

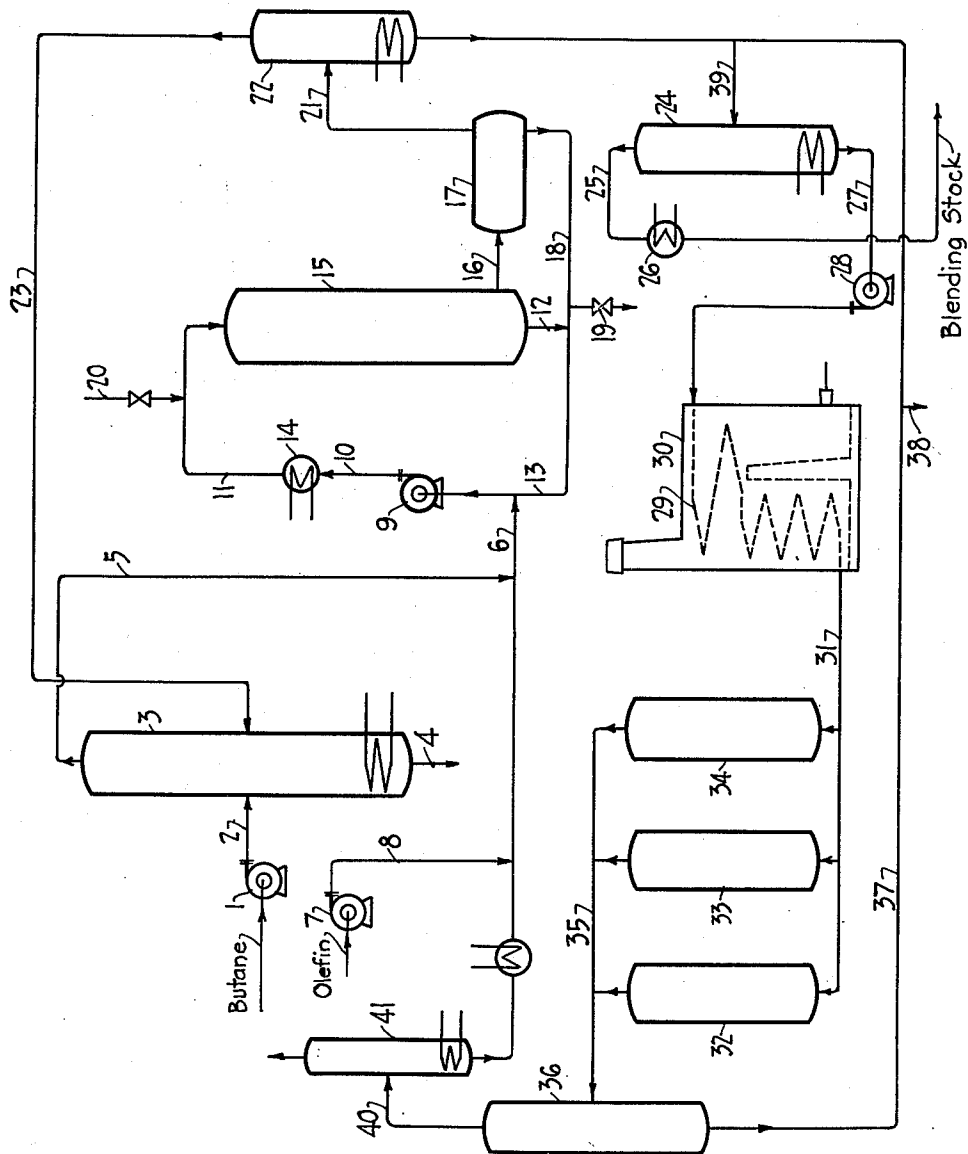
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PRODUCTION OF HIGH OCTANE BLENDING STOCKS

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PRODUCTION OF HIGH OCTANE BLENDING STOCKS

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This invention relates to an improved process for the production of high octane blending stocks. More particularly, the invention relates to a process for obtaining maximum yields of low boiling high octane blending stocks by means of alkylation.

