

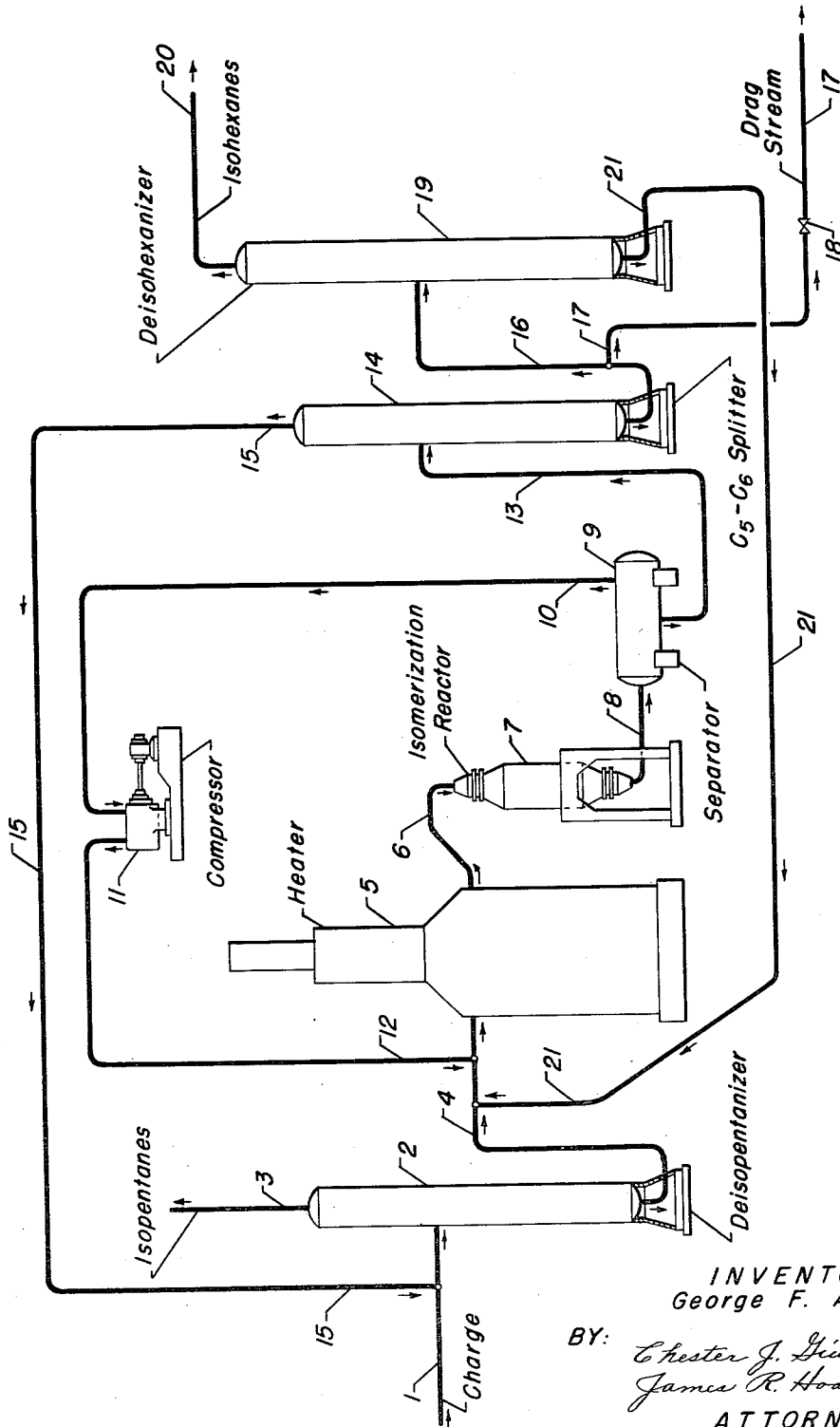
April 28, 1964

G. F. ASSELIN

3,131,235

SIMULTANEOUS ISOMERIZATION OF PENTANE AND HEXANE
WITH SELECTIVE FRACTIONATION

Filed Nov. 23, 1960



INVENTOR:
George F. Asselin

BY: *Chester J. Giuliani*
James R. Hoatson Jr.
ATTORNEYS.

