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HIGH-COMPRESSION MOTOR FUELS AND THEIR MANUFACTURE

Pharis Miller, Elizabeth, N. J., assignor to Standard Oil Development Company, a corporation of Delaware

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This invention relates to high-compression motor fuels constituted to be knock-free in road performance and to their manufacture.

Gasoline-type fuels of improved anti-knock qualities are needed in greater volume for high-powered motors being increasingly used, yet the principal fuel manufacturing processes continue to yield motor fuels which do not give knock-free performance in these motors at all speeds with practical additions of anti-knock agents, such as tetraethyl lead. An object of this invention is to provide fuels which give uniformly knock-free road performance in motors having compression ratios above 6.5:1 with a minimum of processing and economy in the use of the anti-knock addition agents.

In order to make the advantages of this invention more clearly understood, it is considered desirable to briefly discuss differences between methods used in rating the anti-knock value of motor fuels and the significance of these methods.

The anti-knock rating of a motor fuel is basically obtained by direct comparison of the knock intensity it produces with that produced by a standard fuel, i. e., a fuel consisting of normal heptane and iso-octane (2,2,4-trimethylpentane).

In the standardized laboratory test developed by the Cooperative Fuel Research Committee, a C. F. R. engine operated at 600 R. P. M. at room temperature is used in testing the fuel, and the fuel is determined to have an octane number in terms of the per cent by volume of iso-octane in the standard fuel which matches the knock intensity of the fuel being rated.

More recently the described laboratory method, known as the research method, was modified to what is called the C. F. R. motor method, because results of the research method do not correlate with service results. The C. F. R. motor method differs from the earlier procedure in that the engine is operated at 900 R. P. M. instead of 600 R. P. M., the mixture temperature is at 300° F. instead of room temperature, and the spark timing is advanced 3.5°.

To determine actual service performance of motor fuels, a road rating method has been developed. The road rating differs from the laboratory ratings in that the test engines are run at various speeds, are multicylinder, are subjected to variations in spark timing, and by other factors, such as fuel mixture distribution. Just as there are discrepancies between the motor method and the research method ratings, there

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are discrepancies between these laboratory ratings and the road ratings for fuels. The difference between the research method and the motor method ratings has been called the sensitivity of a fuel, which is somewhat a measure of relative susceptibility of a fuel to changes in operating conditions, and fuels with the greatest sensitivity, in general, show the greatest increase or appreciation to higher road ratings.

Motor fuel compositions for spark-ignition engines with high-compression ratios are efficiently modified in accordance with the present invention to have satisfactorily improved road octane ratings and responsiveness to anti-knock addition agents so that they give knock-free performance at all speeds. This improvement is important for securing greater thermodynamic efficiency in the operation of the high-compression motors.

At present, commercial gasolines of highest anti-knock quality are manufactured principally by cracking, reforming, gas polymerization, and alkylation processes. Some of these gasolines contain substantial proportions of olefins ranging from 5% to 50% or higher, but the olefins therein, if present in any such substantial amounts, are distributed throughout the boiling range of the fuel and volatilize mostly with the major portion of the fuel boiling above 158° F.

There are considerable differences between the road performances of commercial gasolines obtained by these various processes. In one respect or another, they have not given satisfactory knock-free performance with practicable additions of anti-knock agents when used in modern high-powered motors.

In accordance with the present invention, gasoline products are improved in appreciation for securing knock-free road performance at both low and high speeds by a treatment which radically modifies the fuel compositions, so that the fuels contain a certain high concentration of low boiling olefins in the fraction distilling off below 158° F., and a minimum content of the higher olefin or non-benzenoid unsaturated hydrocarbon components boiling above 158° F., such higher olefins being eliminated to the extent that the volume ratio of said low boiling olefins to said higher olefins is preferably less than 9:1, without a substantial change in the desired volatility or boiling characteristics of the fuel and without detrimental effects on the vapor pressure.

