

UNITED STATES PATENT OFFICE

2,399,765

ISOMERIZATION OF LIGHT NAPHTHA
PARAFFINIC HYDROCARBONS

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Application September 18, 1943, Serial No. 502,876

13 Claims. (Cl. 260—683.5)

This invention relates to the isomerization of light naphtha paraffinic hydrocarbons and it pertains more particularly to improved methods and means for isomerizing such hydrocarbons in an integrated unitary system wherein one hydrocarbon such as pentane or butane is isomerized in the absence of added hydrogen and another hydrocarbon such as hexane or heptane is isomerized in the presence of added hydrogen.

Although butane, pentane (with an added cracking inhibitor such as benzene) and naphthenes may be isomerized on a commercial scale by Friedel-Crafts type catalysts in the absence of added hydrogen, there is a considerably greater tendency toward cracking in the case of light normally liquid paraffins such as hexanes and heptanes. For isomerizing these light normally liquid hydrocarbons it has heretofore been deemed essential to employ substantial added hydrogen pressures. This in turn necessitated the use of expensive equipment for withstanding necessary high pressures not to mention the considerable expense of obtaining the required hydrogen. An object of our invention is to materially decrease the amount of added hydrogen required for such processes and the amount and size of the necessary high pressure equipment. A further object is to provide an isomerization system which will utilize catalyst more effectively and more efficiently and which will produce larger quantities of aviation motor fuel stocks per unit of catalyst than has heretofore been possible. A further object is to obtain larger yields of neo-hexane and isopentane from a given light naphtha charge than could be produced by any prior process. A further object is to decrease capital expenditure, material requirements and operating costs of an isomerization system of given capacity. Other objects will be apparent as the detailed description of our invention proceeds.

In practicing our invention we isomerize normal pentane or butane in the absence of added hydrogen while we isomerize hexanes or heptanes in the presence of added hydrogen. By eliminating the use of hydrogen in the pentane isomerization step we substantially decrease material requirements, construction expense and operating costs. Both product streams are depentanized in one and the same depentanizer. The isopentane from both streams as well as from the original charge is separated from normal pentane in one and the same isopentane tower which produces the charge for the pentane isomerization step. Any C₆ or heavier hydrocarbons produced in the pentane isomerization step are

fractionated with the hexane isomerization products in one and the same neo-hexane tower so that any neo-hexane therein may be recovered and all heavier products may be recycled to the hexane isomerization step. Higher boiling naphthenes are eliminated from the system at the base of a rerun tower. Thus certain products from each isomerization step serve as a part of the charge to the other isomerization step. Maximum yields of neo-hexane and isopentane are obtained and the system is constantly purged of higher boiling naphthene bottoms.

When normal pentane is contacted under isomerization conditions with a Friedel-Crafts type catalyst and a hydrogen halide in the absence of hydrogen and cyclic hydrocarbons the reaction is chiefly disproportionation and there results a product of which about one-third is butanes, one-third pentanes and one-third hexanes and heavier. By effecting the conversion in the presence of a critically small amount of a cyclic liquid cracking inhibitor this disproportionation may be substantially repressed and ultimate isopentane yields of 85 to 90% may be obtained together with only relatively small amounts of butanes and C₆ and heavier hydrocarbons. The preferred inhibitor is benzene in amounts of the order of .1 to 1%, e. g. about .5% based on charging stock. Amounts of benzene as low as .02% may have a beneficial effect in preventing disproportionation and may be employed where maximum isopentane production is not essential. Amounts up to 2% and higher are even more effective in inhibiting disproportionation but are usually undesirable (except perhaps in starting up procedures) because increased amounts of benzene impair catalyst activity and particularly in the case of aluminum chloride-hydrocarbon complexes tend toward altering the type of complex to undesirable form. Other aromatics may be employed instead of benzene but they are not as desirable since alkyl benzenes are even worse than benzene itself in their tendency toward causing catalyst deterioration and the formation of undesirable complexes. Naphthenes may be employed as cracking inhibitors in amounts about ten times as great as the required amounts of aromatics, i. e., about 1 to 10% by weight based on charge but in view of the required concentration and availability thereof, they are usually not as practical as benzene. It should be emphasized that the critically small amount of benzene should be present in the reaction zone in the charging stock which is undergoing conversion and not chemically combined with the aluminum

chloride because our preferred complex is a complex resulting from the reaction of paraffinic, particularly isoparaffinic, hydrocarbons with aluminum halides, the naphthene complexes being satisfactory but less active and the olefinic and aromatic complexes being undesirable.

