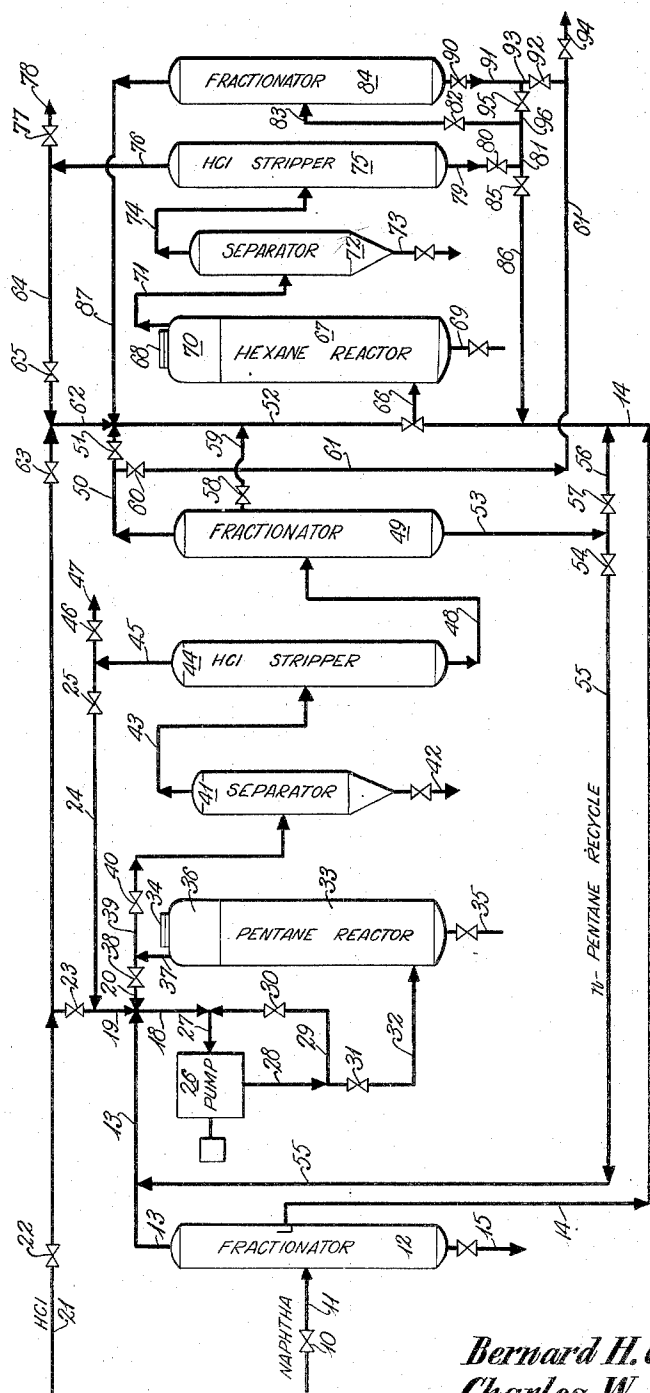


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B. H. GWYNN ET AL
ISOMERIZATION OF LIGHT NAPHTHA

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Inventors

Bernard H. Gwynn and
Charles W. Montgomery

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A. M. Houghton
their Attorney

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ISOMERIZATION OF LIGHT NAPHTHA

Bernard H. Gwynn, Tarentum, and Charles W. Montgomery, Oakmont, Pa., assignors to Gulf Research & Development Company, Pittsburgh, Pa., a corporation of Delaware

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1 Claim. (Cl. 260—683.5)

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This invention relates to the isomerization of a light naphtha of the pentane-hexane boiling range and is particularly concerned with a process of increasing the isoparaffin content of light naphtha with a minimum amount of cracking.

Catalytic naphtha isomerization processes have heretofore been proposed wherein increased yields of isopentane, neohexane and isohexanes have been obtained by employing various cracking inhibitors, such as hydrogen, benzene, and naphthenes. These processes require somewhat higher temperatures and thereby higher pressures thus introducing into the processes the difficulties accompanying high temperature-high pressure operation and they introduce into the processes undesirable materials which must be subsequently removed. It has also been proposed heretofore to isomerize naphthas in the presence of a large proportion of a low boiling isoparaffin, such as isobutane or isopentane. A large proportion of isopentane added to a naphtha, however, has a tendency to subdue the isomerization of normal pentane in favor of the isomerization of normal hexane.

It is an object achieved by this invention to provide an improved light naphtha isomerization process in which increased yields of isopentane, neohexane and isohexanes are obtained.

Another object achieved by this invention is to provide a process for improving the isoparaffin content of a light naphtha wherein the amount of added isopentane cracking inhibitor is materially decreased.

Another object achieved by this invention is to provide an improved process for the isomerization of a light naphtha at a relatively low temperature in which a product consisting essentially of pentanes and hexanes is obtained without resorting to fractionation for the separation of a diluent cracking inhibitor.

A further object achieved by this invention is to provide an improved process for the isomerization of a light naphtha of the pentane-hexane boiling range in which the pentane fraction of the product consists of an equilibrium mixture of normal pentane and isopentane.

