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[54] HEXANE CONVERSION

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[58] **Field of Search**.....260/676, 683.65

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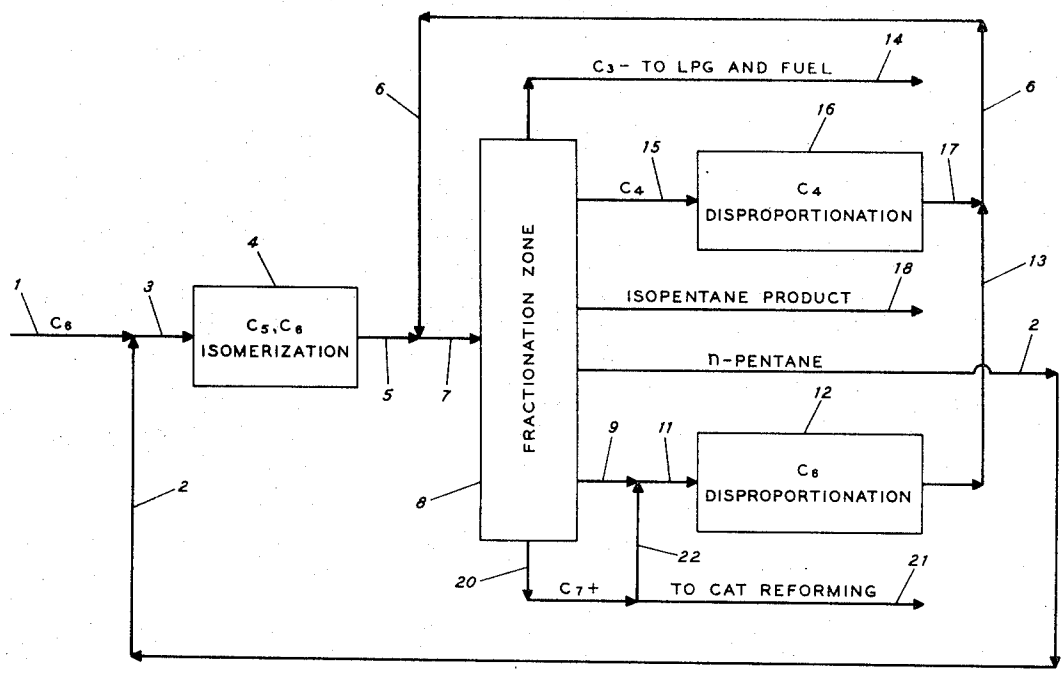
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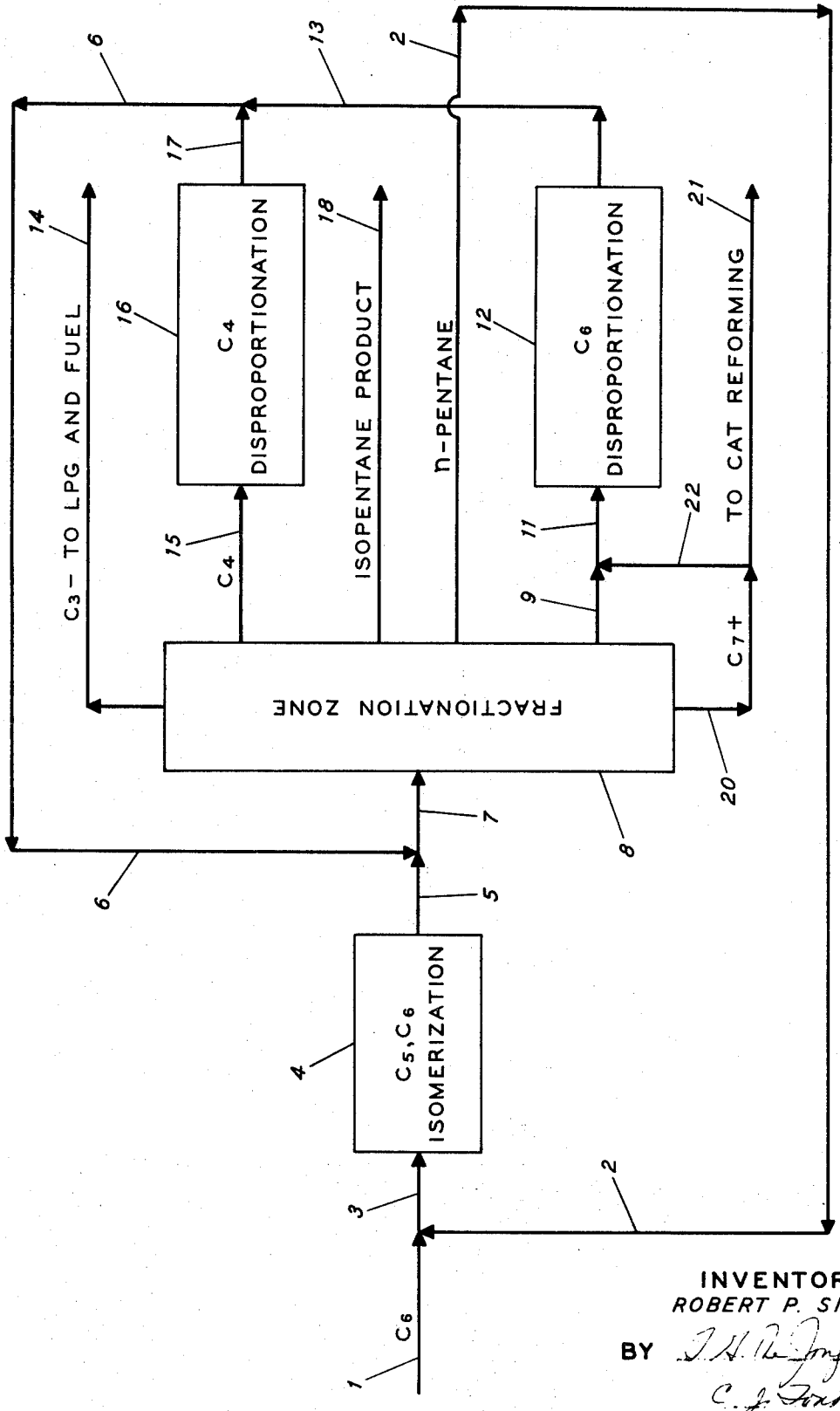
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[57] **ABSTRACT**

