

[54] HYDROCARBON ISOMERIZATION AND SEPARATION PROCESS

[75] Inventor: **George F. Asselin**, Mt. Prospect, Ill.

[73] Assignee: **Universal Oil Products Company**,
Des Plaines, Ill.

[22] Filed: **Oct. 13, 1971**

[21] Appl. No.: **188,792**

[52] U.S. Cl. **208/95, 208/139**

[51] Int. Cl. **C10g 39/00**

[58] Field of Search..... 208/95, 139, 92;
260/683.68

[56] References Cited

UNITED STATES PATENTS

2,918,511 12/1959 Carter et al. 260/683.65
2,921,104 1/1960 Haensel 260/683.65

FOREIGN PATENTS OR APPLICATIONS

110,716 3/1960 Pakistan

Primary Examiner—Delbert E. Gantz

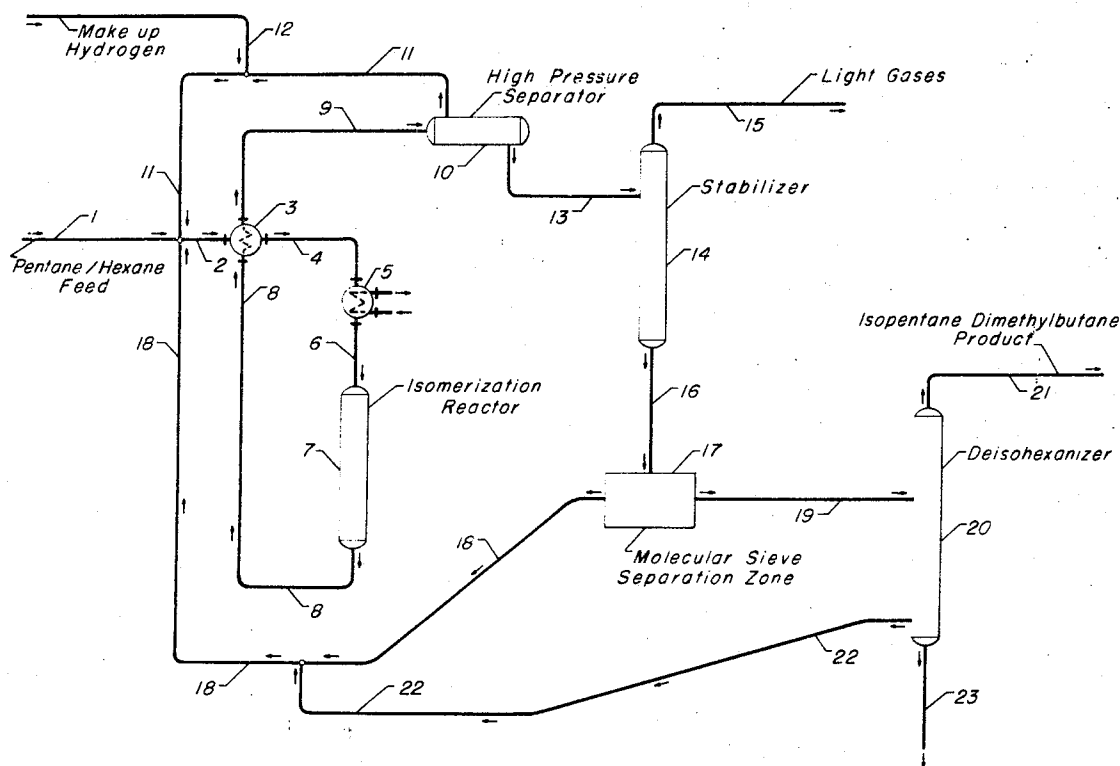
Assistant Examiner—S. Berger