A further object achieved by this invention is to provide an improved process for the isomerization of a light naphtha of the pentane-hexane boiling range wherein the isopentane produced in the isomerization of the normal pentane serves as a cracking inhibitor during the isomerization of the normal hexane.

A still further object achieved by this invention is to provide an improved light naphtha isomerization process in which the formation of aluminum halide-hydrocarbon complexes is minimized and improved use is made of the catalytic activity of the aluminum halide.

Other objects achieved by this invention will

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become apparent in the following detailed description thereof.

We have discovered that increased yields of isopentane, neohexane, and isohexanes can be obtained during the isomerization of a light naphtha of the pentane-hexane boiling range in the presence of an aluminum halide catalyst and a hydrogen halide promoter if the light naphtha is fractionated into a C₅ fraction and a C₆ fraction, each fraction then being separately isomerized in the presence of a predetermined amount of isopentane.

In practicing our invention, we fractionate a light naphtha into a C₅ hydrocarbon fraction, a C₆ hydrocarbon fraction, and a C₇ and heavier hydrocarbon fraction. The latter fraction may be blended with the final product or may be discarded. The C₅ hydrocarbon fraction is treated according to our copending application, S. N. 717,010, whereby a mixture of liquid normal pentane and isopentane, said mixture containing about 33 to 50 per cent by weight of isopentane, is contacted with an aluminum halide and hydrogen halide in a reaction zone at a temperature below about 70° C.; a reaction mixture containing substantially more isopentane than was present in the charge and not more than about 60 per cent by weight of isopentane is withdrawn from said reaction zone. According to the present invention, an equilibrium mixture consisting of about 85 to about 90 per cent by weight of isopentane and about 15 to about 10 per cent by weight of normal pentane is obtained from the reaction mixture produced in the pentane isomerization step. The equilibrium mixture is mixed with the C₆ hydrocarbon fraction in an amount sufficient to produce a mixture containing at least about 45 per cent by weight of isopentane. The pentane-hexane mixture is contacted with an active isomerization catalyst, such as an aluminum halide and a hydrogen halide promoter in a hexane reaction zone at a temperature below about 75° C. whereby normal hexane is converted predominantly to neohexane and isohexanes. An improved light naphtha is recovered, the pentane content of said improved light naphtha consisting essentially of an equilibrium mixture of normal pentane and isopentane. If desired, the product recovered may contain pentanes and hexanes in the same relative proportion as was present in the light naphtha prior to its initial fractionation into a C₅ hydrocarbon fraction, a C₆ hydrocarbon fraction and a C₇ and heavier hydrocarbon fraction. The C₅ fraction of the product, however, would consist of an equilibrium mixture or about 85 to about 90 per cent by weight of isopentane.

As pointed out in our copending application, S. N. 717,010, increased yields of isopentane can be obtained during the isomerization of normal

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pentane in the presence of an aluminum halide catalyst and a hydrogen halide promoter if a predetermined amount of isopentane is introduced with the normal pentane to be isomerized. For example, we determined that isopentane yields above about 50 per cent could be obtained if the normal pentane to be isomerized is mixed with isopentane in an amount corresponding to about 33 to about 50 per cent by weight of the mixture. If less than about 33 per cent or more than about 50 to 52 per cent by weight of isopentane is present initially in the normal pentane feed, the yield of isopentane is less than the yield without the presence of any initial isopentane. Particularly good yields of isopentane are produced without substantial cracking if the proportion of isopentane in the pentane feed is maintained at between about 35 per cent and about 45 per cent by weight of the total pentane feed and best yields are obtained with an initial isopentane concentration of about 40 to 41 per cent. We determined that for the greatest efficiency the reaction mixture withdrawn from the pentane reaction zone should contain not more than about 50 per cent by weight of isopentane. The process can be operated to produce a product containing more than about 60 per cent of isopentane, but when greater than about 60 per cent of isopentane is obtained in the product stream, there also are obtained considerable amounts of cracking and decomposition products with accompanying side reactions and deterioration of the catalyst taking place. Accordingly, when the product stream contains more than about 60 per cent by weight of isopentane, the advantage gained by the initial isopentane concentration is offset by the formation of side reaction products. The pentane isomerization step is, therefore, most advantageously carried out with an initial isopentane concentration of about 40 to 41 per cent and a final isopentane concentration not greater than about 60 per cent. Conversion of normal pentane to isopentane taking place during a single pass through the reactor is relatively small; however, the circulation rate is sufficiently fast to give a commercially attractive process.

