consistent behavior enables one to make an appraisal of what the possibilities are in the way of fuels whose thermodynamic efficiency in an engine may be very high, or of what efficiencies are possible when the present barriers of lack of knowledge as to chemical conversions are removed or reduced. This consistent behavior may also serve as a guide in evaluating theories of the mechanism of hydrocarbon combustion and the incidence of knock in engines. For these reasons it may be valuable in a symposium of this type to review these consistencies, in order that the facts upon which theories or predictions may be based may be clearly in mind.

It is convenient for the sake of simplicity to consider the hydrocarbons in classes, such as paraffins, olefins, etc., and the relationships are most readily expressed graphically. Figure 1 summarizes the relationships for the paraffin hydrocarbons. The knocking characteristics are expressed in terms of "aniline equivalent," which is a measure of the knocking behavior in relatively dilute solution in which concentrations are on the basis of the same number of molecules (12). In order, however, to convey some concept of the scale of aniline equivalent, it may be said that *n*-heptane with an aniline equivalent of -14 and 2,2,4-trimethylpentane, which has a

value of +16, begin to knock when burned undiluted at compression ratios of 2.7 and 6.9, respectively. While such values do not permit a direct conversion of all values, because the relative values obtained in dilute solution with gasoline are not necessarily an index to behavior in the undiluted state, nevertheless they do give an idea of the great range covered by the vertical scale.

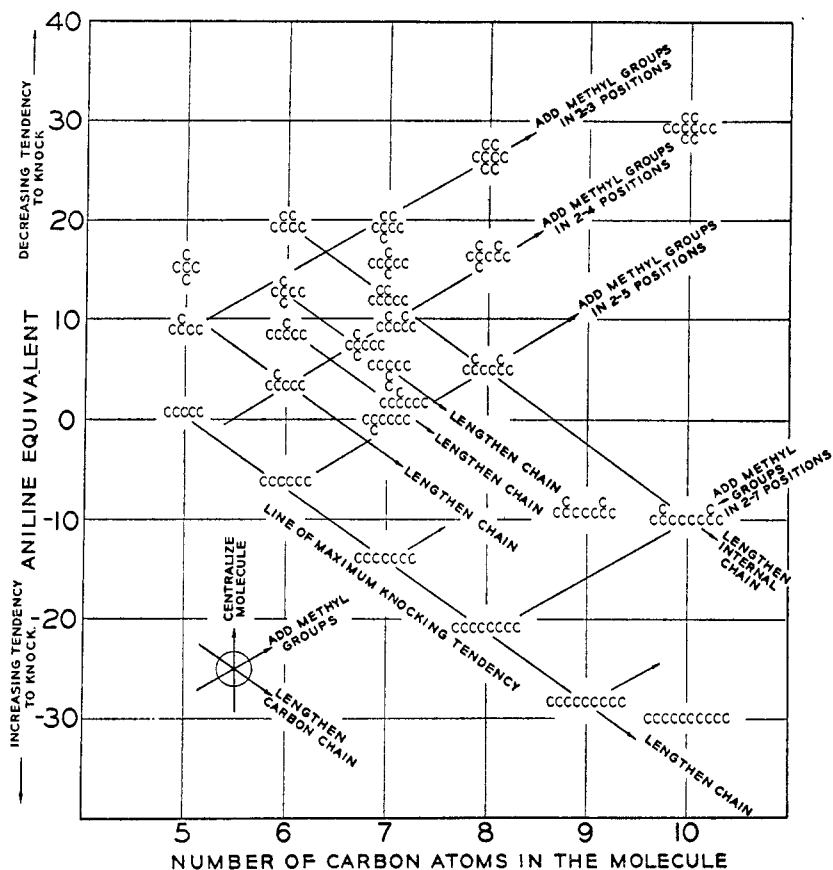


FIG. 1. Relationship of molecular structure to knocking characteristics of paraffin hydrocarbons

From this diagrammatic representation it may be seen that in a very general, and consistent way the addition of methyl groups improves the molecule from a knock standpoint; lengthening the straight chain of a molecule makes the knocking characteristics worse, and centralizing the molecule, without changing the number of atoms, makes a much better

molecule as far as knock is concerned. On this molecular basis it is a fair approximation to say that the knock depends roughly upon the length of the unbranched straight chain of carbon atoms in the molecule. This is a fact that is probably of considerable significance as far as theories of the mechanism of combustion and knock are concerned.

