

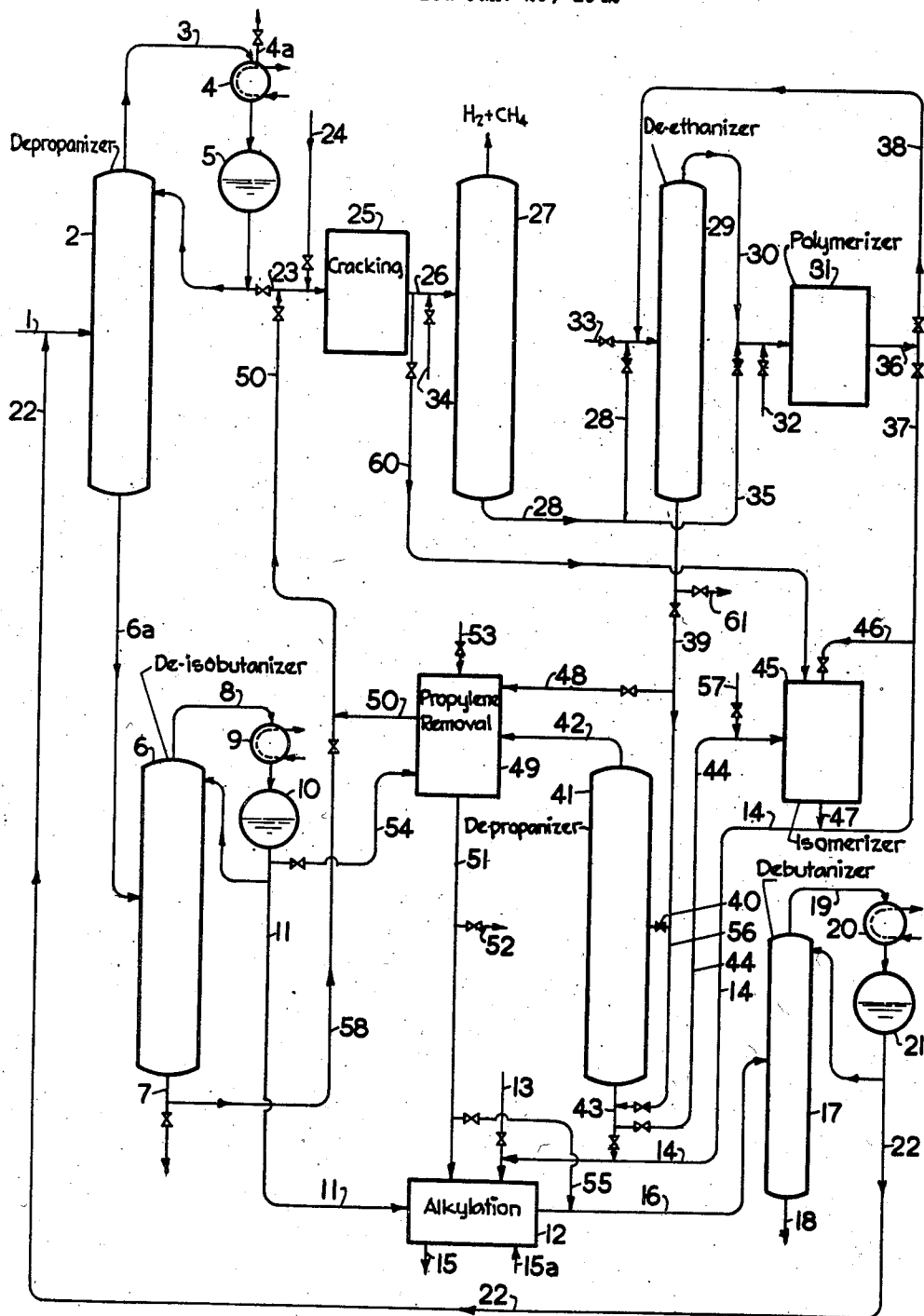
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GASOLINE MANUFACTURE

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GASOLINE MANUFACTURE

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This invention relates to the production of motor fuel and deals particularly with a new and more efficient method of increasing the yield of high anti-knock value hydrocarbons obtainable from petroleum products and the like.

