

MORE EFFICIENT UTILIZATION OF FUEL

BY CHARLES F KETTERING¹

IN general, this article, which was presented to awaken interest and stimulate curiosity in a subject of vital importance to the automotive industry, deals with the fundamentals of combustion of various fuels in internal-combustion engines. The discussion includes broadly

- (1) The importance of chemical structure in the study of fuels. Such knowledge is necessary to understand refining processes and the reactions taking place during combustion in a gas engine.
- (2) Boiling points versus specific gravity of fuels. Specific gravity is a term of slight moment; it has nothing to do with what fuel really is or how it performs in service. The distillation curve is the best index of a fuel's suitability
- (3) Benzol and alcohol as engine fuels. Further proof that chemical structure plays a prominent part in fuel performance
- (4) The phenomenon called "engine knocking." Theory is proposed that knocking is caused largely by change of fuel structure into secondary or intermediate compounds, the so-called "detonable compounds," during combustion. This theory is based upon the fact that fuels, capable of high compression without any knocking tendency, are compounds which do not decompose at low temperatures and pressures
- (5) Pressure-volume and pressure-time indicator cards and their interpretation. The cards show genuine preignition, normal combustion and fuel knocks
- (6) High-compression fuels and engine performance; again showing that certain chemical structures possess high critical temperatures and pressures
- (7) Some of the specific fuel problems

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- (8) The need of more effective co-operation. On account of the constantly decreasing quality of fuels, investigation and study of the situation become imperative

As far as the automotive engineer is concerned, there are two problems involved in the fuel situation, each of which is of great importance. These have to do with the application of fuel to an internal-combustion engine. One is getting the fuel into the engine, and the other is burning it there.

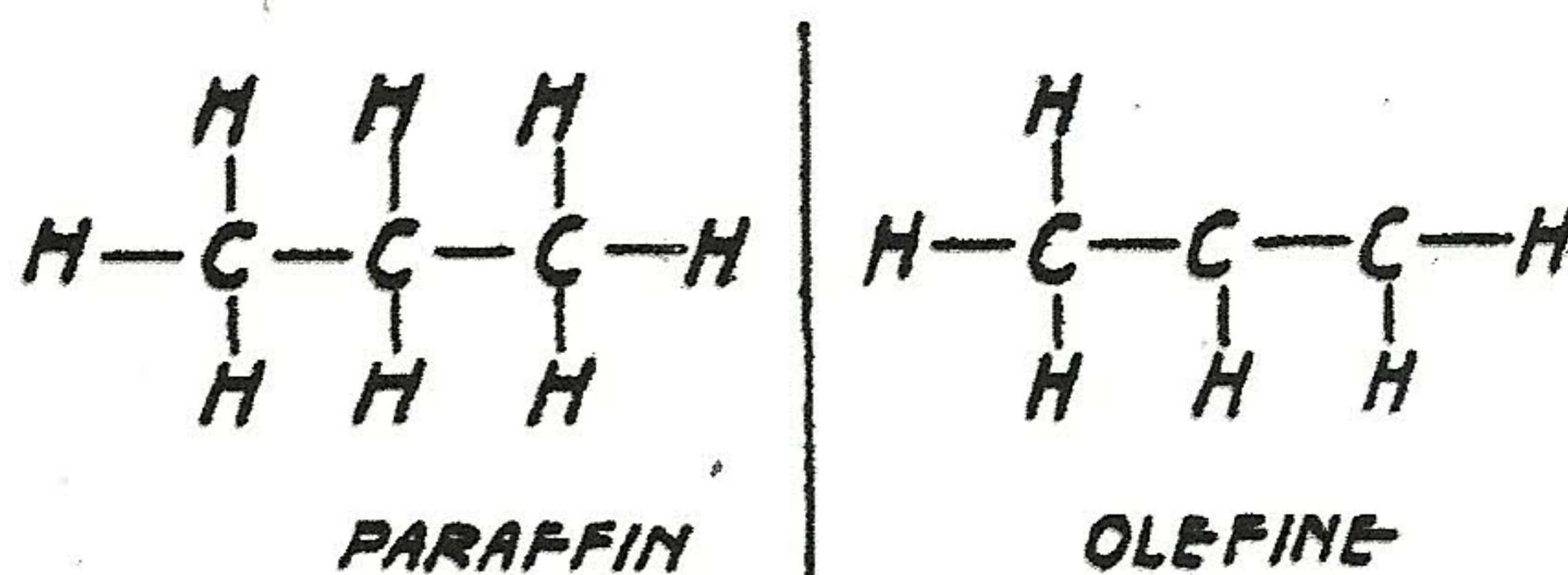
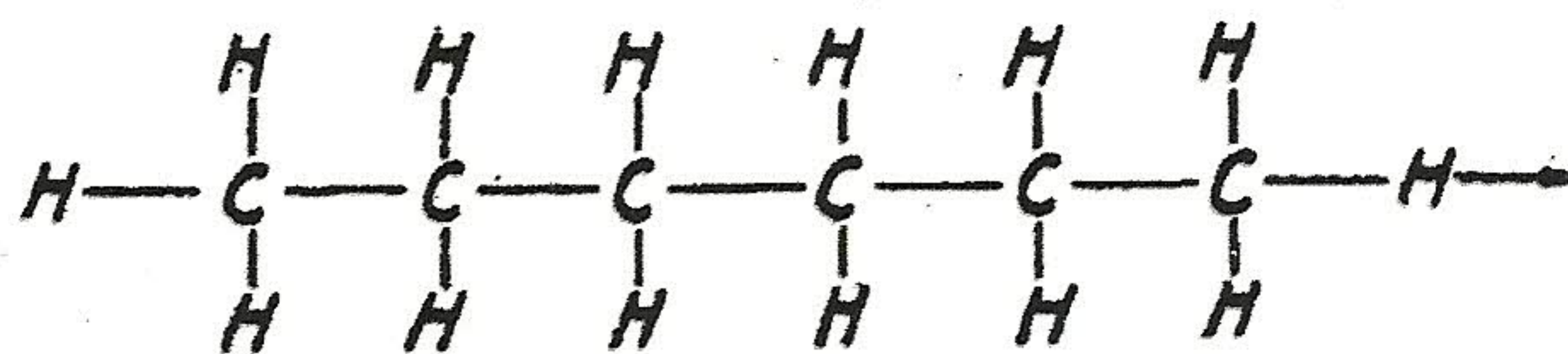
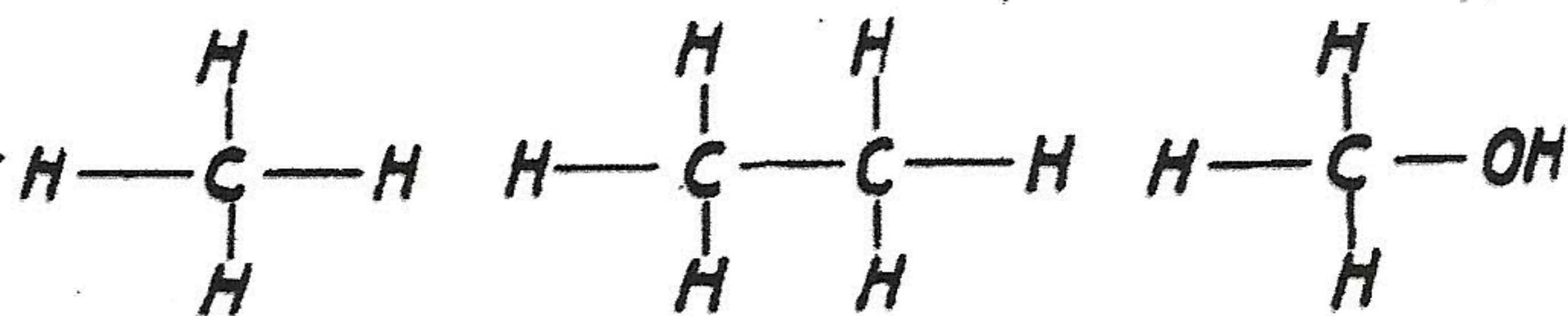
To get the fuel into the engine, innumerable devices have been constructed and given consideration, and yet I think we all recognize that the results from these have been disappointing, because they did not solve the problem that really needed solving; namely, what happens inside of the cylinder. Having recognized this condition of practically complete ignorance as regards what goes on within the cylinder of an engine during operation, we started to see what we could find out about it. Naturally it is a little difficult to sit around in a cylinder while it is in operation and tell just what happens there, so we had to devise means of staying outside and still telling what was going on inside. In doing this, we had to build some new instruments, and theorize. The result is that some things I am going to tell you may not be true, but it is not my fault if they are not.