1

3,131,235

SIMULTANEOUS ISOMERIZATION OF PENTANE AND HEXANE WITH SELECTIVE FRACTIONATION

George F. Asselin, Mount Prospect, Ill., assignor to Universal Oil Products Company, Des Plaines, Ill., a corporation of Delaware

Filed Nov. 23, 1960, Ser. No. 71,278

6 Claims. (Cl. 260—683.68)

The present application is a continuation-in-part of my copending application Serial No. 698,991, filed November 26, 1957, now abandoned. The present invention relates to the isomerization of saturated hydrocarbons in the presence of hydrogen and an isomerization catalyst. More specifically, the present invention is directed toward a combination process involving selective fractionation and the simultaneous isomerization of pentane and hexane. The unique combination of the particular series of process steps, encompassed by the present invention, results in three individual product streams, each of which possesses a higher octane blending value than the original fresh hydrocarbon charge to the process.

The relatively recent introduction, within the automotive industry, of internal combustion engines having a high compression ratio has necessitated the utilization of motor fuels possessing unusually high anti-knock characteristics. Motor fuels possessing high octane blending values, an indication of the anti-knock characteristics thereof, are required for the purpose of utilizing the maximum horsepower output of the internal combustion engine. In turn, the demand for higher and higher octane motor fuels has resulted in the need for steadily increasing quantities of these high-quality hydrocarbons. The group of iso-paraffinic hydrocarbons, containing from about five to about six carbon atoms per molecule, is one particular source of hydrocarbons possessing unusually high octane blending values. The object of the present invention is to provide a series of particular processing steps for the simultaneous isomerization of pentanes and hexanes, resulting in significantly increased volumetric yields of iso-paraffinic hydrocarbons, with respect to the yields heretofore obtained.

Therefore, in a broad embodiment, the present invention relates to a process for effecting the isomerization of a hydrocarbon charge containing hydrocarbons having from about five to about six carbon atoms per molecule, which process comprises removing isopentane from said hydrocarbon charge, reacting the resulting deisopentane hydrocarbon charge in a reaction zone containing an isomerization catalyst and maintained under isomerization conditions, separating the reaction zone effluent into a hydrogen-rich gaseous phase and a liquid phase, separating the latter into a first hydrocarbon fraction containing pentanes, and a second hydrocarbon fraction containing hexanes, combining said pentane containing fraction with the hydrocarbon charge prior to removing isopentane therefrom, removing at least a portion of said second fraction from said process and isohexanes from the remainder, and combining the deisohexanized portion with the aforesaid deisopentane charge prior to reacting the same in said reaction zone.

Another embodiment of the present invention involves a process for isomerizing an isomerizable hydrocarbon charge containing hydrocarbons having from about five to about six carbon atoms per molecule, which process comprises combining said charge with a pentane-containing isomerized product, removing isopentanes from the resulting mixture and passing the deisopentane portion of said mixture, along with hydrogen, into a reaction zone maintained under isomerization conditions and having disposed therein a catalytic composite of alu-

2

mina, combined halogen and a platinum-group metallic component, separating the resulting reaction zone effluent to provide a hydrogen-rich gaseous phase and a liquid phase containing isopentane and isohexane, separating said liquid phase into a first hydrocarbon fraction containing pentanes and a second hydrocarbon fraction containing hexanes, recycling said pentane-containing fraction to combine with said hydrocarbon charge prior to the removal of isopentane therefrom, withdrawing at least a portion of said second fraction from said process, removing isohexanes from the remainder of said second fraction, and combining the deisohexanized portion of said second fraction with the aforesaid deisopentane charge and hydrogen prior to reacting the same in said reaction zone.