Great advances have been made in the production of high octane gasoline within recent years, but large amounts of available hydrocarbons, particularly gaseous hydrocarbons such as ethane, ethylene and propane, are still unused because no satisfactory method for efficiently converting them to saturated liquid hydrocarbons has been available. It is an important object of the present invention to overcome this disadvantage of prior methods of gasoline manufacture. More particularly, it is an object of the invention to provide a method whereby hydrocarbons are treated in a series of cooperating steps to produce higher yields of isoparaffins boiling in the gasoline range than have been obtainable heretofore from the same starting materials. A specific object is to provide an improved, continuous and cyclic process of polymerization and alkylation of high efficiency. Another special object is to make propane and ethylene available as starting materials for the production of branched chain octanes. Still other objects and advantages of the process of the invention will be apparent from the following description.

Various proposals have been made for producing gasoline by procedures involving polymerization of olefines and alkylation of isoparaffins, but none of these methods have proved to be satisfactory because of the difficulties of correlating the polymerization with the requirements of the alkylation step. This is accomplished by the process of the present invention by the use of special polymerization conditions which insure high yields of high octane gasoline and long catalyst life in the alkylation step. The new process has the additional advantage that it makes more effective use of ethylene and propane than has heretofore been possible.

For the purpose of making the invention more clear, it will be described with particular reference to its application to the improvement of the commercially established method of alkylating isobutane with butylenes in the presence of concentrated sulfuric acid as the catalyst, in which propane is a component of the starting material. The accompanying drawing illustrates diagrammatically an assemblage of apparatus particularly adapted to this application of the process. It will be understood, however, that the invention is not limited to this application and that not

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only may other feed stocks and other alkylating methods be employed, but also that the other arrangements of apparatus and other operating procedures may be used.

Referring to the drawing, a charge of isobutane- and propane-containing hydrocarbon from any suitable source, for example, from the fractionation of natural gas or straight run gasoline, or residual paraffins from olefinic conversion processes, and hydrocarbons from the alkylation step of the invention, to be more fully described hereinafter, introduced via line 22, are fed, as by line 1, to a depropanizer column 2. The hydrocarbon feed to this column may be introduced at a plurality of points, instead of the single line shown, if streams of different composition are being employed. In column 2 all hydrocarbons of less than four carbon atoms, usually mainly propane, are taken off overhead via line 3 to condenser 4, preferably provided with an outlet 4a through which lower boiling components such as ethane may be removed, and accumulator 5, while the higher boiling components are removed as bottom product by line 6a and conducted to deisobutanizer column 6. In column 6 a separation of isobutane from normal butane is made, the latter being removed as bottoms via line 7, for use in adjusting the vapor pressure of gasoline and dehydrogenation to butylenes which may be used in the alkylation step or for other purposes. Isobutane of high purity is taken off via line 8 and condenser 9, and is fed from accumulator 10, by line 11, to the alkylation system, represented by 12. In the alkylation step, preferably carried out by the method disclosed and claimed in U. S. Patent 2,232,674, the isobutane is reacted with olefines to form branched chain hydrocarbons of high anti-knock value, boiling in the gasoline range. Olefines from a suitable outside source may be supplied by line 13. Such olefines may, for example, be a butane-butylene fraction of gases obtained in the stabilization of a cracked naphtha or the like and in such case will usually contain a small amount of propane. To the olefine or olefines admitted by line 13 are added olefines by line 14, which are derived from treatment of the propane collected in accumulator 5, as will be described more fully later. To maintain the activity of the alkylation catalyst at a high level, catalyst may be withdrawn from the system by line 15 and replaced by fresh or reactivated catalyst, introduced by line 15a. Reacted hydrocarbons from the alkylation system, comprising excess isobutane, diluents introduced with the olefine, including propane and normal

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butane for example, and alkylation products, are withdrawn by line 16 to a de-butanizer column 17. From column 17 alkylation products are withdrawn by line 18 for further fractionation, if desired, into cuts having boiling ranges appropriate for the particular use to which the products are to be applied. The separated lower boiling components are removed by line 19 to condenser 20 and accumulator 21, whence they are conducted by line 22 to column 2, in which the propane content is removed as previously described.