For hexane isomerization the aromatic or naphthene cracking inhibitors are desirable but usually they do not have to be separately added because they are present in required amounts in most virgin naphtha charging stocks. In this case, however, hydrogen pressures must be employed to maintain catalyst life and catalyst activity. By isomerizing the hexanes in a separate system from the pentanes the requirements of both hydrogen and high pressure equipment may be greatly reduced.

An important feature of the separate isomerization steps is the savings in catalyst requirements. Make-up aluminum chloride must be continuously or intermittently added to the pentane isomerization system in order to maintain catalyst activity at the desired level. If the bound hydrocarbon content of the complex falls below about 23% there is a tendency for aluminum chloride to be carried over with the hydrocarbon product while with hydrocarbon contents greater than 23-25% the complex selectively removes any dissolved aluminum chloride from hydrocarbon solutions so that the products leaving the reactor will not contain much more than approximately .01% of aluminum chloride. On the other hand, if the hydrocarbon content of the complex is permitted to increase substantially about 30 or 40%, the activity of the catalyst is markedly reduced and the amount of conversion that can be effected in a given unit is accordingly reduced. In the hexane system the aluminum chloride catalyst which tends to form inactive complex is continuously regenerated by the hydrogen present in the reactor so that the catalyst requirements are relatively low. The inactive catalyst from the pentane isomerization zone, which forms relatively rapidly, has heretofore been replaced by an equivalent amount of fresh aluminum chloride or regenerated in a separate regeneration zone. According to our invention this inactive catalyst is regenerated by introducing it into the hexane isomerization zone. Thus we minimize the amount of catalyst which must be withdrawn from the system by continuously circulating it between the pentane and hexane isomerization steps. Also by our invention the preferred activity level of the catalysts in the two isomerization zones tend to be automatically controlled.

By employing tower-type reactors we may maintain an activity gradient from the base to the top of each tower. Make-up aluminum chloride enters the low point in the tower at such a rate as to keep the hydrocarbon content of the complex at that point in the general vicinity of about 20 to 25%. In the upper part of the tower the hydrocarbon content of the complex may be as high as 30 to 40%. Instead of discarding all of the excess catalyst of such low activity from the system we introduce a major part of it to the top of the hexane isomerization tower thereby minimizing any tendency toward aluminum chloride carry-over from the hexane reactor. As this catalyst passes downwardly in the hexane isomerization tower it is regenerated by hydrogen simultaneously with the isomerization of the hexanes so that by the time the complex reaches the base of the tower its hydrocarbon content may be reduced once more to about 20 or 25%. The de-

sired catalyst level in the hexane tower is maintained by returning complex from the bottom of the hexane tower to a low point in the pentane tower. This system of operation effects substantial savings in aluminum chloride and hydrogen chloride and it minimizes the problem of aluminum chloride carry-over in the hexane system and spent complex disposal from the pentane system. A much smaller amount of complex has to be withdrawn from the combined systems than would otherwise be withdrawn and the withdrawn portion is of very low activity.

The invention will be more clearly understood from the following detailed description of a specific example thereof read in conjunction with the accompanying drawing which constitutes a part of this disclosure and which is a schematic flow diagram of a pentane-hexane isomerization system.

The charging stock may be a light virgin naphtha or any other hydrocarbon charge of similar boiling range provided that it is rich in paraffins and substantially free from olefins and excessive amounts of aromatics. Such a charge from source 10 is fractionated by conventional means diagrammatically illustrated by column 11 into a pentane-and-lighter fraction withdrawn through line 12, a hexane fraction withdrawn through line 13 and a heptane-and-heavier fraction withdrawn through line 14. All of the fractionating towers herein described are diagrammatically illustrated by showing a reflux coil at the top and a reheater coil at the base but it should be understood that conventional reflux and reboiling means are contemplated and that these diagrammatical showings are merely to simplify the drawing.

The pentane-and-lighter fraction from line 12 together with any pentanes from any extraneous source 15 and product pentanes from line 16 are introduced into isopentane tower 17. Isopentane-and-lighter hydrocarbons are taken overhead through line 18 to debutanizer tower 19, the butanes and lighter hydrocarbons being removed through line 20 and the isopentane product stream being removed through line 21.

