

[54] **GASOLINE PRODUCTION**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 3,303, Jan. 16, 1970, and a continuation-in-part of Ser. No. 3,306, Jan. 16, 1970.

[52] U.S. Cl.208/93, 208/79, 208/141, 260/676

[51] Int. Cl.C10g 39/00

[58] Field of Search208/65, 92, 93, 141-149; 260/683 D, 676

[56] **References Cited**

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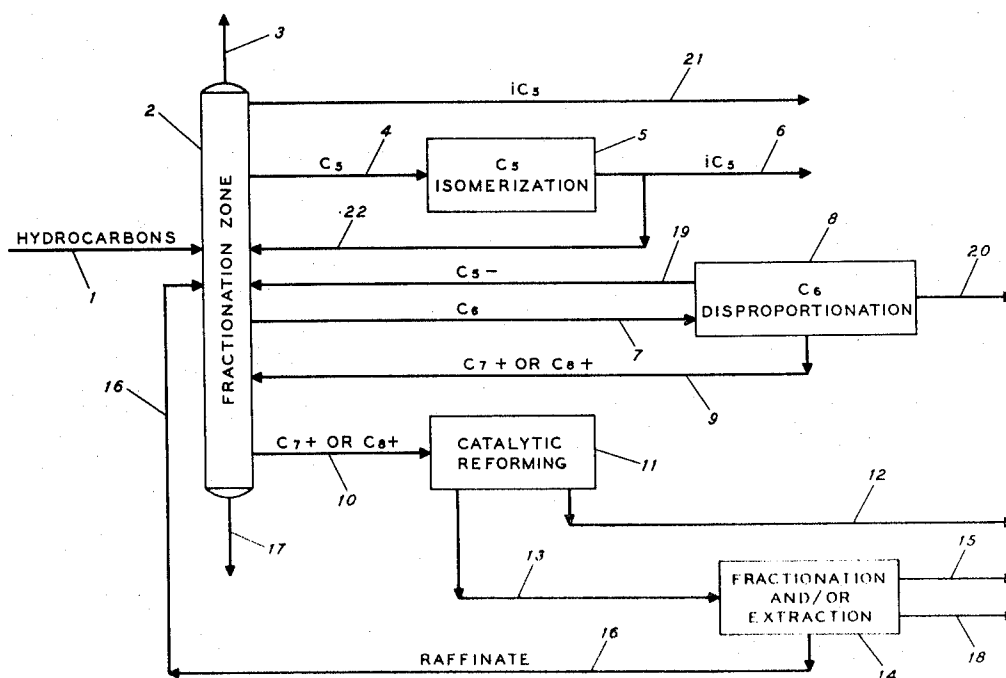
Primary Examiner—Herbert Levine