The separated propane collected in accumulator 3 is fed by line 23, together with propane from any extraneous source if desired introduced by line 24, to cracking unit 25 in which it is the object to produce as high conversions to unsaturates as possible. This may be advantageously achieved by non-catalytic cracking at atmospheric pressure and about 1200 F. to 1400° F., using a residence time of about 1 to 2 seconds. Under these preferred conditions, ethylene and propylene are the main reaction products and the formation of paraffins, such as ethane, is minimized. Other conversion methods, either catalytic or non-catalytic, may, however, be employed. Thus, for example, methods such as are described in U. S. Patents 2,168,840 and 2,217,865 may be used. As a rule, conditions of operation at which substantial amounts of ethylene are formed are preferred since highest conversions to unsaturates can be most economically obtained in this way. The conversion products, after suitable cooling or other desired treatment, not shown, are conducted by line 26 to separating unit 27, in which the components lower boiling than ethylene, mainly hydrogen and methane, are removed for use in supplying heat for the process or for other purposes. This separation may be effected by fractionation or by absorption of the higher boiling components in a suitable liquid such, for example, as pentane, followed by stripping of the absorption product. The remaining hydrocarbons, principally unreacted propane, ethylene and propylene, together with a small amount of higher hydrocarbons, mainly butylenes, are fed by line 28 to a fractionating column 29 in which the ethylene is removed as overhead by line 30 and fed to polymerization unit 31. Additional ethylene from any suitable source may be used in the polymerization, such ethylene being introduced by line 32, if sufficiently free from undesirable lower or higher boiling components, or by lines 33 or 34 if removal of such components is considered advisable.

The object of the polymerization step of the process is to produce, in high yield, olefines which are especially suitable for use in the alkylation step of the process, for example to convert ethylene as completely as possible to butylene. It is desirable to carry out the polymerization, whatever the olefine or olefines used as feed, so as to produce substantial amounts of normal olefines instead of branched chain polymers, since the former give improved results in the alkylation of isoparaffins. These objectives may be most advantageously achieved by effecting the polymerization in the presence of catalysts consisting of the metals of the 8th group of the periodic table. Of particular use for this polymerization are cobalt and nickel, cobalt being the preferred catalyst. The metals employed as the polymerization-promoting catalysts are used in a reduced state and are preferably employed in the form of finely divided particles disposed on suitable car-

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riers. The use of activated carbon as the carrier for the reduced metal, for example reduced cobalt, has been found to be of particular benefit for the conversion of ethylene to produce polymers containing high percentages of the desired butylenes, but other supports may be used. The use of the carriers for the active catalyst metals is advantageous since it permits an accurate control of the olefines to be polymerized and the metal catalyst in the reaction zone, while maintaining other operating conditions, such as the reaction temperature, pressure, space velocity, contact time, etc., constant. The metal catalyst, e. g. reduced cobalt, whether employed alone or in the preferred form of a finely divided metal deposited on activated carbon, or the like, may be prepared and employed in a variety of ways. For example, it may be used in the form of compact masses, granules, chips, powder, etc. One method of preparing the catalyst for the polymerization according to the present invention includes the steps of absorbing aqueous cobaltous nitrate on activated carbon or the like, decomposing the nitrate to the corresponding oxide by a prolonged heating at an elevated temperature, and finally reducing the oxide by heating, preferably while passing an inert or a reducing gas, for example hydrogen, through the catalyst mass. Other methods of preparing the reduced catalyst metal, as well as the incorporation thereof onto porous carriers, may be employed. The concentration of the active reduced metal catalyst may vary within relatively wide limits, depending on the specific metal employed, the desired contact time, and the like. When ethylene is polymerized according to the present invention and this primary material is conveyed through the reaction zone at the rate of about 250 grams per hour per liter of catalyst space, good conversions have been obtained when the cobalt-to-carbon ratio is in the neighborhood of 14:86. However, much higher or lower concentrations of the catalyst may also be used.

Instead of using a solid catalyst bed through which the reactants are conveyed, it is also possible to effect the polymerization according to the present invention by maintaining the catalyst, e. g. reduced cobalt, whether used alone or on a carrier, in suspension in the reaction zone. This may be effected, for instance, by suspending the catalyst in the liquid polymer and by conveying the olefine to be polymerized therethrough.

The catalyst employed for the polymerization of the unsaturated hydrocarbons may also contain various promoters which when used alone will not catalyze the reaction. As such, reference may be made to the oxides and/or salts of lithium, thorium, copper, silver, zinc, and the like, as well as some of these metals per se, for example small amounts of silver or reduced copper with finely divided cobalt or the like.