The normal pentane stream leaves the base of isopentane tower 17 through line 22. A portion of this stream is passed by pump 23 through heater 24 and thence through one of the aluminum chloride solution tanks 25 into which make-up solid aluminum chloride may be charged from time to time from source 26. By employing at least two solution tanks, one may be on-stream while another is being recharged. The amount of the charge which is passed through the solution tank and the temperature to which it is heated in heater 24 should be sufficient to introduce about .1 to 1, e. g. about 0.3 pound of aluminum chloride per barrel of total stock charged and this amount and temperature can be determined from the following solubility table assuming of course that sufficient time and intimacy of contact is employed to permit saturation and sufficient pressure to maintain liquid phase conditions.

Temperature	Wt. per cent of AlCl ₃ dissolved	Lbs. of AlCl ₃ per barrel of pentane
150° F.	0.2-0.3	0.4-0.6
200° F.	0.2-3	1.9-5.0
212° F.	1.4-3.3	3.0-7.2
250° F.	4.3-7.3	9.3-15.8

The lower limit of each of these ranges is the amount dissolved at the stated temperature, while the higher limit of each range is the amount held in solution if said solution is effected at about 30° F. higher than the stated temperature and then cooled thereto. The solution tanks may be operated downflow instead of upflow and if desired a small amount of hydrogen may be employed therein for preventing complex formation, particularly at high temperatures. The resulting solution is passed by line 27 to a low point in pentane isomerizing tower 28.

The remainder of the normal pentane charge is passed by pump 29 through heater 30 and line 31 to a suitable distributor at the base of pentane isomerizer 28. Hydrogen chloride may be introduced into the stream through line 32 in amounts within the approximate range of 2 to 10%, e. g., about 6% by weight, based on total charge. A cracking inhibitor such as benzene may be introduced into line 22 from source 33 and line 34 (or into line 31 from source 33' and line 34') in amounts of about .5% by volume based on total stock charged.

In starting up the reaction, tower 28 may be about one-half to three-fourths filled with an aluminum chloride-hydrocarbon complex prepared by reaction of aluminum chloride in the presence of hydrogen chloride with a paraffinic hydrocarbon such as a portion of the light naphtha which is to undergo isomerization. A suitable complex for example is that described in U. S. Letters Patent 2,300,249 but it should be understood that the complex may be prepared from saturated hydrocarbons generally, provided that they are substantially free from olefins and that they do not contain excessive amounts of aromatics.

The pentane isomerization is preferably effected at a temperature within the approximate range of 150 to 350° F., for example about 212° F., and under a pressure within the approximate range of 200 to 600 pounds per square inch, for example about 300 pounds per square inch gauge, preferably sufficient to maintain liquid phase reaction conditions. The rate of flow may be within the approximate range of .3 to 3, e. g., about 1 volume of charging stock per hour per volume of complex in the tower but will depend on catalyst activity and may be somewhat higher or lower than this preferred range. The column of complex in the tower is at least 5 feet in height and preferably about 20 feet in height and the vertical flow rate of charge may be of the order of about .1 to 1 foot per minute.

A certain amount of the catalyst complex is entrained with the product stream leaving the top of the catalyst column and such entrained catalyst settles back to the column in the upper part of the tower. Any remaining entrained complex is carried by the product stream through line 35 and cooler 36 to settler 37 which may be operated at about 150 to 250 pounds per square inch, e. g., 185 pounds per square inch gauge and at about atmospheric to 100° F. temperature. Any light hydrocarbon gases formed may be purged from the system through line 38 since the hydrogen chloride under the separation conditions will remain in solution. Complex settles out of the liquid products in the settler and will be withdrawn through line 39. The remaining product stream passes over weir 40 and is introduced by line 40a into stripping column 41 which may operate at a gauge pressure slightly above 300 pounds

per square inch with a top temperature of about 130° F. and a bottom temperature of about 320° F. The hydrogen chloride may be returned by lines 42, 32 and 31 to the base of the isomerizer without the necessity of employing a blower or compressor. Make-up hydrogen chloride may be introduced to line 32 from source 43.

The product stream leaving the base of stripper 41 through line 44 is treated with caustic from source 45 in a neutralizing system 46, then washed with water in system 47 and introduced through line 48 to depentanizer tower 49.