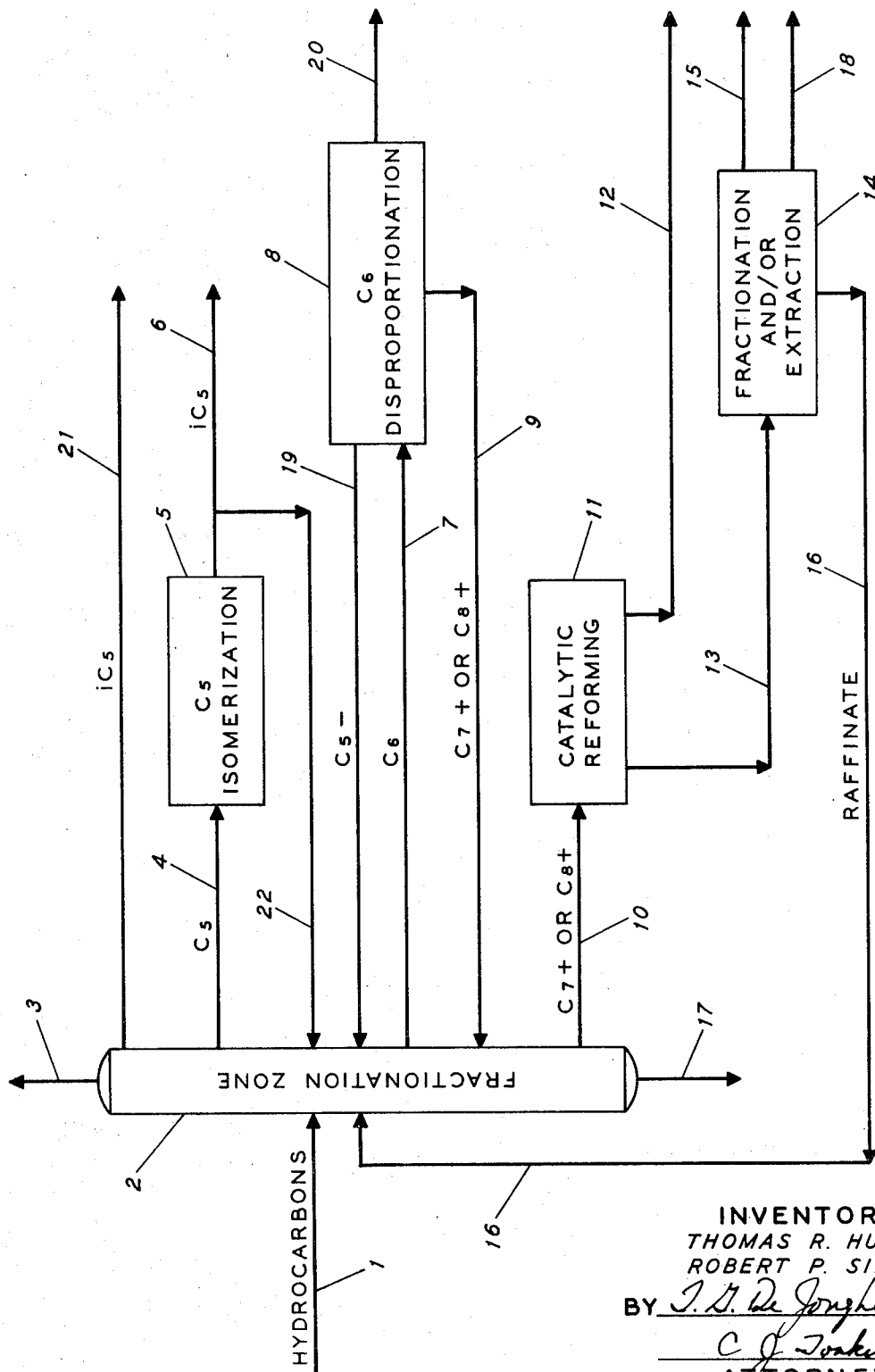
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[57] **ABSTRACT**

A process for producing gasoline from a hexane-rich hydrocarbon feed which comprises disproportionating the hexane-rich feed to obtain at least C₅ hydrocarbons and C₇+ hydrocarbons, and catalytically reforming the C₇+ hydrocarbons to obtain reformate. Preferably, the normal pentane hydrocarbons obtained from disproportionating the hexane are fed to a C₅ isomerization process to obtain isopentane. Preferably, a common fractionation zone is used for the disproportionation, catalytic reforming and C₅ isomerization processes.

6 Claims, 1 Drawing Figure





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GASOLINE PRODUCTION

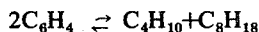
CROSS REFERENCES

This application is a continuation-in-part of Applications Ser. Nos. 3,303 and 3,306, filed Jan. 16, 1970, the disclosures of which applications are incorporated by reference into the present patent application.

BACKGROUND OF THE INVENTION

The present invention relates to disproportionation and catalytic reforming. More particularly, the present invention relates to the disproportionation of alkanes, especially hexane, and the catalytic reforming of hydrocarbons. The present invention also relates to normal pentane isomerization integrated into combined hexane disproportionation and naphtha reforming.

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



Disproportionation, particularly disproportionation of alkanes, is discussed further in Applications Ser. Nos. 3,303 and 3,306.

The disproportionation processes disclosed in Ser. Nos. 3,303 and 3,306 are preferably carried out at relatively low temperatures, usually below 850°F. and more preferably below 800°F. The Ser. Nos. 3,303 and 3,306 processes are particularly directed to the disproportionation of alkanes to higher and lower molecular weight hydrocarbons with the reaction preferably being carried out in the presence of no more than a small amount of olefins.

