Better Gasoline for Postwar Engines

By George A. Miller

Americans like engines, but more than anything they like powerful engines, and next to that they want them quiet, silent, smooth; perhaps a slight purr might be permitted, but they must not knock. To provide a gasoline to fit all these requirements, American petroleum technologists have experimented for years, and mounting octane numbers of the gasolines the refiners have produced both before and during the war bear witness to their success.

The question on everyone's mind now is what may we expect in the way of engine fuel in the postwar period? The gasoline drought during the war, rationing, the inconvenience of doing without a car were major annoyances to all motorists, but they put up with them pretty cheerfully for the most part. However, now that the war is over, and the jalopies are all out and the better cars have been taken off the roads and brought out on the road, the call is for "Some of that good gas—fill her up, if you please."

The solution of this problem of better gasoline for internal combustion engines, and better engines for the better gasolines, started, according to Graham Edgar of the Ethyl Gasoline Corp., with the genius of Charles F. Kettering, of the General Motors Corp., in recognizing the problem of knock. Next came the researches of Thomas Midgley and T. A. Boyd and their associates on antiknock agents which led to the discovery of the effectiveness of tetraethyl lead, the most satisfactory of some 33,000 chemical compounds tested in the development of a practical antiknock compound.

Discovered in 1859 by Bucton, tetraethyl lead remained a chemical curiosity until it was found to be a powerful antiknock agent in gasoline motor fuels. From then on it was the subject of much study and almost continuous research right up to the present day. It has been a decided problem child of the laboratory, but whatever problems it has entailed it has been an economic good, and as long as it continues to enable gasoline to produce the power men want from their motor cars and airplane engines it is likely to find a definite place in postwar fuels.

Launched on Feb. 1, 1923 at a single service station in Dayton, Ohio, under the name of "Ethyl" gasoline, now widely known the world over, gasoline containing tetraethyl lead found ready acceptance from a public that wanted more power and less knock from its fuel. A manufacturing accident in 1924 led to fears that the new antiknock fluid might be a menace to health and caused sales to be suspended in 1925 while the U. S. Public Health Service made a thorough investigation of the entire problem. Given a clean bill of health, ethyl fluid sales were resumed in 1926 and continued to rise rapidly through 1931. However, by 1932 the depression caught up with ethyl gasoline and a decline in sales was noticeable as with other premium products of that period. But in 1933 improvements in the refining of regular-grade gasoline raised its antiknock quality, and competition led to the introduction of tetraethyl lead into this type of gasoline further to reduce knock.

Growth in Use of Lead as Tetraethyl Lead in the United States From 1935 Through 1944.

(American Bureau of Metal Statistics)

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<tr>
<th>Year</th>
<th>Lead in Form of Tetraethyl Lead (tons of 2000 lb.)</th>
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<tr>
<td>1935</td>
<td>15,000</td>
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<td>1936</td>
<td>17,900</td>
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<td>1937</td>
<td>21,400</td>
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<td>1938</td>
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<td>1939</td>
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<td>1940</td>
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<td>1941</td>
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<td>1942</td>
<td>48,800</td>
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<tr>
<td>1943</td>
<td>60,300</td>
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<td>1944</td>
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In 1939 about 75 percent of all gasoline sold in the United States contained tetraethyl lead. In the aviation field, almost all gasoline of 80 octane number or better contained tetraethyl lead; in fact the performance of the modern military and transport plane was due in large part to the development of high-octane gasoline, a development in which tetraethyl lead played an important part.

Outside the United States the use of tetraethyl lead caught on rapidly in Canada, England, France, Australia, New Zealand, and Germany. Canada in 1939, according to the last official figures before World War II opened on Sept. 1 of that year, was using about the same percentage of leaded gasolines as was the United States, namely 75 percent.

Figures from a special report made by the Ethyl Gasoline Corp. in 1941 to the Office of Production Management indicated that 85 percent of all the motor fuel produced in the United

One unit of an alkylation plant

Photo courtesy Standard Oil Co. of N. J.

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States contained tetraethyl lead, and depended on this ingredient for much of its antiknock quality.

One of the unusual features about tetraethyl lead is that it has been on the market for 22 years and has experienced no serious competition. In fact its only competition has been that provided by refinery processes, developing unleaded gasolines. But according to Dr. Kettering, "the freer from knock the hydrocarbon is of itself, in general but not always, the more effective lead is in making it still better."