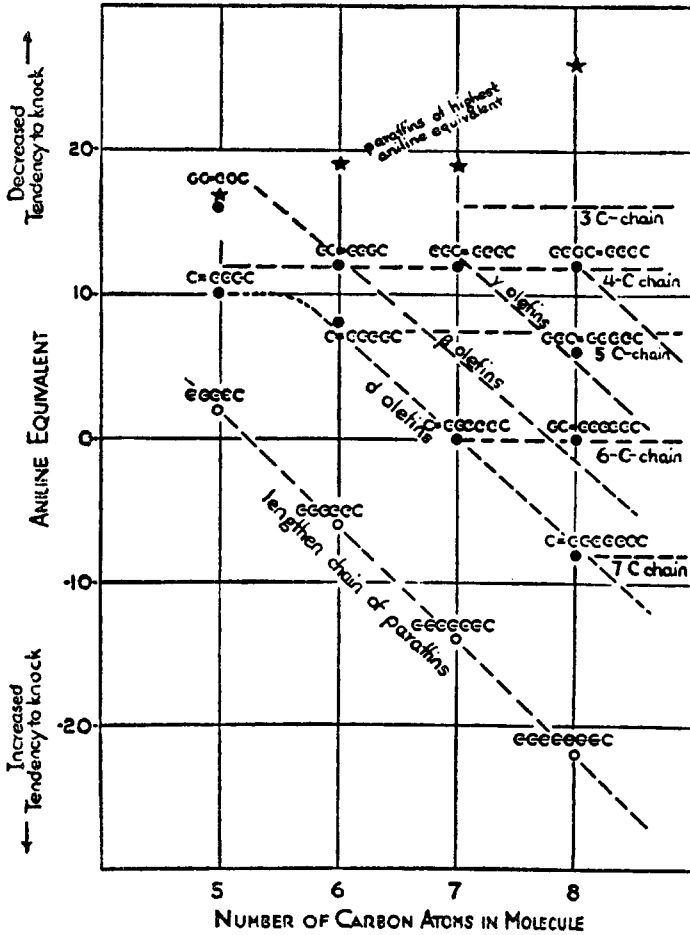


FIG. 2. Knocking characteristics of straight-chain olefins

This same behavior is also exhibited by the straight-chain olefin hydrocarbons, whose properties in this regard are represented graphically in figure 2 (13). The effect of an increase in the straight paraffin chain is similar, both qualitatively and quantitatively, to that observed in the case of the paraffin hydrocarbons. It is also probably significant that,

within the range covered, the knock seems to depend upon the length of the straight paraffin chain, irrespective of the size of the molecule.

Branched-chain olefins behave very much as might be expected from what might be termed the effect of the double bond, as revealed by the straight-chain olefins, combined with the effect of branching, as shown by