Catalytic reforming has been practiced increasingly in petroleum refineries since about 1940. Nearly all of the conventional present catalytic reforming processes use a catalyst comprising platinum on alumina. Usually, the reaction temperature for catalytic reforming is between about 850° and 1100°F., and the reaction is carried out in the presence of hydrogen. Catalytic reforming in general, and a particularly preferred catalytic reforming process, are described in U.S. Pat. No. 3,415,737, the disclosure of which patent is incorporated by reference into the present application.

The present invention is particularly concerned with the integration of alkane disproportionation and catalytic reforming and the present invention is especially concerned with the upgrading of hexane or hydrocarbon feedstocks containing hexane, to obtain higher octane gasoline boiling range hydrocarbons.

The hexane isomers present a unique problem among the alkanes of the gasoline boiling range. The butanes have high blending octane numbers and are limited as gasoline components only by their high vapor pressure. Normal pentane can be isomerized to produce a blend with a fairly acceptable octane number. The C₇ to C₉ alkanes can be converted into high octane number aromatic hydrocarbons by catalytic reforming. However, isomerization of hexanes produces a blend with low octane number, and reforming of hexanes produces only low yields of benzene. One purpose of the present invention is to provide a means for conversion of hexanes into compounds with higher octane numbers.

SUMMARY OF THE INVENTION

According to the present invention, a process is provided for producing gasoline from a hexane-rich hydrocarbon feed stream which process comprises disproportionating the hexane-rich feed to obtain C₅-hydrocarbons and C₇+ hydrocarbons, and catalytically reforming at least a portion of the C₇+ hydrocarbons to obtain reformate.

The term "hexane-rich" is used herein to connote a stream containing a substantial amount of C₆ hydrocarbons, usually at least one or two weight percent hexane and preferably at least 5 or 10 weight percent hexane. The process of the present invention can, of course, be applied to pure hexane streams, but in most instances, the hexane will be present together with other hydrocarbons.

The disproportionation of the hexane will result in hydrocarbons having lower molecular weight than the hexane, i.e., C₅ and lower hydrocarbons, as well as hydrocarbons having a molecular weight higher than the hexane, i.e., C₇ and higher boiling hydrocarbons. The C₅ and lighter hydrocarbons are herein sometimes referred to as C₅-hydrocarbons and the C₇ and higher boiling hydrocarbons are sometimes referred to herein as C₇+ hydrocarbons. The C₅-hydrocarbons are primarily C₅, C₄, C₃ and C₂ hydrocarbons. The C₇+ hydrocarbons are primarily C₇, C₈, C₉, C₁₀, C₁₁ and C₁₂ hydrocarbons, but the C₇+ hydrocarbons can boil as high as about 400° to 500°F.

Preferably, the disproportionation is carried out by contacting the hexane with a catalytic mass having catalytic activity for paraffin dehydrogenation as well as catalytic activity for olefin disproportionation. A particularly preferred catalyst for the disproportionation of hexane or in general, for the disproportionation of the hexane-rich feed to the disproportionation zone in the present invention comprises platinum on alumina and a Group VIB metal on a refractory support.

Preferred catalysts for use in the disproportionation zone in the process of the present invention are disclosed in Ser. Nos. 3,303 and 3,306.

As indicated previously, it is advantageous to combine normal pentane isomerization with the disproportionation and catalytic reforming steps of the present invention. Thus, according to a particularly preferred embodiment of the present invention, a combination process is provided for converting paraffinic hydrocarbons into gasoline which comprises (a) separating a C₃+ hydrocarbon feed stream into a C₅ rich stream, a C₆ rich stream and a C₇+ stream, (b) isomerizing the C₅ rich stream to obtain iC₅, (c) disproportionating the C₆ rich stream to obtain at least hydrocarbons lighter than hexane and C₇+ hydrocarbons, and (d) catalytically reforming at least a portion of the C₇+ stream and the C₇+ hydrocarbons from disproportionation to produce reformate. The term "C₅ rich" connotes a C₅ of at least 20 weight percent C₅ and usually at least 70 weight percent C₅.

The isomerization step according to the above preferred embodiment can operate on all or only on a portion of the normal pentane present in the hexane-rich feed to the process of the present invention. However, it is particularly preferred to feed at least a portion of the normal pentane produced in the disproportionation step to the C₅ isomerization step. Isopentane produced by the isomerization is a high octane gasoline blending component.

