May 15, 1962 P. P. McCALL 3,034,878

HIGH OCTANE MOTOR FUELS

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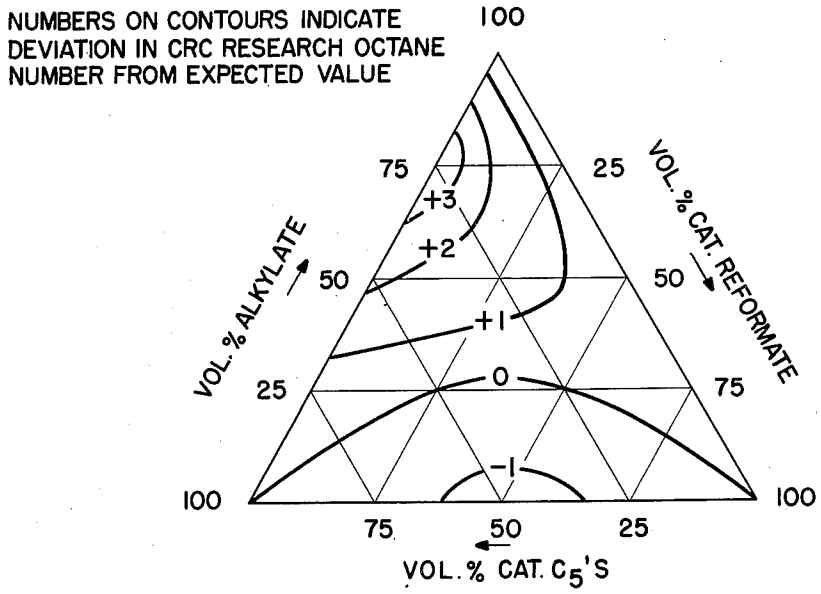


FIG.-1

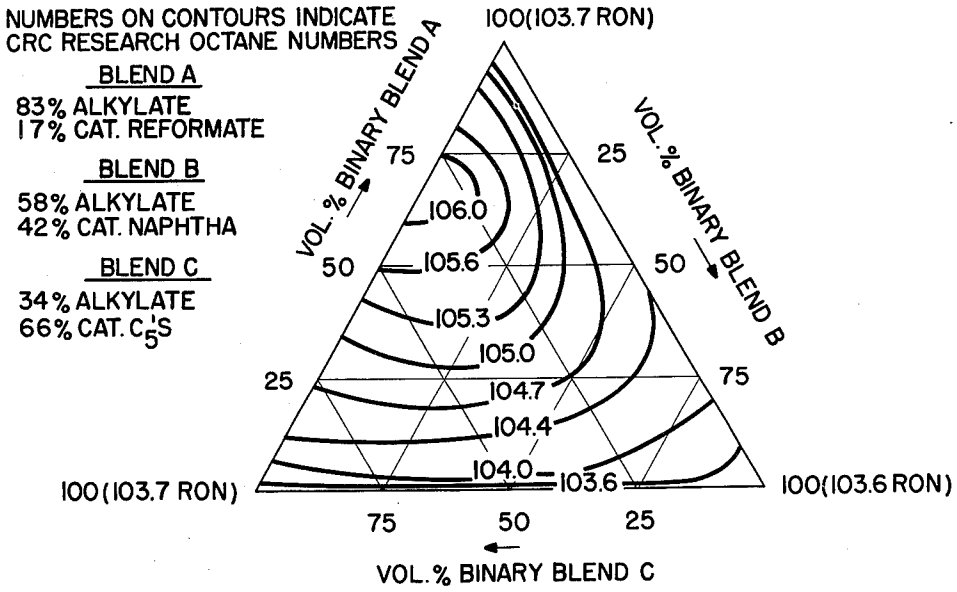


FIG.-2

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HIGH OCTANE MOTOR FUELS

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The present invention relates to fuels for use in spark-ignition internal combustion engines and more particularly relates to improved gasolines of surprisingly high octane quality produced by the blending of selected petroleum refinery process streams in critical proportions.