Instead of polymerizing individual olefines separately, mixtures of olefines may be treated. Thus, for example, column 29 may be by-passed and the ethylene- and propylene-containing mixture conducted by line 35 to polymerizer 31, in which these olefines may be co-polymerized. It has been found that there are critical ranges of temperature and pressure which should be maintained in order to insure highest yields of products most desirable for use in alkylation. Thus, the polymerization of ethylene in the presence of reduced cobalt deposited on activated carbon is preferably carried out at temperatures of about 35° C. to 150° C., most preferably between 80° C. and 120° C., using pressures above about 300 lbs.

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per sq. in., most preferably between 600 and 900 lbs. per sq. in. The same range of temperatures and pressures have also been found to be highly suitable for the co-polymerization of ethylene with other unsaturated hydrocarbons such as propylene. The rate of conversion of ethylene to butylene under the same conditions is considerably higher than the conversion rate of propylene to hexylenes. It is, therefore, preferred to use somewhat more rigorous conditions for the polymerization of higher boiling olefines.

Depending upon the contact time allowed in polymerizer 31, more or less complete conversion of ethylene may be effected. Where complete or substantially complete polymerization is carried out the reaction products may be conducted by lines 36 and 37 to line 14 connecting with the alkylation unit. It is frequently more advantageous, however, to use higher throughput rates, for example about 200 to 500 grams of ethylene per liter of catalyst per hour, in polymerizer 31 as under such conditions not only may higher production rates be achieved but also products of better quality for alkylation may be obtained, particularly through a reduction in the amount of higher boiling products formed. Under such conditions it is preferred to return the polymerization products by lines 38 and 33 to column 29. The polymers will then appear in the bottoms removed by line 39 along with the unreacted propane. This mixture is fed by line 40 to fractionation column 41, in which the propane is taken off overhead by line 42, and the polymers, mainly normal butylenes if ethylene has been polymerized alone or a mixture of mainly normal butylenes and amylenes if the ethylene has been co-polymerized with the propylene, are removed by line 43 and fed to the alkylation unit by line 14, or, particularly where the residence time in polymerizer 31 is insufficient to effect the desired degree of isomerization of the polymers formed, the olefine or olefines may be conducted by line 44 to an isomerization unit in which substantial conversion of the olefines to beta-olefines is effected before using them in the alkylation step. For this isomerization catalysts of the same type as used in the polymerization step are particularly suitable. With these catalysts the isomerization is advantageously effected at about 60° C. to 120° C., and production of higher boiling compounds is preferably avoided. Where the polymers are not de-ethanized they may be fed to the isomerization unit by lines 37 and 46. In either case, products consisting substantially of olefines having the double bond between carbon atoms removed from the end of the chain are conducted by lines 47 and 14 to the alkylation unit 12, in which they give higher yields of high quality products and a materially longer catalyst life than when the previously employed olefine mixtures are used.

The propane-propylene mixture removed by line 42 or the similar mixture supplied by lines 39 and 48, when de-ethanization of the polymerization products is not essential, is conducted to a propylene separating unit 49. This separation may be carried out in a number of different ways. It may consist of an efficient fractionation, after which propane is returned by lines 50 and 23 to cracking unit 25, and propylene is conducted by line 51 to the alkylation unit, or by lines 51 and 52 to some other use. An extraction treatment, for example with sulfuric acid, may be used to effect the separation, the solvent being admitted by line 53 and the extract itself, 75

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or the propylene recovered therefrom, fed to the alkylation unit by line 51, or withdrawn by line 52 for isopropyl alcohol production or other use. Particularly when feeding a sulfuric acid solution of propylene by line 51 to the alkylation unit, a part or all of the acid normally admitted by line 15a may be omitted. In certain cases the separation of propylene from the propane may be advantageously effected by an alkylation treatment using isobutane, for example, supplied through line 54. In this case the hydrocarbon products are conducted by lines 51 and 55 to line 16, and the alkylate recovered with the products of alkylation from unit 12. It may even be feasible to carry out the alkylation with the propylene in unit 12, where the amount of propane present is such that it does not too greatly reduce the isoparaffin concentration in the reaction, and line 56 is provided for use in such operations.