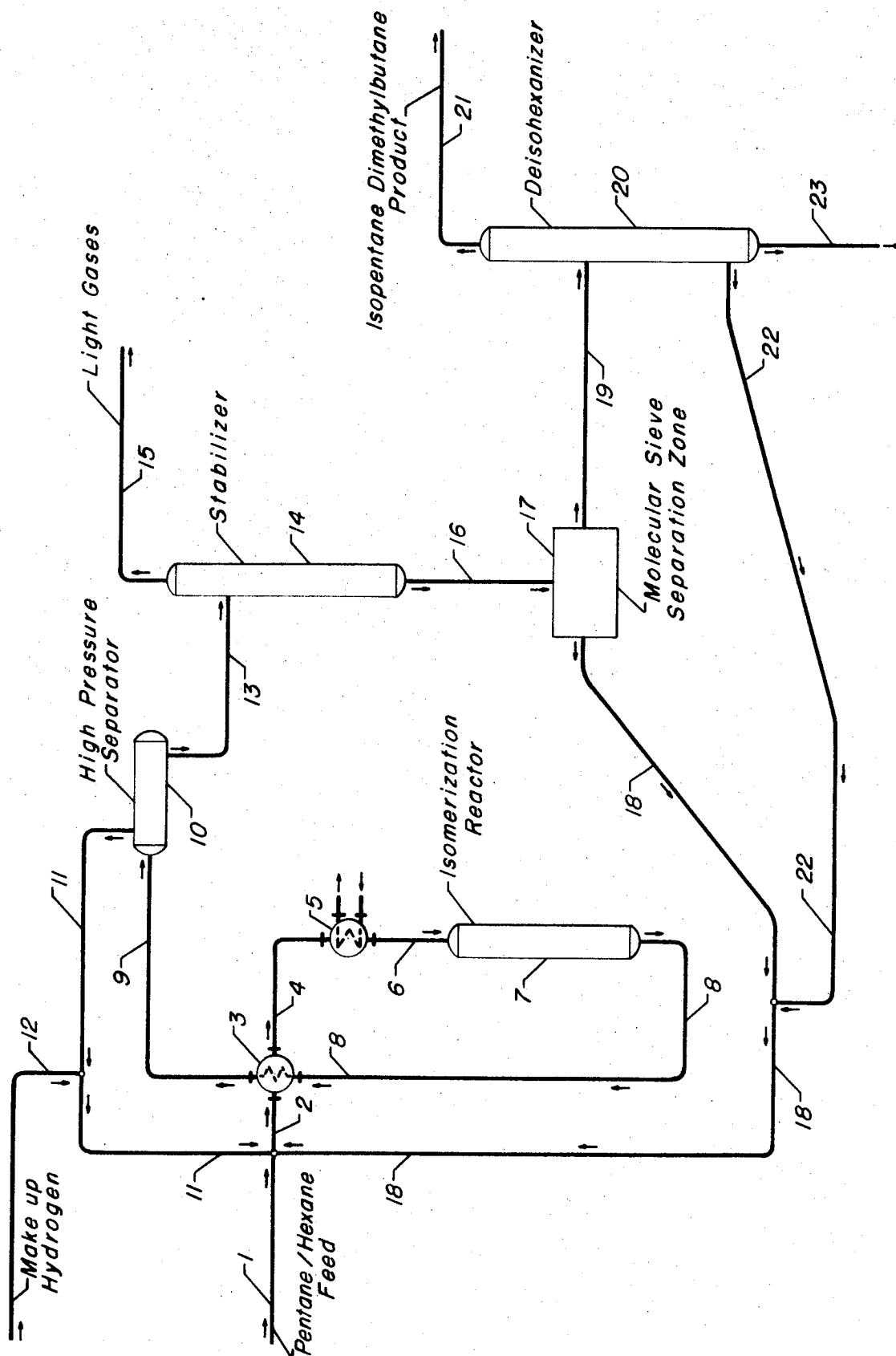
Attorney—James R. Hoatson, Jr. et al.

[57] ABSTRACT

A process for isomerizing and separating a low octane C_5 - C_6 hydrocarbon charge stock to provide a branched hydrocarbons product in which the charge stock is contacted with an isomerization catalyst in an isomerization zone, the effluent from the isomerization zone is separated, in a sorption zone employing a molecular sieve sorbent, into a branched hydrocarbons stream and a normal hydrocarbons stream; the branched hydrocarbons stream is fractionated, and a methylpentanes-free stream of branched hydrocarbons is recovered from the fractionation step as the product of the process.