As is well known, there is an ever-increasing demand for high octane fuels of the gasoline boiling range. This demand has been satisfied in the past primarily by means of thermal and, to some extent, by catalytic cracking of higher boiling hydrocarbons. More recently the demand for premium fuels has been met by the production of certain synthetic blending stocks of exceptionally high octane rating. One method in wide use is, for example, the synthesis of so-called iso-octane by the polymerization of isobutylene to di-isobutylene followed by hydrogenation. This method has the advantage that it utilizes as a raw material the isobutylene which is obtained from thermal cracking processes. It has the disadvantage, however, that it is a two-step process. Still more recently, processes have been developed for the production of such blending stocks by means of alkylation. In the alkylation processes saturated hydrocarbons of high octane number and excellent lead susceptibility are produced in a single step by the reaction of an isoparaffin (usually isobutane) with an olefin or a mixture of olefins such as butylene, amylene, and olefinic cracked gasoline distillates. The present invention relates to an improved method for the production of high octane blending stocks by alkylation.

The production of high octane blending stocks by alkylation is probably the most economical method for the utilization of certain by-product refinery materials such, in particular, as normal butylenes. In view of the great demand for higher octane blending stocks of the type produced by alkylation processes, every effort is made to produce the maximum quantity of these stocks from the raw materials available. In normal refinery operations, it is, however, not usually possible to obtain the maximum quantities of high octane alkylate due to an unfavorable balance of raw materials. Thus, normal refinery operations usually lead to an excess of isobutylene and other less desirable olefins and a deficiency of normal butylene and particularly isobutane. The amount of high octane blending stock which can be produced by alkylation, as presently practiced, is therefore limited by the availability of the least abundant reactant, which is usually isobutane. Also, the quality of the product which

may be produced is usually impaired to a certain extent by an unfavorable balance of the olefins in the feed stocks available.

The object of the present invention is to provide an improved combination process whereby better yields of superior blending stocks may be obtained from a given supply of alkylation feed. This object is realized by the combination process described hereinafter.

The process of the invention may conveniently be described in connection with the description of an operation comprised within its scope. To aid in this description there is provided the attached diagrammatic drawing which shows by means of conventional figures, not drawn to scale, an arrangement of elements in which the process may be conducted. For convenience, the description will be made with reference to the production of high octane blending stocks by the alkylation of isobutane with a butylene fraction employing a conventional sulfuric acid alkylation catalyst. Referring to the drawing, the isobutane from any suitable source such, for instance, as a saturated butane fraction consisting essentially of normal and isobutane is fed via pump 1 and line 2 into a suitable fractionating tower 3 wherein the isobutane is separated from the normal butane. Normal butane and any higher boiling material is removed as a bottom product from column 3 via line 4. The isobutane is removed overhead via line 5 and is fed to the alkylation reaction zone via line 6 in admixture with the desired proportion of olefin entering the system via pump 7 and line 8. The proportion of isobutane to olefins entering the reaction zone via line 6 is at least mol per mol and is preferably in substantial molar excess.

The mixture of butylene and isobutane entering the reaction zone via line 6 immediately contacts a rapidly flowing stream of recycled catalyst and reaction mixture containing an appreciable excess of isobutane. In such alkylation processes the maintenance of a considerable molar excess of isobutane to olefin in the reaction mixture at the point of introduction of the reactant leads to the formation of alkylation products of superior octane number. By means of reactors of specific design and/or by rapid recycle rates, it is possible to maintain this ratio exceedingly high. In practice, however, it is found that ratios of the order of from about 30:1 to 500:1, and preferably from about 100:1 to 500:1, give excellent products and are quite suitable. The reaction mixture is recycled via pump 9 and lines 10, 11, 12 and 13 through a cooler 14 and a time