The hexane stream from line 13 is introduced by pump 50 into the top of hydrogen chloride absorber 51 for picking up hydrogen chloride from a recycled gas stream introduced at the base of this absorber through line 52, any unabsorbed gases leaving the top of the tower through line 53. Make-up hydrogen chloride may be introduced from source 54 either at the base of absorber tower 51 or into line 55 and the hydrogen chloride solution from line 55 is passed by pump 56 through heater 57 to the base of hexane isomerizing tower 58. Hydrogen from source 59 is introduced at the base of this tower through line 60 at the rate of about 50 to 300, e. g., about 200 cubic feet per barrel of stock charged. The complex for the hexane isomerizing tower may be that which is produced in the pentane isomerizing tower or it may be initially prepared from suitable hydrocarbons as hereinabove described. Make-up aluminum chloride may be introduced into the hexane isomerizer by by-passing a portion of the charge from line 13 through a solution tank system similar to that hereinabove described (23, 24, 25, 26, 27) but since the hexanes would tend to form complex in such solution tanks, we prefer to obtain any necessary make-up aluminum chloride as a solution in pentane. Thus a portion of the solution from tanks 25 may be passed by line 61 to surge tank 62, and it may be introduced into the higher pressure conversion zone in tower 58 by means of pump 63 and line 64. The pentane thus introduced into tower 58 is isomerized along with the hexanes, and the resulting isopentane is recovered in our fractionation system. Usually only a small amount of make-up aluminum chloride, if any, has to be introduced into hexane tower 58 because of the catalyst circulation system which will be hereinafter described.

It should be understood that instead of employing only one isomerizing tower in either or both isomerizing steps we may employ two or more towers either in series or in parallel and we may employ higher temperatures in the first tower than in the second. The hexane isomerization temperature should be within the approximate range of about 150 to 350° F., e. g., about 250° F. The pressure should be of the order of about 500 to 1500 pounds per square inch, e. g., about 850 pounds per square inch. The total space velocity may be of the order of about 2 to 4 volumes of charging stock per hour per volume of complex in the total contacting zone and we prefer to employ columns of at least 5 feet in height and preferably about 20 to 30 feet in height.

Any complex which does not settle back to the column from the liquid products in the upper part of tower 58 are taken overhead through line 65 to hot settler 66 from which settled complex is returned by line 67. The product stream then passes through line 68 and cooler 69 to cool settler 70 from which any additional catalyst may be returned by pump 71 and line 72 to the hexane

isomerizer tower 58. Settler 70 is preferably operated from about atmospheric temperature to 100° F. and at a sufficient pressure so that gases may leave the top through line 73 and be returned by line 52 to absorber 51 without further compression. The product stream flows over weir 74 and thence through line 75 to hydrogen chloride stripper 76, the hydrogen chloride being returned by lines 77 and 52 to the base of absorber 51. The stripped products are then neutralized with caustic in neutralizing system 78, water washed in washing system 79 and introduced by line 80 to rerun tower 81. Any hydrocarbons boiling above about 175° F. are removed from the system as naphthene bottoms through line 82 and may be employed as motor fuel components or as a charging stock for hydroforming or aromatization in the manufacture of aromatics, particularly toluene.

The hydrocarbons boiling below about 175° F. are taken overhead through line 83 and introduced through line 48 to depentanizer 49. All pentanes and lighter hydrocarbons pass from the top of tower 49 through line 16 to isopentane tower 17 which has been hereinabove described. The hexanes are removed from the base of depentanizer 49 through line 84 to neohexane tower 85. The neohexane product stream is drawn from the top of tower 85 through line 86. Other hexanes (chiefly methyl pentanes) with a small amount of naphthenes are recycled from the base of tower 85 through line 87 to the top of absorber 51.

The continuous introduction of make-up aluminum chloride solution at the base of pentane tower 28 is at such a rate as to maintain a catalyst activity at the base of the tower corresponding to a bound hydrocarbon content in the general vicinity of 20 to 25%. At the top of tower 28 the catalyst activity may be considerably lower corresponding to a hydrocarbon content of the order of about 30 to 50%. Since complex is continuously being formed from make-up catalyst in the tower it is necessary that complex be continuously removed in order that a substantially constant complex liquid level be maintained in tower 28. Catalyst may thus be removed from the upper part of tower 28 to a trap 90 for separating any product or unconverted hydrocarbons therefrom, such product or unconverted hydrocarbons being returned to the tower through line 90a or introduced to settler 37. Liquid complex may then be introduced by pump 91 through line 92 to the upper part of tower 58. We may, however, dispense with trap 90 and simply rely on the product stream leaving through line 35 to carry a sufficient amount of entrained complex to maintain the column of complex at the desired level in tower 28. A part of the settled catalyst from line 39 may be discarded, but most of it may be introduced by pump 91' and 92 to the upper part of tower 58.