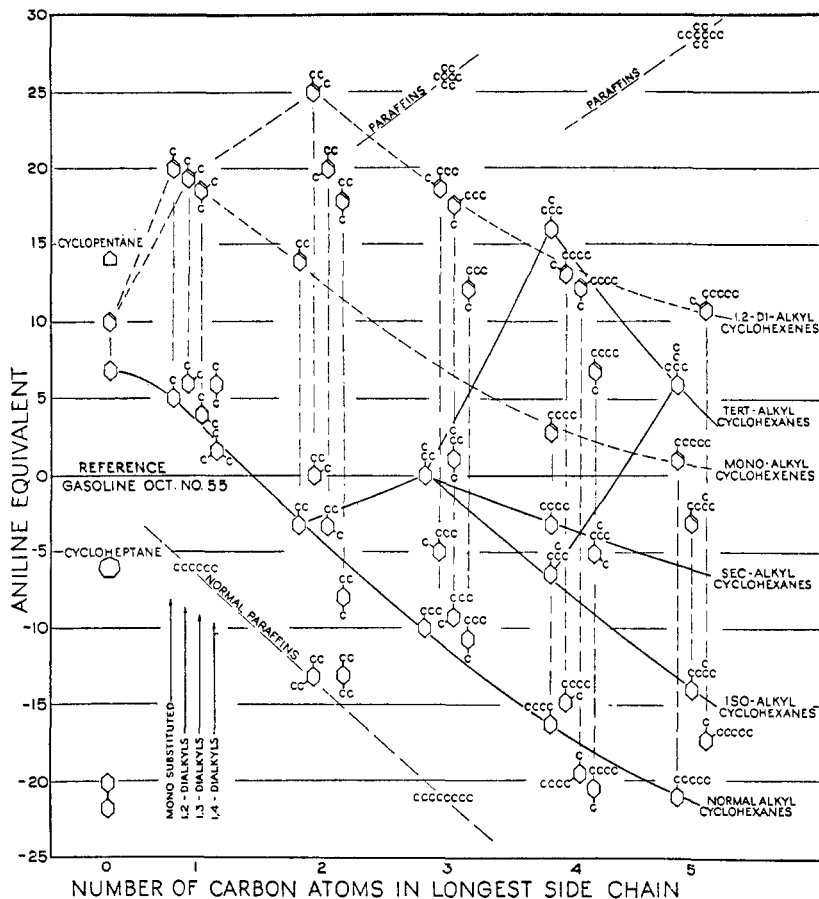


FIG. 3. Relative knocking characteristics of alkyl cyclohexanes and cyclohexenes

the behavior of the paraffins. The great numbers of isomers of such compounds, however, make the obtaining of a complete picture of their behavior a very difficult and tedious matter.

Another class of hydrocarbons is that of those containing a cyclopentane or a cyclohexane ring (14). In general the formation of a ring, as indicated by the behavior of cyclopentane, cyclohexane, and cycloheptane, is to

enhance the degree of freedom from knock of the compound as compared with the paraffin containing the corresponding number of carbon atoms. The possibilities of isomerization in this class of compound are somewhat different from those in the aliphatic compounds, although the effect of changes in the arrangement of an alkyl side chain is similar to that which might be expected by analogy with the paraffin hydrocarbons. This is shown by the graphical representation of the data on the cyclohexanes and cyclohexenes in figure 3, plotted in a manner similar to the preceding data. The possibilities of isomerism due to variations in the positions of two or more side chains have not seemed to be a relatively great factor in determining knock. However, the available data do seem to indicate that, as far as isomerism with respect to a different distribution of carbon atoms between chains is concerned, the most favorable condition from the standpoint of knock prevails with the most centralized structure. If we should define such a rough concept as centralization by a compact arrangement of the plane structural formula ordinarily used, this generalization seems to apply quite generally to all types of compounds investigated. It is also interesting in connection with these cyclic compounds that an introduction of a double bond in the ring increases the freedom from knock of the compound by an amount which seems quite constant.

Cyclopentanes and cyclopentenes seem to behave, as far as their knocking characteristics are concerned, in a manner quite analogous to that of the six-membered rings.

Another class of hydrocarbons of considerable interest in connection with the problem of knock is that of the aromatic compounds containing a single benzene ring (15). Data on these are represented graphically in figure 4. The behavior of these compounds is different from that of the naphthenes as far as the effect of an increasing length of side chain is concerned. The addition of a side chain and its progressive lengthening first results in an increase in freedom from knock; further lengthening of the chain results in a decrease. While this peculiarity might suggest some analogy to be expected with the behavior of these compounds on oxidation, at present this is largely speculative. The effect of the initial methyl substituents, however, is very pronounced, as toluene is much better than benzene, and the xylenes and mesitylene are still better; the effect of position isomerism seems to be a large factor. The aromatic compounds behave with respect to knock as if the benzene ring were of paramount importance and as if the addition of one or more carbon atoms to it were of much greater effect than the arrangement of the atoms within the chain which is added. Most of the aromatic compounds are relatively good from the standpoint of knock as compared with the other conventional classes of hydrocarbons; it is, however, quite difficult if not impossible to assign

relative values to these classes as a whole, since the range covered by the different classes is widely, if not almost completely, overlapping.