We have found that increased yields of neohexane and isohexanes can be obtained during the isomerization of normal hexane in the presence of an aluminum halide catalyst and a hydrogen halide promoter if a predetermined amount of isopentane is introduced with the normal hexane to be isomerized. For example, we have found that neohexane and isohexanes are produced with a minimum amount of cracking occurring if the normal hexane to be isomerized is mixed with isopentane in an amount corresponding to at least about 45 per cent by weight of the mixture. If less than about 45 per cent by weight of isopentane is present initially in the normal hexane feed, the amount of cracking occurring is substantially increased and the yield of isomerized hexanes is substantially decreased. Particularly good yields of neohexane and isohexanes are produced without substantial cracking if the proportion of isopentane in the hexane feed is maintained at between about 45 per cent and 55 per cent by weight of the total hydrocarbons present in the hexane reactor. The isopentane concentration may be as high as 75 per cent or even higher; however, from an economic standpoint it is generally desirable to use not more than about 55 per cent by weight. The isopentane used as the cracking inhibitor in the hexane reactor may

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be substantially pure isopentane but more advantageously it is an equilibrium mixture of normal pentane and isopentane; that is, a mixture consisting of about 85 to about 90 per cent isopentane and about 15 to about 10 per cent normal pentane. We have found that when substantially pure isopentane is used, there is a tendency for a portion of the isopentane to be isomerized to normal pentane until an equilibrium mixture is obtained. When using an equilibrium mixture of normal pentane-isopentane, the amount of mixture used as inhibitor is greater than the amount of pure isopentane used because in the mixture the normal pentane acts only as a diluent. Therefore, if an equilibrium mixture consisting of 10 parts normal pentane and 90 parts isopentane is used as the cracking inhibitor, the minimum amount of mixture that can be used is 50 per cent by weight of the final pentane-hexane mixture. In such a case, a mixture will result consisting of 5 per cent normal pentane, 45 per cent isopentane, and 50 per cent hexanes.

The amount of isopentane reported herein above to be required to inhibit cracking reactions during the separate isomerization of normal pentane and normal hexane is based upon the use of an aluminum halide catalyst and a hydrogen halide promoter. The particular ranges of isopentane concentration cited, however, may vary depending upon the particular catalyst employed and depending upon the operating conditions such as temperature, pressure and space velocity. It should be understood, therefore, that the optimum isopentane concentration at a given temperature, pressure and space velocity will vary with the particular catalyst but can readily be determined in a few trial runs.

The embodiments and examples recited herein have, for the sake of simplicity, been restricted to aluminum chloride as the catalyst and hydrogen chloride as the promoter. It should be understood, however, that we do not wish to limit this invention either with respect to a particular catalyst or with respect to a particular promoter.

The yields referred to herein are a measure of the efficiency of the conversion of normal hydrocarbons to isomerized hydrocarbons and are calculated by dividing the moles of isomerized hydrocarbons formed by the moles of normal hydrocarbon converted all multiplied by 100.

The naphtha employed as charge stock, according to the process of our invention, may be a light virgin naphtha or any naphtha fraction having an end point of about 160° F., provided that it is substantially paraffinic and that only minor amounts of aromatics, about 0.5 per cent or less, are present. Olefinic and aromatic hydrocarbons are undesirable constituents in a charge for our process because these constituents react with metallic halide catalysts to form metallic halide-hydrocarbon complexes, thus causing substantial catalyst deterioration.

The catalyst used in either the pentane reactor or the hexane reactor can be any of the active isomerization catalysts such as metallic halides, boron trifluoride, hydrofluoric acid, and the like. While any of the anhydrous metallic halides will function as isomerization catalysts, for practical purposes aluminum halides, such as aluminum chloride and aluminum bromide are preferred. These halides can be used alone or in combination with a carrier or support material, such as zeolite, permutite, and the like. If desired, the aluminum halide can be suspended or dissolved

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in an inert liquid or can be reacted with unsaturated hydrocarbons to form active aluminum halide-hydrocarbon complexes. If a solid aluminum halide is used as catalyst in the pentane reactor, the sludge which forms therein can, if desired, be used as catalyst in the hexane reactor. Likewise, if a solid aluminum halide catalyst is used in the hexane reactor, the sludge which forms therein can be used as catalyst in the pentane reactor.

The promoter used to increase the activity of the aluminum halide catalyst in accordance with our invention can be a hydrogen halide, such as hydrogen chloride or hydrogen bromide. The amount of the hydrogen halide used is not particularly critical; however, we advantageously use an amount corresponding to between about 2 and about 4 per cent by weight based on the weight of the hydrocarbons present in the reaction zone. We have found that if less than about 2 per cent by weight of a hydrogen halide is used, the rate of normal hydrocarbon conversion drops rapidly and that if more than about 4 per cent of a hydrogen halide is used, the amount of cracking increases rather rapidly.

The operating conditions, such as temperature, pressure, and space velocity, employed in the two reactors are substantially the same. Naturally, these conditions will vary depending upon the particular catalyst chosen. The reactions can be effected, for instance, over a wide range of space velocities. In general, space velocities of from about 0.1 to 4 or 5 volumes of liquid feed per volume of catalyst per hour are employed. The particular space velocity employed is adjusted so as to obtain satisfactory conversions at the temperature chosen.