In discussing the question of fuels I think it would be well to go back a little. Our present idea of fuel is that a satisfactory fuel must have a certain gravity. I want to go into the fuel situation a little more deeply than merely determining its uses according to its gravity. It has been a general observation that as we lower the gravity of a fuel, such as the present commercial fuels on the market, even though we get the fuel properly distributed, we have to lower the compression of the engine because of the knock which results. This knock is the kerosene knock, preignition, pinging, or whatever it is called. To make my subsequent discussion somewhat more intelligible I want to first discuss briefly the construction of a fuel, its relation to gravity, etc., and then what happens when we try to burn it.

CHEMICAL COMPOSITION

All of our fuels are hydrocarbons. I think we have all studied the subject enough to know that a hydrocarbon is a very uncertain and miscellaneous individual,

consisting of varying combinations of carbon and hydrogen. If we start out with carbon we see that it is a four-valent element, that is, it has the ability to combine with four uni-valent atoms, such as hydrogen. The simplest hydrocarbon combination is that in which four hydrogen atoms are combined with a single carbon atom, the bonds uniting the hydrogens with the carbons being as indicated. This compound is methane, which is a large constituent of natural gas. The chemistry of the hydrocarbons would not be very difficult if it always worked out as in the case of methane; that is, if each carbon atom always united with four hydrogen atoms, or four uni-valent atoms. But the carbon also has the ability to combine with itself, that is, to satisfy certain of its chemical bonds by combining with other carbon atoms. It is quite possible to have another compound in which two carbon atoms are united, each in addition having certain hydrogen atoms united with it. The first compound referred to above is said to have the formula CH_4 , and the second the formula C_2H_6 ; but I will show that such a formula really means nothing. If we insert another carbon atom between the other two and



SOME OF THE SIMPLER HYDROCARBON COMPOUNDS AND WHAT HAPPENS WHEN A COMPLEX ONE IS CRACKED

add the two hydrogen atoms to it, we get a third hydrocarbon, the formula for which is C_3H_8 . In other words, if we take a series like this and add a carbon atom each time, with its corresponding hydrogen atoms, we get a general formula which may be expressed thus: C_nH_{2n+2} . In this series the compounds become very long, and increase correspondingly in gravity. This increase in gravity gives a corresponding increase in the boiling point, and that boiling is only a simple way of measuring the weight of a molecule.

We have heard considerable talk about cracking. Now suppose we take one of these big-molecule compounds and break it in two. We will get two smaller compounds. We might have to throw away some of the carbon because if we break such a compound in two we will not have enough hydrogen for the end carbons. This does not necessarily follow, however, for it is possible to have a compound which apparently has not enough hydrogen in it. If we take one of these heavier hydrocarbons, for instance, and crack it in two we have as one compound a paraffin which is analogous to the compounds shown above, and as the remainder another compound which is obviously different from those called paraffins; such compounds being given the general name of olefins. The olefins have a general chemical formula of C_nH_{2n} . The cracking process then consists in breaking up these larger molecules into smaller ones. In breaking up hydrocarbons we put them in a big drum, hit them and hammer around and finally they get sore, as it were, and say, "What's the use? We might as well break up." That is exactly the way we get an increased volume of gasoline. There is, of course, some loss in throwing away carbon. I want you to keep this in mind, however: that, if heating under pressure and high temperature produces disintegration of these molecules in a cracking still, the same identical thing may happen when you maltreat the fuel in a gas engine. I want you to keep this specifically in mind because heat and pressure have about the same effect regardless of where they happen to be, in a gas engine or in some other place.

I want to impress upon you another very important fact. If you take the heat of a pound of carbon and the heat of a pound of hydrogen, you will find, if you burn the gas CH_4 , mentioned above, that you will not get the same amount of heat from this gas as you would expect if you added up the heat contained in the corresponding

amounts of carbon and of hydrogen. It will always be somewhat less. This apparent loss in heat value is a result of what is known as energy of combination and enters largely into the study of chemical compounds. I want to impress on you the fact that each of these compounds has a certain heat value which is always less than the total heat value of an equal quantity of carbon and hydrogen in an uncombined state.

SPECIFIC GRAVITY OF FUELS

The question of gravity and the size of a molecule is a very interesting thing. If we start with the simplest compound of the paraffin series, CH_4 , and add carbon and hydrogen atoms to it, one of carbon and two of hydrogen at a time, we find that the first few compounds are normally a very light gas and extremely difficult to liquefy. As we come down the line, we find that the compounds would become normally liquid, and finally solid, in form. Carbon has an atomic weight of twelve and hydrogen of one, so that CH_4 has a weight of sixteen. As these compounds increase by CH_2 each time, which means an increase of fourteen in the molecular weights for each compound, it is quite obvious that the molecular weights will mount up rather fast. It is easy to see that these are actually physical things. There has always been one trouble with all of our theoretical work. We take up this molecule as though it were simply something to think about and to talk about. But these are real physical things and the combination and decomposition of these things are real physical facts. I think that if we all could get the point of view that this is not complex at all, and we could get somebody to write a chemistry that would make it appear simple instead of complex, we would all get interested in this and be able to do much good by actually studying the fundamental phenomena.

As I mentioned before, the more carbon atoms we get into the compounds, the heavier the fuel becomes. It was for this reason that we, a long time ago, began to measure our fuel by hydrometers. If it measured 72 deg. it was fine. Finally it began to go down and down, and we tried to force upon our oil people the idea that gravity had something to do with a fuel's desirability. Now gravity has not a thing to do with it.