Improvements in engine design, particularly increased compression ratios, have made modern gasoline engines very sensitive to fuel octane quality. Many late model automobiles now require gasolines of 100 research octane number and it is anticipated that automobile engine octane requirements may rise to even higher levels in the future. In order to keep pace with the increased demand for high octane fuels, gasoline octane levels in general have been raised appreciably in recent years and new "super grade" fuels have been introduced. There has been little or no corresponding increase in the octane levels of the blending stocks available for manufacturing gasolines. As a result, fuel octane levels are in many cases now approaching the octane levels of the best available blending stocks and it is becoming increasingly more difficult for the petroleum industry to provide gasolines of the requisite octane quality.

The present invention provides a new class of gasolines of surprisingly high octane quality which can be readily blended from presently available petroleum refinery process streams. The invention is based upon the discovery that certain high octane process streams interact when they are blended together and that the resulting blends have octane values which are either higher or lower than would normally be expected, depending upon whether the interaction is a positive or a negative one. It has been found that when high octane alkylate, catalytic reformate, catalytic naphtha and catalytic C_5 petroleum fractions are blended in critical proportions, positive interactions take place. Blends making use of these positive interactions have octane numbers much higher than those predicted by octane blending correlations and in some cases considerably higher than those of any of the individual streams. In other proportions, blends of the same constituents have the octane numbers predicted by the blending correlations. In still other proportions the octane values are considerably lower than would be expected due to negative interactions. Since the upgrading of gasoline one octane number at present octane levels may increase the cost of the fuel to the consumer by as much as one cent per gallon, the advantages of gasoline blending to effect positive interactions are obvious.

The exact nature of the invention can be best understood by first considering the methods generally used to predict octane levels in blending gasolines. Research octane numbers are usually computed by first converting the octane numbers of the individual blending stocks to research blending numbers which have been developed empirically from data obtained by actual comparative engine tests of an extremely large number of blends of various constituents. Those blending numbers are then averaged volumetrically to obtain the research blending number of the blend for which the determination is being

made. This calculated blending number is then converted to the research octane number. The method for determining motor octane numbers is similar except that empirically determined motor blending numbers rather than research blending numbers are used.

Although both of these methods give accurate results when applied to conventional gasolines and are quite dependable, they do not take into account the interactions which have been found to occur when high octane alkylate, catalytic reformate, catalytic naphtha and catalytic C_5 fractions are blended in accordance with the invention. Catalytic reformate normally has a somewhat higher octane number and a higher blending number than alkylate and therefore it has generally been thought that high octane gasolines should contain catalytic reformate as the major constituent and that alkylate and other high octane blending stocks should be used in much lesser quantities. High octane aviation gasolines blended in the past have, for example, generally contained 50% or more catalytic reformate, about 30% alkylate and up to about 20% catalytic naphtha and other constituents. Since conventional octane blending correlations accurately predict the octane numbers of such gasolines, there was no reason to suspect that higher octane numbers could be obtained by employing alkylate in relatively large amounts and using lesser quantities of the catalytic reformate and other constituents.

In accordance with the present invention, however, it has now been discovered that due to positive or synergistic interactions which occur when alkylate, catalytic reformate, catalytic naphtha and catalytic C_5 hydrocarbons are blended together, surprisingly high octane gasolines can be produced by using relatively small amounts of catalytic reformate and larger amounts of alkylate, catalytic naphtha and catalytic C_5 hydrocarbons. Blends containing from about 40 to about 95% alkylate, about 0 to about 35% catalytic reformate and from about 5 to about 60% catalytic naphtha and C_5 hydrocarbons have octane ratings which are as much as 3 octane numbers above those which they would have in the absence of interactions and are therefore highly valuable for use as high octane gasolines. Blends containing from about 50 to about 90% alkylate, about 0 to 20% catalytic reformate and about 10 to about 50% catalytic naphtha and C_5 hydrocarbons have particularly high octane ratings and are therefore preferred.

