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2,591,367

ALKYLATION OF ISOPARAFFINS WITH ISOMERIZED OLEFINS

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This invention relates to the manufacture of motor fuel and deals particularly with a new and more efficient method of producing products of improved anti-knock value by alkylating isoparaaffins with olefins.

Great advances have been made in the production of high octane gasoline within recent years, particularly as a result of the large scale adoption of isoparaaffin alkylation. In the alkylation of isoparaaffins to produce gasoline components, a wide variety of olefins have been suggested, but the olefins produced by the thermal or catalytic cracking of higher boiling hydrocarbons have been used almost exclusively. These olefins are made up of mixtures of straight and branched chain compounds which have the double bond at different locations in the chain. It has been proposed to segregate these olefins into fractions composed predominantly of olefins having the same number of carbon atoms per molecule and to alkylate isoparaaffins with the separated fractions, which, in the case of fractions having olefins of more than three carbon atoms, are still mixtures comprising branched chain tertiary olefins with secondary olefins having the double bond at the end of the chain as well as removed therefrom, e. g. secondary 1-olefins, 2-olefins, etc. In some cases the tertiary olefin content of such mixtures has been selectively removed prior to alkylation with the remaining secondary olefins. However, it has always been considered heretofore that all olefins having the same number of carbon atoms per molecule were substantially equivalent as isoparaaffin alkylating agents, and it has been the practice to use olefinic mixtures containing both 1-olefins and 2-olefins as the alkylation feed stock.

It has now been found that superior results may be obtained in the catalytic alkylation of isoparaaffins by using olefins having the double bond removed from the end of the chain as the alkylating agent. Typical examples of such more advantageous olefins are, for example, the 2-olefins such as 2-butylene, 2-amylene, 2-methyl butene-2, 2-hexylene, and the like. The secondary 2-olefins are preferred alkylating agents in the process of the invention, but olefins having the double bond further removed from the end of the chain, as in 3-hexylene, 2-methyl hexene-3, etc., may also be used. In one specific embodiment the process of the invention comprises isomerization of a secondary 1-olefin to a 2-olefin using any suitable isomerization catalyst, and alkylating an isoparaaffin, preferably a

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low boiling isoparaaffin such as isobutane and/or isopentane, with the resulting 2-olefin in the presence of an alkylation catalyst. By the method of the invention not only may the yield and quality of the alkylate be increased but also the effective life of the alkylation catalyst may be extended, thus reducing the cost of alkylation, compared to the results obtainable by alkylation of the isoparaaffin with the original 1-olefin.

A number of different methods are available for carrying out the isomerization of secondary 1-olefins to 2-olefins. U. S. Patent 2,379,731, for example, describes a particularly suitable method using sulfuric acid as the catalyst. Other catalysts include alumina, preferably acid-treated, e. g. by soaking in 1 normal hydrochloric acid and then drying, zinc chloride, silica or silica-alumina gels, alkaline earth oxides, preferably calcined, "Superfiltral," oxides of titanium, beryllium, zirconium, chromium and the like, etc. With solid granular catalysts such as these, the isomerization may be carried out, for example, by passing the 1-olefin or the 1-olefins in the gaseous state through tubes or towers packed with the catalyst. Preferably, however, the feed stock is maintained at least partly in the liquid phase and most advantageously the reaction is carried out under conditions such that the desired isomerization product is continuously separated from the unreacted 1-olefin and removed from the reaction zone substantially as fast as formed, leaving the 1-olefin therein for further reaction. One method of achieving this end is by use of a distillation column containing the solid isomerization catalyst. The 1-olefin-containing feed may be supplied in the liquid phase to the top of the column and is isomerized as it flows downward through the catalyst, the feed rate and temperature being preferably regulated so that the olefinic mixture corresponds substantially to the equilibrium mixture for the existing temperature when the hydrocarbons have traversed the catalyst bed. The product then passes into a fractionating zone (free from catalyst) which may be a part of the same column or a separate unit. In either case the unreacted 1-olefin is returned to the catalyst zone for further reaction. Where the fractionator is the lower part of the reaction column, the separated 1-olefin may pass directly up the catalyst column as vapor in countercurrent to the descending 2-olefin since, at least among the lower olefins, the 1-isomers boil sufficiently below the boiling point

of the desired 2-olefins to make this method of operation feasible. However, particularly when using a separate distillation column, it is generally more satisfactory to return the separated unreacted 1-olefin to the reaction with the feed.