Suppose we started a food law in this country that we had to sell potatoes not by the bushel or by the pound, but that there must be so many potatoes to the

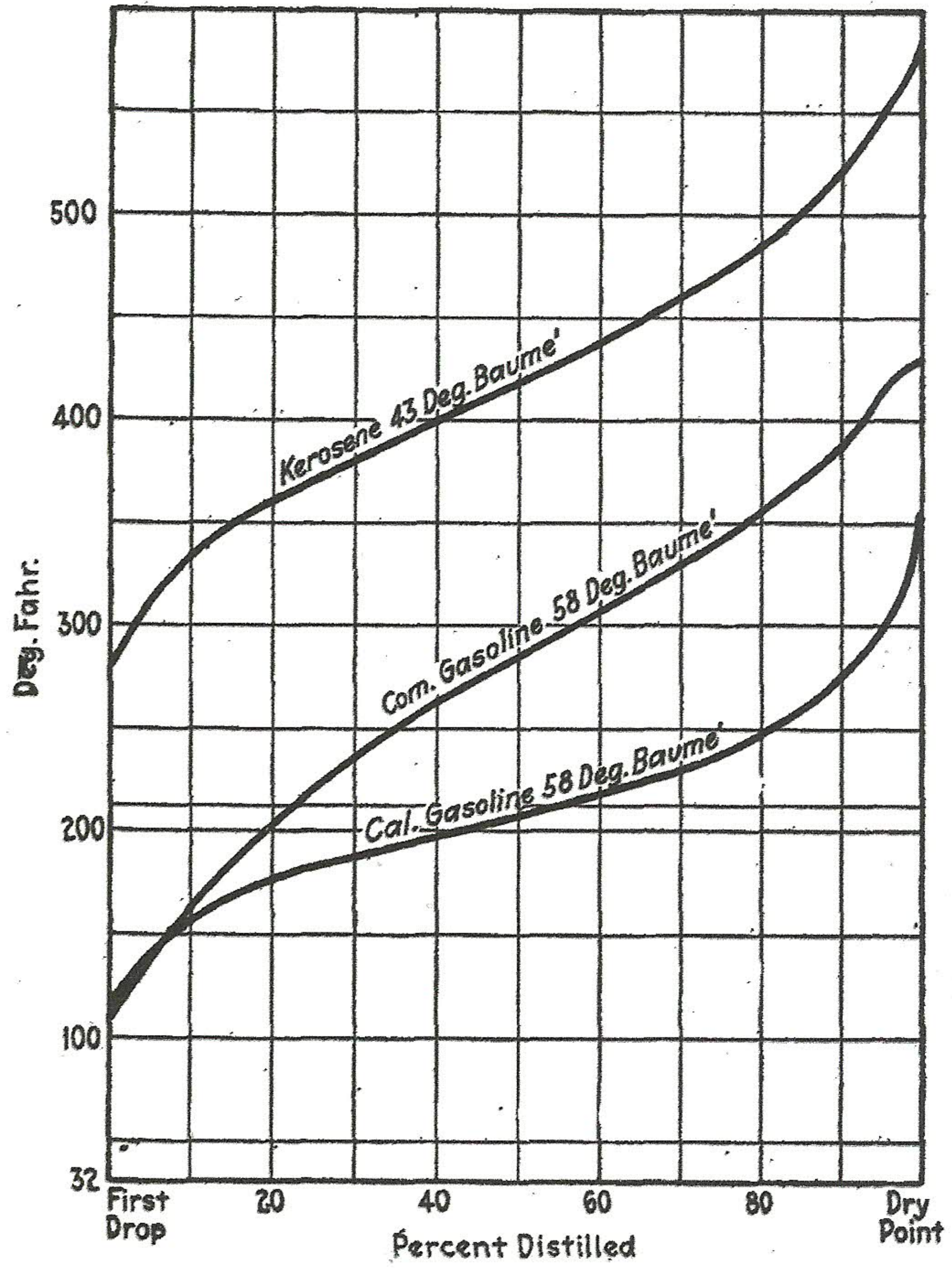
bushel, and that they must have an average weight per bushel. This is actually what we asked the fuel people to do. Suppose the food inspector comes around and examines a bushel of potatoes. He counts the potatoes and says, "There are not enough"; so he takes out one big potato and puts in a couple of small ones and the potatoes are O K'd by him. Then, after the potatoes are sold, they are placed in a pan and put into an oven to bake. And if we leave them in there for an hour, the little potatoes are burned to a crisp and the big ones are not cooked through. Exactly the same thing happens with fuel. There is no difference whatsoever. The average of our fuel may be all right, but that does not mean that we have anything like a good fuel.

Distillation curves have come to be a measure of fuel suitability. They are of a great deal more importance than its gravity. I have had charts showing certain distillation curves prepared. In the chart there is shown a kerosene curve. This kerosene had a gravity of 43 deg, and it started to distill off at about 275 deg. fahr., the percentage evaporated increasing with continued heating and a rising temperature until it finally goes dry at 600 deg. fahr. This is a characteristic curve. This chart also shows commercial gasoline having a gravity of about 58. It shows, in addition, a very interesting and significant fact. When the curve of a California gasoline of 58 gravity is compared with the curve of this other gasoline of 58 gravity, it is seen that the California gasoline has a considerably flatter curve. The reason for this I will show later. We all know that there have been developed in California many wonderful kerosene carbureters which were sent to us here in the East, but which, when put on our engines, failed signally to live up to the claims made for them. This is easily explained. The fact is, California kerosene is often a great deal better than our gasoline, so far as carburetion is concerned.

BENZOL AND ALCOHOL AS FUEL

In addition to the types of hydrogen and carbon compounds already discussed, which, because of the arrangement of the atoms therein, are called "chain" compounds, there are certain other hydrogen and carbon combinations called "ring" compounds. One of the simplest and probably the best known of these is benzol. In this there are six carbon atoms, with three single and three double bonds connecting them, each carbon atom

having a single hydrogen atom attached to it. The formula for this compound is C_6H_6 . As you no doubt remember, when Mr. Crane was discussing his paper on Possible Effect of Aircraft Engine Development on Automobile Practice he mentioned the fact that by the addition