In carrying out the present invention, first it is desirable to prepare gasoline base stocks of suitable boiling range, volatility, and good in-

herent anti-knock quality, i. e., having boiling ranges within the limits of 75° F. and 450° F., more preferably between 100° F. and about 300° F. or 400° F. with mid-boiling points above 158° F., preferably between 200 and 250° F., and inherent A. S. T. M. octane ratings of 70 or better, and to form and treat the fuels in such a manner, that upon analysis, the finished fuel shows a total olefin content of from at least 10% to 50% and preferably about 12% to 30% by volume, with the olefins concentrated principally in the front volatile portion of the fuel to an extent that most of the total olefin content, preferably more than 90% thereof, boils off with the portion distilled off up to 158° F. and constitutes the bulk of this portion.

In the interest of economical processing, the hydrocarbon components of the fuel other than the olefins, in general, comprise paraffinic, isoparaffinic, naphthenic, aromatic, or mixed hydrocarbon compounds of these types, as they result from various refining and conversion processes applied to petroleum oils in making commercial gasoline fuel products.

The present procedure is valuable in treating mixed gasoline fuel stocks which separately or blended in a conventional manner do not have suitable road octane ratings for use in high-compression motors. However, the present procedure is very useful in processing a single fuel stock; for example, if it is desired to modify a cracked gasoline, the cracked gasoline is subjected to operations designed to enrich the olefin content of the fuel in the portion boiling below 158° F. and to reduce the olefin content of the fuel fraction boiling above 158° F. to a minimum without detracting from the boiling characteristics of the fuel so that the finished fuel has the desired overall content of olefins, principally concentrated in the front end portion.

The gasoline to be modified may be obtained by vapor phase cracking of gas oil or by polymerization of normally gaseous olefins, thermal or catalytic, under conditions to form a large amount of olefins in the fuel. The low boiling olefins may be concentrated by fractional distillation or selective solvent treatment to supply the desired front end composition of the improved fuels. As needed, low boiling hydrocarbon fractions, rich in these low boiling olefins, are obtainable by dehydrogenating processes to fill in the front ends of the modified fuels.

In treating the gasoline stocks for the purpose of eliminating olefins from the fractions boiling above 158° F., such higher boiling fractions may be treated by hydrogenation or polymerization properly controlled to reduce olefinicity while keeping the distillation characteristics substantially unchanged. Also, they may be refined by means of sulfuric acid or olefin extracting agents, and further have incorporated correspondingly high boiling non-olefinic hydrocarbons to replace the olefins removed, but advantageously the need of blending certain individual synthetic hydrocarbons to maintain proper distillation characteristics and high anti-knock quality is dispensed with by the preferred method of manufacture herein described.

If the sulfur content of the resulting fuel product is too high, either for the reason that the sulfur content in the initial material is too high or due to insufficient removal of the sulfur during the processing, suitable additional treatment may be given to reduce the sulfur content to below 0.1% or still lower without affecting the hydrocarbon composition. The reduction of the sulfur content may be accomplished by known methods such as soda washing or sweetening.

In the treatment of the fuel for the purpose of the present invention, the non-benzenoid unsaturated hydrocarbons having undesirable gum-forming tendencies, such as particularly diolefins, cyclic olefins, and triolefins will be effectively removed from the higher boiling portions of the fuel, and such unsaturates are readily reduced to a negligible amount of less than 1% in the low boiling portions of the fuel by an adsorptive clay treatment or other established refining methods without substantially diminishing the desired high concentration of mono-olefins. However, the presence of certain low molecular weight diolefins containing only 4 to 6 carbon atoms per molecule, particularly such as butadiene or methyl-butadiene, may be permitted to remain in the front ends without serious impairment to the stability of the fuel in the presence of a gum inhibitor, since such low boiling diolefins are sufficiently stable, provided higher diolefins are absent, to prevent any marked deterioration of the fuel over a normal storage period with a small amount of inhibitor present. Nevertheless, it is intended to have preferably the more common and more stable mono-olefins or alkenes as the olefinic constituents of the improved fuel.