The C_7+ feed to the catalytic reforming step of the process of the present invention can be altered somewhat by feeding the C_7 hydrocarbons to the disproportionation step and feeding only the C_8+ hydrocarbons to the catalytic reforming step. In either case, the C_7+ or C_8+ feed to the catalytic reforming step usually will boil in the naphtha boiling range or from about C_7 or C_8 up to about 400° or 450°F.

The catalytic reforming step is generally carried out using a platinum on alumina catalyst. Preferably, the catalyst also contains between about 0.01 and 5 weight percent rhodium. In any event, the catalytic reforming step will operate to substantially increase the octane number of the naphtha feed to the reforming step.

In general, substantial amounts of aromatics including xylenes will be produced in the catalytic reforming step. According to a preferred embodiment of the present invention, at least a portion of the aromatics present in at least a portion of the effluent from the catalytic reforming step are fractionated or extracted from the reforming effluent and the remaining paraffinic-rich raffinate is recycled at least in part to the disproportionation step. Recycling the paraffinic raffinate to the disproportionation step is especially advantageous because the paraffinic raffinate usually has a relatively low octane and the disproportionation step can operate to substantially raise the quality of the raffinate by disproportionating the raffinate to C_7+ hydrocarbons, which hydrocarbons can be advantageously catalytically reformed.

It is particularly advantageous to feed the raffinate to a common fractionation zone so that C_5 hydrocarbons can be separated from the raffinate and then isomerized in an isomerization zone. The C_6 or C_6 and C_7 hydrocarbons in the raffinate preferably are fractionated from the raffinate and fed to the disproportionation zone for upgrading, at least in part, to higher molecular weight hydrocarbons which, in turn, can be fed to the catalytic reforming step of the present invention.

BRIEF DESCRIPTION OF THE DRAWING

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

DETAILED DESCRIPTION OF THE DRAWING

Referring now more specifically to the drawing, a hydrocarbon stream preferably rich in paraffins and containing at least hexane is fed via line 1 to fractionation zone 2. The hydrocarbon fresh feed stream to the process of the present invention can boil over a wide range such as C_3 up to $C_{10}+$ (C_{10} to about C_{16}) hydrocarbons. Highly paraffinic feedstocks boiling up to about 500° or 600°F. are preferred hydrocarbon feeds. To a large extent, as is schematically indicated in the drawing, the effluent streams from the processing steps of the present invention and the fresh feed can be handled in one common fractionation zone. The fresh feed stream is separated in the fractionation zone into a number of hydrocarbon cuts, most of which are indicated on the drawing. In many instances, it is advantageous to use more than one fractionation column in the fractionation zone.

To aid in the use of a common fractionation zone, in some instances it is preferable to employ vapor side

draws from the fractionation column or columns, as well as liquid side draws. Thus, the hexane-rich withdrawal from the fractionation zone schematically indicated by arrow 7 from the fractionation zone to disproportionation zone 8 can be a vapor withdrawal.

The C_5- feed to the fractionation zone via line 19 from disproportionation zone 8 usually will contain substantial amounts of C_2 and C_3 hydrocarbons in addition to butanes and pentanes. The C_2 , C_3 and C_4 hydrocarbons can be withdrawn from the fractionation zone via line 3 and processed further, if necessary, to obtain liquefied petroleum gas (LPG).

Isopentane present in the fresh feed to the fractionation zone and/or isopentane recycled together with normal pentane via line 22 to the fractionation zone is preferably withdrawn as an isopentane rich stream via line 21.

C_5 hydrocarbons, particularly normal pentanes, are withdrawn via line 4 from the fractionation zone. Preferably, this C_5 rich hydrocarbon stream is fed to isomerization zone 5 for the conversion of normal pentane into isopentane, which is a much higher octane constituent for gasoline. The isopentane is advantageously blended with high octane reformat produced in catalytic reforming zone 11.

A number of different catalysts can be used for normal pentane isomerization. Catalysts such as two percent aluminum chloride dissolved in antimony trichloride have been used for pentane isomerization carried out under a hydrogen pressure of about 60 – 100 psig to suppress side reactions. Other acidic-type solid isomerization catalysts can be used to effect the normal pentane isomerization. Particularly preferred catalysts comprise layered clay-type crystalline aluminosilicate catalysts, such as described in U.S. Pat. No. 3,252,757.