DISTILLATION CURVES OF VARIOUS INTERNAL-COMBUSTION ENGINE FUELS

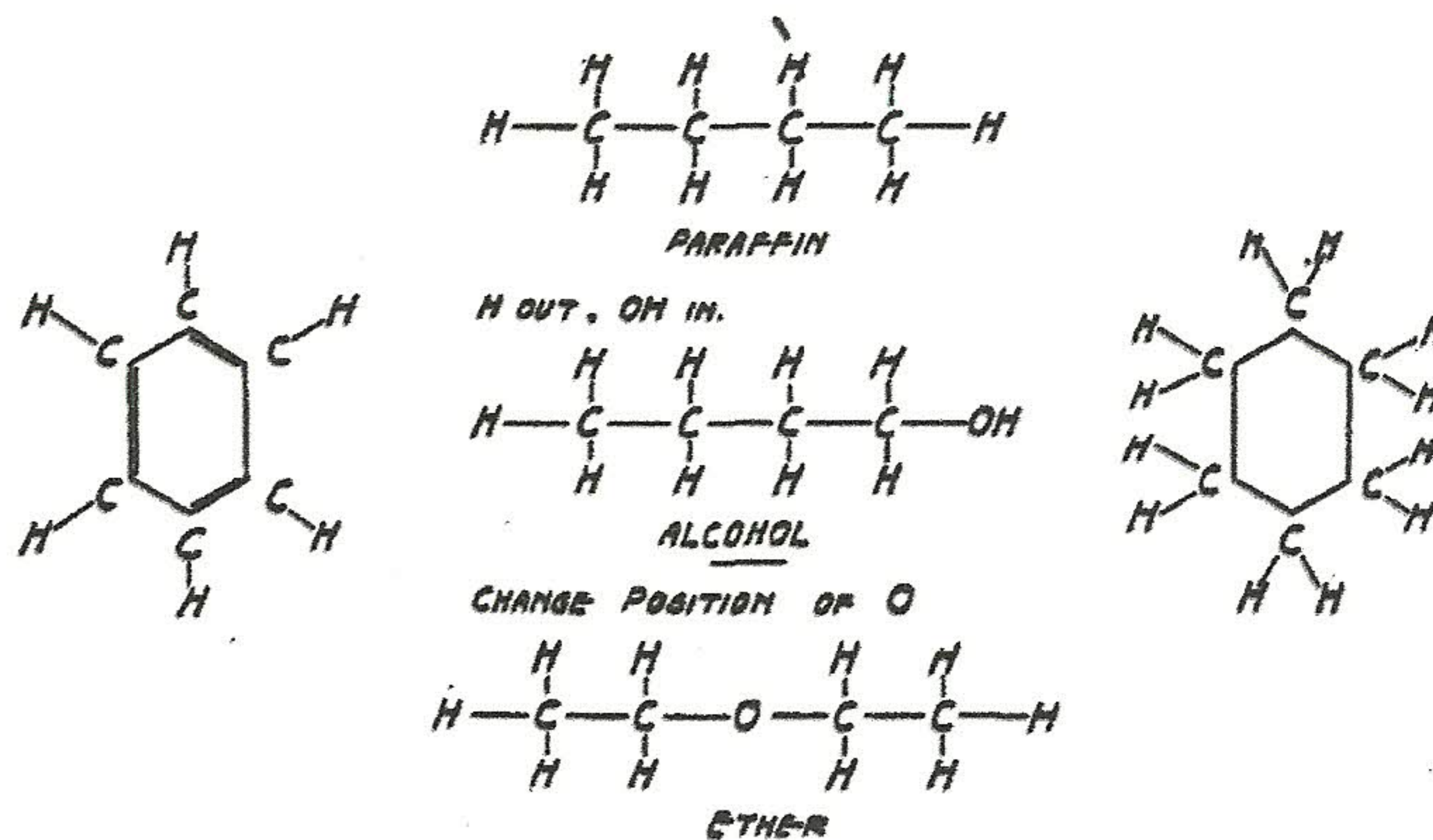
of a certain amount of benzol to a fuel, certain very interesting results are obtained. That does not of itself mean that benzol will necessarily make a good fuel, because there happen to be other considerations involved.

If we run benzol on full load it gives satisfactory results. It is so high in carbon as compared with the amount of hydrogen that if we do not run it on full load very copious productions of carbon in the engine result. This carbon, however, is quite different in character from the carbon which results from the burning of kerosene. It is a fine, fluffy or flaky deposit, not at all gummy or sticky like a kerosene carbon deposit and is blown out readily in the engine exhaust. It does carbonize the spark-plugs badly, however, and will interfere seriously with the running of the engine.

An interesting thing about this type of fuel is that all of the "potatoes" are exactly the same size. The benzol distillation curve represents a mixture of certain of these uniformly sized "potatoes," and we can see what happens. After we get up to a certain temperature, the fuel begins to distill off and practically all of the fuel goes off at that temperature. In other words, all the molecules weigh the same and they all get out at the same time. At the very end of the distillation curve the end point goes up rapidly. A fuel having this characteristic may or may not have desirable characteristics from the standpoint of distribution, but its functioning after it once gets into the engine may be of an entirely different order from the functioning of another fuel having a corresponding gravity. This fuel may be of much lower gravity than another type and yet function very much better under combustion conditions within a cylinder. The gravity of a fuel has absolutely nothing to do with what the fuel really is, or how it performs in service. The main point I want to present is that the fuel proposition, so far as future engine design is concerned, is practically a question of chemical construction and make-up, together with energy of combination that exists within the fuel itself.

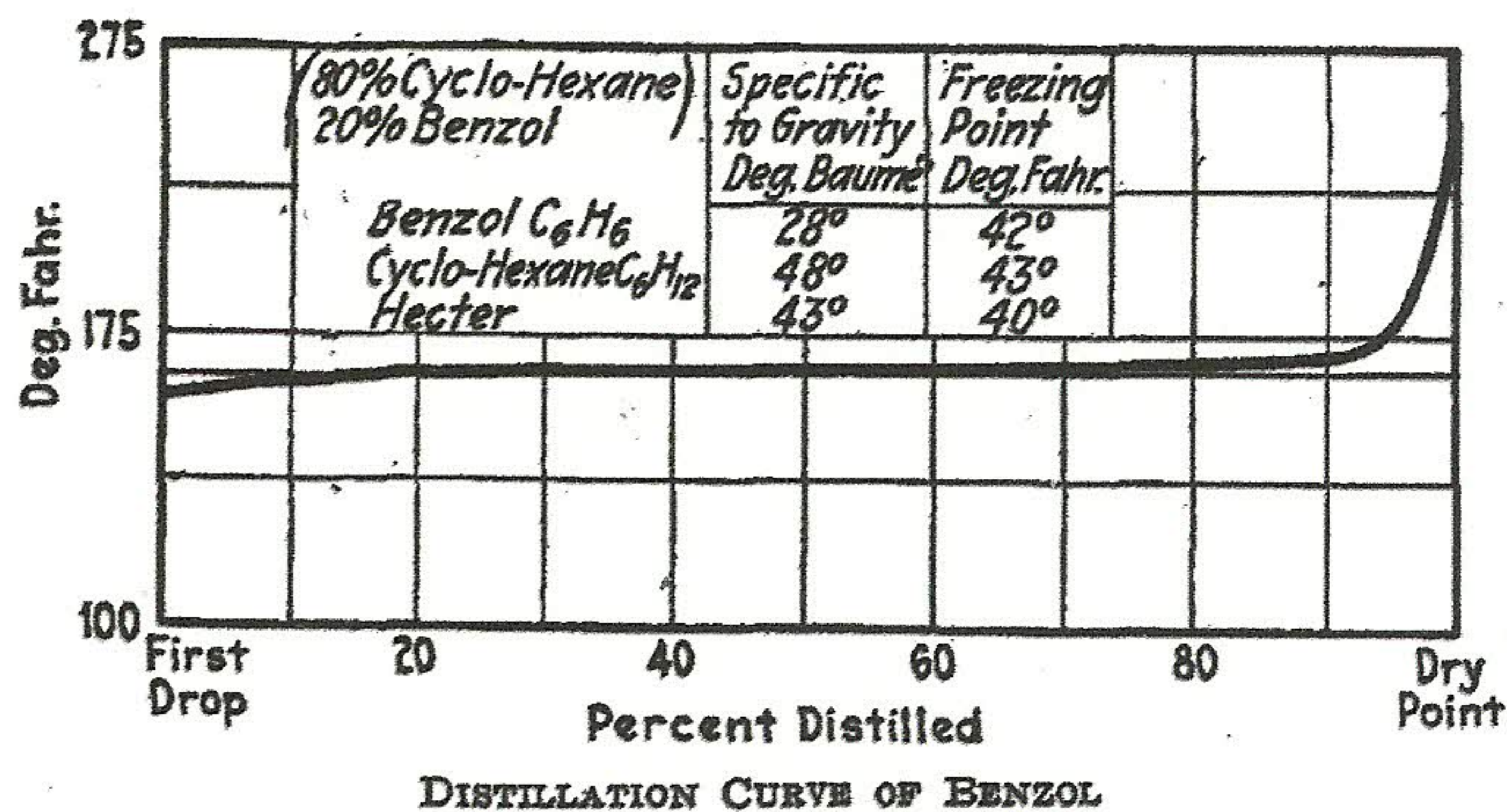
There is still another illustration of the fact that the chemical formula does not mean anything. If we take benzol and break the double bonds existing in the benzol ring and add a hydrogen atom to each carbon atom we will get a compound having the formula C_6H_{12} , which represents a certain thing and a certain specific gravity.