The relationships just discussed relate to dilute solutions and are upon a molecular basis; they are of primary interest because of the suggestive consistencies of the correlations between knock and structure. From the standpoint of the fuel and the engine they are of particular interest,

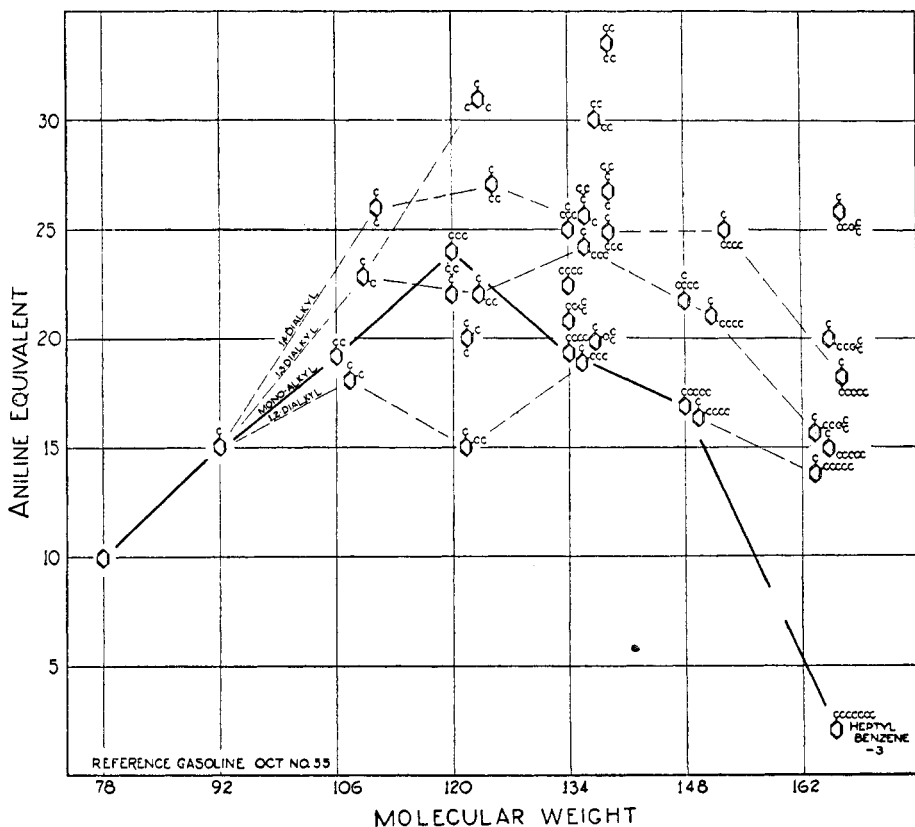


Fig. 4. Relative knocking characteristics of aromatic hydrocarbons

as indicating what may be obtained in practice from relatively small additions of different hydrocarbons in making up fuels better than those now commercially available and with a fairly wide range of constituents.

From the standpoint of making large advances in fuel technology, the knocking behavior of individual hydrocarbons in the pure state is of special importance. Considerable data are available on pure hydrocarbons in terms of the compression ratios that may be used with them, although of

necessity, as previously mentioned, they are of more limited extent. The general qualitative correlations between knocking characteristics and molecular structure previously observed for such hydrocarbons when measured in dilute solutions hold in general, but there are some notable exceptions. These arise from the fact that the critical compression ratio of a mixture of two compounds is not always directly proportional to the concentration of each in the mixture. There is also another contributing factor which will be discussed later, namely, that the engine operating con-