A process for producing isopentane which comprises: (a) isomerizing a C_6rich fraction in an isomerization zone to obtain at least isopentane and C_6 alkanes, (b) fractionating the isopentane from the C_6 alkane to obtain an isopentane product, (c) disproportionating at least a portion of the C_6 alkanes in a C_6 disproportionation zone to obtain at least n-pentane and C_7 hydrocarbons, and (d) isomerizing the n-pentane in the isomerization zone. Preferably, the isomerizing zone uses a sulfactive isomerization catalyst so that the isomerization zone serves not only an isomerization function but also a purification function for subsequent disproportionation. Normal butane produced in the C_6 disproportionation zone is preferably disproportionated in a separate disproportionation zone to produce normal pentane which is isomerized to isopentane. It is particularly preferred to further integrate the disproportionation with the isomerization using common fractionation facilities.

14 Claims, 1 Drawing Figure





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HEXANE CONVERSION

BACKGROUND OF THE INVENTION

The present invention relates to a combination process involving isomerization of saturated hydrocarbons. More particularly, the present invention relates to isomerization operated in combination with saturated hydrocarbon disproportionation, and preferably with integrated common fractionation facilities.

Isomerization is a well-known and frequently used step in petroleum refining. It enables the adjustment of the octane number upwards by converting normal paraffins, such as normal hexane, to isoparaffins, such as 2,2-dimethylbutane. A blend of various isomeric paraffins provides a gasoline which has a higher octane number than a gasoline consisting of normal paraffins. Isomerization is generally performed by passing isomerizable hydrocarbons together with hydrogen through a reaction zone containing an isomerization catalyst. The hydrogen-to-hydrocarbon mol ratio varies within a wide range, generally from 0.05:1 to 5:1, preferably within the range of about 0.5:1 to 2:1 for pentanes and hexanes and 0.1:1 to 1:1 for butanes. The reaction temperature will depend upon the specific hydrocarbons being isomerized and the nature and type of catalyst employed. Hydrocarbon streams consisting chiefly of pentanes and hexanes are usually isomerized at temperatures within the range of 200°–900°F. The isomerization, normally effected under pressure, may be carried out in the liquid or vapor phase. Generally, pressures within the range of 300–1000 psig have been used. A liquid hourly space velocity (LHSV), that is, the volume of liquid charged per hour per volume of catalyst, within the range of 0.5 to 10.0 and preferably within the range of about 0.75 to 4.0 is employed.

Various catalysts have been suggested for use in isomerization processes. In general, the isomerization can be effected at low temperatures (ca. 300°F.) with a Friedel-Crafts catalyst, such as aluminum chloride, or at high temperatures (ca. 750°F.) with a supported metal catalyst, such as platinum on halogenated alumina or silica-alumina. Thermodynamic equilibrium for isoparaffins is more favorable at low temperatures; however, the low-temperature process has not received wide application because the Friedel-Crafts catalyst is quite corrosive and therefore expensive metals or alloys must be used. Of the high temperature isomerization processes, the noble metal catalysts such as platinum or palladium are perhaps considered to be the most effective.

As indicated in U.S. Pat. Nos. 2,951,888 and 3,472,912, minor amounts of sulfur compounds in the feed to isomerization processes are harmful for the typical isomerization processes. Catalysts used in typical isomerization processes include composites of a hydrogenating component on an amorphous acidic silica-alumina support and more usually composites comprising halogenated alumina or aluminum, either of which latter composites are herein referred to as halogenated aluminum catalysts.

According to U.S. Pat. No. 2,951,888, a C_4–C_7 paraffinic feedstock is desulfurized to a sulfur content less than 1 ppm so that better results are achieved in hydroisomerization of the paraffinic feedstock with a catalyst selected from the group consisting of nickel, nickel-molybdenum, and palladium, supported on an acidic silica-alumina support containing 50–90 percent silica, at a temperature of 650°–800°F., pressure of 100–1000 psig, and hydrogen-hydrocarbon mol ratio of 0.5–5.0.

U.S. Pat. No. 3,472,912 also discloses an over-all combination process involving hydrotreating and isomerization wherein a nickel molybdenum-on-alumina catalyst is used under hydrotreating conditions to remove sulfur from C_4–C_7 saturated hydrocarbons so that the hydrocarbons can be isomerized with increased life for the isomerization catalyst. Preferred isomerization catalysts according to the process of U.S. Pat. No. 3,472,912 are platinum-alumina composites activated by the addition of carbon tetrachloride (thereby resulting in a catalyst which is herein classified as a catalyst containing halogenated aluminum).

Recently, catalysts comprising either natural or synthetic crystalline aluminosilicates have been suggested for isomerization processes. Included among the crystalline aluminosilicates which have been suggested are the type X and type Y silicates, mordenite, and layered aluminosilicates such as described in Granquist U.S. Pat. No. 3,252,757.

U.S. Pat. No. 3,507,931, titled "Isomerization of Paraffinic Hydrocarbons in the Presence of a Mordenite Catalyst" discloses the isomerization of straight run distillates rich in C_4–C_6 normal paraffins using a catalyst having a high silica-to-alumina ratio, preferably above 20:1, and operating the isomerization reaction at relatively low temperatures, such as 250°–400°F.

U.S. Pat. Nos. 3,280,212 and 3,301,917 also disclose hydroisomerization processes using crystalline aluminosilicate-type catalysts.

As indicated above, the present invention is directed to both isomerization and disproportionation.