We have heard a great deal of discussion about alcohol. The formula is $C_nH_{2n}O$; but that is not a very good way to write it. It is better to write it in the manner illustrated herewith. If we take a "chain" compound of the structure shown there and trade the hydrogen atom



TYPICAL "RING" AND "CHAIN" HYDROCARBON COMPOUNDS AND THE CHANGES PRODUCED BY VARYING THE RELATIVE POSITIONS OF THE DIFFERENT ATOMS

for a hydrogen and oxygen atom, we get a compound having the structure shown there as alcohol. That hydrogen substitution is the only difference between paraffins and alcohol. The paraffin compound has a certain gravity and will function in a certain way. The alcohol corresponding thereto has a certain gravity and functions in a certain way. The fuel value of these two compounds following the substitution of OH for H is quite different. The alcohol does not burn the same way or act the same way. We have the same amount of carbon in each and practically the same amount of hydrogen, but we have an oxygen atom hooked up in connection with one of the hydrogen atoms. Investigation will show that it takes practically one-half the total amount of heat



available in the fuel to get an oxygen atom into the compound, and yet consideration of the actual atoms within the compound would tend to show that it should have about the same amount of heat as before the change occurred.

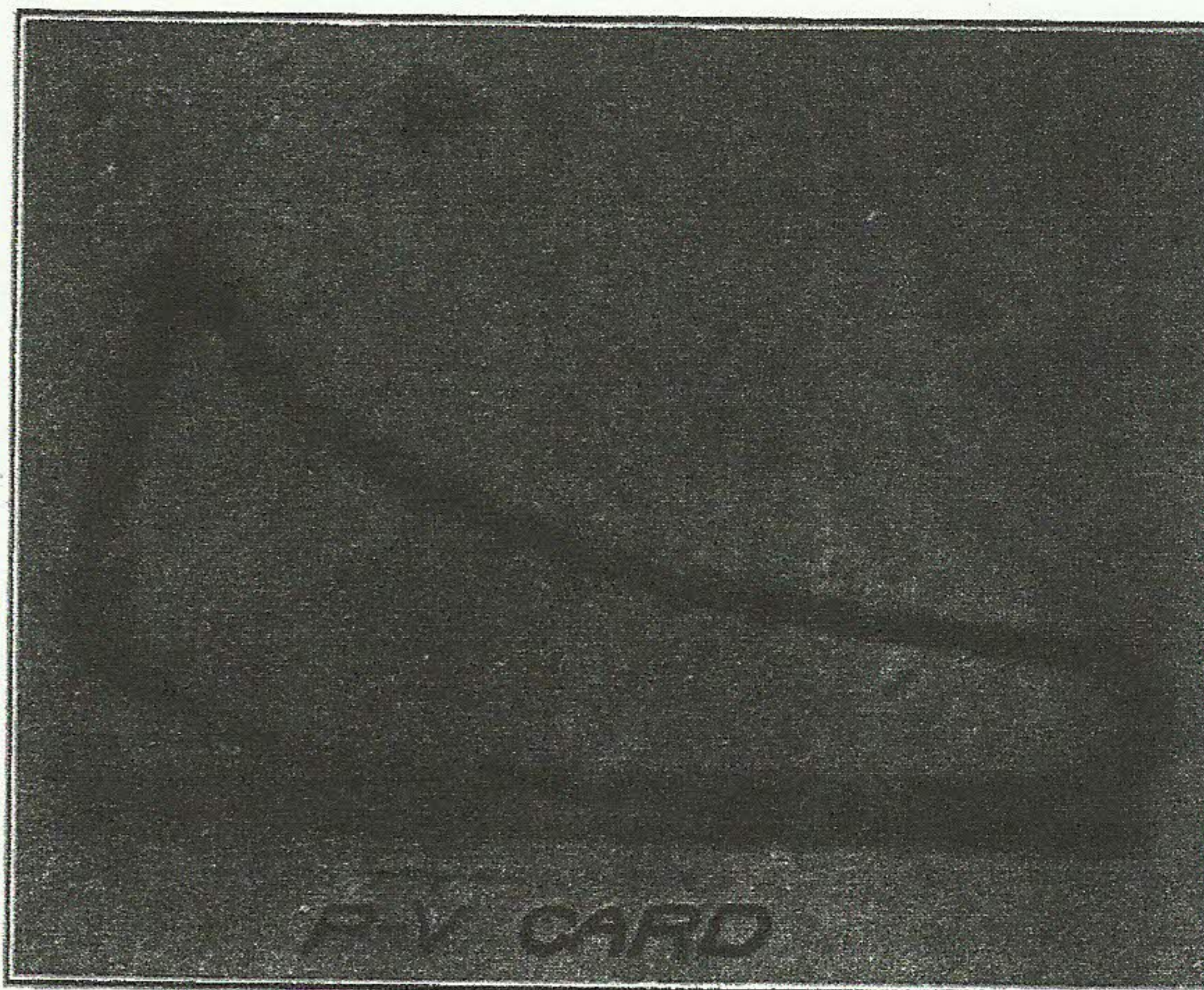
Suppose we take the alcohol illustrated and use exactly the same atoms, but simply shift the arrangement of them a little, so that the oxygen is connected to two carbon atoms and not directly to any hydrogen atoms as shown; in this case we have the hydrogen atoms in the same place and the carbon atoms in the same place, except with relation to the oxygen atom, but we now have ether instead of alcohol. The two have exactly the same composition so far as the number of atoms is concerned; so that the chemical formula, if merely written out, would be exactly the same thing, $C_4H_{10}O$. If we bought alcohol according to chemical formula, we might easily make a mistake and put ourselves permanently to sleep. Also, performance in an engine is entirely different. The gravity of these two is practically the same, but the boiling point of the ether shown is 95 deg. fahr., while that of the alcohol shown is about 243 deg. fahr. Inasmuch as they have exactly the same chemical formula, it is obviously of great importance to know something about their structure and make-up, to determine performance as fuel. If we refine our shale oils, and are going to make the right kind of engine to run on such oils, we have to know what kind of business relationship the atoms have gone into with each other before we can handle the oils properly.

CYLINDER KNOCKS

I have mentioned energy of combination because to us it has proved very, very interesting, inasmuch as it apparently affects fuel action very directly. As I said before, as fuels of lower gravity came into use it became necessary to lower compressions. The general idea has been that this lowering of compressions has been necessary because of preignition. To study this problem we developed an indicator which gave us a new but very satisfactory type of indicator card. This indicator is different in that it gives pressure-time indications and not pressure-volume. As a result of our work with this indicator, we discovered that the knock which comes from kerosene is an entirely different thing from actual preignition. We have made hundreds of indicator diagrams

or cards with this instrument and each of them is very different from the usual pressure-volume card secured with the ordinary indicator.