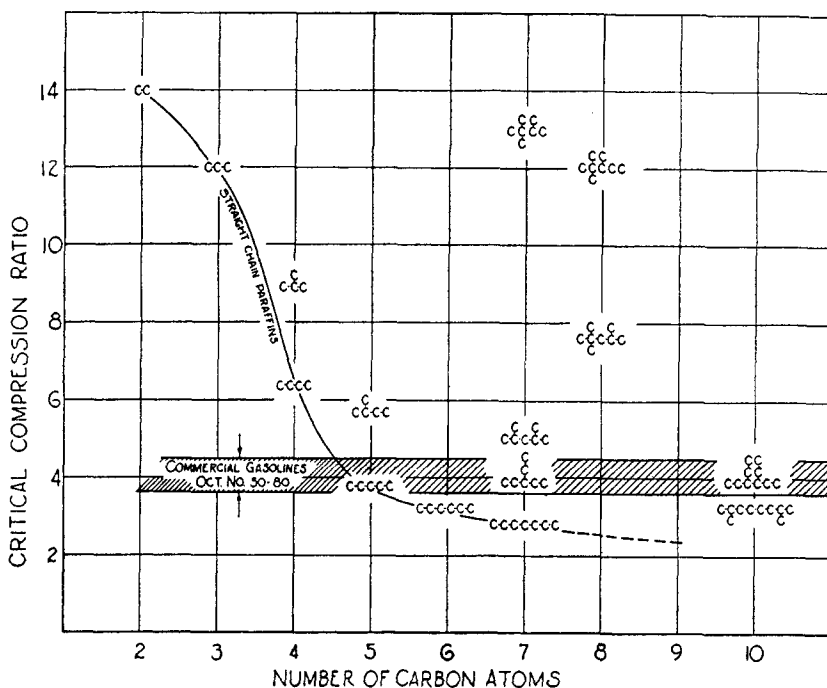


Fig. 5. Critical compression ratios of paraffin hydrocarbons

ditions make a considerable difference in the relative values obtained for some fuels when they are tested in the pure state.

However, a general picture of the relationships among the paraffin hydrocarbons is shown in figure 5, where the knocking characteristics of the pure paraffin hydrocarbons are evaluated in terms of the critical compression ratio or the highest ratio at which they can be used without knocking (16). Most apparent, of course, are the very great differences between the different compounds.

A similar picture for the cyclic compounds is shown in figure 6. Outstanding here are the very great differences between the aromatic com-

pounds and the corresponding saturated compounds, a phenomenon which does not appear with measurements made under conditions of dilute solutions. The knocking tendency of a mixture is not necessarily a linear function of the concentration. This behavior is shown by the data of figure 7, in which the critical compression ratio of some two-component mixtures is plotted against the mole fraction in the solution. The curves are not linear and show a wide variety of characteristics, some being convex and some concave downward. In general, extrapolation of knock-con-

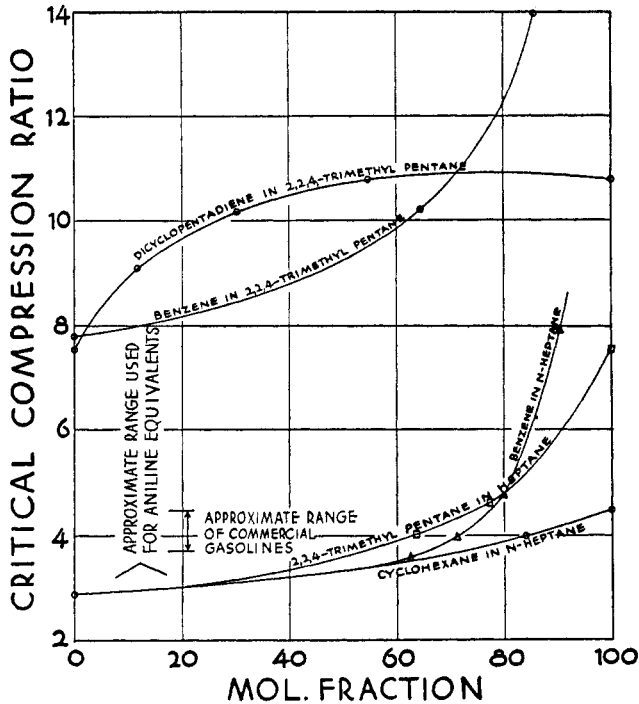


Fig. 7. Knocking characteristics of two-component hydrocarbon mixtures

centration curves over a considerable range is not justified. The reasons for these departures from mere simple relationships are of considerable speculative interest, but our present knowledge of hydrocarbon combustion is possibly too limited to warrant extensive discussion of this here.

The relationships among hydrocarbons with respect to knock and utility are also of interest from the viewpoint of the mechanism of combustion, because of the way in which antiknock compounds act upon them (3, 5, 6). The mechanism of antiknock action seems to be tied up with the molecular structure of the hydrocarbon, probably as a result of the intermediate

compounds formed. In some compounds lead tetraethyl, for instance, may be twenty times as effective as a knock suppressor as in others; in some compounds it may even be a knock inducer.