chamber 15. A portion of the reaction mixture is continuously withdrawn from the cyclic system via line 16 to a separator 17 wherein the hydrocarbon phase and catalyst phase are allowed to stratify. The catalyst phase is returned to the reaction system via line 18. In order to maintain the activity of the catalyst, a portion of the partially spent catalyst from separator 17 may be continuously or periodically withdrawn via outlet 19 and an equivalent amount of fresh catalyst may be introduced into the reaction system via inlet 20. The separated hydrocarbon phase comprising excess isobutane, any normal butane introduced into the system with the olefin, and the high boiling products passes via line 21 to a suitable fractionating column 22. Column 22 is preferably operated in such a manner that all of the unreacted isobutane and any lower boiling materials not desired in the final product are removed overhead. This overhead product is recycle via line 23 back to column 3 wherein the isobutane is separated and returned to the alkylation system. The bottom product from column 22 comprising the total reaction product is, according to the process of the invention, preferably passed to a second fractionating column 24 wherein it is separated into a lower boiling fraction of high octane number and a higher boiling fraction, hereinafter referred to as "higher boiling products," consisting principally of hydrocarbon products boiling above about 130° C. The lower boiling hydrocarbon product is removed overhead via line 25 and condenser 26, and removed from the system as a finished product. The higher boiling products are passed via line 27 and pump 28 through a coil 29 in a suitable heater 30 wherein they are vaporized. The preheated vapors of higher boiling products from coil 29 pass via manifold line 31 into one or more catalytic converters 32, 33 and 34 wherein they are subjected to a selective splitting treatment with catalysts of the type more fully hereinafter described. The vapors from the catalytic cracking reactors pass via manifold line 35 to a suitable fractionating column 36 wherein they are separated into a normally gaseous fraction consisting largely of butane and butylene and a normally liquid bottom product. The bottom product from column 36 consists essentially of saturated hydrocarbons having the desired volatility and excellent octane number. This product, withdrawn via line 37, may, if desired, be withdrawn from the system via line 38 and utilized as a suitable blending stock. In many cases, however, the normally liquid product from column 36 contains appreciable quantities of unreacted hydrocarbon. In such cases it is usually more desirable to recycle the total bottom product via lines 37 and 39 back to fractionating column 24. In this way only the hydrocarbon products boiling below about 130° C. are collected and such higher boiling material is recycled through the catalytic converters 32, 33 and 34 until it is finally converted into hydrocarbon material of the desired boiling range. The normally gaseous fraction from column 36 is preferably passed via line 40 to a fractionating column 41 wherein a butane-butylene fraction is separated as a bottom product from any lighter boiling materials which may be present. The butane-butylene fraction from said column is returned via line 6 in admixture with added butylene from line 8 and added isobutane from line 5 to the alkylation reactor system.

In the above, the process of the invention has

been illustrated with reference to the alkylation of isobutane with butylene employing concentrated sulfuric acid as the alkylation catalyst. This is the specific embodiment of the process which is of the greatest interest at the present time. The invention is, however, not in any sense limited to this embodiment. Thus, the process is applicable generally to the alkylation of saturated hydrocarbons such as paraffins and naphthenes which have a tertiary carbon atom with any suitable alkylating agent. In general, the preferred alkylating agents are the olefins and olefin mixtures such as ethylene, propylene, the butylenes, amylenes, etc., and the cracked gasoline distillates. In lieu of the olefins their equivalents in the reaction such as the esters, particularly the alkyl sulfates, may also be employed. When using sulfuric acid as the catalyst, it is generally preferable from the commercial standpoint to alkylate olefins having at least three, and preferably four, carbon atoms. The invention is, however, in no way limited to the use of sulfuric acid as the alkylation catalyst. Thus, the process may be suitably effected with any of the known alkylation catalysts. Suitable catalysts other than sulfuric acid are, for example, the Friedel-Crafts alkylation catalysts such as aluminum chloride and/or aluminum bromide and certain other mineral acids such as phosphoric acid. Also, the catalyst may, if desired, contain various promoting materials such as boron fluoride, hydrogen fluoride, cupric sulfate, copper pyrosulfate, mercuric sulfate, nickel sulfate, cobalt sulfate, vanadium pentoxide, phosphorus pentoxide, zinc phosphate, and the like, which have been found to be beneficial in certain cases. Also, the invention is not limited by the physical limitations of the apparatus described for the purpose of illustration. Thus, any of the reactors and/or reaction systems suitable for the efficient execution of the alkylation step may be employed instead of the simple cyclic system shown.

In the alkylation reaction the primary reaction product is a saturated hydrocarbon or mixture of saturated hydrocarbons formed by the union of one molecule of the olefin with one molecule of the isoparaffin. There is, however, always an appreciable amount of higher boiling materials formed. Consequently, the crude product formed in such processes invariably consists of a complicated mixture of hydrocarbons boiling essentially in the gasoline boiling range. If the crude hydrocarbon product is fractionated and the properties of the various fractions determined, it is found that there is a gradual falling-off of the octane number and lead susceptibility and an increase in the bromine number of the fractions as the average boiling point is raised. Thus, the highest quality product is that boiling in the lower range and the poorest quality product is that boiling in the upper range of the total boiling range of the total product. It would be desirable therefore from the standpoint of quality to recover and utilize as a blending stock only the lower boiling fraction of the product. This, however, greatly decreases the economy of the process due to the considerable decrease in yields obtained. In the production of high octane blending stocks for aviation gasoline, however, this is the practice and the less desirable higher boiling product is used as a component of ordinary gasoline. The present invention provides process whereby substantially complete yields of the more desirable lower boil-