In carrying out the process of our invention, the pentane isomerization reaction and the hexane isomerization reaction are carried out at a temperature below about 70° C. and about 75° C., respectively. The reactions are preferably carried out at a temperature within the range of about 40° C. to about 60° C. In general, temperatures higher than about 70° C. in the pentane reactor and 75° C. in the hexane reactor are undesirable because at these temperatures the isomerization reaction is accompanied by increased cracking and other decomposition reactions. The minimum temperature at which our invention may be practiced in either reactor depends upon whether the process is being carried out in the liquid phase or the vapor phase. Our process can be carried out in the liquid phase at a temperature less than 40° C., but from a commercial standpoint, the temperature is advantageously above about 40° C. If a highly active catalyst and promoter are used, we may employ temperatures even as low as 25° C. Vapor phase isomerization naturally must be carried out above the boiling point of the normal pentane and normal hexane, respectively. Liquid phase isomerization is carried out under a pressure sufficient to maintain the reactants in liquid phase. A pressure of 200 to 250 p. s. i. should be adequate to maintain the reactants in a liquid phase at a temperature of 75° C. or less.

Our invention may be applied to isomerization in liquid phase, vapor phase, and mixed liquor-vapor phase. However, our invention is most advantageously applied to liquid phase isomerization because of certain economic advantages obtained by liquid phase isomerization. Therefore, while our invention is hereinafter described in connection with its preferred embodiment,

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liquid phase isomerization, it is also within the scope of our invention to carry out the isomerization process in vapor phase and mixed liquid-vapor phase.

Our invention is particularly advantageous in that no diluent is introduced into the pentane reaction system. Accordingly, the process of our invention is economical in that fractionation of a diluent cracking inhibitor is avoided. Our invention is further advantageous from an economic standpoint in that the reaction product from the pentane isomerization reactor serves as the cracking inhibitor during the isomerization of normal hexane. A still further advantage of our process develops from the fact that a greater yield of high octane rating blending fuel is obtained than has heretofore been obtained. For example, the pentane fraction in the final blend may contain upwards of 80, for example, 85 to 90 per cent or more of isopentane, whereas usually not more than about 50 to 55 per cent isopentane is present in the pentane fraction.

Other advantages of our invention will become apparent to those skilled in the art upon consideration of the following detailed description illustrating the preferred methods of practicing the process of our invention. It is to be understood that numerous modifications may be made in the schematic flow diagram shown in the accompanying drawing without deviating from the present invention.

Now referring to the figure, light naphtha consisting predominantly of C₅ and C₆ paraffinic hydrocarbons is introduced by valve 10 and conduit 11 into fractionator 12 where it is fractionated into a fraction consisting essentially of pentanes withdrawn through conduit 13 and a fraction consisting essentially of hexanes withdrawn through conduit 14. If any heptanes and heavier hydrocarbons are present, they may be withdrawn through valved-conduit 15.

The pentane fraction withdrawn through conduit 13 from the top of fractionator 12 is mixed with normal pentane recycle coming from the bottom of fractionator 49 through conduit 53, valve 54, and conduit 55. The combined pentane feed then passes into conduit 18 where it is mixed with hydrogen chloride from conduit 19 and product recycle stream from conduit 20 containing not more than about 60 per cent by weight of isopentane. The hydrogen chloride in conduit 19 consists of fresh hydrogen chloride introduced through conduit 21 and valves 22 and 23 and recycled hydrogen chloride introduced through conduit 24 and valve 25.

The pentane-hydrogen chloride solution which is formed at the intersection of conduits 13, 19 and 20 enters pump 26 through conduit 27. The pentane-hydrogen chloride solution is then pumped into conduit 28 from which a major proportion is circulated by pump 26 through conduit 29 containing valve 30 to conduit 27. A minor proportion of the pentane-hydrogen chloride solution from conduit 28 is withdrawn through valve 31 and conduit 32 into the lower portion of a pentane reactor 33 which is advantageously maintained at a temperature of 40° to 60° C.

The circulation of a major proportion of the pentane-hydrogen chloride solution through conduit 29 insures thorough mixing of the normal pentane introduced through conduit 13 with the hydrogen chloride and the recycle product stream introduced through conduits 19 and 20, respectively. By this mixing procedure, the isopentane

in the recycle product stream is thoroughly mixed with the incoming pentane prior to its introduction into the reactor so that no charge containing less than about 33 per cent of isopentane can come in contact with the catalyst. Thorough mixing of the isopentane with the normal pentane is necessary in order to avoid local decomposition reactions which would otherwise occur near the point of feed introduction into the reactor.

In continuous operation, pentane reactor 33 containing an aluminum halide catalyst is advantageously filled at the start of a run with a mixture consisting of about 40 per cent isopentane and about 60 per cent normal pentane. The reactor is then heated to about 50° C. and a normal pentane-isopentane-hydrogen chloride solution containing at least 33 per cent and not more than 50 per cent of isopentane and 2 to 4 per cent of hydrogen chloride is then charged to the reactor.

Only one pentane reactor is shown in the figure; however, continuous operation may require several reactors so that when the catalyst in one reactor is reduced below an economic level, the flow can be diverted to another reactor while the depleted reactor is being recharged with fresh catalyst. Pentane reactor 33 may contain solid aluminum chloride or aluminum chloride deposited on a suitable support or it may contain one of the various liquid catalysts wherein aluminum chloride is dissolved, suspended, or reacted with some organic or inorganic material. If solid aluminum chloride is used as catalysts in hexane reactor 67, the sludge which forms therein can, if desired, be used as catalysts in pentane reactor 33. Pentane reactor 33 may be provided at its top with a plate 34 which can be removed when it is necessary to charge the reactor with fresh solid catalyst. The reactor may also be provided at its bottom with a valved conduit 35 through which catalyst sludge, if formed, may be withdrawn or through which liquid catalysts may be introduced if desired.