But before we go any further into the story of tetraethyl lead let's look into some of the causes that led to its development. In the early days of the automobile, gasoline was of high quality, much better in volatility, judged by its gravity reading, than any usually sold at the service station today. Oldtimers can remember when kerosine was the main business of an oil company, and gasoline was merely a by-product, something to be disposed of, and cheaply. Undoubtedly the abundance and cheapness of this "high-test" gasoline, often running around 77° Bé, had much to do with the speedy development of the automotive industry. Those were the days of surface paddle-type carburetors, magneto ignition, and strong-right-arm starters. Had the early motor car owners had the additional problem of low-grade gasoline added to their troubles with short-lived tires, chain drive, inefficient spark plugs, and imperfect lubrication they might have given up in disgust and stuck to horses.

However, with the invention of the electric lamp by Edison in 1888 the kerosine lamp was doomed, and by 1902 the excess of by-product gasoline began to dwindle. This made it possible for the refiner to use more and more of the unwanted kerosine to supply the higher volatile fractions to be dumped into the vanishing supplies of gasoline. By 1905 that good 77° Bé, gas was almost a thing of the past and the average had sunk to from 65° to 66° gravity. Of course, the refiner did not change the quality arbitrarily. He simply couldn't deliver enough of the original by-product gasoline—the demand was too great. He either had to lower the volatility or stop furnishing gasoline.

As the urgency increased for a solution of the problem—either to produce more high-quality gasoline or develop an engine that would use the lower grade more efficiently—inventive genius came forward with the jet carburetor, the self-starter, the exhaust manifold system for preheating the air before mixing with the gasoline, and the "hot spot," designed to deliver a dry gas-air mixture to the cylinders.

If one can forget for a moment the kind of gasoline he has been getting during the war, motorists have been enjoying a higher and higher grade of gasoline during the last two decades, thanks largely to tetraethyl lead, now a component of practically all motor gasoline, both "Regular" and "Ethyl." With the better gasoline came a gas of higher compression, to use the improved gas more efficiently. But something far better is in store—a plane-which has much greater antiknock properties than the best aviation gasoline of today can be used in much more efficient engines operating at far higher compression. Whether it can be sold cheaply enough to make its use economical seems to be a question yet to be answered.

The story of the jet carburetor is by no means over. It is in making it still better.

As the quality of the gasoline was degraded to increase its quantity, the automotive engineer designed an engine to take the new fuel. He cut the 95-lb. cylinder compression to 65 lb., but to make up for the motorist's demand for flexibility and power he gave him more cylinders with greater diameter and longer piston stroke. Even with the coming of World War I, refiners, under pressure of demand for more and more motor fuel and particularly for a better-quality fuel for the newly developed airplane engine, found it impossible to furnish the domestic market with a high-quality gasoline.

With the return of peace, benzol, a by-product of excess coking plants erected during the war was discovered to be of great value in boosting the antiknock quality of gasoline for our market. It was mixed with gasoline, two fifths benzol to three fifths gasoline and soon became a premium fuel, selling for as much as 5¢. a gallon more than straight gasoline in some localities.

In 1914 the invention of the thermal cracking process allowed the oil industry to increase the volatility of its now principal product—gasoline—whereupon the automotive engineers promptly restored the old compression pressures. However, they soon discovered limits beyond which it was not safe to go. Nevertheless, these limits aroused General Motors which set up special research agencies to study automobile fuels and find a way to turn out higher-compression engines. The customer who was at first curious and mildly interested in the one-cylinder automobile engine was becoming more and more excited, and demanding engines with two, four, six, eight, and even twelve cylinders—and the self-starter.

The result was that the automobile engine of 1920 started, warmed up, and ran more efficiently and quietly on 58° gasoline than its predecessor in 1900 had operated on a 76° gravity fuel. Nevertheless, the better type of the early models delivered more horsepower hours per pound of fuel than the sophisticated models in use after the war. The answer—the loss in efficiency—was to be found in the dropping of the compression ratio to accommodate the engine to the lower-gravity fuel.

This poor grade of gasoline led to knocks when the engine was put under full load. The cure was easy—lower the compression ratio, but this cut power and fuel economy. The customer desired power, but he didn't want the knock.

This led Dr. Kettering to state the problem clearly at a meeting of the American Petroleum Industry held in Washington, D. C., in 1920. "We cannot raise the compression of our engines," he said, "because of the fact that if we do, when the driver opens his throttle, or when the motor gets a little bit dirty, the spark so hard that it fractures the porcelains in the spark plugs, breaks down the bearings and does all sorts of things. It wrecks the engine. It would be possible by cooperation between the petroleum and automotive industries to increase the efficiency of our machines by from one third to one half. If you can raise the compression of your motors you can do a lot of things. You can increase the economy and you can keep out crankcase dilution."