It might be noted that whereas in conventional refining practice an over-all reduction of olefin content is frequently made, or the olefin content of the fuel is particularly reduced in the front ends by refining or in special processing, such as by alkylation or polymerization, the present invention quite differently provides for substantially raising the concentration of the low boiling olefins while eliminating the higher boiling olefins and reducing the content of low boiling saturates.

As illustrative of the invention, the following examples are given:

Example

An East Texas gas oil, when subjected to intensified dehydrogenation conditions in catalytic cracking is made to form a gasoline product having an exceptionally high olefin content. Satisfactory conditions used in this operation are summarized as follows:

Type of Catalyst	Activated clay, silica-alumina gels, silica-magnesia gels
Catalyst Temperature, ° F.	900–950
Catalyst to Oil, Wt. Ratio	3–5:1
Contact Time, Secs.	16–40
Yield, Based on Output, Vol. percent	20–55

Gasoline products obtained by the described cracking operation have the following compositions:

Components	Volume, percent
Total Olefins	58–74
Aromatics	9– 5
Naphthenes	12–11
Paraffins, normal and branched	21–10
Olefins Distilled Off Below 158° F. (Percentage of Total Olefins)	5–12

By varying the conditions in the catalytic cracking operation, the olefin content and the olefin concentration in the front ends are varied to some degree, but nevertheless the resulting fuel

product contains a considerable excess of higher boiling olefins which distill off at above 158° F.

A gasoline product resulting from cracking processes with intensified dehydrogenation, as described, contains large amounts of olefins, hence it can be fractionated to separate the front end fraction boiling below about 158° F. and a fraction boiling from about 158° F. to about 350 or 400° F., thus furnishing a gasoline which is well adapted for processing in accordance with the present invention. The front end fraction may be enriched in C_4, C_5, and C_6 olefins in proper amounts, with decrease in corresponding amounts of analogous paraffins to obtain suitable volatility characteristics depending upon the needs of the fuel. This increase in the concentration of any of these particular olefins is easily made without giving the fuel an excessive vapor pressure by simply making sharp cuts above the initial point of the front ends where desired and adding the desired low boiling olefins to replace low boiling saturated hydrocarbons eliminated in making the cut.

The separated higher boiling fraction of the cracked gasoline, which is cut between about 158° F. to about 350 or 400° F., when subjected to a hydrogenation treatment under controlled conditions to avoid substantial change in boiling characteristics undergoes a reduction in olefin content to a very low amount, and the conditions can be made such that the olefin content is reduced to well below 10% and preferably to below 5%. Then upon recombining the thus treated fraction boiling above 158° F. of lowered olefin content and the thus treated front end fraction boiling below 158° F., enriched in olefins, the resulting modified fuel composition has in every respect desired physical characteristics of volatility and distillation with a considerable improvement in the road octane rating over the initial gasoline product which was treated as is denoted in the following data.

A very effective method for eliminating olefins from the gasoline fraction boiling above 158° F. is one in which this fraction is subjected in vapor phase to a catalyst that selectively promotes hydrogenation of the olefins with a limited amount of cracking so as to avoid changes in the boiling characteristics of the fraction treated. There may be in this treatment some rearrangement or combination of the molecules, but the main effect is the reduction in olefin content to less than 10% and as low as about 1%. Satisfactory conditions for this type of operation are summarized as follows:

Type of Catalyst	Activated alumina or magnesia impregnated with 1 to 50% by weight of a sulfide or oxide of metals in Groups 4, 5, 6, and 8 of the Periodic Table; preferably with oxides of chromium or molybdenum
Catalyst Temperature, ° F.	800–950
Space Velocity (Liq. Vol. Oil per Vol. Catalyst per Hr.)	0.2–3
Pressure, Lbs. per sq. in. gauge	100–500
Gas Recycle Rate, Cu. Ft. per Bbl. Oil Input	500–10,000
Hydrogen in Recycled Gas, Vol. per cent	20–90