A more limited embodiment of the present invention is directed toward a process for isomerizing an isomerizable hydrocarbon charge containing hydrocarbons having from about five to about six carbon atoms per molecule, which process comprises combining said charge with a pentane-rich isomerized product, removing isopentane from the resulting mixture and passing the deisopentane portion of said mixture, along with hydrogen, into a reaction zone maintained at a temperature within the range of from about 200° F. to about 800° F., and under a pressure of from about 100 to about 2000 pounds per square inch, and having disposed therein a catalytic composite of alumina, platinum and from about 2.5% to about 5.0% by weight fluorine, calculated as the element, separating the resulting reaction zone effluent to provide a hydrogen-rich gaseous phase and a liquid phase containing isopentane and isohexane, separating said liquid phase into a first hydrocarbon fraction containing pentanes and a second hydrocarbon fraction containing hexanes, recycling said pentane-containing fraction to combine with said hydrocarbon charge prior to the removal of isopentane therefrom, withdrawing at least a portion of said second fraction from said process, removing isohexanes from the remainder and combining the deisohexanized portion of said second fraction with the aforesaid deisopentane charge and hydrogen prior to reacting the same in said reaction zone.

From the foregoing embodiments, it is seen that the process of the present invention involves the particular steps of selective fractionation and simultaneous isomerization of a hydrocarbon mixture containing pentanes and hexanes. A typical hydrocarbon mixture, to be utilized as charge to the present process, contains isopentane, normal pentane, 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, normal hexane, methyl cyclopentane, and cyclohexane, etc. In accordance with the present invention, a hydrocarbon charge, of the foregoing composition, is admixed with a previously isomerized product consisting essentially of isopentane and normal pentane. This mixture is introduced into a first fractionation zone serving as a deisopentane separator, from which an isopentane-rich stream is withdrawn as an overhead product, the deisopentane portion of the remainder of the mixture being admixed with a hexane-containing stream derived from an isomerized product by fractionation, and hydrogen, this mixture being passed into an isomerization reaction zone. The total reaction zone effluent, rich in iso-paraffinic hydrocarbons having from about five to about six carbon atoms per molecule, is passed into a suitable separation zone from which a hydrogen-rich gaseous phase is removed and recycled to combine with the mixture of deisopentane charge, and hexane-containing isomerized product. The normally liquid hydrocarbons are passed into a fractionation zone serving as a C₅-C₆ splitter, from which a pentane-rich overhead fraction is removed and recycled to combine with the fresh charge prior to passing the latter into the deisopentane separator. The heavier C₆ hydrocarbons are removed as a bottoms fraction from the

C₅-C₆ splitter, and passed into a fractionation zone serving as a deisohexanizer, from which an overhead product of isohexanes is removed. An essential feature of the present invention is the withdrawal of at least a portion of the C₅-C₆ splitter bottoms fraction from the process, to prevent the accumulation of cyclic hydrocarbons in the charge to the isomerization reaction zone. As hereinafter indicated, another essential feature of the present invention is the point at which the cyclic hydrocarbons, as a drag-stream, are withdrawn from the process. According to the process of the present invention, the drag-stream is a portion of the bottoms fraction from the C₅-C₆ splitter prior to introducing the bottoms fraction into the deisohexanizer for the purpose of recovering an isohexane fraction. Following the removal of isohexanes, as overhead product from the deisohexanizer, the remainder of the C₆ hydrocarbons are passed as a bottoms product recycle to combine with the deisopentanized hydrocarbon mixture and hydrogen, prior to passing the same into the isomerization reaction zone.

The combination of isomerization and selective fractionation steps, as hereinabove set forth, produces three individual product streams, all of which possess octane blending values substantially in excess of the octane rating of the original hydrocarbon charge stock, and the total volumetric yield of which is as high as about 94.0%, based upon the quantity of hydrocarbons initially charged to the process. The low octane rating components of the original hydrocarbon charge stock are converted into high octane products through the combination isomerization and selective fractionation process as hereinabove set forth. The process of the present invention selectively separates the low octane components, and independently converts them to high octane components. By separating the low octane components, the charge to the isomerization reaction zone consists primarily of normal paraffinic hydrocarbons having from about five to about six carbon atoms per molecule. The numerous advantages of the foregoing particular processing steps include high over-all yields of high octane products, mild operation of the isomerization reaction zone, inherently resulting in an extended catalyst life, and conversion of the low octane rating normal paraffinic hydrocarbons in the absence of the high octane rating isomers. In addition, the foregoing processing procedure, in which the original hydrocarbon charge is initially subjected to fractionation to remove isopentane, and the liquid reactor effluent is segregated into a pentane-containing fraction and a hexane-containing fraction, affords lesser over-all fractionation duty: fractionation duty refers to the size of the various fractionators, the quantity of heating required to effect proper, acceptable fractionation therein. In addition to the economic considerations involved in fractionation duty, the process of the present invention affords the very substantial advantage of producing a total C₆-paraffinic hydrocarbon product which possesses an octane rating (F-1 with 3.0 cc. TEL/gal.) 3.4 units higher than produced from conventional processes in which the total reaction zone effluent is first deisopentanized, or where the initial hydrocarbon charge is first introduced into a C₅-C₆ hydrocarbon fractionation zone together with the total reaction zone effluent, etc. Furthermore, the withdrawal of a drag-stream, containing cyclic hydrocarbons, from the C₅-C₆ splitter bottoms fraction, results in the need for a smaller fractionator, to serve as the deisohexanizer, in addition to other advantages resulting from the withdrawal at this particular point.