The refiners were not slow to take up the challenge so definitely issued and at once began to plan and execute a large amount of research. However, the outstanding discovery came from the research laboratories of General Motors Corp., a discovery by Thomas Midgely that a small quantity of tetraethyl lead, less than half a teaspoonful, mixed with a gallon of gasoline instantly eliminated knock from a high-compression or badly carbonized motor. This led to the manufacture of ethyl gasoline now the most widely distributed and best known of all antiknock fuels.

In addition the petroleum industry co-operated by selecting special crudes for refining, which permitted production of gasoline of greater antiknock propensities than the average run from a refinery. It also began the study of
changing methods of processing in the hope of reducing the knock tendency of gasoline.

The results of all this research soon enabled the automotive manufacturers to build engines with greater compression ratios. In 1927 only five manufacturers produced cars with a compression ratio of 5 to 1. In 1928 eighteen manufacturers were building cars with a compression ratio between 5 to 1 and 5.50 to 1, and one builder was making a model with a ratio of 6 to 1. By 1929, thirty companies were building standard engines with ratios of 5 to 1 or higher, and eight companies offered optional models with compression ratios running from 5 to 1 to 6.56 to 1.

Confusion resulting from a statement made by an official of the automotive power plant section of the Bureau of Standards relative to the characteristics of "high test" and "antiknock" gasolines in articles published in November 1929 called forth a series of demands from manufacturers of motor fuels for a statement in detail from the Bureau as to facts ascertained by scientific and practical tests.

These demands brought forth a statement by H. C. Dickenson, then chief of the division of heat and power at the Bureau of Standards, Jan. 30, 1930, which defined the different types of gasoline as follows:

There is a clear distinction between "high test" and "antiknock" gasolines. The former is a gasoline of high volatility ordinarily sold at a premium over ordinary or straight commercial gasoline. Especially in cold weather, it gives quicker response and less trouble from crankcase dilution. In warm weather the high temperatures increase the effective volatility of ordinary gasoline, so that there is little or no advantage from using "high test."

"Antiknock" gasolines are an entirely different product. They include, in general, gasolines made from certain petroleum stocks, gasolines made by certain special cracking processes, gasolines blended with benzol, and ethyl gasolines or those containing tetraethyl lead. They differ from ordinary gasolines in that they are less likely to detonate or knock. A fuel which knocks in any particular engine gives less power and less miles per gallon than a similar fuel which does not.

Ethyl gasoline, which is perhaps the most widely used of the special antiknock fuels, is understood to be a commercial gasoline containing a small amount of ethyl fluid. The latter is made up of tetraethyl lead plus certain other chemicals added to prevent the deposit of lead oxide in the engine. The amount of ethyl fluid added varies in different brands, depending upon the character of the particular commercial gasoline used, but is always small, being generally less than 1 part in 1300 parts of gasoline by volume.

The sole effect of adding ethyl fluid to a given gasoline is to lessen the tendency to knock or detonate. The volatility of the gasoline, its heat value, and its specific gravity remain those of the commercial gasoline used. Ethyl gasolines consequently vary somewhat as to their volatility, starting qualities, acceleration, and other characteristics dependent on the gasoline alone.

If the knock is due to carbon, ethyl gasoline removes the knock, but not the carbon. Under certain conditions and in certain engines the untreated gasoline would knock unless the spark were excessively retarded. In such cases the use of ethyl gasoline permits normal spark advance without detonation and thereby improves power and fuel economy.

Since the advantage of using premium gasolines of the "high test" or of the "antiknock" variety may be considerable or may be nil, depending upon the weather and the kind and condition of the engine, the user must decide when the added cost is justified.

About this time the organic chemists began in earnest to unravel the secrets of the hydrocarbons found in petroleum, referred to by some as "nature's cocktail." They began to separate the different kinds of molecules found in petroleum and test each one separately as to its power and efficiency as an engine fuel. The found among other things that the heavier the molecule the higher its boiling point, in other words a molecule with many carbon atoms would require considerable heat to vaporize it, whereas a light one, with just a few carbon atoms, would vaporize immediately. These light fractions formed the early gasoline of the 1900's of 76° gravity. As the cracking devices and methods improved the chemists discovered they could break up the heavy molecules containing many carbon atoms so as to form lighter molecules which would prove ideal in making gasoline. Hence they began to make vast amounts of gasoline from the light oils and heavier types of crude.