The term "disproportionation" is used herein to mean the conversion of hydrocarbons to new hydrocarbons of both higher and lower molecular weight. For example, butane may be disproportionated according to the reaction:

$$2C_4H_{10} \rightleftarrows C_3H_8 + C_5H_{12}$$

As can be seen from the above disproportionation reaction, the butane is in part converted to a higher molecular weight hydrocarbon, namely, pentane. Various processes have been suggested for converting hydrocarbons to higher molecular weight hydrocarbons.

U.S. Pat. No. 1,687,890 is directed to a process of converting low-boiling-point hydrocarbons into higher-boiling-point hydrocarbons by mixing a hydrocarbon vapor with steam and then contacting the steam-hydrocarbon mixture with iron oxide at temperatures in excess of 1112°F. It is theorized in U.S. Pat. No. 1,687,890 that the following reactions may be involved to a greater or lesser extent:

"1. Paraffin hydrocarbons on being brought into contact with ferric oxide at elevated temperatures are oxidized or dehydrogenated, forming unsaturated hydrocarbons.

"2. Unsaturated hydrocarbons of low molecular weight polymerize into unsaturated hydrocarbons of higher molecular weight when subjected to

elevated temperatures, the extent of polymerization depending upon the temperature and duration of treatment.

"....

"7. Unsaturated hydrocarbons are hydrogenated by nascent hydrogen."

Another process which has been proposed for converting hydrocarbons to higher molecular weight hydrocarbons is olefin disproportionation. Numerous methods and catalysts have been disclosed for the disproportionation of olefins. In most of these processes, the olefin is disproportionated by contacting with a catalyst such as tungsten oxide or molybdenum oxide on silica or alumina at a temperature between about 150°–1100°F. and at a pressure between about 15 and 1500 psia. These prior art processes have been directed to an effective method to convert essentially only olefins, not saturated hydrocarbons, to higher molecular weight hydrocarbons by disproportionation.

For example, in U.S. Pat. No. 3,431,316, an olefin disproportionation process is disclosed, and it is stated that, if desired, paraffinic and cycloparaffinic hydrocarbons having up to 12 carbon atoms per molecule can be employed as diluents for the reaction; that is, the saturated hydrocarbons are non-reactive and merely dilute the olefins which are the reactants.

A process for the direct conversion of saturated hydrocarbons to higher molecular weight hydrocarbons would be very attractive because in many instances saturated hydrocarbons are available as a relatively cheap feedstock. For example, in many instances, excess amounts of propane and/or butanes are available in an over-all refinery operation.

Processes which have been previously reported wherein saturated hydrocarbons are disproportionated include contact of saturated hydrocarbons with solid catalyst comprised of $AlCl_3$ on Al_2O_3 and contact of saturated hydrocarbons with a promoter comprised of alkyl fluoride and BF_3. The use of the $AlCl_3$ solid catalyst was uneconomic because, among other reasons, the catalyst was non-regenerable. The use of alkyl fluoride and BF_3 was unattractive because of severe corrosion, sludge formation and other operating problems.

In the past it has been the practice to convert saturated hydrocarbons, particularly normal alkanes, to olefins as a separate or distinct step and then to disproportionate the olefins to valuable higher molecular weight hydrocarbons.

For example, in U.S. Pat. No. 3,431,316, saturated light hydrocarbons are cracked to form olefins, and then the olefins are separated from the cracker effluent and fed to a disproportionation zone wherein the olefins are disproportionated to higher molecular weight hydrocarbons. Thus, a separate step is used to obtain olefins because, according to the prior art, no economically feasible process is available for the direct disproportionation of saturated hydrocarbons.

U.S. Pat. No. 3,445,541 discloses a process for the dehydrogenation-disproportionation of olefins and paraffins, using a combined dehydrogenation and disproportionation catalyst. According to U.S. Pat. No. 3,445,541, a hydrocarbon feed which is either an acyclic paraffin or acyclic olefin having 3–6 carbon atoms is contacted with the catalyst at conditions of temperature and pressure to promote dehydrogenation and disproportionation. It is said that the process can be carried out at temperatures between 800°F. and 1200°F.; however, the lowest temperature used for processing a paraffin in accordance with any of the examples of U.S. Pat. No. 3,445,541 is 980°F., and typically the temperature used is between 1040°F. and 1125°F.

The high-temperature process disclosed in U.S. Pat. No. 3,445,541 is shown therein to result in only relatively low yields of saturated higher molecular weight hydrocarbons. The U.S. Pat. No. 3,445,541 process operates with a substantial amount of olefins in the reaction zone and with about **10** to **50** volume percent or more olefins in the effluent from the disproportionation reaction zone. U.S. Pat. No. 3,445,541 does not disclose or suggest any advantages for disproportionation of hexanes and butanes in combination with C_5 and C_6 isomerization.

SUMMARY OF THE INVENTION

According to the present invention, a process is provided for producing isopentane which comprises: (a) isomerizing a C_6-rich fraction in an isomerization zone to obtain at least isopentane and C_6 alkanes, (b) fractionating the isopentane from the C_6 alkanes to obtain an isopentane product, (c) disproportionating at least a portion of the C_6 alkanes in a C_6 disproportionation zone to obtain at least n-pentane and C_7 hydrocarbons, and (d) isomerizing the n-pentane in the isomerization zone.

The process of the present invention results in the production of high-octane isopentane from low-octane hexane (such as normal hexane, which has an octane rating of about 26). The isopentane which is produced in the process of the present invention has an octane rating of about 92 and is particularly useful in high-octane unleaded or low-lead-content gasolines.

Isomerization of C_6 hydrocarbons can be used to upgrade the octane rating of normal hexane-rich hydrocarbon fractions. However, the octane can be increased only to about 70–75 (motor octane) by isomerization because the main hexane isomers produced, namely, 2-methyl pentane and 3-methyl pentane, have an octane rating of only 73 and 75, respectively. Although increasing the octane rating of a C_6 fraction from the vicinity of about 26, which is the octane of normal hexane, to about 70–75 by isomerization to produce isohexanes represents a substantial increase, it is generally not a sufficient increase to produce high-octane gasoline components for use in unleaded or lead-free gasolines.