The pentanes, upon entering the lower portion of pentane reactor 33 through a suitable distributing means (not shown), pass upwardly in contact with the catalyst during which passage a portion of the normal pentane is isomerized to isopentane so that the resulting product stream contains not more than about 60 per cent isopentane. The concentration of isopentane in the incoming stream is maintained between about 33 per cent and about 50 per cent. The upper portion of pentane reactor 33 is provided with a settling zone 36 to minimize catalyst carry-over into the product and recycle lines. From the top of settling zone 36, a product stream containing not more than about 60 per cent of isopentane is withdrawn through conduit 37. One portion of the product stream is recycled through valve 38 and conduit 28 to conduit 18 wherein it is mixed with a predetermined quantity of normal pentane so that the resulting mixture contains less than about 50 per cent but more than about 33 per cent of isopentane. The portion of the product stream not recycled through conduit 28 passes from conduit 37 through conduit 39 and valve 40 into separator 41 where any dissolved or entrained catalyst is settled out. The amount of product stream removed through conduit 39 is controlled by valve 40 so that the isopentane concentration at the top of the reactor does not exceed about 60 per cent.

Separator 41 is provided at its bottom with a valved conduit 42 through which settled catalyst can be periodically withdrawn. If desired, the settled catalyst can be recycled to pentane reactor 33. From the top of separator 41 a product stream is removed through conduit 43 to hydrogen chloride stripper 44. From the top of hydrogen chloride stripper 44, hydrogen chloride and non-condensable gases are removed through conduit 45 and recycled in part through conduit 24 to the beginning of the process. A portion of the hydrogen chloride recycle may be removed by valve 46 through conduit 47 to prevent light hydrocarbon gases that might be formed from building up in the system. From the bottom of hydrogen chloride stripper 44, a liquid product is removed through conduit 48 to a fractionator 49.

Fractionator 49 may be operated according to several modifications depending upon the amount of pentanes in the original naphtha charge. For example, if the naphtha charge consists of equal parts of normal pentane and normal hexane, the flow might be as follows: one hundred parts of a 50-50 mixture of normal pentane-normal hexane enters fractionator 12 through conduit 11. Fifty parts of normal pentane are removed from fractionator 12 through conduit 13 wherein the 50 parts of normal pentane are mixed with 40 parts of normal pentane recycle coming from the bottom of fractionator 49 through conduit 53, valve 54 and conduit 55. The 90 parts of normal pentane are then mixed with at least 180 parts of a 50-50 mixture of normal pentane-isopentane recycle coming from the top of pentane reactor 33 through conduit 37, valve 38 and conduit 28. The hydrocarbons thus entering the bottom of pentane reactor 33 consist of 90 parts of isopentane and 180 parts of normal pentane. The isopentane concentration in the mixture accordingly is about 33 per cent. From the top of pentane reactor 33, 270 parts of a 50-50 mixture of normal-pentane-isopentane are withdrawn through conduit 37; 180 parts are recycled as mentioned above and the remaining 90 parts pass through separator 41 and hydrogen chloride stripper 44 to fractionator 49. From the top of fractionator 49, 45 parts of isopentane are removed through conduit 50. From the bottom of fractionator 49, 45 parts of normal pentane are withdrawn through conduit 53. Forty of the forty-five parts of the normal pentane are recycled through valve 54 and conduit 55 and the remaining 5 parts are passed through conduit 56 and valve 57 into conduit 14. An alternate procedure would be to remove these 5 parts of normal pentane together with the 45 parts of isopentane through conduit 50. The 45 parts of isopentane and 5 parts of normal pentane thus removed from fractionator 49 are mixed with the 50 parts of normal hexane coming from fractionator 12 through conduit 14. The hydrocarbon charge thus entering hexane reactor 67 consists of a mixture of normal hexane and pentanes, said mixture containing 45 per cent of isopentane. An isomerized product consisting of 50 parts pentanes and 50 parts hexanes is withdrawn from the top of hexane reactor 67 and passes through separator 72 to hydrogen chloride stripper 75. In this particular case, fractionator 84 may be by-passed and the final products withdrawn from the bottom of hydrogen chloride stripper 75 through conduit 79, valve 80, conduit 81, conduit 96, valve 95, conduit 93, valve 92, and valved conduit 94 to

storage. The pentane content of the final product consists of 90 per cent isopentane and 10 per cent normal pentane.