Furthermore, as they broke down these heavy hydrocarbons and tested the different types separately they found that some of them were more efficient in cutting down knock than others. One of these, iso-octane, was so effective in reducing knock that they gave it an octane number of 100. By comparison with this gasoline they measured the other more and less efficient types of knock-preventing gasolines.

One of the least effective of the antiknock types was a straight-chain heptane. Its carbon atoms were placed one behind another. It was given an octane rating of zero because when used in internal-combustion engines it produced persistent knocking.

It might be well to look at some of the accompanying diagrams of the various hydrocarbons which are found in connection with petroleum and are at present changed about by cracking methods to produce tailor-made gasoline, gasoline to fit any engine, or perform most any job. In these diagrams those with the smaller number of atoms are gases, as methane, that is, they have much lower boiling points than do the heavier or longer-chained ones such as heptane and octane. Naturally many of the higher numbered hydrocarbon molecules contain several multiples of the carbon atoms shown in the diagrams. These are the ones that make
up the light and heavy oils, and the paraffins, etc. It is these large ones that are broken down by thermal cracking processes, alkylation processes, and vastly improved catalytic cracking methods into the more efficient types used in internal-combustion engines.

Next we put three carbon atoms in a row at the top of the chain, and we have another iso-heptane which has still better antiknock qualities.

Finally we take another carbon atom off the end of the chain and place it on the side, and we have an iso-heptane known as triptane which has the best antiknock quality of any hydrocarbon.

Following is a diagram of this super-fuel, known as triptane, also one of iso-octane:

![Diagram of iso-octane]

One of the first things discovered by the research workers in this field was that by taking up any one type as, say, heptane, many changes can be made in the position of its carbon atoms. For instance if a carbon atom on one end is detached and placed on one side you still have heptane, but of different antiknock properties. This is called an iso-heptane. The interesting feature about this iso-heptane is that it has much better antiknock qualities than the straight-chained heptane. If we ar-

![Diagram of iso-heptane]

The old gasoline used in the early Model T Ford had an octane number of about 40 to 60. Most thermally cracked gasoline had an octane number of less than 70 but by adding tetraethyl lead the number could be upped to about 80. Iso-octane set the standard at 100-octane but the new triptane actually is gauged at about 110 octane but it produces or can deliver about 50 per cent more power than 100-octane gasoline. If tetraethyl lead is added to triptane the power obtained is nearly three times (performance index numbers) as great as with iso-octane, according to Dr. Kettering.

This then is the new superfuel which may revolutionize the motor car and aviation industry after the war. It was first made, according to Dr. Kettering, in 1922 by Chavanne, a Belgian. Later it was made by the Ethyl Gasoline Corp. and tested in 1926 in the General Motors laboratories. In 1939 the Dow Chemical Co. made some 300 gallons for the Ethyl Gasoline Corp. at a cost of about $35 a gallon. Later researches in the General Motors laboratories developed a cheaper way to make it, and a small-scale pilot plant capable of making from five to ten barrels of triptane a day was built. Approved by the War Department and the Army Air Forces it was completed in 1943 and in January 1944 began operations, producing better than expected yields with a purity of about 99 per cent.

According to Dr. Kettering, tests have been made at Wright Field in Dayton, at the Aircraft Engine Research Laboratory of the National Advisory Committee for Aeronautics in Cleveland, at the Allison Engine Division of General Motors Corp., and at the General Motors Research laboratories.

Some of these tests, run on a variety of engines, some single and some multiple-cylinder types, have shown that remarkable gains can be made in the fuel-engine combination. "The magnitude of such gains, " says Dr. Kettering, "depends upon the particular engine and condition of operation, and with triptane containing tetraethyl lead they have amounted to as much as four times the power and to as much as 25 percent gain in fuel economy over iso-octane or 100-octane gasoline.

"A twelve-cylinder Allison airplane engine," he says, "has been operated on triptane blends at an output of well over 2500 hp. although the rated take-off horsepower with 100-octane aviation gasoline is about 1500 hp."

Dr. Kettering stated further in an address before the American Chemical Society in September 1944, that "studies were under way to evaluate the commercial possibilities of triptane and related compounds with some preliminary indication that the value of the fuel may justify the present projected cost per gallon, which is relatively high as compared with fuels of lower quality. More importantly an engine program is contemplated to see what may be done with engines and their application to various uses, once the barrier of uncontrollable combustion has been removed to such an important degree. The objective is to find the best combination of engine and fuel to give the greatest value per total dollar, irrespective of what form it may take. This phase of the problem is how to design engines to take advantage of their greater possibilities."