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PRODUCTION OF HIGH OCTANE NUMBER FUELS

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The present invention is concerned with providing a method of treatment which is particularly applicable to low boiling components of naphthas formed under intensive dehydrogenation conditions which obtain in low pressure vapor phase cracking of petroleum distillates.

It is designed to derive high anti-knock ingredients efficiently from a low quality portion of naphthas which have a high content of low boiling olefins.

Low pressure vapor phase cracking is a development which has become important in the manufacture of highly aromatic naphthas. The high aromatic content of these naphthas is accompanied by a high content of olefins and other unsaturated hydrocarbons, particularly in the low boiling range, and it is found that these olefins, to a large extent, are detrimental to the quality of the naphtha as a motor fuel.

The low pressure vapor phase cracking is characteristically performed in the vapor phase at pressures ranging from about 0 to 250 lbs./sq. in. gauge, or lower, and at a temperature in the range of about 900° F. to 1400° F. It may also be conducted with a cracking catalyst, in which event the temperature range is somewhat lowered, i. e., to about 850° F. to 1050° F.

When a naphtha product from a low pressure vapor phase cracking is subjected to fractionation or stabilization, and the low boiling cuts separated are inspected for anti-knock characteristics, it is observed that debutanizer tops or C_4 cuts have high octane numbers while the debutanizer bottoms composed predominantly of C_5 and C_6 hydrocarbons have very low octane numbers. It is appreciated by those skilled in the art that it is commonly desirable to stabilize a gasoline, yet important to avoid completely omitting C_4 to C_6 hydrocarbons from the gasoline motor fuel if the fuel is to have proper volatility. Thus, the problem created is how this low boiling part of the unsaturated gasoline should be treated to produce higher octane number fuels efficiently and economically.

A specific object of the present invention is to provide an efficient treatment for converting C_5 and C_6 cuts of high olefin content into higher octane number fuel ingredients.

In accordance with the present invention, C_5 and C_6 olefins are effectively transformed in molecular structure without cracking and without change in molecular weight by catalytic reaction in the presence of bauxite under proper conditions, and thereafter the transformation products thus obtained are conveniently purified for blending with a gasoline fuel and in a definitely better form for alkylation to derive a high quality alkylate useful for blending, particularly when it is desired to manufacture aviation gasolines.

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Bauxite is hydrated alumina which has found usefulness in a variety of petroleum refining processes and which has also been proposed to be used as a cracking catalyst, but in these operations the bauxite functions in a very different manner with respect to the types of materials treated, the conditions of the treatment, and results. When it is used as a cracking catalyst under cracking conditions, it acts to promote the breakdown of higher boiling hydrocarbons into gasoline and gas. When it is used in a low temperature purification treatment, it acts to adsorb color- and gum-forming unsaturated hydrocarbons from an oil and to desulfurize an oil containing sulfur compounds without altering the hydrocarbons which remain in the oil. In the present instance, the bauxite is made to have a specific transformation action on olefinic C_5 and C_6 hydrocarbon fractions to change the molecular structure of olefins which remain in the treated fractions without cracking.

In the operation of the present invention, it is preferred to have the low boiling hydrocarbon fraction used for the transformation reaction made up mainly of C_5 and C_6 chain olefins. It may contain some amount of C_4 and C_7 hydrocarbons. In the preferred operation, the selected feed stock for the catalytic transformation with bauxite is carried out at a temperature between 750° F. and 850° F., and with the space velocity regulated to come within the range of about ½ volume to 2 volumes of liquid hydrocarbons per volume of catalyst per hour. The contact time may be decreased within the range of about 2 minutes to ¼ minute with increase in temperature. Hot vapor products emerging from the reaction zone are then readily purified by being subsequently passed at a temperature of about 400° F. to 500° F. through an adsorbent, such as clay, under a superatmospheric pressure of, for example, 100 lbs./sq. in. gauge.

In the purification treatment, clay effectively serves to eliminate diolefins. Bauxite may be used also as an adsorbent in the purification step at temperatures below 750° F. and preferably no higher than 500° F. Following the purification treatment with a solid adsorptive material, the products separated from the polymers may be fractionated prior to blending or further processing, and at the same time be freed of any gaseous impurities and any entrained polymers.