If the naphtha charge consists of 40 per cent normal pentane and 60 per cent normal hexane, the flow might be as follows: one hundred parts of a 40-60 mixture of normal pentane-normal hexane enters fractionator 12 through conduit 11. Forty parts of normal pentane are removed from fractionator 12 through conduit 13 wherein the 40 parts of normal pentane are mixed with 28 parts of normal pentane recycle coming from the bottom of fractionator 49 through conduit 53, valve 54 and conduit 55. The 68 parts of normal pentane are then mixed with at least 136 parts of a 50-50 mixture of normal pentane-isopentane recycle coming from the top of pentane reactor 33 through conduit 37, valve 38 and conduit 20. The hydrocarbons thus entering the bottom of pentane reactor 33 consist of 68 parts of isopentane and 136 parts of normal pentane. The isopentane concentration in the mixture accordingly is about 33 per cent. From the top of pentane reactor 33, 204 parts of a 50-50 mixture of normal pentane-isopentane are withdrawn through conduit 37; 136 parts are recycled as mentioned above and the remaining 68 parts pass through separator 41 and hydrogen chloride stripper 44 to fractionator 49. From the top of fractionator 49, 34 parts of isopentane are removed through conduit 50. From the bottom of fractionator 49, 34 parts of normal pentane are withdrawn through conduit 53. Twenty-eight of the 34 parts of the normal pentane are recycled through valve 54 and conduit 55 and the remaining 6 parts are passed through conduit 56 and valve 57 into conduit 14. An alternate procedure would be to remove these 6 parts of normal pentane together with the 34 parts of isopentane through conduit 50. The 34 parts of isopentane withdrawn through conduit 50 are mixed with 20 parts of isopentane recycle coming from the top of fractionator 84 through conduit 87. At the start of a run the 20 parts of isopentane are added from an outside source (not shown). The 54 parts of isopentane are then mixed with the 60 parts of normal hexane coming from fractionator 12 through conduit 14 and 6 parts of normal pentane coming from the bottom of fractionator 49 through conduit 53. The hydrocarbon charge thus entering hexane reactor 67 consists of a mixture of normal hexane and pentanes, said mixture containing 45 per cent of isopentane. An isomerized product is withdrawn from the top of hexane reactor 67 and passes through separator 72 and hydrogen chloride stripper 75 to fractionator 84. From the top of fractionator 84, 20 parts of isopentane are recycled through conduit 87. From the bottom of fractionator 84 a final product consisting of 40 parts pentanes and 60 parts hexanes is withdrawn through valve 90, conduits 91 and 93, valve 92 and valved conduit 94 to storage. The pentane content of the final product consists of 85 per cent isopentane and 15 per cent normal pentane.

If the naphtha charge consists of 60 per cent normal pentane and 40 per cent normal hexane, the flow might be as follows: one hundred parts of a 60-40 mixture of normal pentane-normal hexane enters fractionator 12 through conduit 11. Sixty parts of normal pentane are removed from the fractionator 12 through conduit 13 wherein the 60 parts of normal pentane are mixed with 52 parts of normal pentane recycle coming from the bottom of fractionator 49 through conduit 53,

valve 54 and conduit 55. The 112 parts of normal pentane are then mixed with at least 224 parts of a 50-50 mixture of normal pentane-isopentane recycle coming from the top of pentane reactor 33 through conduit 37, valve 38 and conduit 20. The hydrocarbons thus entering the bottom of pentane reactor 33 consist of 112 parts of isopentane and 224 parts of normal pentane. The isopentane concentration in the mixture accordingly is about 33 per cent. From the top of pentane reactor 33, 336 parts of a 50-50 mixture of normal pentane-isopentane are withdrawn through conduit 37; 224 parts are recycled as mentioned above and the remaining 112 parts pass through separator 41 and hydrogen chloride stripper 44 to fractionator 49. From the top of fractionator 49, 56 parts of isopentane are removed through conduit 50. From the bottom of fractionator 49, 56 parts of normal pentane are withdrawn through conduit 53. Fifty-two of the 56 parts of the normal pentane are recycled through valve 54 and conduit 55 and the remaining 4 parts are passed through conduit 56 and valve 57 into conduit 14. An alternative procedure would be to remove these 4 parts of normal pentane together with 36 parts of isopentane as a side stream from fractionator 49 through valve 58 and conduit 59. From conduit 50, 20 parts of isopentane are removed through valve 60 and conduit 61 wherein it is mixed with the bottoms from hydrogen chloride stripper 75 thus forming the final product. The remaining 36 parts of isopentane from conduit 50 pass through valve 51 and conduit 52 to conduit 66 wherein they are mixed with 40 parts of normal hexane coming from fractionator 12 through conduit 14 and 4 parts of normal pentane coming from the bottom of fractionator 49 through conduit 53. The hydrocarbon charge thus entering hexane reactor 67 consists of a mixture of normal hexane and pentanes, said mixture containing 45 per cent of isopentane. An isomerized product is withdrawn from the top of hexane reactor 67 and passes through separator 72 to hydrogen chloride stripper 75. In this case, fractionator 84 may be by-passed and the isomerized product withdrawn from the bottom of hydrogen chloride stripper 75 through conduit 79, valve 80, conduit 81, conduit 96, valve 95, conduit 93 and valve 92 to conduit 61 wherein it is mixed with the 20 parts of isopentane withdrawn from conduit 50. The final blended product consisting of 60 parts pentanes and 40 parts hexanes is withdrawn through valved conduit 94 to storage. The pentane content of the final blended product consists of 93.3 per cent isopentane and 6.7 per cent normal pentane.