A card made with our indicator is also shown illustrating the normal burn in an engine cylinder, without any evidence of a knock. As you can see from this card, pressures begin to go up at the instant the compression stroke of the piston is started and increase uniformly until ignition, after which pressures go up rapidly to a maximum and then taper off gradually during the work



A TYPICAL PRESSURE-VOLUME CARD SECURED FROM AN INTERNAL-COMBUSTION ENGINE

stroke of the piston. The difference between the cards made on these two types of indicator is quite obvious and needs no explanation.

Another card made with our indicator and illustrating a case of true preignition is reproduced. The kerosene knock occurs in a region of from 10 deg. after ignition to 25 deg. past top center on the down stroke. In one card shown, the knock occurs fairly early in the combustion stroke, while in another its occurs at approximately 25 deg. after top center and on the down stroke of the piston.

These cards proved tremendously interesting to us and we began to study the knock to see what it is and why it is. In the course of our study we have been theorizing

and reached the following conclusion. If we take a complex molecule and start to burn it, it will not burn by a single step from the carbon and hydrogen in it to carbon dioxide and water, but as it starts to break down it may be decomposed into a variety of compounds. If during this burning we should happen to liberate, for an instant, as intermediate products of combustion, some compounds of an extremely explosive or detonable nature, we would, upon explosion of these compounds, get such a sudden rise in pressure as is indicated in the cards shown. Now the compounds which form, if these big molecules do break down in this way, will differ, depending upon the temperature and pressure conditions at the time combustion takes place. That is, the type of compounds which are formed will vary with the compression, explosion pressures and the temperatures which exist in the cylinders.

In studying the conditions existent within the cylinder during knocking we endeavored to get an actual view of conditions within the cylinder at the time the knocking took place. To do this we put a window in the cylinder and pointed a spectroscope at this window. In this way we were able to reach some rather definite ideas as to the substances or compounds actually present and causing the knock. As a result of these observations we came to the conclusion that the compound which caused the trouble is acetylene. I will admit that this is one of the things that we have only theorized about so far and that we do not know now that this is really true.

What takes place within a cylinder when the knock occurs may readily be in accordance with my previously mentioned conception. You have all seen the grains of powder used in big guns. It comes in little sticks with perforations through them. Now you can take one of these sticks and light it with a match and hold it in your hand as it burns and it is perfectly harmless. But if you stuff that powder into an iron pipe and screw the end on it and light it, and then get away in time, you would witness quite a different reaction. The reason is that when you vary the pressure and temperature conditions you change the entire nature of the burn. In other words, in the first case you are simply burning the stick of powder as you would any other inflammable hydrocarbon, while in the second case you are releasing its energy of combination in a very short space of time. The resulting variation in the chemical reaction which

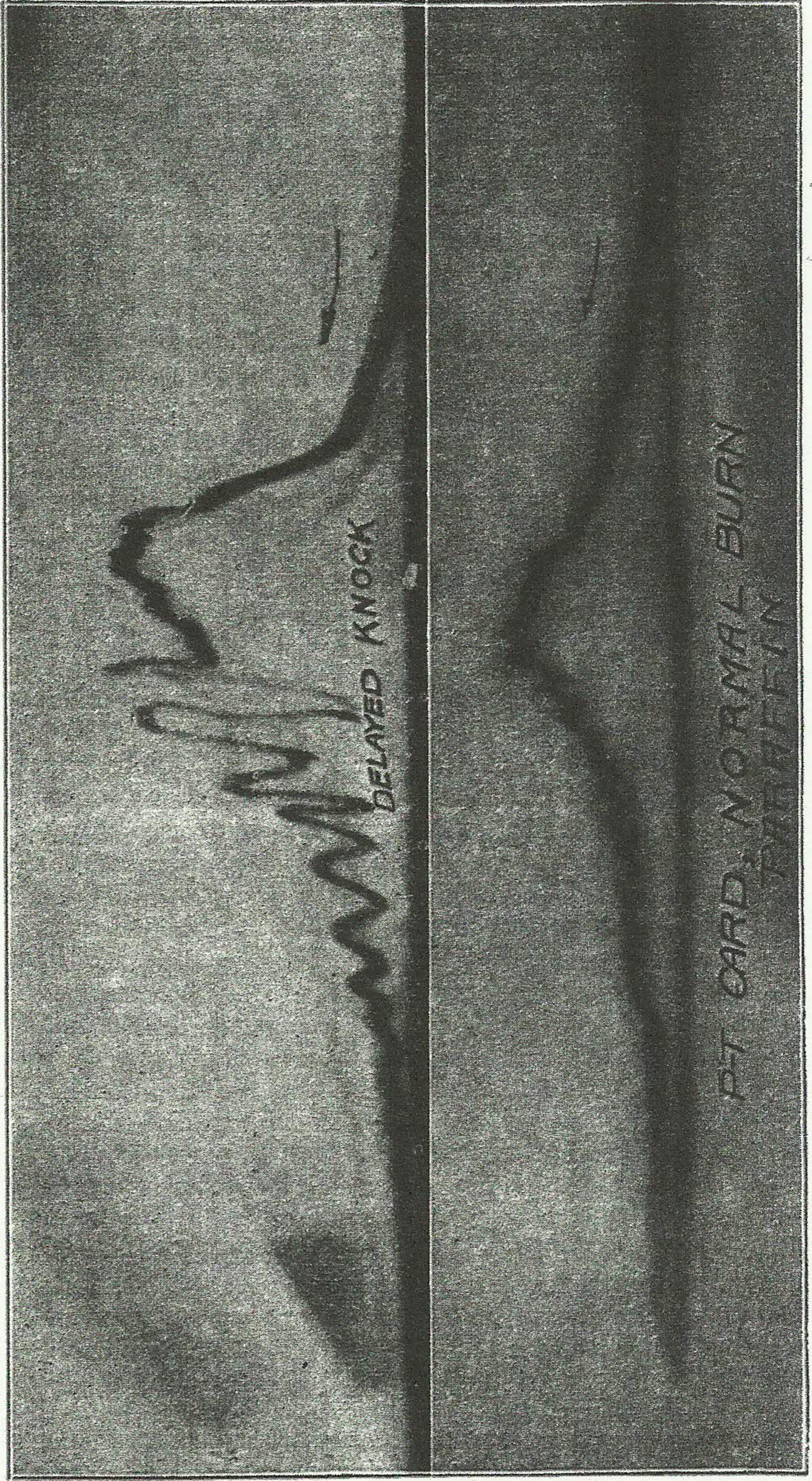
takes place causes the sudden building up of pressure that we call an explosion.

If our idea of the formation of secondary compounds is a true one, then if a fuel can be found which will burn by a single step from carbon to carbon dioxide and from hydrogen to water, it should be a fuel which does not give a knock. We started out by taking benzol. But we found that it was not a satisfactory fuel because of its free liberation of carbon upon burning. So we took this benzol and broke the double bonds between some of the carbon atoms and hitched on an extra hydrogen atom to each carbon atom, so that instead of being C_6H_6 , it became C_6H_{12} . This, of course, made a material difference in the gravity of the fuel. And, incidentally, I might state that the gravity of benzol is only 28 deg., so that if a man were buying it by gravity he would imagine himself to be getting a very poor fuel. The gravity of C_6H_{12} , the name of which is cyclohexane, is 48 deg.