The alkylate component employed as a blending stock in preparing the fuels of the invention is a product consisting essentially of branched chain paraffins prepared by reacting isobutane, isopentane or a similar low molecular weight isoparaffin with a C_3, C_4 or C_5 olefin such as propylene, butylene, isobutylene or the like under alkylation conditions. The reaction is carried out in the presence of concentrated sulfuric acid, hydrofluoric acid, aluminum trichloride, boron trifluoride or a similar catalyst at a temperature in the range of from about 30 to about 100° F. The alkylate product normally boils in the range between about 100° and about 360° F. Alkylate prepared by reacting isobutane and butylene under conditions to yield a maximum of C_8 isoparaffins, particularly trimethylpentanes, is preferred for purposes of the present invention because of its high octane value. Alkylation processes are widely used throughout the petroleum industry for producing high octane blending stocks and need not be described at length for purposes of this invention.

Typical alkylate inspections are as follows:

	I	II
Gravity, °API	70.2	70.7
Distillation, ASTM:		
Initial Boiling Point, °F	120	106
5% Point, °F	172	153
10% Point, °F	185	163
20% Point, °F		185
30% Point, °F		198
40% Point, °F		207
50% Point, °F	221	213
60% Point, °F		217
70% Point, °F		220
80% Point, °F		223
90% Point, °F	246	231
95% Point, °F	271	238
Final Boiling Point, °F	333	291
Recovered, Percent	98.0	99.0
Residue, Percent	1.4	0.7
Loss, Percent	0.6	0.3
Aromatics, Percent	1	1.4
Olefins, Percent	0	0
Saturates, Percent	99	98.6
Research Octane No., Clear	95.1	95.5
+3 ml. TEL/gal	106.05	107.53
Motor Octane No., Clear	93.5	94.1
+3 ml. TEL/gal	106.33	107.40

The catalytic reformate which is utilized as a blending stock in preparing the fuels of the invention is produced by subjecting a naphtha to elevated conditions of temperature and pressure in the presence of a reforming catalyst such as platinum-on-alumina, molybdena, chromia or cobalt-molybdenia. Under these conditions, naphthenes in the naphtha are dehydrogenated and isomerized to benzenes, straight chain paraffins are aromatized and isomerized to benzenes and isoparaffins, and normal paraffins are hydrocracked to form shorter chain compounds. The resulting product boils in the range between about 100° F. and about 400° F. and is a highly aromatic stream having a significantly higher octane number than the feed naphtha. There are numerous catalytic reforming processes, all generally similar and well known in the art. In a typical process the feed naphtha is contacted with a platinum-on-alumina catalyst in the presence of 1000–6000 cu. ft./bbl. feed of H_2 at a temperature in the range of from about 900 to 1000° F. and at a pressure of from about 200 to 300 p.s.i.g. with a space velocity of from about 2 to 4 pounds of feed per hour per pound of catalyst.

Typical catalytic reformate properties are as follows:

	I	II
Gravity, °API	44.2	35.5
ASTM Distillation:		
Initial Boiling Point, °F	100	207
5% Point, °F	192	232
10% Point, °F	227	237
20% Point, °F	260	
30% Point, °F	274	
40% Point, °F	285	
50% Point, °F	292	257
60% Point, °F	299	
70% Point, °F	306	
80% Point, °F	316	
90% Point, °F	327	295
95% Point, °F	239	307
Final Boiling Point, °F	370	336
Recovery, Percent	98.0	98.8
Residue, Percent	0.9	0.8
Loss, Percent	1.1	0.4
Aromatics, Percent	58.8	85.0
Olefins, Percent	0.9	0.9
Saturates, Percent	40.3	14.1
Research Octane No., Clear		
+3 ml. TEL/gal	100.53	108.94
Motor Octane No., Clear	85.1	94.1
+3 ml. TEL/gal	91.1	100.0

The catalytic naphtha and C_5 hydrocarbons used as blending stocks in accordance with the invention are obtained by fractionation of the product stream from a catalytic cracking unit to recover products boiling from the C_5 range up to about 300° F. The catalytic pentanes and pentenes may be separately recovered and used as blending stocks or instead may be recovered and used with the heavier material in the form of a C_5 to about 300° F. catalytic naphtha. Catalytic cracking is a well known method for producing relatively low boiling hydrocarbons from gas oils and other high boiling petroleum fractions by contacting such fractions with a silica-alumina, silica-magnesia, clay or similar catalyst at a temperature in the range of from about 900 to about 1000° F. Numerous cracking processes familiar to those skilled in the art may be employed.