The C_6-rich hydrocarbons also have been considered as feedstocks for catalytic reforming in order to reform the C_6 material into reasonably low volatility gasoline boiling range hydrocarbons in the **90+** octane range. However, the C_6 hydrocarbons have been found to make a relatively unattractive feedstock for catalytic reforming processes.

Thus, it is desirable to provide a process for upgrading C_6-rich hydrocarbon fractions into 90+ octane rating components. The process of the present invention achieves these desired results by the combination of isomerization with disproportionation. In addition, the isomerization step is particularly advantageously em-

ployed with the disproportionation step in the present invention as the isomerization step serves the dual function of (1) purifying C_6-rich hydrocarbons which are subsequently disproportionated, and (2) isomerizing a portion of the C_6 hydrocarbons.

The isomerization zone serves to purify the feed for the disproportionation zone by converting sulfur compounds in the C_6-rich feed to the isomerization zone to hydrogen sulfide, which can be readily removed from the isohexane-rich effluent from the isomerization zone before the isohexane-rich effluent is fed to the disproportionation zone. The preferred catalyst used in the disproportionation zone is sensitive to even small amounts of H_2S, and H_2S will be formed in the disproportionation zone unless the organic sulfur compounds are substantially completely removed ahead of the disproportionation zone.

Also, the isomerization zone can serve to increase the amount of isopentane produced in the disproportionation zone by providing a branched-chain C_6 feed for the disproportionation zone. Using the preferred dual-function dehydrogenation-olefin disproportionation catalyst for the disproportionation zone, there is substantially no production (or depletion) of branched-chain hydrocarbons in the disproportionation reaction zone.

According to a preferred embodiment of the present invention, the isomerization zone is further integrated with the disproportionation zone by using common fractionation facilities, at least in part. The term "fractionation facilities" is used herein to mean distillation columns or the like and associated equipment.

The effluent from the C_5–C_6 isomerization zone is usually composed primarily of isopentane, normal pentane, isohexanes and normal hexane. However, there also is present minor or small amounts of propane, isobutane, normal butane and C_7+ hydrocarbons. It will, of course, be understood that the amount of these secondary hydrocarbons will depend upon several factors, including the composition of the feed to the isomerization zone, the type catalyst used in the isomerization zone (some isomerization catalysts have higher per-pass conversions but lower selectivities to the desired isopentane and isohexane products), and the temperature used in the isomerization zone (higher temperatures usually resulting in more light hydrocarbons such as propane and butanes). The effluent hydrocarbons from normal hexane disproportionation according to the preferred embodiments of the present invention using the two-component disproportionation catalyst usually are primarily propane, normal butane, normal pentane, normal hexane and C_7+ hydrocarbons. However, there will also be minor or small amounts of isobutane, isopentane, and isohexane. The amounts of these iso- or branched-chain hydrocarbons will increase if increased amounts of isohexane are fed to the C_6 disproportionation step. Thus, it is particularly advantageous to use common fractionation facilities for the isomerization zone effluent hydrocarbons and the disproportionation zone effluent hydrocarbons when substantial amounts, for example more than 5 or 10 weight percent, isohexane is fed to the C_6 disproportionation zone because, in this instance, there is an increased amount of common hydrocarbons from both the isomerization zone and the disproportionation zone.

The fractionation facilities required for the effluent from the isomerization zone and for the effluent from the disproportionation zone can range from one or two columns up to about 8 sequential columns. For example, a propane splitter to separate propane from isobutane+; an isobutane splitter to separate isobutane from normal butane+; a normal butane splitter to separate normal butane from isopentane+; an isopentane splitter to separate isopentane from n-pentane+; a normal pentane splitter to separate normal pentane from isohexane+; an isohexane splitter to separate isohexane from normal hexane+; and a normal hexane splitter to separate normal hexane from C_7+. The fractionation of the aforementioned hydrocarbon cuts can be carried out in sequential separate columns or, at the other extreme, one column can be used similar to crude oil distillation with side streams being withdrawn from the column and stripped, if necessary. As indicated previously, the amounts of the various components present in the effluents from the isomerization zone and the disproportionation zone can vary. Thus, in some instances, only part of the fractionation for the two zones will be carried out in common fractionation facilities with the other part being carried out in separate fractionation facilities for the respective zones. Because there are usually substantial amounts of normal pentane and C_6 alkanes in the effluent hydrocarbons in both the isomerization zone and the disproportionation zone, it is particularly preferred to carry out the separation of normal pentane from C_6 alkanes in a distillation column common to both the isomerization zone and the disproportionation zone.

In the process of the present invention, the feed to the C_6 disproportionation zone can be a normal hexane feed or a feed containing substantial amounts of isohexane in addition to normal hexane. Usually it is preferred to feed the isohexane as well as the normal hexane to the disproportionation zone so as to produce isopentane (as well as normal pentane from the normal hexane). Isopentane has a substantially higher octane than the isohexanes 2-methyl pentane and 3-methyl pentane, which are the primary isohexane products from C_6 isomerization using sulfactive isomerization catalysts and isomerization conditions (500°–800°F.) suitable for hydrodesulfurization.

As indicated above, one of the important purposes which the isomerization zone serves in the process of the present invention is to remove sulfur impurities from the C_6 fraction before the C_6 fraction is fed to the disproportionation zone. In broad scope, the process of the present invention can be applied to the isomerization and subsequent disproportionation of C_6-rich hydrocarbon streams which are essentially free of sulfur impurities as, for example, C_6 hydrocarbon streams obtained from a catalytic reforming unit. However, the process combination of the present invention has particular advantage when applied to C_6-rich hydrocarbon streams containing minor amounts of sulfur impurities, usually at least 5 ppm sulfur.