The combination process of the present invention may be further understood through reference to the accompanying drawing. In the drawing, numerous valves, controls, coolers, condensers and other miscellaneous appurtenances have been eliminated as not being essential to the complete understanding of the present invention. The incorporation of these, and other modifications, may be made by one possessing sufficient skill within the art of petroleum processing, and are not considered to be out-

side the broad scope and spirit of the present invention as set forth in the appended claims.

A hydrocarbon charge stock, containing hydrocarbons having from above five to about six carbon atoms per molecule, enters the process through line 1, being admixed with a pentane-containing isomerized product in line 15, the mixture being introduced into deisopentanizer 2. It is understood that the pentane-containing stream in line 15 may be combined with the charge in line 1, or may enter deisopentanizer 2 at a point slightly above that at which the charge in line 1 is introduced, and that the latter scheme is intended to be included within the scope of the present invention. The combined hydrocarbon charge is separated in deisopentanizer 2 such that a substantially pure isopentane fraction is removed via line 3 as an overhead product. The deisopentanized portion of the combined charge is removed from deisopentanizer 2 via line 4, is admixed with a hexane-containing isomerized product in line 21 and passed into heater 5 wherein the temperature of the hydrocarbon mixture is raised to the desired operating level. As indicated in the drawing, the combined deisopentanized hydrocarbon charge passing into heater 5 is admixed with a gaseous recycle stream, rich in hydrogen, entering via line 12 from compressor 11. Although not indicated in the drawing, in some instances the recycled hydrogen-rich gaseous phase from compressor 11 may be passed via line 12 to combine with the heated hydrocarbon charge in line 6 prior to passing the same into isomerization reaction zone 7.

Isomerization reactions may be effected in isomerization reaction zone 7 at varying conditions of temperature, pressure, liquid hourly space velocity, and hydrogen to hydrocarbon mol ratio to convert the normal paraffins into isoparaffins. The temperature will generally be dictated by the particular isomerization catalyst disposed within isomerization reaction zone 7, and will be within the range of from about 200° F. to about 800° F. The pressure selected for the isomerization reaction zone 7 will be within the range of from about 100 to about 2000 pounds per square inch. The liquid hourly space velocity (defined as the volume of liquid charge per hour per volume of catalyst disposed within the reaction zone) will range from about 0.1 to about 10.0 or more, the only limitation being that nearly equilibrium mixtures of isomerized hydrocarbons are obtained in the reaction zone effluent. Hydrogen is utilized to minimize cracking, and to maintain the surface of the catalyst in a carbon free condition. The quantity of hydrogen utilized will range from about 0.25 to about 10.0 mols, or more of hydrogen per mol of hydrocarbon. The consumption of hydrogen will be exceedingly small, and will be within the range of from about 30 to about 100 standard cubic feet per barrel of total liquid hydrocarbon charge to the reaction zone.