As an index of this effectiveness, we may consider the increase in critical compression ratio which the addition of 1 cc. of lead tetraethyl will permit. It is possible to correlate such values upon the basis of the branching of carbon chains, upon the position of double bonds in a chain or in a ring, and so on. These manifold and consistent relationships may not well be detailed here. However, as a rough general correlation, the data shown

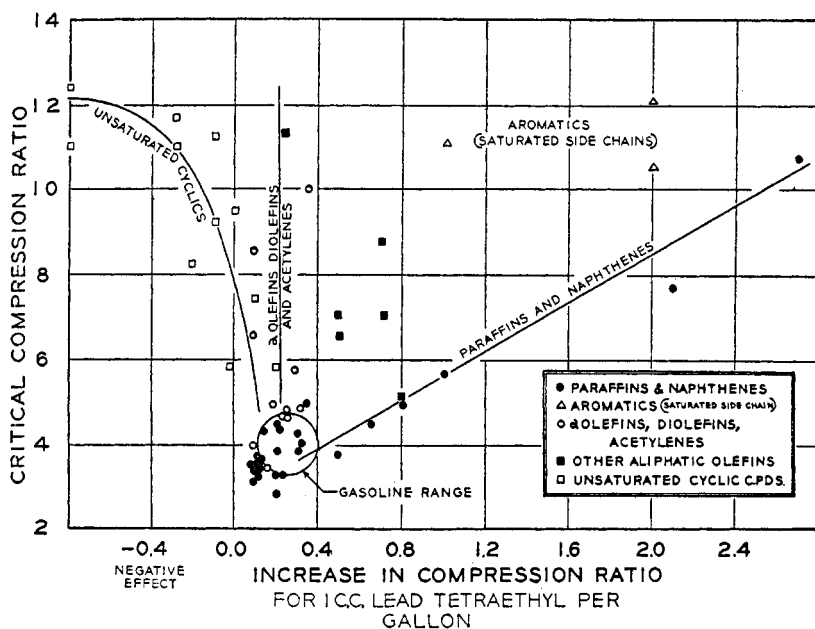


FIG. 8. Relative antiknock effect of lead tetraethyl in various types of hydrocarbons

graphically in figure 8 indicate the extent of the variation, since the addition of 1 cc. of lead tetraethyl to a hydrocarbon may permit an increase of 2.7 ratios without knock, or may necessitate a decrease of 0.8 of a compression ratio. As a single example of how specific this effect is, there are the data of figure 9, which are self-explanatory. Since any consistent theory of knock must include the action of antiknock compounds, it is important to note that some antiknock compounds or catalysts may under some circumstances act as knock-inducing compounds.

An evaluation of the relative utilities of fuels of different molecular structures is essentially a measurement of the thermodynamic efficiency

with which each may be burned in an engine suited to that particular fuel. As mentioned previously, this is a property not entirely of the fuel but also of the engine; the engine must to a considerable extent be adapted to the fuel in other respects than simply in regard to the compression ratio.

A concept of why this comes about may be readily gained by thinking of the phenomenon of knock as essentially a race between two combustion processes in the engine cylinder. The first is the spread of flame across the cylinder; the second is the series of steps leading up to ignition of the fuel-air mixture ahead of the flame. Which phenomenon takes place first determines whether or not there is knock. Both processes are influenced

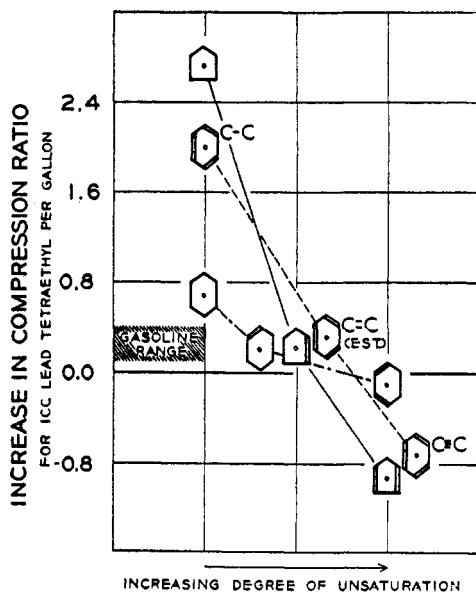


FIG. 9. Effect of double bonds in cyclic compounds on effectiveness of lead tetraethyl

by the time available, by temperature, and by pressure, so that the outcome of the race will depend upon such conditions. Furthermore, the extent to which these different processes are affected by temperature and pressure will vary from one hydrocarbon fuel to another. It is to be expected, consequently, that the attainment of the greatest efficiency is to be had only by the best fitting together of fuel and engine. This amounts to selecting a raw material (fuel) and carrying out a chemical reaction on it (combustion with air) under conditions best adapted to secure the greatest yield of work with it. The selection of the initial fuel material is influenced, first, by the relative ease with which it may be made from petroleum or

other raw material, and, second, by the conditions which it requires for its best combustion.