It will be apparent from this description of the invention that it offers many advantages over prior methods of operation. Not only does it make it possible to efficiently utilize propane and ethylene in the process, but also it gives improved results in the alkylation as a consequence of the fact that normal olefines are used therein in place of branched chain products of polymerization. As a result of isomerization of the olefines in unit 45, or, where long contact times are used in polymerization, in unit 31, the process gives more uniform results because the olefines are more uniform and longer catalyst life in alkylation because the isomerized olefines are predominantly beta-olefines. These latter advantages may be extended by using in the process only isomerized olefines conveniently obtained, for example by supplying the olefines, preferably normal olefines, to the process by line 57 instead of line 13.

Many variations may be made in the process, the various steps of which may be carried out batch-wise or intermittently instead of continuously. The process is not limited to alkylation with sulfuric acid as described as a preferred example, but may be carried out using other alkylation catalysts, such as boron fluoride, hydrogen fluoride, phosphoric acid, aluminum chloride, etc. Instead of the single reaction units indicated in the drawing, a plurality of units in series or parallel may be used. Also, it is not essential to re-employ all the hydrocarbon streams in the process as shown in the drawing since corresponding hydrocarbons from other sources may be used instead. In fact, it may be advantageous in some cases to use other hydrocarbons than those described in the illustrative example in the various steps of the process. Thus, isopentane may be alkylated instead of isobutane, and normal butane, for example, supplied to line 23 by lines 58 and 59 may be cracked instead of, as well as in addition to, the propane. Alternatively, the normal butane may be catalytically dehydrogenated in unit 25 instead of cracked and line 60 may be used to conduct the resulting butylenes to the isomerization. The alkylation with the products of polymerizer 31 and/or isomerizer 45 may be carried out separately from the alkylation with olefines from other sources. Column 29 may be operated so as to separate propylene along with the ethylene, higher boiling products being removed as bottoms and either withdrawn from the system by line 61 or treated along with, or similarly to, the hydrocarbons in line 39, as previously described.

The polymerization products in this case are preferably deethylenized in a separate column, not shown, the bottom product of which is fed to line 38. Propylene or other olefine separated in unit 49 may be fed to polymerizer 31 by connecting lines 52 and 52, it being generally desirable when such olefine is to be interpolymerized with ethylene to maintain an excess of the less reactive higher olefine, preferably 2 to 10 mols of higher olefine (such as propylene) per mol of ethylene during the polymerization. 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.

We claim as our invention:

1. A process of producing motor fuel components from normally gaseous hydrocarbons which comprises contacting a mixture of ethylene and propylene with reduced cobalt deposited on activated carbon at a temperature between 30° C. and 150° C. and, under a pressure of above about 300 pounds per square inch, isomerizing the resulting normal alpha olefines of four and five carbon atoms per molecule to the corresponding beta olefins and reacting the isomerized olefins with an isoparaffin under alkylating conditions, and recovering high anti-knock value saturated liquid hydrocarbon reaction products.

2. A process of producing motor fuel components from normally gaseous hydrocarbons which comprises cracking propane to produce a mixture of ethylene, propylene and unreacted propane, separating the ethylene from the propylene and propane, converting the separated ethylene substantially to a mixture of alpha and beta butylenes by contact with a metal of the eighth group of the periodic table at between 30° C. and 150° C. substantially isomerizing the alpha butylene content of said mixture to beta butylene, and alkylating an isoparaffin with the resulting beta butylene.

3. A process of producing motor fuel components from normally gaseous hydrocarbons which comprises contacting ethylene with reduced cobalt deposited on activated carbon at a temperature between 30° C. and 150° C. and, under a pressure above about 300 pounds per square inch, separating unreacted ethylene from the resulting butylene, contacting the latter with reduced cobalt deposited on activated carbon at a temperature between 60° C. and 120° C. to substantially convert the butylene to beta butylene, and alkylating isobutane with said beta butylene to produce high anti-knock value gasoline components.