A hexane-rich hydrocarbon stream is withdrawn via line 7 from the fractionation zone and is fed to disproportionation zone 8. The hexane-rich feed usually contains at least about 10 weight percent hexane and preferably 35 weight percent or more hexane. The hexane-rich stream can contain both lighter and heavier hydrocarbons than hexane. According to the present invention, the two most preferred hexane-rich feed streams are (a) a predominantly C_6 paraffin stream boiling between about 136° and 156°F. or (b) predominantly C_6 and C_7 paraffins boiling between about 136° and 209°F.

As indicated previously, preferably the disproportionation of the hexane is carried out at a temperature below 850°F., and more preferably, below 800°F., and in the presence of no more than about five weight percent olefins, by contacting the hexane with a catalytic mass having catalytic activity for dehydrogenation of hydrocarbons as well as catalytic activity for olefin disproportionation. The catalytic mass can comprise a physical mixture of catalyst particles which are active for hydrocarbon dehydrogenation and catalyst particles which are active for olefin disproportionation. Preferably, the catalytic mass comprises a noble metal or a noble metal compound on a refractory support, in addition to an olefin disproportionation component. Thus, preferred catalyst masses include platinum on alumina particles mixed with tungsten oxide on silica particles. Catalyst masses comprising a Group VIII

component in addition to a Group VIB component are generally suitable in the process of the present invention.

It is preferred in the process of the present invention to operate the disproportionation reaction zone at a pressure above about 200 psig, more preferably above about 400 psig, and still more preferably above about 800 psig. The elevated pressure has been found advantageous because it leads to higher disproportionation conversion. The residence time of the reactant in the reaction zone increases with increasing pressure. Also, the equilibrium partial pressures of both olefin and H_2 formed from dehydrogenation of saturated hydrocarbons rise in direct proportion to the square root of the total pressure. Thus, relatively high pressure, of the order of 500–1,500 psig, are particularly preferred.

C_7+ or C_8+ hydrocarbons produced in disproportionation zone 8 are removed via line 9 and fed to fractionation zone 2. It is to be understood that in most instances, there will be some fractionation or separation facilities as part of disproportionation zone 8 in order to separate the lighter hydrocarbons, for example, C_5- , from the heavier hydrocarbons, for example, C_7+ , formed from the disproportionation of the hexane-rich feed to the disproportionation zone. In some instances, the C_7+ fraction from the disproportionation zone is preferably fed directly to catalytic reforming zone 11. But usually, it is preferred to feed the C_7+ material from the disproportionation zone to common fractionation zone 2 so that the desired C_7+ feed comprising a mixture of C_7+ hydrocarbons in the initial feed added via line 1 and the C_7+ hydrocarbons obtained by disproportionation can be withdrawn together from the common fractionation zone via line 10 and fed to catalytic reforming zone 11. The feed to the reformer in the process of the present invention preferably boils from about C_7 up to about 300° to 425°F. or from C_8 up to about 300° to 425°F. To increase jet fuel production, the feed to the reformer preferably boils from about C_8 to 300° or 350°F. Jet fuel boiling range hydrocarbons (about 350° to 600°F.) are withdrawn from the fractionation zone via line 17.

A portion of the disproportionation zone effluent can be withdrawn via line 20. Build up of highly branched chain hexanes, which are not as readily disproportionated as straight chain hexanes, can be avoided by withdrawal of a bleed stream via line 20.

Catalytic reforming zone 11 is preferably operated at a temperature between 850° and 1,100°F. and at a hydrogen partial pressure between about 40 and 1,000 psig. Preferred catalysts are catalysts containing one or more noble metals on a refractory support such as platinum on alumina. Preferably, the reforming catalyst also contains a small amount of a halide to promote the activity of the catalyst for isomerization. The platinum or noble metal component of the catalyst is believed to be mainly responsible for the reaction (which may be characterized as a dehydrocyclization reaction) necessary to convert paraffinic hydrocarbons to aromatics. The term "catalytic reforming" is used herein to refer to hydrocarbon processing wherein substantial amounts of paraffins are converted to aromatics so as to obtain a reformate which, usually after removal of at least some light ends, has a substantially increased oc-

tane rating relative to the paraffinic feedstocks to the reforming process. Particularly preferred catalysts for upgrading the octane level of the paraffinic feed to catalytic reforming zone 11 are catalysts comprising platinum and rhenium on alumina such as described in U.S. Pat. No. 3,415,737.