The first factor, that of the preparation of the fuel from petroleum or other sources of raw material, is dealt with in other papers of this symposium; the conditions for best combustion may be outlined here so as to show some of the controlling conditions influencing the selection of fuels.

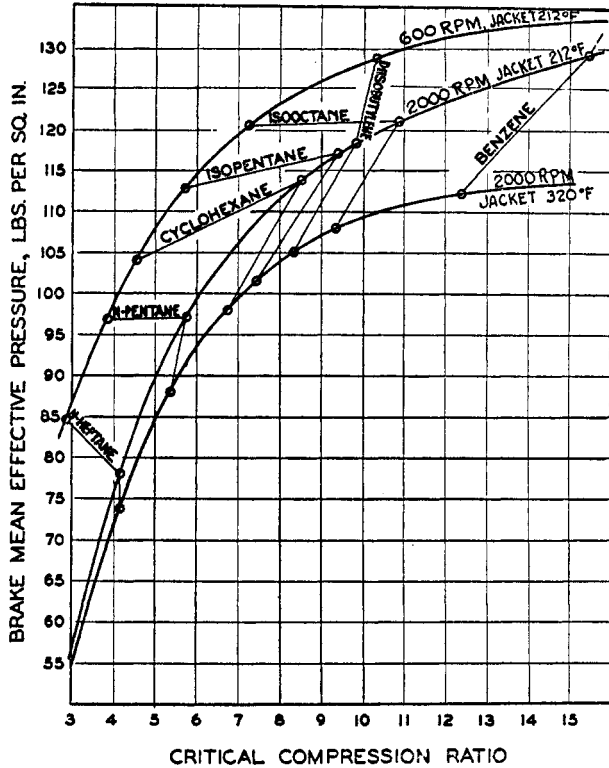


FIG. 10. Power characteristics of a $3\frac{1}{2}$ in. x $4\frac{1}{2}$ in. single-cylinder, variable-compression engine. Mixture ratio and spark timing for maximum power. Mixture temperature approximately 60°F .

As is well known, the compression ratio gives a fair index of the relative thermodynamic efficiency of combustion, if and only if other factors are kept constant. The numerical values of compression ratio so obtained, however, are quite without absolute significance, except as they pertain to the particular conditions utilized. An evaluation of such a scale is figure 10, where, taking the data from one variable compression engine, brake mean effective pressures are plotted against the compression ratios at which the engine was operated. Spotted along the curve are a number of

points which represent the highest compression ratio at which the hydrocarbons indicated may be used without knock, under the particular conditions of the tests. Three such curves are shown, representing different engine speeds and different temperatures of the cylinder jacket. It is obvious from the three curves that with different fuels there are very great differences between the efficiencies or power outputs possible with knock-free operation.

Equally important are the changes in the relative behavior of different hydrocarbons when burned in an engine under different operating conditions. The paraffins and cyclohexane decreased in knocking tendency as the speed was increased. Diisobutylene, an olefin, knocked more with increasing speed, as shown by the lowering of the critical compression ratio with increased speed. Increasing the jacket temperature resulted in general in an increase in knocking tendency, although the change varied greatly from one fuel to another.

The comparison between isoöctane and diisobutylene is of particular interest because it illustrates the differences in knocking characteristics, as affected by engine conditions, that may exist between an olefin and the corresponding paraffin. At 600 R.P.M. diisobutylene has much less tendency to knock than isoöctane under the engine conditions represented in figure 10. But at 2000 R.P.M. the relative knocking tendencies of these two hydrocarbons are completely reversed and the saturated paraffin, isoöctane (2,2,4-trimethylpentane), becomes the superior fuel.

These data indicate that the relative knocking tendencies of different hydrocarbons may be expected to be affected to a considerable degree by changes in engine conditions. Consequently the choice of fuel and engine conditions to be used for the production of maximum output involves an evaluation of the relative effects of a number of different variables, of which only two of the more outstanding ones—engine speed and jacket temperature—have been discussed herein.

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