5 Claims, 1 Drawing Figure





HYDROCARBON ISOMERIZATION AND SEPARATION PROCESS

BACKGROUND

This invention relates to a process for isomerizing and separating a lower octane C_5 - C_6 hydrocarbon charge stock containing normal paraffinic hydrocarbons to provide higher octane products. In one aspect, this invention relates to a hydrocarbon isomerization process utilizing fractionation and a solid sorbent to separate branched chain C_5 and C_6 hydrocarbons from normal C_5 and C_6 hydrocarbons.

More specifically, this invention relates to a process for isomerizing and separating an isomerizable hydrocarbon charge stock containing hydrocarbons having from about five to about six carbon atoms per molecule to provide a branched hydrocarbons product, which process comprises: contacting said charge stock with an isomerization catalyst in an isomerization zone at isomerization conditions; separating the effluent from said isomerization zone in a sorption zone, employing a solid sorbent, to provide a normal hydrocarbons stream and a branched hydrocarbons stream; and, fractionating said branched hydrocarbons stream to provide a methylpentanes stream and a products stream and withdrawing said products stream as said branched chain hydrocarbons product.

Hydrocarbons comprising primarily pentanes and hexanes, such as those available in petroleum refineries, for example, as straight-run fractions of crude oil or as raffinate from reforming processes, represent a substantial potential source of high octane motor fuel components. However, these C_5 - C_6 fractions normally have an unleaded research octane rating of only about 65-70, and the octane rating of such fractions is raised to only about 85-90 by the addition of 3 ml. of an alkyl lead compound per gallon of hydrocarbon. Present premium fuels for automobile engines must have an octane rating of about 100. One method of upgrading these C_5 - C_6 fractions, to improve their utility as motor fuel components, is by eliminating low octane normal paraffins from them by isomerizing the normal paraffins to higher octane branched isomers. It is well known that the more highly branched hydrocarbons such as isopentane and the dimethylbutanes possess a higher unleaded octane than do normal pentane and normal hexane. For example, isopentane and 2,2-dimethylbutane each have an unleaded research octane of about 93, while n-pentane and n-hexane have unleaded octane ratings of about 62 and 30 respectively. By eliminating at least a part of the n-pentane and n-hexane from a typical C_5 - C_6 refinery fraction, the octane rating of the fraction can, therefore, be substantially improved. With the advent of a strong demand for unleaded motor fuel for automobiles, there is an even more pressing need for motor fuel components which have a high octane rating without the addition of alkyl leads. It is essential to upgrade the available C_5 - C_6 fractions if they are to be useful in unleaded motor fuels. The process herein disclosed provides a novel and economically superior method for producing high octane products from these low octane petroleum fractions.

Isomerization of hydrocarbons is well known in the petroleum refining art. Generally, hydrocarbon stocks have been isomerized and fractionated to recover valuable components. The combination of isomerization with fractionation and molecular sieve separation dis-

closed in the process of this invention makes possible a sharper separation, smaller isomerization reactor requirement and higher quality product than is generally available from current commercial processes.

SUMMARY

It is an object of this invention to provide a process for isomerizing and separating a lower octane pentane/hexane hydrocarbon fraction to produce a higher octane hydrocarbon product. Another object of this invention is to provide a hydrocarbon isomerization process utilizing a solid molecular sieve sorbent to separate normal hydrocarbons from branched and cyclic hydrocarbons to produce a higher octane, more highly branched product from a lower octane, less branched hydrocarbon fraction.

Therefore, in an embodiment, this invention relates to a process for isomerizing and separating an isomerizable hydrocarbon charge stock containing hydrocarbons having from about five to about six carbon atoms per molecule to provide a branched hydrocarbons product, which process comprises: (a) containing said charge stock with an isomerization catalyst in an isomerization zone at isomerization conditions; (b) separating the effluent from said isomerization zone in a sorption zone, employing a solid sorbent, to provide normal hydrocarbons stream and a branched hydrocarbons stream; and, (c) fractionating said branched hydrocarbons stream to provide a methylpentanes stream and a products stream and withdrawing said products stream as said branched chain hydrocarbons product.

Further objects and embodiments of the process of this invention will be more readily apparent from the following description of the accompanying drawing and detailed description of the invention.

DESCRIPTION OF THE DRAWING

An understanding of the process of this invention may be aided by referring to the accompanying drawing which represents a schematic diagram of an embodiment of the process of this invention.