The resulting modified gasoline obtained by the described treatment for reduction of olefins boiling within the range of about 158° F. and 400° F.

and increase in the proportion of lower boiling olefins has substantially the same distillation characteristics as the initial gasoline treated, as illustrated in the following table:

	Initial Gasoline From Catalytically Cracked Gas Oil	Modified Gasoline
Gravity, ° A. P. I.	59.8	52.6
Reid Vapor Pressure (lbs./sq. in.)	8.0	7.0
A. S. T. M. Distillation Per cent Distilled at ° F.:		
158	14.5	13.0
212	46.0	45.0
257	75.0	76.0
266	80.0	81.5
302	93.5	95.0
Final Boiling Point	333	318
Total Olefin Content, Vol. Per cent	50	13
Olefins Boiling Above 158° F., Vol. Per cent	40	1
Olefins Boiling Below 158° F., Vol. Per cent	10	12

Anti-knock rating tests were made on the initial gasolines and the modified gasolines, separately and blended, and with an addition of 2.75 cc. of tetraethyl lead (T. E. L.) per gallon. The initial gasoline products from the catalytically cracked gas oil showed a definite tendency to knock in a 7.3:1 compression-ratio Chrysler automobile engine at high speeds (35 to 60 miles per hour). A road rating test with the same type of engine run on a gasoline formed by the described hydrogenation treatment so that the gasoline had a total olefin content of less than 10% by volume showed that this type of fuel of extremely low total olefin content has a tendency to knock in the same type of high-compression engine at low speeds (10 to 35 miles per hour). The modified gasoline containing more than 10% by volume of olefins but with at least 90% of these olefins concentrated in the front ends which distill off below 158° F. gave entirely knock-free performance in the same type of high-compression engine at both the low and high speeds.

	Road Octane Ratings With 2.75 cc. T. E. L./Gal.	
	10–35 Miles Per Hour	35–60 Miles Per Hour
Initial Cracked Gasoline	93.0	87.8
Hydrogenated Gasoline	86.3	96.0
Modified Gasoline	93.7	93.7

The marked improvement in the gasoline cannot be accounted for by the reduction in total olefin content but is indicated to be dependent on the modification treatment, whereby the olefins are present in a substantial proportion of at least 10% but are concentrated in the front ends distilling off below 158° F.

A further illustration of how the road octane ratings of the motor fuels are improved by increasing the proportion of the low boiling olefins is demonstrated in a series of tests on a variety of modified gasoline samples from catalytically cracked gas oil, these samples having nearly identical physical inspection properties and chemical composition but differing essentially in the boiling range distribution of the olefins. Representative of these tests, gasoline sample II was richer in its concentration of low boiling olefins or alkenes, namely butenes, pentenes, and hexenes, by the amount of 6% by volume over gasoline sample I. The finished gasolines having

nearly the same total olefin content were tested for anti-knock value to obtain the following data:

Fuel Sample	Total Olefin Content, Volume Per Cent	Octane Rating		Road Rating Average Car At 70° F.	
		A. S. T. M. Motor Method	C. F. R. Research Method	Clear	+1.5 cc. TEL/Gal.
I	49	79.7	90.9	87	90
II	46	79.7	92.1	89	94

It is important to note that it is not the total olefin content which is the determining factor of appreciation toward improved road rating, but more particularly the concentration of the low boiling olefins having from 4 to 6 carbon atoms per molecule.