The introduction of this complex containing 30 to 50% hydrocarbon in the upper part of tower 58 minimizes any tendency for aluminum chloride carry-over through line 65. The complex introduced through line 92 gradually flows downwardly in tower 58 and during the course of its flow it is hydrogenated and thus regenerated so that by the time it reaches the bottom of tower 58 its hydrocarbon content may be decreased to approximately 20 to 25%. Complex from the base of tower 58 may then be returned through line 93 back to a low point in pentane isomerizer 28. To avoid possibility of hexanes finding their way

to the pentane tower 28 we may pass complex from the base of tower 58 by line 93a to settler 93b, return hexanes to tower 58 through line 93c and transfer hexane-free complex through lines 93d and 93 back to tower 28. Some catalyst will have to be discarded from the system and such discard is effected through line 94. The catalyst withdrawn from the system is the least active catalyst. A large amount of the catalyst may be continuously recirculated from the pentane tower to the hexane tower and thence back to the pentane tower for alternate operation in the presence and absence of hydrogen. This recirculation effects marked savings in the required amount of make-up aluminum chloride, it minimizes the amount of complex which must be withdrawn from the system and disposed of and it likewise minimizes hydrogen chloride losses.

In a pentane isomerization system small amounts of hexanes are formed and in the hexane isomerization system small amounts of pentanes are formed. Our system provides not only for common product fractionators but for a fractionation system which permits a portion of the products from each conversion system to be combined with the charge entering the other conversion system. This integrated unitary system thus results in maximum production of isopentane and neohexane, minimum catalyst requirements and operating costs and exceptionally small losses on account of complex discard. The pentane-hexane charge is converted substantially quantitatively into isopentane and neohexane together with small amounts of butanes and lighter hydrocarbons and small amounts of naphthene bottoms suitable for hydroforming. Our system gives a greater yield of high quality aviation motor fuel blending stocks from a given pentane-hexane mixture than could be obtained by any process heretofore known to the art.

While we have described a particular example of our invention in great detail it should be understood that this example is given by way of illustration and that it is not limitative. Other modifications and alternative operating conditions will be apparent to those skilled in the art from the above detailed description. The principles of our invention with appropriate modifications are equally adaptable to the isomerization of butane and hexanes or butanes together with mixed pentanes and hexanes. In the latter system n-butane is isomerized in the absence of hydrogen with a liquid aluminum chloride complex and the spent complex is pumped to the pentane-hexane unit operating in the presence of hydrogen where the spent catalyst is regenerated as it isomerizes the latter feed. The changes in the fractionation columns and the lines will be apparent to those skilled in the art in the light of the above disclosure.

In another modification of our process the naphthenic bottoms from the common fractionation are employed as a cracking inhibitor in the pentane isomerization step. The naphthenic bottoms may be used in entirety or may be fractionated to produce a cyclohexane and/or a methylcyclohexane rich fraction for such use when operating the pentane reactor as an isomerization reactor.

An alternative method is to operate the pentane reactor in the absence of an added inhibitor, thereby altering the type of reaction therein from to predominantly isomerization reaction to a predominantly disproportionation reaction. The product of the pentane reactor under these con-

ditions consists principally of about equal volumes of butanes, pentanes and hexanes. The product is fractionated together with the hexane isomerization product in the common fractionation system, the n-pentane fraction being recycled to the pentane reactor and the less branched hexanes recycled to the hexane reactor operating in the presence of hydrogen. Such a mode of operation, together with hexane isomerization in the presence of added hydrogen, makes it possible for us to convert n-pentane into butane (principally isobutane), isopentane and neohexane. The overall production of neohexane by this method of operation is greater than the production of neohexane when operating the pentane reactor in the presence of an inhibitor.

Features of the invention are applicable when catalysts other than aluminum chloride-hydrocarbon complexes are employed. For example, any Friedel-Crafts or hydrogen halide type of catalyst may be employed under conditions suitable for the particular catalyst in accordance with the general principles set forth in connection with the above examples of our invention hereinabove described.