Referring to the drawing, hydrocarbon charge stock, comprising primarily pentanes and hexanes, is introduced through conduit 1 and passed through conduit 2 to heat exchanger 3 wherein the charge stock is heated in indirect heat exchange with effluent from isomerization zone 7. Hydrogen is commingled with the charge stock in conduit 2. The partially heated charge stock is withdrawn from exchanger 3 and passed through conduit 4 to heater 5 wherein the charge stock is further heated to the desired temperature for isomerization conditions. The heated charge stock is passed from heater 5 via conduit 6 to isomerization reactor 7. Isomerization reactor 7 contains a fixed bed of isomerization catalyst. The hydrocarbons charged to reactor 7 are passed over the fixed bed of catalyst, maintained at a temperature and pressure sufficient that at least a part of the charged hydrocarbons are isomerized, and withdrawn from reactor 7 through conduit 8. The isomerization reactor effluent is passed from conduit 8 into heat exchanger 3 in indirect heat exchange with fresh feed stock as described above. Cooled reactor effluent is withdrawn from heat exchanger 3 and passed through conduit 9 to high pressure separator 10, wherein the effluent forms a liquid phase and a hydrogen-rich gaseous phase. The hydrogen-rich gaseous phase is withdrawn from separator 10 through conduit

11. Make up hydrogen is charged to conduit 11 by way of conduit 12 as needed, and the combined hydrogen stream continues through conduit 11 to conduit 2 where the hydrogen is commingled with fresh charge stock as described above. The liquid phase in high pressure separator 10 is withdrawn through conduit 13 and passed to stabilizer 14. In stabilizer 14, any light gases, such as butanes, propane, ethane and methane, as well as any other normally gaseous materials such as hydrogen halides, are separated from C_3/C_6 hydrocarbons, passed overhead in conduit 15 and withdrawn from the process. The C_3/C_6 hydrocarbons in stabilizer 14 are withdrawn and passed through conduit 16 to molecular sieve separation zone 17. In separation zone 17, normal C_3 and C_6 hydrocarbons are separated from branched chain and cyclic C_3 and C_6 hydrocarbons. The normal hydrocarbons are withdrawn via conduit 18 and passed therethrough to conduit 2, wherein they are commingled with fresh charge stock from conduit 1 and hydrogen from conduit 11. The branched and cyclic hydrocarbons in molecular sieve separation zone 17 are withdrawn through conduit 19 and passed to deisohexanizer 20, which comprises a fractionation vessel. In deisohexanizer 20, isopentane, dimethylbutanes and some methylpentanes are withdrawn overhead in the vapor phase and recovered through conduit 21 as the product of the process. A bottoms stream comprising primarily methylcyclopentane, and cyclohexane is recovered from deisohexanizer 20 and withdrawn from the process through conduit 23. A side cut stream of primarily methylpentanes is withdrawn from deisohexanizer 20 and passed through conduit 22 to conduit 18 wherein the methylpentane is combined with normal hydrocarbons from molecular sieve separation zone 17 and recycled to isomerization reactor 7.

DETAILED DESCRIPTION OF INVENTION

The hydrocarbon charge stocks which are suitable for use in the process of this invention include straight and branched chain saturated C_3 and C_6 hydrocarbons and mixtures thereof. Typical of the suitable charge stocks is a C_3/C_6 fraction derived from the fractional distillation of petroleum crude oil. Such a fraction may contain lighter and heavier components such as butanes and heptanes and may contain cyclic and aromatic compounds such as cyclopentane, cyclohexane, benzene, etc. Typically, such straight-run fractions are contaminated by sulfur compounds and water, and it is desirable to eliminate such contaminants before a charge stock is utilized in this process. Generally, the charge stock should comprise less than about 10 wt. percent of C_7 and heavier hydrocarbons, although this requirement is not essential to the operation of the process. It is also desirable to limit the aromatics content of the charge stock to less than about 10 percent of the feed, by weight, primarily because the aromatics have higher octane rating than the products formed from them in the isomerization reaction. Suitable charge stocks may contain unsaturated hydrocarbons, such as pentenes, hexenes, pentadienes, etc. When the charge stock is obtained from the raffinate of a hydrocarbon reforming process, it will usually contain several wt. percent of such unsaturates. Such a feed stock is suitable for use in the present process. It will be obvious to one skilled in the art that the present process is basically applicable to C_3/C_6 charge stocks containing a greater-than-equilibrium fraction of normal pentane