The isomerization may be carried out equally satisfactorily by means of catalysts which need not be solids. Not only the previously mentioned sulfuric acid but also the other acids such, for example, as phosphoric acid, benzene sulfonic acid, hydrogen fluoride, perchloric acid, etc., may be used in the liquid state. However, even these acid catalysts may, if desired, be used as deposits or coatings on carriers such as clay, alumina, silica or other suitable solid materials. The previously discussed solid isomerization catalysts may be similarly used in order to increase their effective surface.

The temperature, pressure and feed rate are adjusted with respect to the particular olefin or olefins involved and the activity of the isomerization catalysts chosen so as to give the desired conversion with minimum side reactions. Thus, temperatures in the general range of about 33° C. to about 425° C. are suitable, the time of contact being preferably reduced as the temperature is increased. Polymerization and/or other side reactions during isomerization with acid catalysts may be reduced by using these catalysts in the form of aqueous solutions; thus, hydrogen fluoride of about 50% to 80%, preferably about 65% concentration, or sulfuric acid of about 70% to 90%, preferably about 80% strength, may be used. It is even feasible to carry out the olefin isomerization non-catalytically, but temperatures of the order of about 600° C. or higher are generally required and these lead to substantial side reactions which make such methods less desirable. The isomerization may be effected under conditions at which rearrangement of the carbon structure takes place in addition to the desired shift in the double bond, but this is not objectionable, and may even be advantageous in some cases, as long as the isomerization product is an olefin having the double bond removed from the end of the chain. Catalysts such as boric oxide on alumina, zeolites, etc. may be used for this type of isomerization.

As previously pointed out, the usual sources of olefins of four or more carbon atoms per molecule are generally mixtures containing both terminally unsaturated secondary olefins and secondary olefins having the double bond further removed from the end of the chain as well as tertiary olefins and diolefins. With such starting materials, it is desirable to separate diolefins and tertiary mono-olefins from the secondary olefins before carrying out the isomerization of the alpha olefin content. Selective polymerization or hydrogenation or reaction with maleic anhydride may be used for the removal of diolefins. The tertiary olefins may be removed by extraction, for example, with sulfuric acid as described in U. S. Patent 2,007,159, or by selective polymerization, for instance, as claimed in U. S. Patent 2,007,160, or by other suitable methods. The starting material may also be treated for the removal of sulfur and/or nitrogen compounds or other impurities, either before or after the removal of the diolefins and/or tertiary mono-olefins. The remaining mixture of secondary olefins, which in the case of petroleum cracking fractions will usually also contain substantial amounts of branched and straight chain paraffins, may be used directly as feed to the previously described isomerization. Alternatively,

the secondary olefin-containing mixture may be distilled to separate a fraction containing the terminally unsaturated olefin from olefins having the double bond removed from the end of the chain. Such distillation may advantageously be carried out in the same unit as is used for the fractionation of the isomerization product. Where the product fractionation unit is an integral part of the isomerization reactor as previously described, the feed mixture containing 1-olefin and 2-olefin may be introduced at a point below the catalyst zone and the separated 1-olefin vapors will pass up the tower and be isomerized while the 2-olefin content will flow out with the isomerization product. Other methods of producing the desired olefin which do not require such isomerization and/or fractionation may also be used. For example, diethyl carbinol may be dehydrated or 3-chloropentane may be dehydrochlorinated to produce 2-amylene suitable for use in the process.

The 2-olefin, or 2-olefins, however produced, is then fed, according to the invention, to the alkylation system for reaction with a paraffin such as isobutane, isopentane, or the like. Acid catalysts, such as sulfuric acid of about 85% to 100% concentration, hydrogen fluoride which may be anhydrous or aqueous, phosphoric acid, chlorosulfonic or fluorosulfonic acids, hydrofluoroboric acid, etc., may be advantageously used in the process. Instead of the individual catalyst acids, not only may mixtures of such acids be employed but also mixtures of one or more such catalysts with other materials having a beneficial effect on the reaction, for example, boron fluoride, phosphorus pentoxide, oxides of vanadium, zinc or cadmium phosphates, sulfur dioxide and/or trioxide, may be used. Another suitable group of alkylation catalysts are the metal halides, particularly the Friedel-Crafts type catalysts. Aluminum chloride, aluminum bromide, ferric chloride, titanium tetrachloride and antimony trichloride have been found to be suitable. Less active catalysts such as stannous or stannic chloride, bismuth chloride, etc. may also be used. The catalysts may be used in solid form as lumps or granules, or finely divided powders, or may be deposited on supports or carriers which may be inert or may have an advantageous influence on the reaction. U. S. Patent 2,295,977, for example, describes a method suitable for the preparation of such supported catalysts. Catalysts in the liquid state offer many advantages in the process. Friedel-Crafts type catalysts such as the aluminum halides may be used in this form by converting them to organic complexes. Organic complexes of active metal halides and ketones such as described in U. S. Patent 2,085,535, or metal halide-alkyl halide complexes such as may be prepared, for example, by refluxing the tertiary alkyl halide to be used in the reaction with the corresponding aluminum halides, may be used. Other suitable complex catalysts are those formed by the union of active metal halides with hydrocarbons, which may be either aliphatic or aromatic, or mixtures of hydrocarbons. The catalysts claimed in U. S. Patent 2,306,261, for example, may be used. Double salts of aluminum chloride such as are described in U. S. Patent 2,076,201 are also useful in the process. Complexes or sludges formed in the course of the reaction may, after addition of fresh metal halide, be used as the catalyst. While boron fluoride may be used as a gas, it is likewise preferable in liquid form. With Friedel-Crafts type cata-