C_6 hydrocarbon cuts obtained by crude oil distillation, i.e., straight run C_6-rich hydrocarbon fractions, contain usually at least 5 ppm organic sulfur compounds (calculated as elemental sulfur by weight) and generally between about 20 and 500 ppm organic sulfur compounds. The isomerization zone can use a hydrotreating step ahead of the isomerization reaction

zone catalyst as in the case of using halogenated aluminum-type catalysts, but it is preferred in the process of the present invention to use a crystalline aluminosilicate-type hydroisomerization catalyst, many of which catalysts we have found can be operated with several hundred ppm sulfur and frequently up to about 500 or 1000 ppm sulfur in the feed without substantially decreasing the life of the hydroisomerization catalyst. Also, the crystalline aluminosilicate-type catalyst can be used to obtain relatively high yields of isohexane per pass at temperatures usually about 100°F. less than is required for a comparable isohexane yield using halogenated aluminum-type isomerization catalysts. Halogenated aluminum-type catalysts which are sensitive to sulfur poisons and thus not as preferred for use in the process of the present invention include the catalyst such as used in the butamer process described in the Oil and Gas Journal, Vol. 56, No. 13, Mar. 31, 1958, pp. 73–76, the BP isomerization process as described in Hydrocarbon Processing, Vol. 45, No. 8, August 1966, pp. 168–170, and the liquid phase isomerization process described in Hydrocarbon Processing, Vol. 42, No. 7, July 1963, pp. 125–130.

Thus, in the process of the present invention, it is preferred to use a hydroisomerization catalyst which is essentially free of halogenated aluminum. Catalysts comprising crystalline aluminosilicates, such as molecular sieves, mordenite, and layered crystalline aluminosilicates, are particularly preferred. It is preferred to use one or more hydrogenation components with the crystalline aluminosilicate. Palladium and platinum are preferred hydrogenation components. Preferred catalysts comprising crystalline aluminosilicate and a hydrogenation component such as palladium or others are described in patent applications Ser. Nos. 776,733 and 839,999, which applications are incorporated by reference into the present patent application, particularly those portions of the afore-identified applications disclosing catalyst compositions. Preferred aluminosilicate-containing catalysts for use in the isomerization zone include catalysts comprising a layered clay-type aluminosilicate cracking component, with 0.01 to 2.0 weight percent, based on said cracking component and calculated as the metal, of a hydrogenating component selected from platinum, palladium, iridium, ruthenium, and rhodium, and also with 0.01 to 5.0 weight percent, based on said cracking component and calculated as the metal, of a hydrogenating component selected from tungsten and chromium. Particularly preferred hydroisomerization catalysts are those as described above wherein the hydrogenating components are palladium and chromium. In the present specification, oxides and other compounds of metals are to be considered as included in reference to a metal simply as an element, i.e., chromium includes the use of chromium in compound forms such as chromium oxide.

The C_6 disproportionation zone operated in accordance with the present invention in combination with the C_5–C_6 isomerization zone will usually produce substantial amounts of butanes in addition to the disproportionation of hexane to pentane and heptane. Butane is produced in accordance with the following disproportionation reaction:

$$2C_6 \rightleftarrows C_4 + C_8$$

Butanes have a high octane rating with normal butane having an octane rating of about 90 and isobutane having an octane rating of about 99. However, only limited amounts of butanes can be used in motor gasolines before exceeding Reid Vapor Pressure limitations for the gasoline.

Thus, it is particularly preferred in the process of the present invention to upgrade butanes produced in the C_6 disproportionation zone to high-octane gasoline boiling range hydrocarbons which are not as volatile as the C_4 hydrocarbons. In accordance with a particularly preferred embodiment of the present invention, this objective is accomplished by operation of a separate butane disproportionation zone in combination with the isomerization zone and the C_6 disproportionation zone. The butane fed to the C_4 disproportionation zone is at least in part derived from the butanes resulting from the C_6 disproportionation. The butanes are disproportionated in the butane disproportionation zone to obtain increased amounts of normal pentane, which is in turn fed at least in part to the isomerization zone to produce the high-octane, relatively low-volatility product, isopentane.

Although the butane disproportionation is preferably carried out in the same plant as the plant used for the hexane disproportionation step, usually, and preferably, separate reactors are used for the C_6 disproportionation and the C_4 disproportionation, respectively.

Preferred catalysts for use in both the C_6 and the C_4 disproportionation reaction zones are catalytic masses having a component with alkane dehydrogenation activity and a second component with olefin disproportionating activity, for example, catalytic masses comprising a Group VIII metal component and a Group VIB metal component. Particularly preferred disproportionation catalysts include catalytic masses comprising a noble metal on a refractory support and a Group VIB metal or metal compound on a refractory support, for example a catalytic mass comprising platinum on alumina and tungsten or tungsten oxide on silica. Preferred temperatures for the disproportionation of normal butane and for the disproportionation of C_6 alkanes using the above-indicated catalytic masses are between about 400°–850°F. and more preferably between 650°–799°F. Pressure maintained in the disproportionation reaction zone is preferably between atmospheric and 2500 psia, and still more preferably between 100 and 1500 psia. In addition to the preferred relatively low temperature for hydrocarbon disproportionation, we have found that it is preferable to carry out the disproportionation reaction in the presence of no more than a few weight percent olefins, preferably less than 5 weight percent olefins. Preferred conditions for the disproportionation of saturated hydrocarbons such as butane or hexane are further discussed in commonly assigned applications Ser. Nos. 3,303 and 3,306, the disclosures of which applications are incorporated by reference into the present application.

Thus some of the important advantages obtained in accordance with particularly preferred embodiments of the present invention include: (1) using sulfactive

isomerization catalysts, particularly layered clay-type catalysts as described above, sulfur-containing C_6 hydrocarbon feed to the process can be desulfurized while it is being isomerized; (2) the isomerization zone is used both for C_6 isomerization and also for the isomerization of normal pentane to isopentane; (3) in utilizing separate C_4 and C_6 disproportionation reactors in the preferred embodiment as described above, the separate disproportionation steps can be operated at the best temperature, space rates and other operating conditions for their respective feeds, whereas if C_4 and C_6 alkanes are interacted together in an averaging reaction, it is necessary to select the best compromise operating conditions; (4) in addition to the C_4 disproportionation zone handling the problem of some C_4 product from the C_6 disproportionation zone, the C_6 disproportionation zone is advantageously used to handle the problem of some C_6 alkane product from the C_4 disproportionation zone. Thus, each disproportionation reactor takes care of a selectivity problem for the other reactor. For example, two C_6's go mainly to a C_5 and a C_7, but they do go partly to a C_4 and a C_8 alkane. Conversely, two C_4's go mainly to a C_3 and a C_5, but do go partly to C_2 and C_6 alkanes; (5) common fractionation facilities can be used to further integrate the disproportionation zone or zones with the isomerization zone. The common fractionation facilities reduce the cost of separating the respective components, reduce the complexity of the combination and make it easier to route undesired products to the proper place to convert them at least partly to the proper product to ultimately produce the desired isopentane product.