We claim:

1. The method of isomerizing paraffin hydrocarbons of the pentane-hexane boiling range which method comprises separating said hydrocarbons into a pentane fraction and a hexane fraction, removing isopentane and lighter hydrocarbons from the pentane fraction, contacting the remaining normal pentane in the absence of any substantial amount of added hydrogen but in the presence of a small amount of a cyclic cracking inhibitor with a column of a halide isomerization catalyst under conditions of temperature, pressure and space velocity to give isomerization as the main reaction in a pentane contacting zone, removing catalyst from the products of the contacting step, contacting said hexane fraction with a hydrogen chloride containing gas stream for absorbing hydrogen chloride therefrom, contacting the hexane together with absorbed hydrogen chloride with a second column of halide isomerization catalyst in a hexane contacting zone under substantial hydrogen pressure and under conditions of temperature, pressure and space velocity to effect isomerization as the main reaction, separating catalyst and a hydrogen chloride gas stream from products leaving the hexane contacting step, returning said gas stream to said absorption step, removing from said product stream hydrocarbons which boil substantially above about 175° F., combining the remainder of the product stream with the pentane isomerization product stream, depentanizing the combined products and introducing said pentanes to said isopentane removal step, fractionating the depentanized products to separate neohexane from heavier hydrocarbons and returning said heavier hydrocarbons to said hexane contacting step.

2. The method of isomerizing paraffin hydrocarbons of the pentane-hexane boiling range which method comprises fractionating a charging stock containing pentanes and hexanes but substantially free from olefins to obtain a pentane fraction and a hexane fraction, introducing said pentane fraction at a low point in a column of liquid aluminum chloride paraffinic hydrocarbon complex in the presence of a small amount of a liquid cyclic hydrocarbon cracking inhibitor and in the absence of substantial amounts of added hydrogen, contacting said hexane fraction with a

second column of liquid aluminum chloride-paraffinic hydrocarbon complex in the presence of hydrogen chloride, introducing hydrogen at a low point in said second column at the rate of about 50 to 250 cubic feet per barrel of stock charged thereto, maintaining said second column at a temperature within the approximate range of 150 to 350° F. and under a pressure within the approximate range of 500 to 1500 pounds per square inch, introducing a solution of make-up aluminum chloride in at least a part of the pentane fraction introduced into said first column whereby complex is formed in said first column, withdrawing complex from an upper part of said first column at such a rate as to maintain a substantially constant complex level therein, introducing the withdrawn complex into an upper part of the second column whereby said complex is regenerated as it passes from the upper part of said second column to the lower part thereof and transferring catalyst from the lower part of said second column to a lower part of said first column.

3. The method of producing isopentane and neohexane from paraffinic hydrocarbons of the pentane-hexane boiling range, which method comprises producing separate hexane and normal pentane charging stocks, contacting said normal pentane charging stock with a first column of halide isomerization catalyst in the absence of substantial amounts of added hydrogen but in the presence of a small amount of a cyclic liquid cracking inhibitor under conditions effective for isomerization, contacting said hexane charging stock with a second column of halide isomerization catalyst in the presence of added hydrogen in amounts of at least 50 cubic feet per barrel of stock charged and under conditions effective for isomerization, separating heavier-than-hexane hydrocarbons from the products from the second column contacting step, combining the remaining hydrocarbons with the products from the first column contacting step, separating an isopentane fraction from the combined products, returning normal pentane from the combined products to the first column contacting step, separating a neohexane fraction from the combined products, returning heavier hexanes from the combined products to the second column contacting step, and transferring catalyst from said first column to said second column whereby it may be regenerated simultaneously with the isomerization of hexanes therein.

4. The method of claim 3 which includes the step of adding benzene in amounts within the approximate range of .02 to 2% to the normal pentane charging stock contacted with said first column of halide isomerization catalyst.

5. The method of claim 3 which includes the further step of transferring catalyst from said second column back to said first column.