Inspections of catalytic naphtha and C_5 hydrocarbons are typically as follows:

	Catalytic Naphtha		Catalytic C_5's
	I	II	
Gravity, °API	67.8	70.6	88.3
ASTM Distillation:			
Initial Boiling Point, ° F	136	97	81
5% Point, ° F	149	111	83
10% Point, ° F	151	115	84
50% Point, ° F	163	133	89
90% Point, ° F	190	203	
95% Point, ° F	199	223	95
Final Boiling Point, ° F	217	243	106
Recovered, Percent		97.4	96.0
Residue, Percent		0.5	0.5
Loss, Percent	0.4	2.1	3.5
Aromatics	5.8	16.2	1.1
Olefins	79.7	42.7	70.2
Saturates	14.5	41.1	28.7
Research Octane No., Clear	93.2		
+3 ml. TEL/gal	98.7	100.94	100.94
Motor Octane No., Clear	78.8	82.1	82.5
+3 ml. TEL/gal	83.8	88.1	86.8

The gasolines of the invention containing the above constituents in critical proportions may boil between about 80° F. and about 450° F. when tested by ASTM Method D–86 and are 95% or more hydrocarbons. They may have vapor pressures between about 7 and 15 pounds per square inch when determined by ASTM Method D–323. Their vapor pressures may, of course, be varied within this range depending upon the season of the year during which they are to be used. The octane numbers of the fuels of the invention are in excess of 100 when determined in accordance with ASTM Method D–908.

The gasolines of the invention may contain from about 2.0 to about 4.6 ml. of tetraethyl lead, tetramethyl lead or a similar volatile metal anti-knock compound per gallon and from about 1.2 to about 3.0, preferably 1.5 to 2.1 "theories" of a halohydrocarbon scavenger agent. One "theory" is the amount of the scavenger agent stoichiometrically equivalent to the antiknock agent in the gasoline. This method of expressing scavenger concentrations is a conventional one and will be familiar to those skilled in the art. Halohydrocarbon scavenger agents suitable for inclusion in the gasolines of the invention include alkyl halides such as chlorobromomethane, tetrabromoacetylene, trichloroethylene, ethylene trichloride and ethylene dibromide; alicyclic halogenated hydrocarbons such as chlorocyclopentane and trichlorocyclopentane; aromatic halohydrocarbons such as chlorobenzene, dibromobenzene, trichlorobenzene, dibromotoluene, and bromoxylene; and mixtures of such compounds. Ethylene dichloride and ethylene dibromide are preferred scavenger agents for use in the fuels of the invention.

In addition to a volatile metal anti-knock compound and a halohydrocarbon scavenger agent as described above, the improved gasolines of the invention may also contain solvent oils consisting of hydrocarbon mixtures having Saybolt viscosities at 100° F. of not more than about 450 seconds, 50% distillation points not more than about 350° F. at 10 mm. Hg and API gravities between about 18 and 28. They may also contain corrosion inhibitors such as amines, amine phosphates and nitrates, and Santolene C, which is a phosphorus-containing dimer of linoleic acid. Also included may be gum inhibitors such as N,N-disecondary butyl p-phenylenediamine, 3,4-dimethyl-6-tertiary butylphenol and 2,6-ditertiary butyl-4-methylphenol; anti-icing agents such as isopropanol, hex-

ylene glycol, carbitol and dimethyl formamide; dyes such as 1,4-diisopropyl amino anthraquinone and p-dimethyl aminoazobenzene; dye stabilizers such as ethylene diamine; and other additive materials commonly employed in gasolines.

The invention may be further illustrated by considering results obtained in a series of experiments in which the octane numbers of various gasoline blends were determined and by referring to the accompanying drawings which illustrate fuel compositions and octane levels.