As a specific embodiment of the present invention, the purified transformation product of an olefinic C_5—C_6 cut obtained in debutanizer bottoms from naphtha products in low pressure vapor phase cracking of a virgin gas oil is subjected to alkylation with isoparaffins in the presence of sulfuric acid to obtain an improved yield of high quality alkylate.

As another specific embodiment of the invention, a purified bauxite transformation product containing C_5—C_6 hydrocarbons is recombined with the stabilized gasoline, with alkylate gasoline, or other higher boiling gasoline fuels to impart thereto normal volatility characteristics and improved octane number.

For the purpose of illustration, the following example is given on the procedure and results:

EXAMPLE 1

For analytical investigation, approximately 100 gallons of cracked naphtha were prepared by cracking 33.3° A. P. I. East Texas virgin gas oil in a once-through coil-only cracking unit at a space velocity of 3 v./v. hr. at a temperature of 960° F. and under a pressure of 200 lbs./sq. in. gauge. The conversion yield was 25% to 30% naphtha distillate per pass. Fractions of the naphtha distillate were finished by a catalytic transformation with bauxite at 800° F., 100 lbs./sq. in. gauge pressure, and a feed rate of 1 v./v. hr. (about 53 seconds contact time) followed by a clay tower purification. Detailed analyses were made of the naphtha fractions before and after the treatment, and the results are shown in the following table:

TABLE I

Detailed analysis of fractions from the cracking process before and after the catalytic transformation with bauxite and clay purification

Fraction	Vol. percent total gasoline	Boiling range		Vol. percent of components		Hydrocarbon and boiling point, ° C.
		° C.	° F.	Untreated	Treated	
1	10.4	28–40	82–104	4	0	C_5 diolefin (isoprene, 34.1° C.).
				35	8	C_5 amylenes (30–31° C.).
				23	50	C_5 amylenes (36–39° C.).
				38	42	C_5 n-paraffins (pentane, 36° C.).
2	3.4	40–60	104–140	16	0	C_5 chain and cyclic diolefins.
				42	50	C_5 naphthene (cyclopentane, 49° C.).
				42	50	C_6 iso-olefins (methylpentenes).
3	11.0	60–70	140–158	0	0	C_6 diolefins (60–65° C.).
				5	0	C_6 diolefins (65–70° C.).
				60	15	C_6 chain olefins (60–65° C.).
				8	52	C_6 chain olefins (65–70° C.).
				6	6	C_6 isoparaffins (60–65° C.).
				21	27	n-Paraffins (hexane, 68.8° C.).
4	4.4	70–82	158–180	19	20	Aromatics.
				5	0	C_6 diolefins.
				9	10	C_6 chain olefins.
				52	54	C_6 cyclic olefins.
				10	11	C_6 naphthenes.
				5	5	C_7 paraffins.

The analyses show that the major changes by the catalytic transformation treatment take place in the two main fractions: fraction 1, boiling from 82 to 104° F., and fraction 3, boiling from 140° F. to 158° F. The main change is a transformation of the relatively low boiling C_5 and C_6 chain olefins (B. pt. 30–31° C. and 60–65° C., respectively) to the slightly higher boiling C_5 and C_6 isomers (B. pt. 36–39° C. and 65–70° C., respectively). This upward shift in boiling points indicates a shift in the double bond toward the center of the olefin molecules. The desired change becomes less pronounced as the boiling points of the fractions are increased above 158° F.

In the C_5 and C_6 fractions there is a substantial increase in the proportions of the higher boiling amylenes and hexenes, and this change is accompanied by a definite octane number improvement for each of these fractions. By actual measurement, an octane improvement of 7.4 octane numbers was obtained.

Further, in order to illustrate how the transformation affects the alkylation properties of the low boiling components, olefinic components of the C_5 fraction present before and after the catalytic bauxite transformation were used as reactants with isobutane under typical low temperature alkylation conditions as set forth below:

TABLE II

Alkylation operating conditions

Catalyst	Concentrated H_2SO_4
Titratable acidity, percent	93–96
Temperature, ° F.	41
Acid to hydrocarbon ratio	1:1
Isobutane to olefin feed ratio	10:1

The results obtained indicate that the bauxite transformation products of the C_5 and C_6 olefins give a much better yield of total alkylate and an alkylate of substantially higher octane number than do the original olefins of lower boiling point. This is exemplified in the following representative data:

TABLE III

Alkylation of isobutane under comparative conditions with different C_5 olefins

Olefin reactants	Alkylate product	
	Wt. percent yield [1]	ASTM O. N.
C_5 amylenes (B. pt. 30–31° C.)	191	89.6
C_5 amylenes (B. pt. 36–39° C.)	201	90.6

[1] Theoretical yield 183%.