As hereinbefore described, highly desirable gasoline fuels of improved road octane rating are prepared from mixtures of hydrocarbons having normal gasoline distillation characteristics, i. e., preferably with initial and final boiling points between 100° F. and 400° F., with a mid-boiling point preferably no lower than about 200° F., and so modified as to contain preferably from 10 to 50% of olefins, with a minimum of mono-olefins boiling above 158° F., so that at least 90% of the olefins are in the front ends boiling below 158° F.

The herein described modification of gasolines is subject to certain variations depending upon the grade and purpose needed. For summer grade fuels, the modified gasoline preferably should have less than 20% distill off at 158° F., and contain from 10% to 20% of C_5 and C_6 olefins. For a winter grade, the modified gasoline may contain from 20 to 30% of C_4 to C_6 olefins, which distill off below 158° F. Also, aviation fuels may be prepared in accordance with the present invention, because the modified fuels contain relatively low total amounts of olefins, have suitably low Reid vapor pressures, and yet have suitable boiling ranges. The modified fuels, in general, have normal Reid vapor pressures in the range of 5 to about 15 pounds per square inch at 100° F., and more particularly between 7 to 12 lbs. per square inch at 100° F., because the C_4 to C_6 olefins are present in balanced concentrations with an extremely low amount of other hydrocarbons in the same distillation range. By having the combined C_4 to C_6 olefins constitute the major part of the front ends boiling below 158° F., with lowering of the C_4 to C_6 alkanes in these front ends in an amount corresponding to the enrichment by the analogous low boiling alkenes and the described treatment of the higher boiling portion of the fuel, the vapor pressure is properly maintained and even somewhat lowered despite an increase in the volume of the front end fraction. The mixture of C_4 to C_6 alkenes, in general, will be made to constitute at least 75% and preferably more than 90% of the front ends boiling below 158° F.

The improved gasolines may contain metallo-organic anti-knock agents other than tetraethyl lead, or other additives, such as a top cylinder lubricant, a gum-fluxing agent, thickening agents, dyes, gum inhibitors, such as amino and phenolic

compounds, or anti-knock blending agents, such as alcohols, branched ethers, or others of this type of agent, corrosion inhibitors, etc.

The foregoing examples are illustrative of the invention, and modifications may be made which come within the spirit of the invention as recited in the appended claims.

I claim:

1. The method of preparing a motor fuel with improved road octane rating and lead susceptibility, which comprises treating a cracked gasoline of high olefin content and containing substantial amounts of aromatic and naphthenic hydrocarbons to replace paraffinic components of a gasoline fraction boiling below 158° F. by mono-olefins having 4 to 6 carbon atoms per molecule until said monoolefins constitute at least 75% by volume of said fraction and from 10 to 30% by volume of the fuel, hydrogenating the fraction of said gasoline boiling above 158° F. with hydrogen in the presence of a catalyst under suitable conditions to reduce the olefin content thereof to less than 10% by volume while maintaining the distillation characteristics substantially unaltered, and recombining the olefin-enriched fraction boiling below 158° F. with the hydrogenated fraction boiling above 158° F.

2. The method of preparing a knock-free motor fuel for spark ignition engines having compression ratios above 6.5:1 from a cracked gasoline mixture of hydrocarbons having a high content of olefins and containing a substantial amount of aromatic and naphthenic hydrocarbons, the major part of which boil above 158° F., which comprises replacing said olefins boiling above 158° F. by hydrogenated derivatives thereof to reduce the olefin content of the hydrocarbons boiling above 158° F. to less than 10% by volume, and concentrating olefins having 1 to 2 double bonds and 4 to 6 carbon atoms per molecule in the fraction of the gasoline distilling below 158° F. so that the gasoline contains from 10% to 50% by volume of non-benzenoid unsaturates with at least about 90% by volume of the total volume of olefins in the fraction of the fuel distilling below 158° F. while maintaining the distillation characteristics of the gasoline so that it has a mid-boiling point in the range of 200° F. to 250° F. and a boiling range within the approximate limits of 100° F. to 400° F.

PHARIS MILLER.

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