The hexane fraction withdrawn from fractionator 12 through conduit 14 is preferably mixed with an equilibrium mixture of normal pentane and isopentane obtained in accordance with one of the above modifications. Hydrogen chloride promoter is introduced into the pentane-hexane charge by means of conduit 62. The hydrogen chloride in conduit 62 consists of fresh hydrogen chloride introduced through conduit 21 and valves 22 and 63 and recycle hydrogen chloride introduced through conduit 64 and valve 65. The pentane-hexane-hydrogen chloride charge passes through conduit 66 into the lower portion of hexane reactor 67 which is advantageously maintained at a temperature of 40° to 75° C.

In continuous operation hexane reactor 67 containing an aluminum halide catalyst is advantageously filled at the start of a run with a

mixture consisting of about 50 per cent normal hexane and about 50 per cent of an equilibrium mixture of normal pentane and isopentane. The reactor is then heated to about 65° C. and a pentane-hexane-hydrogen chloride solution containing at least 45 per cent of isopentane and 2 to 4 per cent of hydrogen chloride is then charged to the reactor.

Only one hexane reactor is shown in the figure; however, continuous operation may require several reactors so that when the catalyst in one reactor is reduced below an economic level, the flow can be diverted to another reactor while the depleted reactor is being recharged with fresh catalyst. Hexane reactor 67 may contain solid aluminum chloride or aluminum chloride deposited on a suitable support or it may contain one of the various liquid catalysts wherein aluminum chloride is dissolved, suspended, or reacted with some organic or inorganic material. If solid aluminum chloride is used as the catalyst in pentane reactor 33, any slurry which forms therein can, if desired, be used as catalyst in hexane reactor 67. Hexane reactor 67 may be provided at its top with a plate 68 which can be removed when it is necessary to charge the reactor with fresh solid catalyst. The reactor may also be provided at its bottom with a valved conduit 69 through which any sludge, if formed, may be withdrawn or through which liquid catalysts may be introduced if desired.

The pentane-hexane-hydrogen chloride charge upon entering the lower portion of hexane reactor 67 through a suitable distributing means (not shown), passes upwardly in contact with the catalyst during which passage the hexane is isomerized. The upper portion of hexane reactor 67 is provided with a settling zone 70 to minimize catalyst carry-over. From the top of settling zone 70, a product stream is withdrawn through conduit 71 to separator 72 where any dissolved or entrained catalyst is settled out.

Separator 72 is provided at its bottom with a valved conduit 73 through which settled catalyst can be periodically withdrawn. If desired, the settled catalyst can be recycled to hexane reactor 67. From the top of separator 72, a product stream is removed through conduit 74 to hydrogen chloride stripper 75. From the top of hydrogen chloride stripper 75, hydrogen chloride and non-condensable gases are removed through conduit 76 and recycled in part through conduit 64. A portion of the hydrogen chloride recycle may be removed by valve 77 through conduit 78 to prevent light hydrocarbon gases from building up in the system. From the bottom of hydrogen chloride stripper 75, a liquid product is removed through conduit 79, valve 80, conduit 81, valve 82, and conduit 83 to a fractionator 84. If desired, all or a portion of the hydrogen chloride stripper bottoms may be recycled to hexane reactor 67, through valve 85 and conduit 86. As shown hereinabove, if the original naphtha charge contains pentanes in an amount at least equal to the amount of hexanes, fractionator 84 may be by-passed and product may pass directly from the bottom of hydrogen chloride stripper 75 through conduit 79, valve 80, conduit 81, conduit 96, valve 95, conduit 93, valve 92 and valved conduit 94 to storage.

Fractionator 84 is provided at its top with a conduit 87 through which isopentane may be recycled. The amount of isopentane removed as overhead from fractionator 84 depends upon the composition of the original naphtha charge. If

the original naphtha charge contains more hexanes than pentanes, it has been shown above that isopentane is recycled from the top of fractionator 84 in an amount sufficient to produce a pentane-hexane mixture containing at least 45 per cent of isopentane. If the original naphtha charge contains either more pentanes than hexanes or equal amounts of pentanes and hexanes, fractionator 84 may be by-passed. The bottoms from fractionator 84 pass through valve 90, conduit 91, valve 92 and conduit 93 into conduit 61. If the original naphtha charge contains more pentanes than hexanes, isopentane coming from the top of fractionator 49 through conduits 50 and 61 are blended with hydrogen chloride stripper bottoms, the final blended product being withdrawn through valved conduit 94.