The catalyst disposed within reaction zone 7 may be any suitable isomerization catalyst comprising a carrier material, an acid-acting component, and a hydrogenation component. The carrier material may be selected from various diverse refractory inorganic oxides, including, silica, alumina, silica-alumina, silica-alumina-magnesia, silica-alumina-zirconia, alumina-zirconia, silica-zirconia, etc. These various carrier materials will have surface areas ranging from about 25 to about 500 square meters per gram, depending upon the particular method selected for the preparation thereof. The effectiveness of the acid-acting component, such as silica-alumina, is controlled by the quantity of silica which is combined with the alumina, and by the treatment of the silica-alumina, particularly the calcination treatment prior to, or after combining the hydrogenation component therewith. Of the various possible carrier materials, alumina is particularly preferred, and especially gamma-alumina having a surface area of from about 150 to 450 square meters per gram. When gamma-alumina is utilized as

the carrier material, the acid-acting function may be added thereto by incorporating therewith quantities of combined halogen. The amount of combined halogen may be varied from about 0.01% to about 8.0% by weight, calculated as the element, and based upon the weight of the carrier material. Both fluorine and chlorine may be used to supply the combined halogen, although the preferred halogen, which will be utilized with the alumina-carrier material, is fluorine in an amount of from about 2.5% to about 5.0% by weight, calculated as the element thereof.

Following the formation of the alumina, the hydrogenation component will be combined therewith. The hydrogenation component will usually be selected from the group consisting of groups VI-A and VIII of the periodic table, or mixtures thereof. Such hydrogenation components include chromium, molybdenum, tungsten, iron, cobalt, nickel, and the platinum group metals including platinum, palladium, ruthenium, rhodium, osmium, and iridium. The platinum-group metals are preferred, and of these metals, platinum is particularly preferred. The hydrogenation component of the catalytic composite disposed in reaction zone 7 will be utilized in an amount of from about 0.1% to about 10.0% by weight, calculated as the element, and based upon the weight of the carrier material. With the particularly preferred platinum-group metals, the quantity utilized will range from about 0.1% to about 2.0% by weight. A particularly preferred catalytic composite will comprise 0.4% by weight of platinum, 4.0% by weight of fluorine, the remainder being alumina.

Due to equilibrium considerations, and because it is often desirable and/or advisable to effect the isomerization reactions at the lowest possible temperature, from about 200° F. to about 500° F., the catalytic composite may also be prepared by impregnating composites as hereinabove described with a metallic halide of the Friedel-Crafts type. For example, an excellent low temperature isomerization catalyst may be prepared by impregnating aluminum chloride onto a composite of platinum, alumina and combined halogen. The process of the present invention may be effected in the presence of other catalysts, but not necessarily with equivalent results. Such other catalysts include aluminum chloride sludge, aluminum bromide sludge, etc., which may be employed along with hydrogen chloride, hydrogen bromide, etc.

The total reaction zone effluent is passed, after cooling, through line 8 into separator 9. A gaseous phase, rich in hydrogen, is removed via line 12 and raised to the reaction zone operating pressure by compressor 11. The hydrogen-rich gaseous phase is recycled via line 12 to combine with the liquid hydrocarbon charge to reaction zone 7. As indicated in the drawing, the hydrogen-rich recycle gas stream is combined with the liquid hydrocarbon reaction zone charge prior to raising the latter to the desired operating temperature. However, as hereinbefore set forth, the recycled hydrogen may enter the process to combine with the previously heated hydrocarbon charge, in line 6. Although not indicated in the drawing, make-up hydrogen, to replace the relatively minor quantity consumed within the process, may be introduced into line 10 or line 12 from any suitable source. The normally liquid hydrocarbons, following the removal of the hydrogen rich gaseous phase, are removed from separator 9 via line 13. The total liquid isomerized product is transmitted via line 13 into C₅-C₆ splitter 14. An overhead product, consisting essentially of pentanes, is removed via line 15, and is combined with the fresh hydrocarbon charge in line 1, prior to passing the latter into deisopentanizer 2, or, as previously stated, passed directly into deisopentanizer 2 at a point above line 1. The heavier, C₆ hydrocarbons are removed from the bottom of C₅-C₆ splitter 14 via line 16 and introduced into deisohexanizer 19. At least a portion of the bottoms product from C₅-C₆ splitter 14, is removed in line 17 containing valve