BRIEF DESCRIPTION OF THE DRAWING

The drawing is a schematic process flow diagram illustrating preferred embodiments of the present invention.

DETAILED DESCRIPTION OF THE DRAWING

Referring now more particularly to the drawing, a C_6-rich hydrocarbon stream is fed via lines 1 and 3 to isomerization zone 4. The C_6 fraction or cut can be obtained from the effluent from a catalytic reforming process and advantageously upgraded in the process of the present invention to isopentane. However, the process combination of the present invention has particular application to straight run hydrocarbon C_6-rich fractions containing organic sulfur compounds, usually in an amount between about 5 ppm and 300 ppm, calculated as sulfur by weight.

The C_6-rich hydrocarbon fraction is isomerized in the presence of hydrogen using a hydroisomerization catalyst which preferably comprises a crystalline aluminosilicate together with a hydrogenation component such as palladium or platinum. Preferred operating conditions for the C_6 isomerization include a hydrogen gas rate in the range of 1000 to 5000 SCF/b., preferably 1500 to 2000 SCF/b.; space velocities in the range of about 0.1 to 20 liquid volumes per hour per volume of catalyst, preferably 1.0 to 5.0 LHSV; temperatures in the range of about 200°–800°F., preferably 250° to 750°F.; and pressures within the range of atmospheric to 3000 psig, preferably in the range of 500–800 psig.

In addition to isomerizing normal hexane in isomerization zone 4, normal pentane derived from disproportionation zone 12 is also isomerized in zone 4. As shown in the drawing, normal pentane from the disproportionation zone is recycled via line 2 and then introduced via line 3 to the isomerization zone. After stripping hydrogen sulfide from the isomerization reaction zone effluent, the isomerization effluent hydrocarbons are fed via lines 5 and 7 to fractionation zone 8.

Fractionation zone 8 typically consists of 3 to 8 distillation columns used to separate the various components obtained both from isomerization in zone 4 and disproportionation in zones 12 and 16, according to the preferred embodiment illustrated in the drawing. As indicated previously, the fractionation zone can have a varying number of distillation columns, and it is preferred to use common fractionation facilities for at least part of the separation of effluent hydrocarbons from isomerization zone 4 and disproportionation zone 12. It is particularly preferred to carry out the fractionation of normal pentane from C_6 alkanes in the same fractionation column for effluent hydrocarbons from disproportionation zone 12 and isomerization zone 4.

C_6 alkanes are removed from the fractionation zone via line 9 and fed to disproportionation zone 12 via line 11. A portion of the C_6 hydrocarbons from the fractionation zone can be recycled back to the isomerization zone instead of feeding all the C_6 hydrocarbons to C_6 disproportionation.

C_6 hydrocarbons are disproportionated in zone 12 at least in part to obtain normal pentane and heptane. Effluent hydrocarbons including normal pentane are removed from disproportionation zone 12 via line 13 and passed via lines 6 and 7 to fractionation zone 8.

In fractionation zone 8 normal pentane is separated. The normal pentane is passed via line 2 and line 3 to isomerization zone 4.

In isomerization zone 4, the normal pentane derived from disproportionation zone 12 is isomerized to isopentane which is ultimately fractionated from the isomerization zone effluent hydrocarbons and recovered as a product withdrawn via line 18.

Propane and other light gases formed in isomerization zone 4 and also in disproportionation zone 12 are removed from the effluent hydrocarbons from these two respective zones by separation in zone 8. Preferably, common fractionation facilities are used to separate the propane and other light gases generated in disproportionation zones 12 and 16 and in isomerization zone 4, particularly when the isomerization is carried out at a high temperature, for example in excess of 700° or 750°F., so as to generate substantial amounts of propane and other light hydrocarbons. When the isomerization zone is operated at relatively mild conditions, for example below 700°F., and with only one or two percent or less weight percent propane produced in isomerization zone 4, depropanizing the effluent hydrocarbons from the isomerization zone could advantageously be carried out separate from the depropanizing of the effluent hydrocarbons from disproportionation zones 12 and 16.

As discussed under Summary of the Invention, according to a preferred embodiment of the present invention butanes generated in disproportionation zone

12 are fed to disproportionation zone 16 for conversion in part to normal pentane, which in turn is converted in isomerization zone 4 to high-octane isopentane. Butanes are withdrawn via line 15 from fractionation zone 8 and fed to disproportionation zone 16. Effluent hydrocarbons including normal pentane are withdrawn via line 17 and passed via lines 6 and 7 to fractionation zone 8. The normal pentane is withdrawn from fractionation zone 8 and passed via lines 2 and 3 to isomerization zone 4.

The disproportionation reaction in zones 12 and 16 is preferably carried out in separate reactors, for example parallel reactors in a single disproportionation plant. The preferred catalyst is a two-component catalyst comprising an alkane dehydrogenation component and an olefin disproportionation component.

Some heavier hydrocarbons, i.e., C_7+ hydrocarbons, are formed in both disproportionation zone 12 and zone 16. These heavier hydrocarbons are withdrawn from fractionation zone 8 via line 20. The C_7+ hydrocarbons can be advantageously used as a feedstock for catalytic reforming to produce high-octane gasoline, for example by reforming using a platinum-rhenium on alumina catalyst. The C_7+ hydrocarbons alternately can be passed at least in part via lines 22 and 11 to C_6 disproportionation zone 12. The C_7+ hydrocarbons are suitable feedstock for disproportionation to lower hydrocarbons including normal pentane.