and normal hexane, since the octane rating improvement resulting from processing stocks having a high branched chain, cyclic and aromatic hydrocarbons content would be negligible. A typical straight run C_3/C_6 feed stock, suitable for use as a feed in the present process, could comprise, by weight, 20 percent isopentane, 30 percent n-pentane, 1 percent cyclopentane, 2 percent dimethylbutanes, 19 percent methylpentanes, 19 percent n-hexane, 5 percent methylcyclopentane, 1 percent benzene and 3 percent heavier hydrocarbons.

Isomerization catalysts suitable for use in the process of this invention include all catalysts capable of isomerizing normal paraffinic hydrocarbons to produce branched chain paraffinic hydrocarbons. Friedel-Crafts metal halides, e.g., aluminum chloride, are well known as isomerization catalysts. These catalysts may be used as such or combined with other materials such as hydrogen halides. Typical catalysts of this type, suitable for use in the present process, are aluminum chloride with hydrogen chloride added as a promoter and antimony chloride having aluminum chloride dissolved therein. Friedel-Crafts metal halides may be utilized suitably in combination with substantially inert supporting materials. Another suitable type of isomerization catalyst which may be used in this process is a composite of a metal from Group VIII of the Periodic Table with a solid support. The platinum group metals, and platinum in particular, are preferred for use as components of such a catalyst in this process. Solid supports which are suitable for a catalyst of this type include silica, alumina, magnesia, zirconia, chromia, titania, bauxite, kaolin, Kieselguhr, vanadium oxide, boron oxide, etc., and combinations thereof. Catalysts comprising a Group VIII metal component and a solid support may be utilized with promoting components such as hydrogen halides, organic halides, etc. For example, the composite may be treated, before or during use, with hydrogen halide or with an organic halide such as carbon tetrachloride, chloroform, etc. A hydrogen halide or organic halide may be admixed with the hydrocarbons to be isomerized in a continuous operation whereby a definite concentration of halide is provided in the feed to the isomerization zone. A similar type of catalyst suitable for use in the process of this invention comprises a Group VIII metal component and one or more combined halogen components on a solid support. For example, a catalyst comprising, by weight, about 0.01 to about 2.0 percent platinum, about 0.01 to about 8 percent chlorine, about 0.01 to about 8 percent fluorine on a silica-alumina support is suitable for use in this process. One isomerization catalyst preferred for use in the present process is described in U. S. Pat. Ser. No. 2,999,074. This preferred catalyst comprises a calcined and reduced composite of a refractory oxide containing chemically combined hydroxyl groups and from about 0.01 percent to about 2 percent by weight of a platinum group metal, said calcined composite being impregnated with from about 10 percent to about 100 percent by weight of an anhydrous Friedel-Crafts metal halide in which the halogen is selected from chlorine and bromine and said hydroxyl groups having been reacted with the metal halide in a reaction resulting in the elimination from the composite of at least 0.5 mole but not more than 2.0 moles of hydrogen halide per mole of Friedel-Crafts metal halide adsorbed thereon.

Various other suitable catalysts have been disclosed in prior art. For example, catalytic composites containing more than one metallic component, e.g., a platinum group metal and a metal from Group VIB or Group IB of the Periodic Table have been found to be useful as isomerization catalysts. Certain forms of crystalline aluminosilicates have also been found to act as isomerization catalysts, and may suitably be used as such in the process of this invention. Such catalytic composites commonly require isomerization conditions very similar to those discussed below in connection with the use of the preferred catalysts, so that the isomerization conditions discussed are generally applicable to them.

Another catalyst preferred for use in the process of this invention comprises a halogen component on a solid support comprising an alumina matrix having suspended therein a finely divided crystalline aluminosilicate and a Group VIII or Group VIB metallic component. Such a catalyst may be prepared by distributing finely divided crystalline aluminosilicate particles throughout an aluminum hydroxyl halide sol, to form a mixture, gelling the resulting mixture to form substantially spherical hydrogel particles, aging, washing and calcining the particles, and adding platinum thereto. The crystalline aluminosilicate, preferably mordenite, should comprise from about 2 percent to about 10 percent by weight, of the support, and the platinum component should comprise from about 0.05 percent to about 2.0 percent of the final weight of the catalyst.