18 as a drag stream from the process, prior to passing the bottoms product into deisohexanizer 19. This drag stream is necessary in order to reject the cyclic hydrocarbons entering the process with the original hydrocarbon charge, thus avoiding an intolerably high cyclic concentration in the reactor feed. Conventional, prior art processes, reject such cyclic hydrocarbons either in a small bottoms stream from deisohexanizer 19, with the recycle hexanes to the reactor being withdrawn as a side-cut, or merely withdraw a portion of the deisohexanizer bottoms prior to introducing the same into the isomerization reaction zone. The process of the present invention, wherein the drag-stream is withdrawn from the bottoms product of the C₅-C₆ splitter, eliminates two serious disadvantages of conventional processes. The present method is much more effective in achieving the desired cyclic rejection, and further, a loss of about 8.0 octane-rating units (F-1 with 3.0 cc. TEL/gal.) will be avoided with respect to the drag stream. Thus, in accordance with the present invention, the drag stream is withdrawn from the present process from line 16 via line 17 containing valve 18. The remainder of the C₅-C₆ splitter bottoms is introduced into deisohexanizer 19 from which an isohexane-rich stream is removed as overhead product through line 20. The remaining portion of the C₅-C₆ splitter bottoms fraction is removed via line 21 and recycled to combine with the deisopentanized hydrocarbon mixture in line 4, prior to passing the same into heater 5 and isomerization reaction zone 7.

To illustrate another of the many advantages inherent in the combination process of the present invention, the fresh charge might be introduced into the pentane-hexane splitter, which arrangement unnecessarily swells the needed volume of the reactor due to the isopentane contained in the fresh feed, which must now enter the reaction zone instead of being short-circuited through the deisopentanizer directly to the iso-pentane products stream. By introducing the fresh hydrocarbon charge first into a deisopentanizing zone, and passing the total reaction zone effluent into the pentane-hexane splitter, the difficulty of splitting the effluent into the desired two fractions is lessened considerably since the feed to the splitter comprises an approximately 60/40 volumetric ratio of isopentane to normal pentanes, instead of an approximately equal volume of total pentanes which are nearly n-pentane, as would be the case if the fresh charge and reactor effluent were combined in a deisopentanizer. In addition, considering the C₅ hydrocarbon load, the present process reduces the load on the C₅-C₆ splitter by about one-half.

Considering the C₆ hydrocarbon performance of the process of the present invention, the hexanes contained in the fresh hydrocarbon charge pass immediately from the deisopentanizer directly to the reaction zone, without mingling with, and degrading the quality of the reactor effluent upstream of the deisohexanizer. By this method it is possible to produce a higher quality hexane-paraffinic product than with the conventional methods of the prior art processes, the increase in quality being about 3.4 octane units.

The following example is given to illustrate further the method of the present invention, and to indicate clearly the benefits to be afforded through the utilization thereof. It is not intended that the process of the present invention be limited unduly to the character of the charge stock, the operating conditions and/or the catalyst employed within the example.

The catalyst disposed within the reaction zone comprises an alumina carrier material with which has been composited 4.0% by weight of combined fluorine, calculated as the element. Following the formation of the alumina-combined fluorine composite, platinum is composited therewith through the use of an impregnating technique. The impregnating technique involves soaking, dipping or otherwise immersing the alumina-combined fluorine composite in an aqueous solution of chloro-

platinic acid containing sufficient platinum to result in catalyst containing 0.4% by weight of platinum, calculated as the element. To illustrate a typical commercial size operation, a fresh hydrocarbon charge in an amount of 1333 barrels per day, comprising 670 b./d. of total pentanes, 530 b./d. of total hexanes, and 133 b./d. of cyclic hydrocarbons, is combined with 679 b./d. of a pentane-containing isomerized product. Following the removal of 637 b./d. of isopentane, having an octane rating of approximately 108.6 (F-1 with 3.0 cc. TEL/gal.), the remaining portion of the mixture, in an amount of about 1375 b./d. is admixed with hydrogen and about 767 b./d. of a hexane-containing isomerized product, the mixture being raised to a temperature of about 700° F., and thereafter passed into the reaction zone containing the aforementioned catalyst. The total reaction zone effluent is passed into a high-pressure separator, operating at approximately room temperature, from which a hydrogen-rich gas stream is recycled to combine with the deisopentane charge and the hexane-containing isomerized product. The total reaction zone liquid effluent, about 2059 b./d., is passed into a fractionation zone which operates to provide a light hydrocarbon fraction containing isopentane and n-pentane, and a second heavier hydrocarbon fraction containing isohexanes, normal hexane and cyclic compounds. The lighter fraction is recycled, in an amount of about 679 b./d., within the process to combine with the 1333 b./d. of fresh charge, the mixture being fractionated to remove the isopentane therefrom. The heavier fraction is passed in an amount of about 953 b./d., following the removal of 427 b./d. as a drag-stream, into the deisohexanizer from which approximately 186 b./d. of isohexanes are removed. The deisohexanized, bottoms material is then recycled, in an amount of about 767 b./d., to combine with the deisopentane charge and hydrogen prior to passing the same into the reaction.