EXAMPLES

Example 1

A C_6-rich fraction was desulfurized from 100 ppm S to less than 0.1 ppm S under the following reaction conditions:

T, °F.	700
P, psig	800
LHSV	1.0
Catalyst composition:	Pd-Cr-layered crystalline aluminosilicate
Hydrogen, SCF/bbl.	10,000

Example 2

Using the same Pd-Cr-layered aluminosilicate catalyst as in Example 1, a C_6-rich fraction free of sulfur was isomerized at 800 psig, LHSV = 1.0 and hydrogen rate = 17,000 SCF/bbl. of feed, with the results as shown in Table I.

Example 3

The data tabulated in Table II below illustrate the results obtained in disproportionating normal butane by contacting normal butane with an alkane disproportionation catalyst mass under the following conditions:

Volume of Catalyst in Reactor: 9 cubic centimeters (cc.)

Type of Catalyst:

2 cc. of 0.5 wt.% Pt; 0.5 wt. % Re; 0.5 wt.% Li on Al_2O_3 7 cc of 8.0 wt.% WO_3 on SiO_2

Both types of catalyst particles were 28 to 60 Tyler mesh size.

Operating Conditions:

Temperature[1]: 650°, 700°, 750°, 800°, 875°F.

Pressure: 900 psig

Feed rate: 9 cc./hour

[1]Successive runs, of several hours each with no regeneration in between, were made at the temperatures specified, except that the catalyst was reactivated by flushing the catalyst overnight with hydrogen before the run at 875°F.

As can be seen from the data tabulated in Table II, the ultimate yield of C_5+ decreases considerably in moving from particularly preferred temperatures below 800°F. to temperatures in excess of 800°F. as, for example, temperatures as high as 875°F., where the ultimate yield of C_5+ drops to about 42 percent vs. approximately 57 percent at 750°F. More importantly, the yield of nC_5 is seen to be greater at temperatures between 700° and 800°F. than at higher temperatures such as 875°F.

TABLE II

Weight % Product Yields at Various Operating Temperatures

Product	650°F.	700°F.	750°F.	800°F.	875°F.
$He + CH_4$	0.2	0.2	0.5	1.1	3.2
C_2H_6	0.8	1.3	2.1	2.8	7.5
C_3H_8	5.9	11.6	15.7	19.8	16.0
iC_4H_{10}	0.1	0.1	0.2 0.4		0.5
nC_4H_{10}	83.1	67.7	56.7	46.9	53.1
ΣC_4H_8	0.5	0.4	0.5	0.5	N.M.[4]
Σ branched C_5C_{12}	0.06	0.1	0.2	0.5	0.8
nC_5H_{12}	4.7	9.5	11.7	13.9	7.2
ΣC_5H_{10}	0.1	0.1	0.2	0.2	N.M.[4]
Σ branched C_6H_{14}	0.03	0.1	0.3	0.8	0.9
nC_6H_{14}	2.3	4.4	5.7	6.3	3.7
ΣC_6H_{12}	0.1	0.1	0.2	0.4	N.M.[4]
Σ branched C_7H_{16}	0.009	0.05	0.2	0.3	0.6
nC_7H_{16}	1.1	2.1	2.8	2.9	1.9
ΣC_7H_{14}	0.02	0.05	0.08	0.06	N.M.[4]
Σ branched C_8H_{18}	—	0.05	0.1	0.5	0.4
nC_8H_{18}	0.5	1.0	1.3	1.3	1.0
Σ branched C_9H_{20}	—	0.05	0.1	—	0.07

TABLE I.—ISOMERIZATION OF SYNTHETIC NAPHTHA

		Catalyst temperature, ° F.													
	Feed	561	577	593	609	625	641	657	673	689	705	721	737	753	769
Methane		0.06									0.18				0.46
Ethane		0.01									0.28				0.8
Propane		0.04									1.91				0.16
Iso-C_4		0.30									0.60				1.34
n-C_4		0.05									0.69				2.12
Total cracked prod., wt. percent		0.45	0.49	0.53	0.63	0.77	0.98	1.33	1.87	2.74	3.66	5.36	7.41	9.30	13.92
Iso-C_5	14.36	14.15	15.05	16.37	17.30	19.97	22.07	25.41	28.48	30.80	32.48	30.71	30.35	29.13	29.34
n-C_5	32.56	35.75	35.06	34.10	32.05	30.13	27.37	25.03	22.71	20.55	19.40	17.44	17.33	17.03	17.26
2,2-dimethyl butane		0.46	0.61	0.93	1.39	2.11	2.90	3.52	4.20	4.27	5.31	5.56	5.40	4.90	
2,3-dimethyl butane		0.75	1.00	1.33	1.66	1.98	2.25	2.40	2.48	2.50	2.60	2.67	2.54	2.39	
2-methyl pentane	10.96	13.17	13.38	14.44	15.33	15.64	15.38	14.97	14.60	13.94	13.41	13.51	13.72	12.99	12.28
3-methyl pentane	11.47	10.22	9.99	10.23	10.66	10.83	10.73	10.52	10.19	9.89	9.46	9.62	9.69	9.28	8.79
n-C_6	21.54	17.20	15.74	14.47	13.17	11.68	10.62	9.98	9.45	9.24	8.99	9.22	9.12	9.00	8.44
Methyl cyclopentane	2.47	4.74	5.63	6.19	6.68	6.72	7.07	6.28	5.64	5.22	4.64	4.73	3.69	3.73	2.42
Benzene	0.79														
Cyclohexane	5.83	3.73	3.03	2.03	1.51	1.21	1.28	1.22	0.82	0.82	0.66	0.83	0.46	1.05	0.2

nC_9H_{20}	0.3	0.4	0.7	—	0.5
$\Sigma C_{10}+$	—	0.3	0.5	—	2.0
ΣC_1–C_3	6.9	13.2	18.3	23.8	26.7
ΣC_5+	9.4	18.4	24.2	28.4	19.7
C_5+ Ultimate Yield[1]	57.7	58.3	56.9	54.4	42.4
Σ Olefins[2]	0.7	0.8	0.9	1.2	N.M.[4]
(% branched chain in C_5–C_9 range)[3]	1.1	2.0	4.3	7.4	19.2

[1]C_5+ Ultimate Yield $= \Sigma C_5+/(\pi C_1$–$C_3 + \Sigma C_5+)$.