4. A process of producing motor fuel components from normally gaseous hydrocarbons which comprises subjecting propane to treatment at an elevated temperature at which substantial conversion to ethylene takes place, separating the ethylene produced from components of the reaction mixture having less and more than two carbon atoms per molecule, contacting the separated ethylene with a polymerization catalyst to produce an alpha butylene-containing product, contacting said alpha butylene with reduced cobalt deposited on activated carbon at a temperature between 60° C. and 120° C. to substantially convert the alpha butylene to beta butylene, and alkylating isobutane with said beta butylene to

produce high anti-knock value gasoline components.

5. A process of producing motor fuel components from normally gaseous hydrocarbons which comprises fractionating an isobutane- and propane-containing hydrocarbon mixture to separate propane therefrom, thermally cracking said propane to produce a substantial yield of ethylene, polymerizing said ethylene mainly to a mixture of alpha and beta butylenes by contact with reduced cobalt deposited on a porous support at a temperature between 30° C. and 150° C. and under a pressure above about 300 pounds per square inch, substantially isomerizing the alpha butylene content of said mixture to beta butylene, alkylating said separated isobutane with the resulting beta butylene in the presence of sulfuric acid of about 90% to 100% concentration, and recovering high anti-knock value gasoline components from the reaction products.

6. A process of producing motor fuel components from normally gaseous hydrocarbons which comprises reacting a butylene- and propane-containing hydrocarbon mixture with isobutane in the presence of an alkylation catalyst under conditions at which alkylation of the isobutane takes place, fractionating the reaction products to separate normally gaseous hydrocarbons from the alkylation products, separating propane from said normally gaseous hydrocarbons, cracking said propane to produce a substantial yield of ethylene, polymerizing said ethylene by contact with reduced cobalt at a temperature between 30° C. and 150° C. and under a pressure above about 300 pounds per square inch to produce an alpha butylene-containing product, isomerizing said alpha butylene to beta butylene, and feeding the resulting beta butylene to said alkylation reaction to produce saturated high anti-knock value gasoline components therefrom.

7. In a process of producing motor fuel components by alkylating isobutane with butylene, the improvement which comprises fractionating a hydrocarbon mixture to separately remove therefrom isobutane, normal butane and propane, reacting the separated isobutane with butylene-containing hydrocarbon under alkylating conditions, separating alkylation products from normally gaseous components of the reacted hydrocarbons, returning the normally gaseous components to the first said fractionation, cracking propane separated from the isobutane therein, removing hydrocarbons having less than two carbon atoms per molecule from the cracking products, separating ethylene produced in said cracking from unreacted propane present therewith, polymerizing the separated ethylene by contact with a metal of the group consisting of cobalt and nickel at between 30° C. and 150° C., returning the alpha butylene-containing polymerization products to said ethylene separation, fractionating the higher boiling products from the latter to separate unreacted propane from said alpha butylene, contacting the alpha butylene with reduced cobalt on activated carbon under conditions at which beta butylene is produced therefrom, and feeding said beta butylene to said isobutane alkylation.

8. A process for producing high octane number gasoline which comprises polymerizing an olefin having at least 3 carbon atoms per molecule, subjecting at least a part of the resulting polymers to catalytic isomerization, and alkylating isobutane by reaction with said isomerized polymer,

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9. A process for producing higher boiling branched chain paraffins which comprises polymerizing propylene, subjecting at least a part of the resulting polymers to catalytic isomerization, and alkylating isobutane with the isomerized polymer by reaction in the presence of sulfuric acid.

10. The process which comprises polymerizing propylene, subjecting at least a portion of the resultant polymers to the action of an olefin isomerizing catalyst at isomerizing conditions, and alkylating an alkylatable hydrocarbon with at least a portion of said isomerized propylene polymer.

11. A process for producing branched chain hydrocarbons which comprises polymerizing propylene, subjecting at least a portion of the resultant polymers to the action of an olefin isomerizing catalyst at isomerizing conditions, and alkylating an alkylatable hydrocarbon with at least a portion of said isomerized propylene polymer.

12. The process which comprises polymerizing a normally gaseous olefin, subjecting at least a portion of the resultant polymers to the action of an olefin isomerizing catalyst at isomerizing conditions, and alkylating an alkylatable hydrocarbon with at least a portion of said isomerized polymer.

13. The process which comprises polymerizing

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a normally gaseous olefin, subjecting at least a portion of the resultant polymers to the action of an olefin isomerizing catalyst at isomerizing conditions, and alkylating a isoparaffin with at least a portion of said isomerized polymer.

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