Product reformate can be withdrawn from zone 11 via line 12, usually after separating a small amount of light hydrocarbons in separation or distillation facilities which are a part of zone 11. However, in the process of the present invention, it is particularly preferred to feed at least a portion of the effluent from catalytic reforming zone 11 to fractionation and/or extraction zone 14 via line 13. Zone 14 is operated so as to separate a paraffinic-rich hydrocarbon stream from higher octane primarily aromatic hydrocarbons. The paraffinic-rich stream is recycled via line 16 to the fractionation zone so that the recycle stream can be upgraded in octane level. The most important means of upgrading the recycle stream in octane level is by the disproportionation of hexanes present in the recycle stream followed by catalytic reforming of the heavier hydrocarbons obtained in the disproportionation of the hexanes. Also, in the process of the present invention, normal pentane present in the recycle paraffin-rich stream can be increased in octane rating by means of isomerization in zone 5.

It is particularly preferred to separate the paraffinic-rich recycle stream by solvent extraction in zone 14 using a solvent which selectively takes aromatics into solution with the solvent such as glycol-water solutions (frequently referred to as Udex) or furfural or other aromatic solvents. The material left after the aromatics have been extracted is generally referred to as raffinate. The raffinate is a preferred paraffinic-rich hydrocarbon stream for disproportionation in zone 8, usually after the raffinate has been further processed by fractionation to obtain a C_6 rich stream for feed to disproportionation zone 8.

Various aromatic-rich fractions can be withdrawn from zone 14 but only two withdrawals via line 15 and line 18 are indicated from zone 14. The two preferred withdrawals are a xylene-rich aromatic stream for use in a chemical plant such as a paraxylene plant, and a high octane aromatic gasoline stream for use as motor fuel.

When carrying out high severity reforming in zone 11, producing predominantly aromatics and using, for example, newly developed catalysts such as Pt-Re on alumina catalysts, it is usually preferably in the process of the present invention to employ fractionation rather than solvent extraction for separating paraffins from aromatics, especially for newly built low pressure catalytic reforming units.

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. It is apparent that the present invention has broad application to increasing the octane rating of hexane-rich hydrocarbons by a combination of at least hexane disproportionation and catalytic reforming of hydrocarbons heavier than hexane. 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.

We claim:

1. A combination process for converting paraffinic hydrocarbons into gasoline which comprises:
- a. separating a hydrocarbon feed stream into a C₅ rich stream, a hexane rich stream and a C₇+ stream,
 - b. isomerizing normal pentane present in the C₅ rich stream to obtain isopentane,
 - c. disproportionating the hexane rich stream to obtain at least C₅- hydrocarbons and a C₇+ hydrocarbon fraction, and wherein the disproportionation of the hexane is carried out by contacting the hexane with a catalytic mass having catalytic activity for paraffin dehydrogenation as well as catalytic activity for olefin disproportionation, and
 - d. catalytically reforming, in the presence of hydrogen gas and using a catalyst containing platinum, at least a portion of the C₇+ stream and the C₇+ hydrocarbon fraction from disproportionation to produce reformate.
2. A process in accordance with claim 1 wherein a normal pentane rich hydrocarbon stream is separated from the C₅ hydrocarbons from disproportionation and

- the normal pentane rich hydrocarbon stream is isomerized to obtain iC₅.
3. A process in accordance with claim 1 wherein the hexane disproportionation is carried out by contacting the hexane with a catalytic mass having catalytic activity for paraffin dehydrogenation as well as catalytic activity for olefin disproportionation.
4. A process in accordance with claim 3 wherein the catalytic mass comprises platinum on alumina and a Group VIB metal on a refractory support.
5. A process in accordance with claim 4 wherein the disproportionation reaction is carried out at a temperature below 850°F. and in the presence of no more than 5 weight percent olefins.
6. A process in accordance with claim 1 wherein at least a portion of the reformate is separated by solvent extraction into an aromatics-rich stream and a raffinate stream rich in paraffins, and at least a portion of the raffinate is disproportionated to obtain C₇+ hydrocarbons which are catalytically reformed.

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