6. The method of isomerizing a plurality of different paraffinic hydrocarbons of the light naphtha boiling range which method comprises fractionating a charging stock containing said hydrocarbons to obtain a first fraction of paraffinic hydrocarbons isomerizable in the absence of added hydrogen and a second fraction of said hydrocarbons to be isomerized in the presence of added hydrogen, contacting said first fraction with a first column of liquid halide isomerization catalyst by dispersing said fraction at the base of said column of liquid catalyst and passing said dispersed hydrocarbons upwardly through said column of catalyst in the absence of any substantial amount of added hydrogen

and under conditions for effecting isomerization, contacting said second fraction with a second column of liquid halide isomerization catalyst by dispersing said second fraction at a low point in said column and passing the dispersed hydrocarbons upwardly therein in the presence of added hydrogen in amounts of at least 50 cubic feet per barrel in said second fraction charged and under conditions for effecting isomerization, removing liquid catalyst from products leaving the upper part of said first column, introducing at least a substantial amount of said removed liquid catalyst at an upper point in said second column and returning liquid catalyst from the lower part of said second column back to said first column.

7. The method of isomerizing a plurality of different paraffinic hydrocarbons of the light naphtha boiling range which method comprises fractionating a charging stock containing said hydrocarbons to obtain a first fraction of paraffinic hydrocarbons isomerizable in the absence of added hydrogen and a second fraction of said hydrocarbons to be isomerized in the presence of added hydrogen, contacting said first fraction with a first column of liquid aluminum chloride-hydrocarbon complex isomerization catalyst by dispersing said fraction at the base of said column of liquid catalyst and passing said dispersed hydrocarbons upwardly through said column of catalyst in the absence of any substantial amount of added hydrogen and under conditions for effecting isomerization, contacting said second fraction with a second column of liquid aluminum chloride-hydrocarbon complex isomerization catalyst by dispersing said second fraction at a low point in said column and passing the dispersed hydrocarbons upwardly therein in the presence of added hydrogen in amounts of at least 50 cubic feet per barrel in said second fraction charged and under conditions for effecting isomerization, introducing relatively active catalyst complex from a low point in the second column to a low point in the first column, removing catalyst complex from a high point in said first column, returning at least a part of said removed catalyst complex to a high point in said second column and adding make-up aluminum chloride to catalyst complex in at least one of said columns.

8. The method of isomerizing a plurality of paraffinic hydrocarbon fractions of which a first fraction is isomerizable in the absence of added hydrogen and a second fraction requires the presence of added hydrogen in the isomerization step, which method comprises dispersing said first fraction at a low point in a first column of liquid aluminum chloride paraffinic hydrocarbon complex and passing the dispersed hydrocarbons upwardly through said column in the presence of

hydrogen chloride but in the absence of added hydrogen under conditions for effecting isomerization, dispersing said second fraction at a low point in a second column of liquid aluminum chloride paraffinic hydrocarbon complex and passing said dispersed hydrocarbon upwardly in said second column in the presence of substantial amounts of added hydrogen and hydrogen chloride under conditions for effecting isomerization, separating relatively spent complex from products leaving the upper part of said first column, discarding a part of said separated complex, introducing another part of said separated complex at an upper point in said second column and returning complex from the lower part of said second column back to said first column.

9. The method of claim 8 which includes the further step of adding make-up aluminum chloride to both columns as a solution in a part of said first fraction.

10. The method of claim 8 wherein the first fraction consists essentially of pentane and the second fraction consists essentially of hexanes.

11. The method of claim 8 wherein the first fraction consists essentially of butane and the second fraction is a normally liquid paraffinic hydrocarbon lower boiling than heptane.

12. In a process wherein a first paraffinic hydrocarbon stream higher boiling than propane and lower boiling than hexane is isomerized in a first column of aluminum chloride-hydrocarbon complex under isomerization conditions in the presence of hydrogen chloride and in the absence of any substantial amount of added hydrogen, and a second paraffinic hydrocarbon stream higher boiling than pentane and lower boiling than octane is isomerized in a second column of aluminum chloride-hydrocarbon complex under isomerization conditions in the presence of hydrogen chloride, in the absence of the first hydrocarbon stream, and in the presence of a substantial amount of added hydrogen, the method of minimizing the amount of required make-up aluminum chloride which comprises transferring relatively spent complex from the upper part of said first column to said second column so that the transferred catalyst may be regenerated simultaneously with the isomerization effected in said second column and transferring active complex from the lower part of said second column back to said first column.

13. The method of claim 12 which includes the steps of transferring complex from an upper part of the first column to an upper part of the second column and transferring complex from a lower part of the second column to a lower part of the first column.

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