[2]All olefins analyses are from an approximate chromatographic analysis.

[3]The decrease in branching with decreasing temperature indicate the process of the present invention is more selective for pure disproportionation without isomerization at lower temperatures. This attribute is important when it is desired to produce n-paraffins, as, for example, in wax production.

[4]N.M. = not measured because products were hydrogenated prior to analysis.

Although various embodiments of the invention have been described, it is to be understood that they are meant to be illustrative only and not limiting. Certain features may be changed without departing from the spirit or scope of the present invention. It is apparent that the present invention has broad application to combined C_5, C_6 alkane isomerization and C_6 disproportionation to produce isopentane. Accordingly, the invention is not to be construed as limited to the specific embodiments or examples discussed, but only as defined in the appended claims or substantial equivalents of the claims.

What is claimed is:

1. A process for producing isopentane which comprises:
   a. isomerizing a C_6-rich hydrocarbon fraction containing C_5 hydrocarbons in an isomerization zone to obtain at least isopentane and C_6 alkanes;
   b. fractionating the isopentane from the C_6 alkanes to obtain an isopentane product;
   c. disproportionating at least a portion of the C_6 alkanes in a C_6 disproportionation zone by contacting the C_6 alkane with a catalyst comprising a Group VIII metal or metal compound and a Group VIB metal or metal compound at a temperature between 400°F. and 850°F. to obtain at least n-pentane and C_7 hydrocarbons; and
   d. isomerizing the n-pentane to iso-pentane in the isomerization zone.

2. A process in accordance with claim 1 wherein the C_6-rich hydrocarbon feed to the isomerization zone contains at least 5 ppm sulfur present as organic sulfur compounds and the isomerization is carried out using a sulfactive isomerization catalyst at conditions sufficient to convert the organic sulfur compounds to H_2S and hydrocarbons, and H_2S is separated from the C_6 alkanes from the isomerization zone before the C_6 alkanes are fed to the disproportionation zone.

3. A process in accordance with claim 1 wherein C_6 alkanes are disproportionated in accordance with step (c) to obtain normal pentane, C_7 hydrocarbons, and normal butane, and wherein the normal butane is disproportionated in a C_4 disproportionation zone to obtain at least normal pentane and propane, and wherein at least a portion of the normal pentane obtained by normal butane disproportionation is isomerized in the isomerization zone.

4. A process in accordance with claim 1 wherein common fractionation facilities are used at least in part for effluent hydrocarbons from the isomerization zone and effluent hydrocarbons from the C_6 disproportionation zone.

5. A process in accordance with claim 4 wherein the same fractionation column is used for the fractionation of normal pentane from C_6 alkanes present as a mixture in effluent hydrocarbons from both the isomerization zone and the C_6 disproportionation zone.

6. A process in accordance with claim 1 wherein the C_6-rich hydrocarbon stream fed to the isomerization zone is a straight run fraction obtained by fractionating a C_6-rich cut from crude oil.

7. A process in accordance with claim 1 wherein the catalyst used in the isomerization zone is substantially free of halogenated aluminum.

8. A process in accordance with claim 1 wherein the isomerization catalyst comprises palladium or platinum and a crystalline aluminosilicate material.

9. A process in accordance with claim 1 wherein the isomerization catalyst comprises 0.05 to 5.0 weight percent palladium and 0.05 to 5.0 weight percent chromium on a layered clay-type crystalline aluminosilicate material.

10. A process in accordance with claim 1 wherein the disproportionation reaction is carried out at a temperature between 400° and 850°F. using a catalyst comprising a noble metal on a refractory support and a Group VIB metal compound on a refractory support.

11. A process in accordance with claim 1 wherein the disproportionation reaction comprises contacting the C_6 alkanes with a catalytic mass comprising platinum on alumina and tungsten or tungsten oxide on silica at a temperature between about 650° and 850°F. and a pressure between about 100 psia and 1500 psia.

12. A process in accordance with claim 11 wherein the olefin concentration in the disproportionation reaction zone is maintained below about 5 volume percent.

13. A process for producing isopentane from C_6 hydrocarbons which comprises:
   a. isomerizing a C_6-rich hydrocarbon stream containing between 5 and 500 ppm organic sulfur compounds in an isomerization zone by contacting the C_6-rich hydrocarbons with a sulfactive isomerization catalyst at a hydrogen partial pressure between about 100 and 1500 psig and a temperature between about 200°F. and 800°F. to obtain a C_6-rich effluent stream containing less than 1 ppm sulfur present as organic sulfur compounds,
   b. disproportionating at least a portion of the C_6-rich effluent stream by contacting the C_6 hydrocarbons with a catalyst comprising platinum on a refractory support and a Group VIB metal or metal oxide on a refractory support at a temperature between 400° and 850°F. to obtain a hydrocarbon stream comprising normal butane, normal pentane and C_7 hydrocarbons,
   c. disproportionating at least a portion of the normal butane in the effluent from C_6 disproportionation by contacting the normal butane with a catalyst comprising platinum on a refractory support and a Group VIB metal or metal oxide on a refractory support at a temperature between 400° and 850°F. to obtain a stream containing propane and normal pentane, and
   d. isomerizing at least a portion of the normal pentane from the C_6 disproportionation and at least a

portion of the normal pentane from the C_4 disproportionation in the isomerization zone to obtain isopentane.

14. A process in accordance with claim 13 wherein common fractionation facilities are used at least in part for the isomerization zone and the C_6 disproportionation zone and the C_4 disproportionation zone.

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