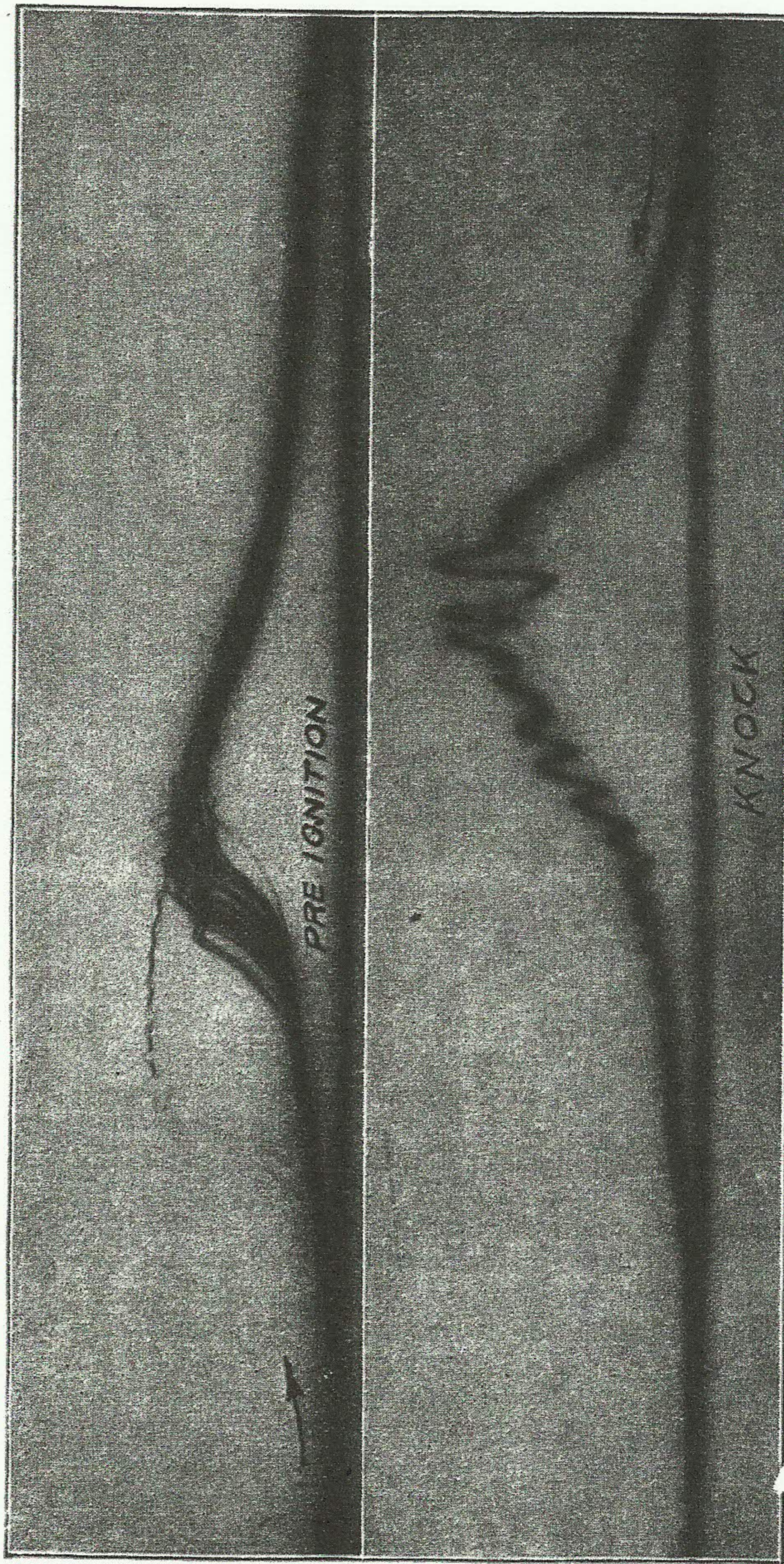
TESTS OF CYCLOHEXANE

Now here is the interesting thing about this cyclohexane. When we made it up and used it in an engine it acted differently from any fuel we had ever had. It took a long time for it to sink into our heads, but finally this fact came home to us: if a fuel burns by a single step from carbon to carbon dioxide and from hydrogen to water, the explosion will be absolutely independent of the compression, because the temperatures and pressures can only rise to such points in the cylinder as the products of combustion permit. That is, the temperatures of combustion cannot rise above the dissociation temperature of the products which result from such combustion. Consequently, when this fuel is used in an engine cylinder we get a pressure-volume card that looks like a steam-engine curve. And we can, without materially raising the explosion pressures, run this fuel on any compression up to the point of actual preignition, caused by the temperature rise due to compression reaching the ignition temperature of the fuel. This brief outline of our work with this fuel seems to indicate that the knock is certainly due to the formation of secondary or intermediate combustion compounds, detonatable compounds we call them, which let go unexpectedly and cause an abnormal rise of pressure.

Why then should lowering of compression prevent the development of the knock? Simply because lowering the



PRESSURE-TIME INDICATOR CARDS SECURED BY A SPECIAL INTERNAL-COMBUSTION ENGINE INDICATOR WHICH SHOW TYPICAL OPERATING CONDITIONS



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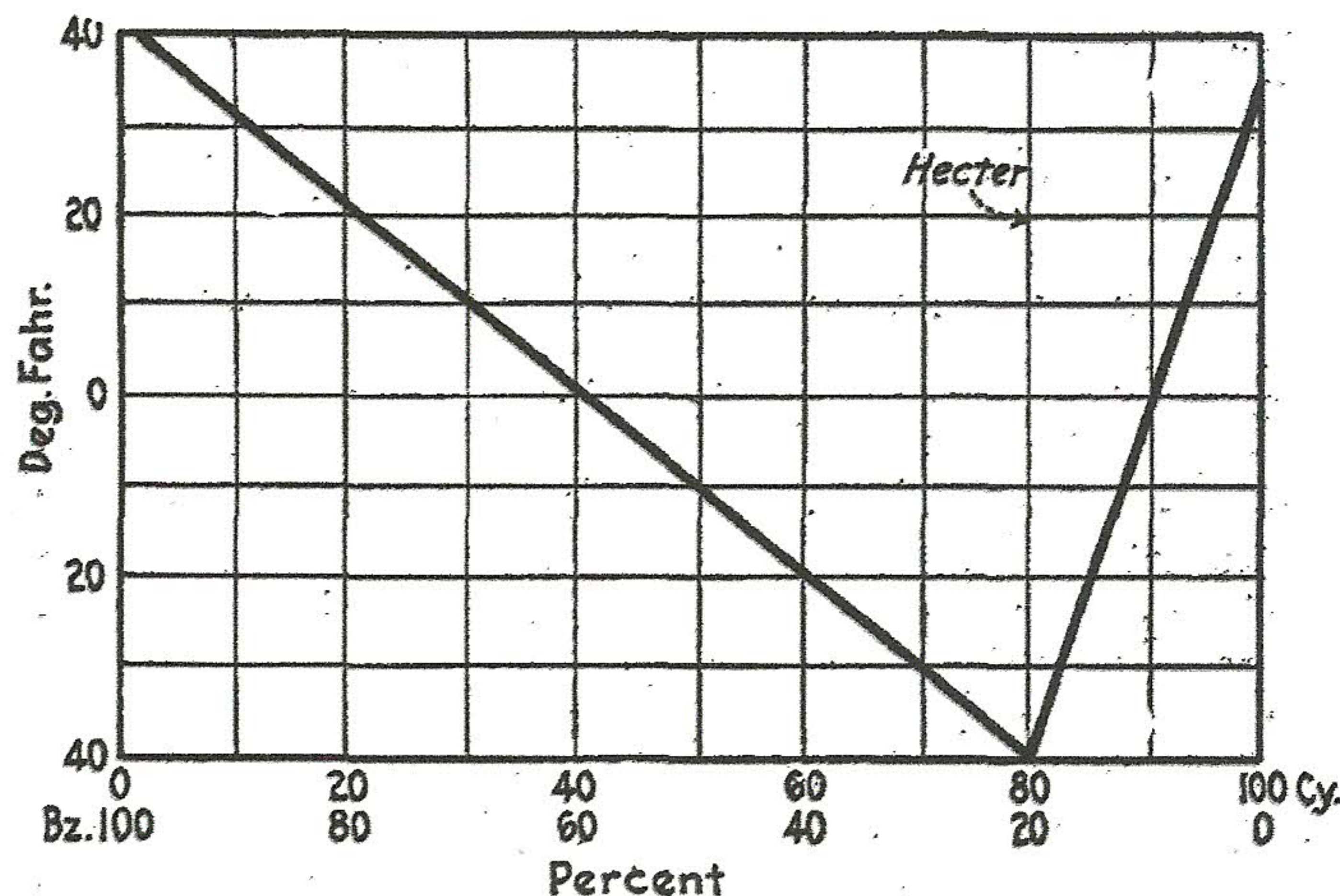
compression results in a substantial lowering of the maximum combustion temperature within the engine cylinder.