The following is given as illustrative of the present invention, but it is to be understood that the invention is not restricted thereto. The data appearing for the four runs listed in the table below afford a comparison of the results obtainable when separately isomerizing normal pentane and normal hexane by contact with an aluminum chloride catalyst and a hydrogen chloride promoter in the absence of and in the presence of isopentane. All of the runs were batch liquid phase experiments, but it is to be understood that our process is also applicable to continuous operation. In each of the runs, 50 mls. of charge was placed in a stainless steel bomb of approximately 100 mls. capacity. To the charge was added 7.4 grams of anhydrous aluminum chloride. The bomb was closed and then immersed in a Dry Ice-acetone bath. When the bomb and its contents reached the approximate temperature of the Dry Ice-bath, 0.6 gram, or about 2 per cent by weight of the hydrocarbons charged, of anhydrous hydrogen chloride was added to the reaction mixture. The bomb was then attached to agitating means and immersed in a constant temperature bath. The pentane isomerization reaction runs 1 and 2 were carried out at a temperature of 48.6° C. for a period of 45 minutes. The hexane isomerization reaction runs 3, 4, 5 and 6 were carried out at a temperature of 30° C. for a period of 24¾ hours. When operating continuously we use a temperature of about 65° C. and a liquid space velocity of about 0.2 to 0.6. After remaining in the constant temperature bath for the required time, the bomb was removed and quickly chilled in a Dry Ice-acetone bath. The bomb was then opened, the contents decanted and fractionated.

Table

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Charge, weight Per cent:						
n-pentane.....	99.0	55.0	100.0	89.3	77.0	51.5
n-hexane.....	1.0	45.0	0	10.7	23.0	48.5
isopentane.....						
Product, weight per cent:						
isobutane.....	21.9	0.5	26.4	25.0	29.0	0.9
n-butane.....			1.4	1.0	0	
isopentane.....	30.5	54.3	17.7	18.2	19.5	46.8
n-pentane.....	28.1	44.0	2.3	2.4	3.0	0
neohexane.....			7.6	8.4	10.4	2.5
isohexanes.....			13.9	13.3	12.9	14.1
n-hexane.....	19.5	1.2	7.0	9.0	3.1	35.7
heptanes+.....			23.7	22.7	22.1	0
Yield, per cent.....	41.5	84.5	23.1	27.0	31.5	105.1

¹ mols. isomerized hydrocarbon formed
mols. n-hydrocarbon converted $\times 100$.

² includes neohexane and isohexanes.

As indicated by the foregoing data, where the isopentane was present during the separate isomerization of normal pentane and normal

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hexane, the yields of isomerized hydrocarbons were substantially increased. For example, in run 1, where only 1 per cent of isopentane was initially present during the isomerization of normal pentane, a yield of only 41.5 per cent resulted. In run 2, however, wherein the initial isopentane concentration was 45 per cent, a yield of 84.5 per cent was obtained. Likewise, in run 3, where no isopentane was initially present during the isomerization of normal hexane, a yield of only 23.1 per cent resulted. While isopentane was present in runs 4 and 5, it was not present in an amount sufficient to suppress cracking as can be noted by the large amount of butanes formed. Also, it can be observed that the yields in runs 4 and 5 were only slightly higher than the yield in run 3 where no isopentane was present. In run 6, however, where the initial isopentane concentration was 48.5 per cent, a yield of 105.1 per cent was obtained. The yield of greater than 100 per cent is attributed to slight unavoidable errors in analytical determination.

This invention has been discussed with particular reference to certain embodiments and specific examples, but it is not limited to such embodiments or examples except as defined in the appended claim.

We claim:

A process of increasing the isoparaffin content of a light naphtha of the pentane-hexane boiling range comprising separating said naphtha into a pentane fraction and a hexane fraction consisting predominantly of normal hexane; admixing with said pentane fraction normal pentane recycle and a proportion of normal pentane-isopentane reaction mixture sufficient to produce a normal pentane-isopentane charge mixture consisting essentially of normal pentane and isopentane and containing about 35 to about 45 per cent by weight of isopentane; isomerizing said normal pentane-isopentane charge mixture in the presence of an aluminum halide catalyst and a hydrogen halide promoter in a pentane isomerization zone at a temperature below about 70° C., said isopentane in said normal pentane-isopentane charge mixture acting to inhibit cracking of said normal pentane and being the

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only cracking inhibitor present in effective amounts in said pentane isomerization zone; withdrawing from said pentane isomerization zone a pentane reaction mixture containing substantially more isopentane than was present in said normal pentane-isopentane charge mixture and not more than about 60 per cent by weight of isopentane; dividing said pentane reaction mixture into two portions; recycling to the pentane isomerization zone one of said portions admixed with normal pentane as aforesaid, fractionating the remaining portion into a cut consisting essentially of normal pentane and a cut comprising isopentane; recycling normal pentane from said fractionation to said pentane isomerization zone; mixing with the aforesaid hexane fraction a mixture of isopentane and normal pentane recovered in said fractionation and containing about 85 to 90 per cent by weight of isopentane in an amount sufficient to produce a hexane charge mixture containing at least about 45 per cent by weight of isopentane; isomerizing said hexane charge mixture in the presence of an aluminum halide catalyst and a hydrogen halide promoter in a hexane isomerization zone at a temperature below about 75° C., withdrawing from said hexane reaction zone an improved light naphtha, said improved light naphtha containing unconverted normal hexane, a substantial amount of isohexane, and a pentane content consisting essentially of an equilibrium mixture of normal pentane and isopentane.

BERNARD H. GWYNN.

CHARLES W. MONTGOMERY.

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