ing product may be produced. According to the present process, the crude product is separated into the desired lower boiling product, for instance boiling below about 130° C.-150° C., and a less desirable higher boiling product. The higher boiling product is subjected to a separate catalytic treatment whereby it is split into high octane hydrocarbons having a more desirable boiling point and a gaseous fraction which is exceptionally suitable as a feed stock in the alkylation reaction. This splitting of the less desirable higher boiling material takes place with regenerative cracking catalysts of the clay type quite selectively and with exceptional ease. This is illustrated by the following examples.

Example I

A higher boiling hydrocarbon product obtained in the alkylation of isobutane with 100° C. end point cracked gasoline in the conventional sulfuric acid alkylation process, and boiling between about 214° C. and 318° C., was contacted with a catalyst consisting essentially of a blend of silica, alumina and zirconia with and without steam under the following conditions:

Temperature	-----°C	500	500
Liquid hourly space velocity	-----	3	4
Diluent	-----	None	None
Mol ratio diluent to feed	-----	5	5
Pressure	-----atm	1	1

About 75% of the treated material was converted into lower boiling material and a gaseous fraction. The composition of the gaseous fraction (about 21% and 23%, respectively, of the higher boiling alkylate) was as follows:

	Without steam	With steam
	Volume %	Volume %
H ₂	12.4	4.6
CH ₄	0.9	0.9
C ₂ H ₄	1.8	1.8
C ₂ H ₂	2.7	1.1
C ₃ H ₆	22.7	28.8
C ₃ H ₈	2.0	0.9
i-C ₄ H ₈	25.4	33.4
n-C ₄ H ₈	15.0	18.4
C ₄ H ₁₀	18.0	10.1

Example II

A heavy hydrocarbon material produced in the alkylation of isobutane with butylenes in the conventional sulfuric acid alkylation process, and boiling in the range between about 170° C. and 288° C., was contacted with a clay-type cracking catalyst without steam under the conditions described above. About 48% of the treated material was converted into lower boiling material. About 21% of the material was converted to a gaseous product having the following composition:

H ₂	-----	5.1
CH ₄	-----	11.8
C ₂ H ₄	-----	2.2
C ₂ H ₂	-----	2.5
C ₃ H ₆	-----	19.4
C ₃ H ₈	-----	7.4
i-C ₄ H ₈	-----	18.8
n-C ₄ H ₈	-----	9.4
C ₄ H ₁₀	-----	23.4

Example III

A higher boiling hydrocarbon material produced by the sulfuric acid alkylation of isopen-

tane with amylenes, and boiling between about 147° C. and 306° C., was catalytically cracked with a silica-alumina cracking catalyst at a liquid hourly space velocity of 3 without diluent under otherwise the same conditions as above specified. About 35% of the treated material was converted into lower boiling material. About 13% was converted to a gaseous fraction having the following composition:

H ₂	-----	10.3
CH ₄	-----	16.0
C ₂ H ₄	-----	32
C ₂ H ₂	-----	1.3
C ₃ H ₆	-----	25.7
C ₃ H ₈	-----	3.3
i-C ₄ H ₈	-----	11.0
n-C ₄ H ₈	-----	11.2
C ₄ H ₁₀	-----	18.0

Example IV

A higher boiling hydrocarbon produced in the alkylation of isobutane with butylene, and boiling in the range of 170° C. to 288° C., was contacted with a catalyst consisting essentially of silica gel promoted with aluminum phosphate and aluminum fluoride at 500° C., a liquid hourly space velocity of 4, 60-minute process periods and 1 atmosphere pressure. About 47% of the treated hydrocarbon was converted to lower boiling products. About 23% was converted to a gaseous fraction having the following composition:

H ₂	-----	5.7
CH ₄	-----	6.9
C ₂ H ₄	-----	2.9
C ₂ H ₂	-----	1.8
C ₃ H ₆	-----	26.4
C ₃ H ₈	-----	5.7
i-C ₄ H ₈	-----	15.0
n-C ₄ H ₈	-----	13.0
C ₄ H ₁₀	-----	22.6

Example V

A higher boiling hydrocarbon obtained by the alkylation of isobutane with butylenes, and boiling between about 185° C. and 265° C., was contacted with a cracking catalyst consisting essentially of a blend of silica, alumina and zirconia under the conditions specified in Example IV. About 36% of the treated hydrocarbon was converted into lower boiling materials. About 16% was converted into a gaseous fraction having the following composition:

H ₂	-----	7.4
CH ₄	-----	10.3
C ₂ H ₄	-----	2.4
C ₂ H ₂	-----	1.0
C ₃ H ₆	-----	29.6
C ₃ H ₈	-----	3.9
i-C ₄ H ₈	-----	14.3
n-C ₄ H ₈	-----	11.7
C ₄ H ₁₀	-----	19.4

Example VI

A higher boiling hydrocarbon produced in the alkylation of isobutane with butylene, and boiling between about 170° C. and 288° C., was contacted with a catalyst consisting essentially of silica gel impregnated with zirconia under the conditions specified in Example IV. About 44% was converted into lower boiling products. About 18%

of the treated material was converted to a gaseous fraction having the following composition:

H ₂ -----	4.3
CH ₄ -----	8.4
C ₂ H ₄ -----	2.3
C ₂ H ₂ -----	1.9
C ₃ H ₆ -----	20.2
C ₃ H ₈ -----	3.0
i-C ₄ H ₈ -----	24.8
n-C ₄ H ₈ -----	11.5
C ₄ H ₁₀ -----	23.6

Example VII

A higher boiling material produced in the alkylation of isobutane with butylene, and boiling between about 197° C. and 280° C., was contacted with a cracking catalyst consisting essentially of a blend of silica, alumina and zirconia under the conditions specified in Example IV. About 53% of the treated hydrocarbon was converted to lower boiling products. About 22% of the treated material was converted to a gaseous fraction having the following composition:

H ₂ -----	6.6
CH ₄ -----	8.3
C ₂ H ₄ -----	2.2
C ₂ H ₂ -----	0.8
C ₃ H ₆ -----	28.4
C ₃ H ₈ -----	4.6
i-C ₄ H ₈ -----	16.9
n-C ₄ H ₈ -----	14.1
C ₄ H ₁₀ -----	18.1

It is seen from the above examples that under relatively mild conditions the variety of higher boiling materials resulting from alkylation were deeply cracked at relatively high space velocities to produce lower boiling materials and gas. By recycling the unconverted starting materials through the cracking reactors a substantially complete conversion into desirable lower boiling products may be obtained. On the other hand, that which remains unconverted in the splitting step may be withdrawn and not recycled. In this case it is found that this unconverted material, although it is relatively high boiling, is greatly improved in quality. This is apparently due to a selective cracking of the less desirable components. It is found that catalysts of the clay type selectively crack the higher boiling and olefinic components of the mixture. Thus, the bromine number of a higher boiling material resulting from alkylation may be reduced from 51 to 5-6 by the described catalytic splitting treatment.

A further particular advantage of the process of the present invention is that it allows a greater yield of alkylate to be produced from a given amount of raw materials. This is due to the fact that by subjecting the higher boiling material of inferior octane number to the described catalytic splitting treatment with catalysts of the clay type, a certain amount of isobutane is actually produced at the expense of less desirable hydrocarbon types. While the mechanisms of the reactions are not clearly understood, it is believed that the additional amounts of isobutane are produced from isobutylene formed by selective splitting of higher boiling hydrocarbons and polymers followed by a hydrogen transfer reaction. Isomerization of normal butane may also possibly take place. Regardless of the cause, it is seen that in general the butane fraction which consists predominantly of isobutane is approximately equal to the butylene fraction. The bu-

tane-butylene fraction produced in the described splitting step is therefore especially suited for alkylation and also serves to increase the yield of alkylate. The remaining portion of the gaseous fraction is seen to consist predominantly of propylene which may be used in alkylation and is also well suited for use in phosphoric acid polymerization and similar processes. The amount of undesirable products such as methane and ethane are, on the other hand, exceptionally small compared to thermal splitting.