From a thorough study of the effects of the bauxite transformation treatment on narrow cut fractions of hydrocarbons formed in low pressure vapor phase cracking, the following observations and conclusions may be made:

1. A very valuable improvement is obtained in the anti-knock quality of the olefinic C_5 and C_6 fractions when subjected to the transformation reaction without cracking. This reaction is catalyzed by bauxite under proper conditions of temperature. The bauxite effectively catalyzes this reaction even when dehydrated.

2. The main observable effect of the bauxite transformation is the formation of higher boiling C_5 and C_6 alkenes from the lower boiling C_5 and C_6 alkenes, indicating the formation of more symmetrical arrangements in amylenes and hexenes.

3. The transformed C_5 and C_6 olefins of higher boiling point have substantially higher anti-knock quality than the initial C_5 and C_6 olefins, and are accordingly much better blending agents and ingredients for a motor fuel.

4. They are of enhanced value for reblending with gasoline distillates whence they originate. They are of particular value for blending with a straight run gasoline to obtain improved road rating fuels and with paraffinic gasoline fractions requiring improved front end volatility as, for example, alkylate gasolines.

5. The transformed C_5 and C_6 olefins are better adapted for alkylation with an isoparaffin than the relatively lower boiling initial C_5 and C_6 olefins. The efficiently accomplished transformation and purification by bauxite and clay places these fractions in improved condition for alkylation. The catalytic transformation with bauxite is preferably performed at a temperature between 750° F. and 850° F.

Motor fuels containing the transformed C_5 and C_6 olefins are further enhanced in blending value with tetraethyl lead. They may contain other useful additives, such as gum inhibitors, anti-corrosion agents, dyes, etc., as needed or desired.

Although the invention has been described with reference to specific detailed examples, it is not intended to be limited thereby. Various modifications which come within the spirit of the invention are intended to be included within its scope.

I claim:

1. A process for the production of high anti-knock fuel ingredients which comprises segregating a C_5 fraction containing predominantly

amylenes boiling at about 30° C. to 31° C. from a naphtha product of low pressure vapor phase cracking, passing said segregated fraction into contact with bauxite at a temperature of about 800° F. until a substantial proportion of said amylenes are transformed to C_5 olefins boiling at about 36° C. to 39° C., then passing the thus treated fraction through clay for purification, and thereafter alkylating the transformed C_5 olefins with isobutane to secure a high quality alkylate.

2. A process for producing high anti-knock quality fuel which comprises segregating a fraction containing predominantly 5 to 6 carbon atom olefinic hydrocarbons from a cracked distillate formed under intensive dehydrogenation conditions, contacting said fraction in vapor phase with bauxite at a sufficiently elevated temperature and for sufficient time to transform 5 to 6 carbon atom alkenes to alkenes having the same number of carbon atoms but with higher boiling points, purifying the thus treated fraction by contact at a lower temperature with an adsorptive material, alkylating at least a portion of the purified product with an isoparaffin to form a high quality alkylate, and blending said alkylate with hydrocarbon constituents of different boiling point to obtain a fuel of suitable volatility.

3. A process for producing motor fuel of improved octane rating which comprises cracking a higher boiling oil under low pressure vapor phase conditions controlled to form a motor fuel fraction having a high aromatic content in the higher boiling portion and a high olefinic content in the lower boiling portion, separating the motor fuel so formed into a higher boiling aromatic fraction and a lower boiling olefinic fraction consisting principally of C_5—C_6 olefins and containing a relatively high concentration of pentene-1 and hexene-1, passing the last-named fraction in vapor phase in contact with bauxite at a temperature between 750° F. and 850° F. for a period sufficient to isomerize the pentene-1 and hexene-1 into higher boiling isomers, thereafter alkylating the isomers so formed with a low boiling isoparaffin capable of forming an alkylate product within the motor fuel boiling range.

4. In the process defined by claim 3, the further improvement which comprises treating the isomers so formed to remove diolefins therefrom prior to the alkylation treatment.

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