The product distribution, resulting from the foregoing example of the process, is given in the following table. The various charge and product streams are indicated, and the concentration of pentanes, hexanes and cyclic hydrocarbons in each stream.

Tabulated Data—Product Distribution

Stream, b./d.	Total Pentanes	Total Hexanes	Total Cyclics	Total Stream	C ₆ -paraffin Octane Rating ¹
Fresh Charge.....	670	530	133	1,333	78.4
Reactor Charge.....	712	1,000	430	2,142	80.7
Reactor Effluent.....	679	950	430	2,059	88.6
C ₅ -C ₆ splitter					
Feed.....	679	950	430	2,059	88.6
Deisopentaneizer					
Feed.....	1,349	530	133	2,012	78.4
Deisohexanizer					
Feed.....		656	297	953	88.6
Isopentane.....	637			637	
Isohexane.....		186		186	102.2
Drag Stream.....		294	133	427	88.6
Total Products.....	637	294	133	1,250	93.9

¹ Octane rating for the paraffinic hexane portion of the various total streams is the F-1 Rating with 3.0 cc. TEL/gal.

As hereinbefore set forth, the 637 b./d. of isopentane, withdrawn as a product stream, possesses an octane rating, F-1 with 3.0 cc. TEL/gal., of about 108.6. The isohexane product stream possesses an octane rating, of 102.2; the 427 b./d. of the drag stream, contains 294 b./d. of a hexane fraction having the indicated octane rating of 88.6; the 133 b./d. of cyclic hydrocarbons possesses an octane rating of about 103.0, the octane blending value of the total drag-stream being approximately 93.0, F-1 with 3.0 cc. TEL/gal.

The total volumetric yield of the three individual product streams is 1250 b./d., or about 94.0% by volume, based upon the total fresh charge to the process. The octane rating of the total quantity of C₆ paraffinic hydrocarbons, contained in the three individual product streams, is indicated as being 93.9. This octane blending value

is approximately 3.4 units greater than that obtained from conventional processes which, as hereinbefore set forth, for example, combine the total reaction zone effluent with the fresh hydrocarbon charge as feed to the C₅-C₆ splitter, and which processes withdraw the drag stream at some other point in the process, for example, following the removal of isohexanes from the total hexane-containing fraction.

The foregoing example and specification illustrates the method of the present invention and indicates the benefits to be afforded through the utilization thereof.

I claim as my invention:

1. A process for effecting the isomerization of a hydrocarbon charge containing hydrocarbons having from about five to about six carbon atoms per molecule, which process comprises removing isopentane from said hydrocarbon charge, reacting the resulting deisopentaneized hydrocarbon charge in a reaction zone containing an isomerization catalyst and maintained under isomerization conditions, separating the reaction zone effluent into a hydrogen-rich gaseous phase and a liquid phase, separating the latter into a first hydrocarbon fraction containing pentanes and a second hydrocarbon fraction containing hexanes, combining said pentane-containing fraction with the hydrocarbon charge prior to removing isopentane therefrom, removing a portion of said second fraction from said process, fractionating the remainder of said second fraction to separate isohexanes therefrom, and combining the deisohexanized portion of said second fraction containing normal hexane with the aforesaid deisopentaneized charge prior to reacting the same in said reaction zone.