In using the preferred isomerization catalysts, it is desirable to eliminate sulfur and water from the feed stock before it is contacted with the catalyst. Typically, C_5 - C_8 fractions available for isomerization have been desulfurized by prior processing, but, if necessary, sulfur may be removed by contacting the feed stock with hydrogen at elevated temperatures and pressures, whereby the sulfur is converted to hydrogen sulfide and is easily separated from the heavier hydrocarbons. Various methods for eliminating water from the feed to the process are known including pre-fractionation and molecular sieve drying. The latter method is preferred. Dual function isomerization catalysts such as the preferred catalysts require that hydrogen gas be present in the isomerization zone. It is necessary to eliminate water from fresh hydrogen which will enter the isomerization zone. It is preferred that the fresh hydrogen be dried using molecular sieves.

The isomerization step in the process of this invention may be performed in a batch reaction scheme or a continuous reaction scheme. The particular manner in which the isomerization step is performed will depend, in part, on the choice of isomerization catalyst. Generally, a continuous operation is preferred. When a batch operation is utilized, a quantity of the charge stock is placed in an appropriate vessel and contacted therein with an isomerization catalyst. The stock is maintained at a particular temperature and pressure for a predetermined length of time and then separated from the catalyst and recovered. In a continuous scheme, the catalyst may be employed as a fixed bed in a suitable reaction vessel and the hydrocarbon stock passed across the bed continuously. In another suitable method, the catalyst may be employed in a moving bed scheme, or a fluidized bed operation in which catalyst and hydrocarbons are continuously contacted, either concurrently or countercurrently, and separated. It is

preferred that a fixed bed of catalyst be maintained in the reaction zone.

Isomerization conditions include a temperature in the range from about 0°F. to about 1,200°F. and a pressure in the range from 1 atmosphere to about 200 atmospheres or more. Preferred isomerization conditions include a temperature of from about 200°F. to about 800°F. and a pressure of from about 10 atmospheres to about 100 atmospheres. It is contemplated that gases such as helium, nitrogen, argon, etc., may be charged to the isomerization zone if desired. In an embodiment of the present process using one of the preferred catalysts, a gas comprising hydrogen is passed to the isomerization zone and commingled with the hydrocarbon to be isomerized. Hydrogen should be charged at a rate in the range from about 0.1 to about 10 moles per mole of charged hydrocarbons. Hydrocarbons, either in the gaseous or the liquid phase, are passed through the isomerization zone at a liquid hourly space velocity (volume of hydrocarbons charged per hour divided by the volume of catalyst in the isomerization zone) of from about 0.1 to about 20 or more.

In using the preferred isomerization catalysts, it is preferred that an organic halide be added to the feed to the isomerization zone. This procedure results in the production of some hydrogen halide in the isomerization zone, and beneficially affects the activity of the catalyst. In embodiments of the present process utilizing hydrogen, organic halide, etc., in the isomerization step, it is necessary to provide equipment for separating hydrogen and other light gases from the heavier hydrocarbons. Various methods for making such a separation are well known. One suitable method employs two separation zones, the first zone operating at high pressure and the second at a lower pressure. In the first, high pressure separation zone a gaseous stream comprising primarily hydrogen is separated. The hydrogen recovered from the high pressure separation zone is recirculated to the isomerization zone. In the second, lower pressure separation zone, any C_4 and lighter hydrocarbons, hydrogen halides, etc., are separated from the heavier hydrocarbons comprising primarily C_5 and C_6 saturates.