In a first series of experiments blends of alkylate, catalytic reformate, and catalytic pentanes and pentenes were blended in various proportions. The leaded research octane number of each blend was first calculated using conventional octane blending correlations. Tetraethyl lead was added to each blend in a concentration of 3 ml. per gallon and the actual research octane number of each blend was obtained by direct match octane number determinations using commercial reference fuels as standards. In each case the octane ratings are expressed as Coordinating Research Council Octane Numbers. This rating method is accepted as standard throughout both the petroleum and automotive industries.

Table I

Blend No.	Alkylate, Vol. Percent	Cat. Reformate, Vol. Percent	Cat. C_5's, Vol. Percent	CRC R.O.N.+ 3 ml. TEL		Δ CRC R.O.N.
				Actual	Computed	
1	100	0	0	107.5	107.5	----------
2	0	100	0	108.9	108.9	----------
3	0	0	100	100.9	100.9	----------
4	0	57.5	42.5	104.1	105.9	−1.8
5	62.5	0	37.5	108.3	105.9	+2.4
6	4.2	50.3	45.5	104.3	105.6	−1.3
7	8.5	43.1	48.4	104.3	105.6	−1.3
8	17.0	28.8	54.2	104.3	105.2	−0.9
9	25.4	14.4	60.2	104.3	105.2	−0.9
10	29.7	7.2	63.1	104.3	105.0	−0.7
11	7.8	87.5	4.7	108.6	107.9	+0.7
12	15.6	75.0	9.4	107.9	107.6	+0.3
13	31.3	50.0	18.7	107.2	106.9	+0.3
14	46.9	25.0	28.1	107.4	106.4	+1.0
15	54.7	12.5	32.8	108.1	106.1	+2.0
16	73.4	21.9	4.7	108.8	107.5	+1.3
17	71.8	18.8	9.4	108.9	107.2	+1.7
18	68.7	12.5	18.8	108.8	106.8	+2.0
19	65.7	6.2	28.1	108.7	106.2	+2.5
20	64.1	3.1	32.8	108.4	106.1	+2.3
21	75.0	25.0	0	108.7	107.9	+0.8

The data shown in Table I and similar data from other tests were plotted to obtain a composition diagram showing the octane ratings of the various blends. This composition diagram is shown in the attached FIGURE 1. It can be seen from FIGURE 1 that blends containing more than about 35% catalytic reformate do not show positive octane number interactions; while blends containing from about 40% to about 95% alkylate, about 0 to 35% catalytic reformate and about 5 to 60% catalytic naphtha or C_5 hydrocarbons have octane ratings which may be as much as 3 CRC octane numbers above the predicted values. The particular advantage of using blends containing from about 50 to 90% alkylate, about 0 to 20% catalytic reformate and about 10 to 50% catalytic naphtha and C_5 hydrocarbons is also shown by FIGURE 1. Blends containing from 65 to 80% alkylate, 0 to 5% catalytic reformate and from 15 to 40% of a catalytic C_5 to 300° F. naphtha are of especially high octane value.

In order to further demonstrate the invention, reference is made to data obtained in a second series of experiments in which a blend of 83% alkylate and 17% catalytic reformate, a blend of 34% alkylate and 66% catalytic C_5 hydrocarbons, and a blend of 58% alkylate and 42% catalytic naphtha were prepared. Each of these three binary blends had a CRC research octane number of about 103.7. The three binary blends were then blended together in various proportions and the octane ratings of the final blends were measured by direct match octane number determinations as in the previous experiments. The data obtained are shown in Table II below.

Table II

Blend	Vol. Percent Blend A [1]	Vol. Percent Blend C [2]	Vol. Percent Blend C [3]	Actual CRC RON+ 3 ml. TEL
1	100	0	0	103.7
2	0	100	0	103.6
3	0	0	100	103.7
4	87.5	0	12.5	105.3
5	75.0	0	25.0	105.8
6	50.0	0	50.0	105.7
7	25.0	0	75.0	104.8
8	12.5	0	87.5	104.4
9	87.5	12.5	0	104.4
10	75.0	25.0	0	104.4
11	50.0	50.0	0	104.4
12	25.0	75.0	0	104.2
13	12.5	87.5	0	103.7
14	0	12.5	87.5	103.6
15	0	25.0	75.0	103.6
16	0	50.0	50.0	103.6
17	0	75.0	25.0	103.6
18	0	87.5	12.5	103.6
19	60.0	30.0	10.0	105.3
20	60.0	10.0	30.0	106.0
21	20.0	60.0	20.0	104.7
22	20.0	20.0	60.0	104.9

[1] Blend A contained 83% alkylate and 17% catalytic reformate.
[2] Blend B contained 58% alkylate and 42% catalytic naphtha.
[3] Blend C contained 34% alkylate and 66% catalytic C_5 hydrocarbons.