For testing cyclohexane we built a Liberty engine having 200-lb. compression, and this fuel burned at such high compressions without any knock whatever. With the best grades of gasoline that we could secure we could not use compressions in excess of 125 lb.; in fact, without very careful selection of gasoline the compression could not be run up to more than 100 lb.

There is another interesting thing leading us to believe that there is a critical temperature beyond which we cannot go without causing an entirely different type of combustion to take place in the engine. If we take an engine operating at 75 to 80-lb. compression, start to run it on kerosene and let it warm up, there will be no knock during this warming-up period. As soon as the engine gets up to operating temperature, however, it will start to knock, and it will immediately heat up, with loss of power and other evidences of poor performance. However, if we introduce into the fuel that is being used 3 or 4 per cent of ethyl iodide, we can run the same engine right up to full compression without knocking and accompanying troubles. In other words, the engine will run as well as it does on gasoline. The reason for this is, we think, that below 1200 deg. fahr. iodine exists in the form of molecular vapor, but between 1200 and 2000 deg. fahr. the iodine vapor breaks part into an atomic vapor and in so doing uses up a considerable quantity of the heat energy resulting from the combustion within the cylinder. And the heat energy so used up will just ease off the temperature curve, flatten it out, in other words, and hold the maximum temperature below the critical line so that the secondary explosive compounds will not be formed.

There are a great many interesting phases and peculiar things in connection with the fuel game. My idea has been to present this subject to you more as a means of stirring up your interest and exciting your curiosity than supplying any fundamental engineering data. As an example of one of these interesting things, we found, when we investigated cyclohexane, that it would freeze at 42 deg. fahr. We also found that benzol freezes at 43 deg. fahr. Consequently, neither of these compounds of itself would make a satisfactory fuel, especially for airplane work where temperatures considerably below the

freezing point of each fuel are prevalent. We found out this very interesting thing, however. If we take some cyclohexane and some benzol and mix them, the freezing point of the mixture is considerably below that of either constituent. By mixing them in the proportion of substantially 20 per cent benzol and 80 per cent cyclohexane, we get a freezing point for the mixture of substantially 40 deg. below zero, fahr. If it were not for the facts in connection with this statement I know you would not believe that if two fuel compounds are taken, each one of which freezes at a comparatively high temperature, and are mixed together in certain proportions, the freez-



MIXING BENZOL AND CYCLOHEXANE REDUCES THE FREEZING POINT OF THE MIXTURE MATERIALLY AS COMPARED WITH THOSE OF THE CONSTITUENTS

ing point of the mixture can be reduced 80 deg. It is simply another case of molecular energy making such a thing possible.

I might go on into various interesting experimental data, but there are one or two other things that I want to bring out. We have all talked about carbon causing the knock in an engine and we know that when we clean the engine out we do not get the knock any more. And we have all had the idea that the reason we have carbon knocks is because some of the carbon heats up and pre-ignites the incoming mixture. That is not what happens at all. One of the best heat insulators we have is

carbon, and the only thing we do when there is a nice little carbon deposit in a gas-engine cylinder is to cut down the rate of thermal transfer.

SECURING BETTER ENGINE EFFICIENCY

One of our big problems in connection with fuels, therefore, seems to be to discover how to lower the temperature peak during combustion. We must remember, however, what happens when a cylinder is cooled too much. The crankcase gets filled up with anything but oil. The big problem then seems to be to get a more efficient regulation of temperatures. And we must make this a problem whether we desire it or not. The factors governing the supply of fuels are now such that we must take our present grade of fuel whether we want to or not. Consequently, we must study the relationship and the conditions which exist after we get the fuel inside the engine cylinder. No matter what the fuel manufacturers hand us, or where it comes from, we have to take it and burn it, and give satisfaction to the customers using it. None of us believes that the internal-combustion engine business is going to die out because we are having difficulty with fuel. But the amount of satisfaction the users of the engine will get is going to be proportional to the enthusiasm, pep, chemical knowledge, etc., that the engineer puts into the engine before he turns it out.

So I think it is only well at this time that we should begin to think in terms of the fuel question, not only from a supply and demand point of view, but also from an efficiency standpoint. We engineers have a lot to do from the latter standpoint; we have hardly touched the subject as yet. The ordinary engine running around the streets of New York has a thermal efficiency of from 5 to 10 per cent. We must make it higher. In our own work we have run some common ordinary engines up to 29 per cent thermal efficiency, and this without any very great amount of work on them. This leads us to believe that there is a possibility of going far beyond the range of our ordinarily prescribed limit of 25 to 30 per cent. I think that in 5 or 10 yr. from now it will be common practice to secure in the neighborhood of 35 or 40 per cent thermal efficiency.

Remember that a problem is what we think it is. If we think an engine can run only 10 hr. without repair it will run just that length of time. If we think it can

run 100 hr., the chances are it will. If there is any one thing the war has demonstrated to us, it is that we have not exhausted anything like the mechanical possibilities of any device. Anything that man creates is only a physical representation of his mental conception of it. If some one should come here from some other world he would get a very bad idea of the mental conception of our automotive engineers, if they do not get busy on the little simple problems of settling this fuel question. In this talk I have shown where I think the problem lies. No matter what kind of injection devices or other instruments we may have, there is the problem of finding out how the fuel acts after it is inside the cylinder, and we must work out this problem. And this problem can never be solved by any one individual. It is going to be solved by cooperation between the oil and the engine people and every one else.