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lysts, it is usually advantageous to use a small amount of an activator such as the corresponding hydrogen halide or the like.

Any suitable method of reacting paraffins with the 2-olefins in the presence of alkylation catalysts may be used in the alkylation step of the process. The alkylation may be carried out with either or both reactants in the vapor phase, but liquid phase reaction is preferred. Any suitable method of intimately mixing the reactants and catalyst acid may be employed. For example, jet mixers, towers provided with suitable baffles or packing, power-driven mixers and the like may be used. For large scale, continuous operation mixing by means of a pump which is in communication with a separator wherein reaction products may be separated at least in part from catalyst acid and the latter returned to the reaction, preferably together with a part of the separated product-containing phase to which fresh reactants are added before being contacted with catalyst acid, is advantageous. A preferred method of operation which is more fully described and claimed in U. S. Patent 2,232,674 comprises circulation of a stream of reacted mixture containing unreacted isoparaffin and continuously feeding into the mixture isoparaffin and olefin to be reacted therewith, the former preferably in molecular excess, while taking off from the circulating emulsion reacted mixture from which product equivalent to the feed is withdrawn and the remainder returned to the system. Preferably a molecular excess of isoparaffin over olefin is used in the reaction and most preferably the pretreated olefin is mixed with a molecular excess of isoparaffin before it is contacted with catalyst acid.

The conditions of alkylation which will be most desirable in any particular case will depend upon the nature of the isoparaffin and olefin involved. Where sulfuric acid is employed as the catalyst, initial concentrations of about 90% to 100% may be used although fuming H_2SO_4 is also suitable provided lower reaction temperatures are used. Temperatures of the order of about 5° C. to 50° C. may be used. The proportion of catalyst to hydrocarbon which will be desirable will depend upon the olefin being reacted. In general, volume ratios of about .5:1.0 to about 4:1 are suitable. Reaction times of about five to thirty-five minutes are preferred but may be varied depending upon the type of apparatus and method of operation from a fraction of a minute to as much as sixty minutes. Most preferably molar ratios of isoparaffin to olefin of at least 20:1 are used in the reaction mixture in order to favor alkylation and to suppress undesirable reactions such as olefin polymerization, and it is usually advantageous to use ratios of the order of 50:1 to 500:1 at the point where the olefin first contacts the acid. While the same ratio of paraffin to olefin may be used in the feed as is employed in the reaction, when the preferred method of feeding reaction mixture into recirculated reaction product is used, ratios of isoparaffin to olefin of about 3:1 to 20:1 in the feed are preferred. Single or multiple stage alkylation with either concurrent or countercurrent flow of reactants and catalyst may be used with either batchwise, intermittent or continuous operation.

Whatever the method of alkylation adopted, the hydrocarbon phase of reaction products may be treated to separate the alkylate from the excess un-reacted isoparaffin and the latter returned to the reaction. Where volatile catalysts

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are used, any small amount remaining in the reaction product after separation of the bulk of the catalyst, as previously described, may be recovered and returned to the reaction with the excess isoparaffin.