The isomerization zone effluent C_5 and heavier hydrocarbons are charged to a sorption zone, wherein normal hydrocarbons are separated from branched chain and cyclic hydrocarbons. The separation of normal hydrocarbons from branched chain and cyclic hydrocarbons is effected utilizing a solid sorbent. Among the solid sorbents which are suitable for use in this process are clathrate-forming organic compounds such as urea and thiourea, and molecular sieve type sorbents. The preferred sorbents are the molecular sieve-type crystalline aluminosilicates. For example, one suitable crystalline aluminosilicate is a Type A zeolite manufactured by the Linde Division of Union Carbide Corp., particularly the 5A zeolites of this type. Zeolites may be characterized as having a porous structure, with the pores being interconnected by smaller diameter pore openings. When the pore openings are about 5 Å in diameter, normal hydrocarbons can enter the pores, but cyclic and branched chain hydrocarbons cannot enter because of their larger molecular diameters. When a mixture of normal, branched and cyclic hydrocarbons is contacted with a zeolite of this type, the zeolite acts as a molecular sieve admitting normal hydrocarbons to the pores but excluding branched and cyclic hydrocar-

bons. The branched and cyclic hydrocarbons are then withdrawn from contact with the zeolite relatively free of normal hydrocarbons, and the relatively branched chain-free normal hydrocarbons are subsequently desorbed from the zeolite.

The zeolite crystal structure consists of three-dimensional networks of the fundamental units, which are silicon-centers SiO_4 and aluminum-centered AlO_4 tetrahedra. These units are interconnected by sharing apical oxygen atoms. To preserve electrochemical neutrality, the AlO_4 tetrahedra are associated with a cation such as an alkaline earth or alkali metal ion. Both natural and synthetic zeolites may be utilized as a sorbent in the process of this invention, including those in which AlO_4 tetrahedra are bonded with alkali and alkaline earth metal cations, as well as those where the cations have been replaced by ion exchange or treatment with acids or bases. The zeolite may be composited with binding materials such as refractory inorganic oxides, preferably those inert with respect to catalytic and molecular sieve properties. The sorbent may be employed in a batch, moving bed, fixed bed or other type of operation. For example, one suitable type of separation technique, employing a simulated moving bed operation, is described in U. S. Pat. No. 2,985,589.

In general, the use of a desorbent is required to recover the adsorbed normal hydrocarbons from a molecular sieve sorbent. Desorbents preferred for use in the process of this invention include those which can be easily separated from normal hexane. In operations making use of a desorbent, the preferentially adsorbed feed component, in this case normal pentanes and hexanes, and the desorbent are removed from the solid sorbent in admixture. Easy separation of the normal hydrocarbons from the desorbent is, therefore, essential to the economy of the operation. One preferred type of desorbent is a normal hydrocarbon having either a higher or lower boiling point than normal hexane or normal pentane, respectively, such as n-octane or n-butane. Another preferred type of desorbent is a mixture of a normal hydrocarbon and a branched hydrocarbon both having lower or higher boiling points than n-pentane or n-hexane such as a mixture of n-butane and isobutane, or a mixture of n-octane and isooctanes. Another method of desorbing the normal hydrocarbons from the solid sorbent is by adsorbing the normal hydrocarbons at a higher pressure, and then desorbing them utilizing a lower pressure to produce a vacuum effect. The normal hydrocarbons may also be desorbed by heating the sorbent, vaporizing the adsorbed normal hydrocarbons and withdrawing them. A desorbent may also be employed in operations utilizing vacuum or heating desorption. For example, a gas such as hydrogen, nitrogen, argon, etc., may be utilized as a desorbent. The desorbent and normal hydrocarbons are subsequently separated, for example, by fractionation when a hydrocarbon desorbent is utilized, or by flash separation when a gas is used. A stream of relatively pure normal hydrocarbons is thereby produced and the desorbent recovered may be recycled for further use.

In the present process, a raffinate of non-adsorbed hydrocarbons, comprising branched and cyclic C_5 and C_6 saturates is withdrawn from contact with the sorbent and passed out of the sorption zone, leaving the adsorbed normal pentane and normal hexane. The adsorbed hydrocarbons are subsequently desorbed, preferably

erably by employing a desorbent. The normal pentane and normal hexane are then separated from the desorbent, if any, and withdrawn from the sorption zone. The stream of normal hydrocarbons so formed is recycled to the isomerization step.