The catalytic splitting treatment may be effected with any of the conventional clay-type cracking catalysts. Such catalysts comprise, for example, certain natural clays and clay-like earths usually consisting of silicates of alumina as well as various synthetic silicates and blends of silica with other earthy materials such as alumina, zirconia, magnesia, etc. Particularly suitable catalysts for the splitting step of the present process are, however, synthetic blends consisting essentially of silica gel or adsorptive alumina, especially when promoted with one or more agents such as alumina, silica, zirconia, magnesia, aluminum fluoride, aluminum phosphate, and magnesium fluoride. With catalysts of the described type the selective splitting of the higher boiling fractions may be effected at temperatures of from about 460° C. to about 560° C. The pressure is preferably substantially atmospheric, that is, from about 0 to about 30 p. s. i. During the catalytic splitting treatment a small amount of carbon is deposited upon the catalyst. This is periodically burned off in the conventional manner with a stream of combustion supporting gas. In the preferred embodiment of the invention the temperature and space velocity are adjusted to convert at least about one-third of the higher boiling material resulting from alkylation into lower boiling products. In view of the relative ease with which the splitting with catalysts of this type takes place, this may be realized with relatively high space velocities, for example liquid hourly space velocities in the order of about 1-5.

I claim as my invention:

1. In a process for the production of high octane blending stocks which comprises the step of alkylating exterior sources of isobutane with butylene, the method of increasing the available alkylation reactants and the ratio of available isobutane to normal butylene and, hence, increasing the potential production of lower boiling alkylate per given quantity of said alkylation reactants from exterior sources, which comprises separating the alkylation product into a lower boiling fraction and a higher boiling fraction boiling above about 130° C., and contacting the higher boiling fraction under cracking conditions with a cracking catalyst of the clay type, thereby to produce a normally gaseous fraction containing at least 40% by volume of C₄ hydrocarbons.

2. In a process for the production of high octane blending stocks which comprises the step of alkylating exterior sources of isobutane with an olefin, the method of increasing the available alkylation reactants and the ratio of available isobutane to olefin and, hence, increasing the potential production of lower boiling alkylate per given quantity of said alkylation reactants from exterior sources, which comprises separating the alkylation product into a lower boiling fraction and a higher boiling fraction boiling above about 130° C., and contacting the higher boiling fraction under cracking conditions with a cracking

catalyst of the clay type, thereby to produce a normally gaseous fraction containing at least 40% by volume of C₄ hydrocarbons.

3. In a process for the production of high octane blending stocks which comprises the step of alkylating exterior sources of an isoparaffin with an olefin, the method of increasing the available alkylation reactants and the ratio of available isoparaffin to olefin and, hence, increasing the potential production of lower boiling alkylate per given quantity of said alkylation reactants from exterior sources, which comprises separating the alkylation product into a lower boiling fraction and a higher boiling fraction boiling above about 130° C., and contacting the higher boiling fraction under cracking conditions with a cracking catalyst of the clay type, thereby to produce a normally gaseous fraction containing at least 40% by volume of C₄ hydrocarbons.

4. In a process for the production of high octane blending stocks which comprises the step of alkylating exterior sources of an isoparaffin with an olefin, the method of increasing the available alkylation reactants and the ratio of available isoparaffin to olefin and, hence, increasing the potential production of lower boiling alkylate per given quantity of said alkylation reactants from exterior sources, which comprises separating the alkylation product into a lower boiling fraction and a higher boiling fraction boiling above about 130° C., and contacting the higher boiling fraction under cracking conditions with a synthetic cracking catalyst comprising a blend of silica and alumina, thereby to produce a normally gaseous fraction containing at least 40% by volume of C₄ hydrocarbons.

5. In a process for the production of high octane blending stocks which comprises the step of alkylating exterior sources of an isoparaffin with an olefin, the method of increasing the available alkylation reactants and the ratio of available isoparaffin to olefin and, hence, increasing the potential production of lower boiling alkylate per given quantity of said alkylation reactants from exterior sources, which comprises separating the alkylation product into a lower boiling fraction and a higher boiling fraction boiling above about 130° C., and contacting the higher boiling fraction under cracking conditions with a synthetic cracking catalyst comprising a blend of silica, alumina and zirconia, thereby to produce a normally gaseous fraction containing at least 40% by volume of C₄ hydrocarbons.

6. In a process for the production of high octane blending stocks which comprises the step of alkylating exterior sources of an isoparaffin with an olefin, the method of increasing the available alkylation reactants and the ratio of available isoparaffin to olefin and, hence, increasing the potential production of lower boiling alkylate per given quantity of said alkylation reactants from exterior sources, which comprises separating the alkylation product into a lower boiling fraction and a higher boiling fraction boiling above about 130° C., and contacting the higher boiling fraction under cracking conditions with a silica-alumina cracking catalyst promoted with aluminum fluoride, thereby to produce a normally gaseous fraction containing at least 40% by volume of C₄ hydrocarbons.

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