The data of Table II were used to prepare the attached FIGURE 2 which shows the octane values for various compositions of the three binary blends. Even though the three starting blends all had octane ratings of 103.6, cross blends of these had ratings of over 106. This octane number increment clearly illustrates the surprising octane number improvement which can be realized by selective blending to take advantage of positive blending interactions.

It will be understood that the fuels of the invention are not limited to fuels containing alkylate, catalytic reformate, and catalytic naphtha and C_5 hydrocarbons alone and that other constituents may be included so long as the alkylate, catalytic reformate and catalytic naphtha and C_5 hydrocarbons are employed in ratios to one another such that positive interactions occur. Polymer gasoline and butane may be added, for example to a blend containing from 40 to 95% alkylate, from 0 to 35% catalytic reformate and from 5 to 60% of catalytic naphtha and catalytic pentenes and pentanes to provide a fuel having the proper volatility characteristics. Although the presence of such other constituents will affect the overall octane rating of the gasoline, the benefit of the synergistic interaction between the alkylate, catalytic reformate and catalytic naphtha and catalytic pentenes and pentanes is not lost and higher octane ratings can be obtained than would be possible if these four constituents were blended in ratios such that positive interactions did not occur.

What is claimed is:

1. A high octane premium gasoline having an octane number in excess of 100 and containing as the hydrocarbon constituents thereof from about 50 to 87.5% by volume of

(*a*) blend A containing 83% by volume of an alkylate boiling between about 100° F. and about 360° F. produced by alkylation of low molecular weight isoparaffin with a C_3 to C_5 olefin and about 17% by volume of a catalytic reformate boiling between about 100° F. and about 400° F. produced by contacting a naphtha with a reforming catalyst in the presence of hydrogen under reforming conditions; and from 12.5 to about 50.0% by volume of

(*b*) blend C containing about 34% by volume of said alkylate and about 66% by volume of catalytic C_5 hydrocarbons derived from the product stream of a catalytic cracking unit, said high octane gasoline

yielding a CRC research octane number higher than that of any individual blend.

2. The gasoline composition of claim 1 wherein incorporated in said gasoline is a minor amount of a volatile lead antiknock agent.

3. A high octane premium gasoline having an octane number in excess of 100 and containing as the hydrocarbon constituents thereof about 60% by volume of

(*a*) blend A containing 83% by volume of an alkylate boiling between about 100° F. and about 360° F. produced by alkylation of low molecular weight isoparaffin with a C_3 to C_5 olefin and about 17% by volume of a catalytic reformate boiling between about 100° F. and about 400° F. produced by contacting a naphtha with a reforming catalyst in the presence of hydrogen under reforming conditions; from 10 to about 30% by volume of

(*b*) blend B containing about 58% by volume of said alkylate and about 42% by volume of a C_5 to 300° F. catalytic naphtha derived from the product stream of a catalytic cracking unit; and from 10 to about 30% by volume of

(*c*) blend C containing about 34% by volume of said alkylate and about 66% by volume of catalytic C_5 hydrocarbons derived from the product stream of a catalytic cracking unit, said high octane gasoline yielding a CRC research octane number higher than that of any individual blend.

4. The gasoline composition of claim 3 wherein incorporated in said gasoline is a minor amount of a volatile lead antiknock agent.

5. The gasoline composition of claim 2 wherein said minor amount is from 2.0 to about 4.6 ml./gallon.

6. The gasoline composition of claim 2 wherein said lead antiknock agent is tetramethyl lead.

7. The gasoline composition of claim 2 wherein said lead antiknock agent is tetraethyl lead.

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