The following examples show specific applications of the process of the invention and illustrate certain of its advantages:

Example I

To show the superiority of the 2-olefins over the corresponding 1-olefins, alpha- and beta-butylenes were separately alkylated under the following conditions, with the results shown below:

10 mols isobutane per mol olefin in the feed
87%–89% isobutane in the feed
100% H_2SO_4 as catalyst
10° C. alkylation temperature
1 vol. acid per vol. of hydrocarbon
20 min. contact time

Butylenes	Alpha	Beta
Acid life.....	10	15
Light alkylate (15° C.–150° C.) in product..... percent..	96–97	97–98
Percent octanes in product..... do.....	93	95
ASTM, ON of product in 95%–97% acidity range.....	96.0	97.2
Light ends..... percent..	3.5	2.5

Example II

Two alkylation runs were made using a C_4 fraction of cracking products as starting material. In one case the alkylation was carried out without any pretreatment of the feed, while in the other case the fraction was treated with sulfuric acid to remove the isobutylene content and to isomerize 1-butylene to 2-butylene. In both cases the alkylation was carried out with 96% sulfuric acid using a ratio of isobutane to olefin of 4.4–4.8:1.

	Untreated Feed	Isomerized Feed
Composition of feed:		
Propane-propylene.....	0.4
Isobutylene.....	5.1	0.1
1-Butylene.....	4.4	1.5
2-Butylene.....	4.9	10.2
Isobutane.....	71.5	53.4
N-butane.....	13.7	34.8
Quality of Product:		
Octane number of alkylate.....	92.5	93.7

It will be apparent from this description of the invention that it offers many advantages over prior methods of operation. Not only does the process give more uniform results because the olefins are more uniform but also longer catalyst life in the alkylation, and alkylation products of improved quality are obtained because the isomerized olefins are predominantly beta-olefins.

Many variations may be made in the process, the various steps of which may be carried out batch-wise or intermittently instead of continuously. Still other variations may be made not only in the materials treated, but also in the details of operation employed, and it will be understood that the invention is not limited to the procedure disclosed by way of example, nor by any theory suggested in explanation of the improved result obtained.

This application is a continuation-in-part of application Serial No. 428,656, filed January 29, 1942, and which issued as Patent No. 2,460,303 on February 1, 1949.

I claim as my invention:

1. A process of producing higher boiling hydrocarbons which comprises treating hydrocarbon containing an alpha-olefin of at least four carbon atoms per molecule under conditions at which said olefin is isomerized to an olefin of the same number of carbon atoms per molecule but having a more centrally located double bond, and alkylating an isoparaffin with the resulting isomerized olefin in the presence of an alkylation catalyst.

2. A process of producing higher boiling hydrocarbons which comprises treating hydrocarbon containing an alpha-olefin of at least four carbon atoms per molecule under conditions at which said olefin is isomerized to a beta-olefin of the same number of carbon atoms per molecule, and contacting a mixture of said resulting beta-olefin and a substantial molar excess of an isoparaffin with an alkylation catalyst under alkylating conditions.

3. A process for producing high octane paraffins from an isoparaffin and secondary olefins, each having four to five carbon atoms per molecule, which comprises isomerizing a mixture of said olefins under conditions effecting conversion of 1-olefins to 2-olefins, admixing the effluent of said isomerization with the isoparaffin, and contacting the resulting mixture with an alkylation catalyst under conditions effecting alkylation of the isoparaffin with said 2-olefin.

4. The improved process of producing high octane paraffins from an isoparaffin and a secondary 1-olefin, each having four to five carbon atoms per molecule, which comprises subjecting said 1-olefin to the isomerizing action of a catalyst capable of isomerizing said 1-olefin to the corresponding 2-olefin, and alkylating said isoparaffin with the resulting isomerization effluent in the presence of an alkylation catalyst.

5. The improved process of producing high

octane motor fuel paraffins from an isoparaffin and a secondary 1-olefin, each having four to five carbon atoms per molecule, which comprises subjecting said 1-olefin to the isomerizing action of a catalyst capable of isomerizing said 1-olefin to the corresponding 2-olefin, alkylating said isoparaffin with the resulting isomerization effluent in the presence of concentrated sulfuric acid, and isolating from the resulting alkylation mixture a motor fuel of high octane rating.

6. The process of claim 5, in which said isoparaffin is isobutane.

7. The process of claim 5, in which said 1-olefin is butene-1.

8. A process of producing higher boiling hydrocarbons which comprises treating hydrocarbon containing alpha-butylene under conditions at which said olefin is isomerized to beta-butylene and contacting a mixture of the resulting beta-butylene and a substantial molar excess of isobutane with sulfuric acid under alkylating conditions.

9. A process of producing high octane motor fuel paraffins which comprises contacting alpha-butylene with sulfuric acid under conditions at which said olefin is isomerized to beta-butylene and contacting a mixture of the resulting beta-butylene and a substantial molar excess of isobutane with an alkylation catalyst under alkylating conditions.

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