The stream of branched and cyclic hydrocarbons recovered as the sorption zone raffinate is further separated by fractionation. It is desirable to recover a branched product comprising isopentane and the maximum fraction possible to dimethylbutanes from this fractionation step, while retaining a recycle stream of as large a fraction of methylpentanes as possible. The very small difference in boiling point between 2,3-dimethylbutane and 2-methylpentane makes a complete separation of these isomers by fractionation virtually impossible. Depending upon the particular embodiment of this invention, the product of the process may comprise substantially methylpentane-free isopentane and 2,2-dimethylbutane, or the product may comprise isopentane, 2,2- and 2,3-dimethylbutane with a fraction of methylpentane. By variations in fractionation conditions well known to those skilled in the art, the amount of methylpentanes taken overhead with the desired products may be varied over a wide range, and the product of the process may be varied in octane rating accordingly. For example, if fractionation conditions are imposed which provide an overhead product consisting essentially of isopentane and 2,2-dimethylbutane, the product will possess an unleaded research octane of about 93. If much of the high octane 2,3-dimethylbutane is also recovered overhead, it is also necessary to take overhead some methylpentane. In this embodiment, a product also having an unleaded research octane of about 93 may be recovered, and a smaller and less costly recycle stream of methylpentanes will result. When fractionation conditions are adjusted to take overhead more than about 10 volume percent of the methylpentanes in the fractionator feed, the octane rating of the product will be correspondingly less, while the recycle stream will be smaller. Regardless of the desired octane of the product, it is essential to the concept of the present process that at least a portion of the methylpentanes in the feed to the fractionation step be separated from the product and, preferably, recycled to the isomerization step.

In general, the feed to the fractionation step will contain at least some methylcyclopentane and cyclohexane. These hydrocarbons will invariably be retained in the recycle, bottoms portion of the fractionator. Although it may be possible to isomerize these cyclic compounds to the desired branched paraffinic isomers by recycling them to the isomerization step, it may be more economical to separate them from the recycle stream of methylpentanes and withdraw them from the process. One preferred method for accomplishing such a separation is to withdraw the recycle methylpentanes stream as a side cut from the lower section of a fractionation vessel and to withdraw the cyclics in the bottoms from the fractionator, while the product of the process is recovered overhead. Thus the desired separation can be produced by simply enlarging the fractionator necessary to the process.

I claim as my invention:

1. A process for the conversion of a C_5 - C_6 hydrocarbon fraction into more valuable products which comprises isomerizing said fraction, separating from the resultant effluent a C_5 - C_6 isomerate, contact-

ing the latter with a solid sorbent to separate the isomerate into a C₅-C₆ normal hydrocarbons stream and a C₅-C₆ branched hydrocarbons stream, fractionating the last-mentioned stream to separate the same into an isopentane-dimethylbutane overhead product, a methylcyclopentane-cyclohexane bottoms product and a methylpentane side cut, recycling said C₅-C₆ normal hydrocarbons stream and said side cut to the isomerizing step, and separately recovering said overhead product and said bottoms product.

2. The process of claim 1 further characterized in that said fraction is isomerized in contact with a catalyst comprising a refractory inorganic oxide component, a combined halogen component and platinum group metal component.

3. The process of claim 1 further characterized in that said solid sorbent is a zeolitic molecular sieve-type sorbent.

4. The process of claim 3 further characterized in that said sorbent selectively adsorbs normal hydrocarbons and rejects branched chain and cyclic hydrocarbons.

5. A process for isomerizing and separating a lower octane isomerizable hydrocarbon charge stock containing hydrocarbons having from about five to six carbon atoms per molecule to produce a higher octane

branched hydrocarbons product, which process comprises the steps of:

- a. contacting said charge stock with hydrogen and with a composite comprising a refractory inorganic oxide component, a platinum group metal component and a combined halogen component, in an isomerization zone at isomerization condition;
- b. separating the effluent from said isomerization zone into a hydrogen-rich gaseous phase and a liquid isomerate phase;
- c. separating said isomerate phase in a sorption zone, utilizing a solid zeolite sorbent, to provide a normal hydrocarbons stream and a branched hydrocarbons stream and introducing said normal hydrocarbons stream into said isomerization zone;
- d. fractionating said branched hydrocarbons stream to provide a product stream comprising isopentane and dimethylbutanes, a recycle stream comprising methylpentane, and a bottoms stream comprising methylcyclopentane and cyclohexane, and recovering said products stream as said branched hydrocarbons product; and,
- (e) withdrawing said bottoms stream from the process and introducing at least a portion of said recycle stream into said isomerization zone.

* * * * *

30

35

40

45

50

55

60

65