2. A process for isomerizing an isomerizable hydrocarbon charge containing hydrocarbons having from about five to about six carbon atoms per molecule, which process comprises combining said charge with a pentane-rich isomerized product, removing isopentane from the resulting mixture and passing the deisopentaneized portion of said mixture with hydrogen into a reaction zone containing an isomerization catalytic composite of a refractory inorganic oxide and a platinum-group metal, and maintained under isomerization conditions, separating the resulting reaction zone effluent to provide a hydrogen-rich gaseous phase and a liquid phase containing isopentane and isohexane, separating said liquid phase into a first hydrocarbon fraction containing pentanes and a second hydrocarbon fraction containing hexanes, recycling said pentane-containing fraction to combine with said hydrocarbon charge prior to the removal of isopentane therefrom, removing a portion of said second fraction from said process, fractionating the remainder of said second fraction to separate isohexanes therefrom, and combining the deisohexanized portion of said second fraction containing normal hexane with the aforesaid deisopentaneized charge and hydrogen prior to reacting the same in said reaction zone.

3. A process for isomerizing an isomerizable hydrocarbon charge containing hydrocarbons having from about five to about six carbon atoms per molecule, which process comprises combining said charge with a pentane-rich isomerized product, removing isopentane from the resulting mixture and passing the deisopentaneized portion of said mixture, along with hydrogen, into a reaction zone maintained under isomerization conditions and having disposed therein a catalytic composite of alumina, combined halogen and a platinum-group metallic component, separating the resulting reaction zone effluent to provide a hydrogen-rich gaseous phase and a liquid phase containing isopentane and isohexane, separating said liquid phase into a first hydrocarbon fraction containing pentanes and a second hydrocarbon fraction containing hexanes, recycling said pentane-containing fraction to combine with said hydrocarbon charge prior to the removal of isopentane therefrom, withdrawing a portion of said second fraction from said process, removing isohexanes from the remainder of said second fraction, and combining the de-

9

isohexanized portion of said second fraction containing normal hexane with the aforesaid deisopentanized charge and hydrogen prior to reacting the same in said reaction zone.

4. The process of claim 3 further characterized in that said catalytic composite comprises alumina, platinum and from about 0.1% to about 8.0% by weight of combined halogen.

5. The process of claim 3 further characterized in that said combined halogen is fluorine in an amount within the range of about 2.5% to about 5.0% by weight, calculated as the element.

6. A process for isomerizing an isomerizable hydrocarbon charge containing hydrocarbons having from about five to about six carbon atoms per molecule, which process comprises combining said charge with a pentane-rich isomerized product, removing isopentane from the resulting mixture and passing the deisopentanized portion of said mixture, along with hydrogen, into a reaction zone maintained at a temperature within the range of from about 200° to about 800° F. and under a pressure of from about 100 to about 2000 pounds per square inch, and having disposed therein a catalytic composite of alumina, platinum and from about 2.5% to about 5.0% by weight of fluorine, calculated as the element, separating the resulting reaction zone effluent to provide a hydrogen-rich

10

gaseous phase and a liquid phase containing isopentane and isohexane, separating said liquid phase into a first hydrocarbon fraction containing pentanes and a second hydrocarbon fraction containing hexanes, recycling said pentane-containing fraction to combine with said hydrocarbon charge prior to the removal of isopentanes therefrom, withdrawing a portion of said second fraction from said process, removing isohexanes from the remainder of said second fraction, and combining the deisohexanized portion of second fraction containing normal hexane with the aforesaid deisopentanized charge and hydrogen prior to reacting the same in said reaction zone.

References Cited in the file of this patent

UNITED STATES PATENTS

2,834,823	Patton et al. _____	May 13, 1958
2,900,425	Bloch _____	Aug. 18, 1959
2,905,619	Sutherland _____	Sept. 22, 1959
2,908,735	Haensel _____	Oct. 13, 1959
2,968,631	Carr et al. _____	Jan. 17, 1961

OTHER REFERENCES

Kellog	"Oil and Gas Journal," vol. 55, No. 12, p. 155, March 25, 1957.
Pure Oil	"Oil and Gas Journal," vol. 55, No. 12, p. 158, March 25, 1957.