June 22, 1948. B. L. EVERING 2,443,607

HEPTANE ISOMERIZATION

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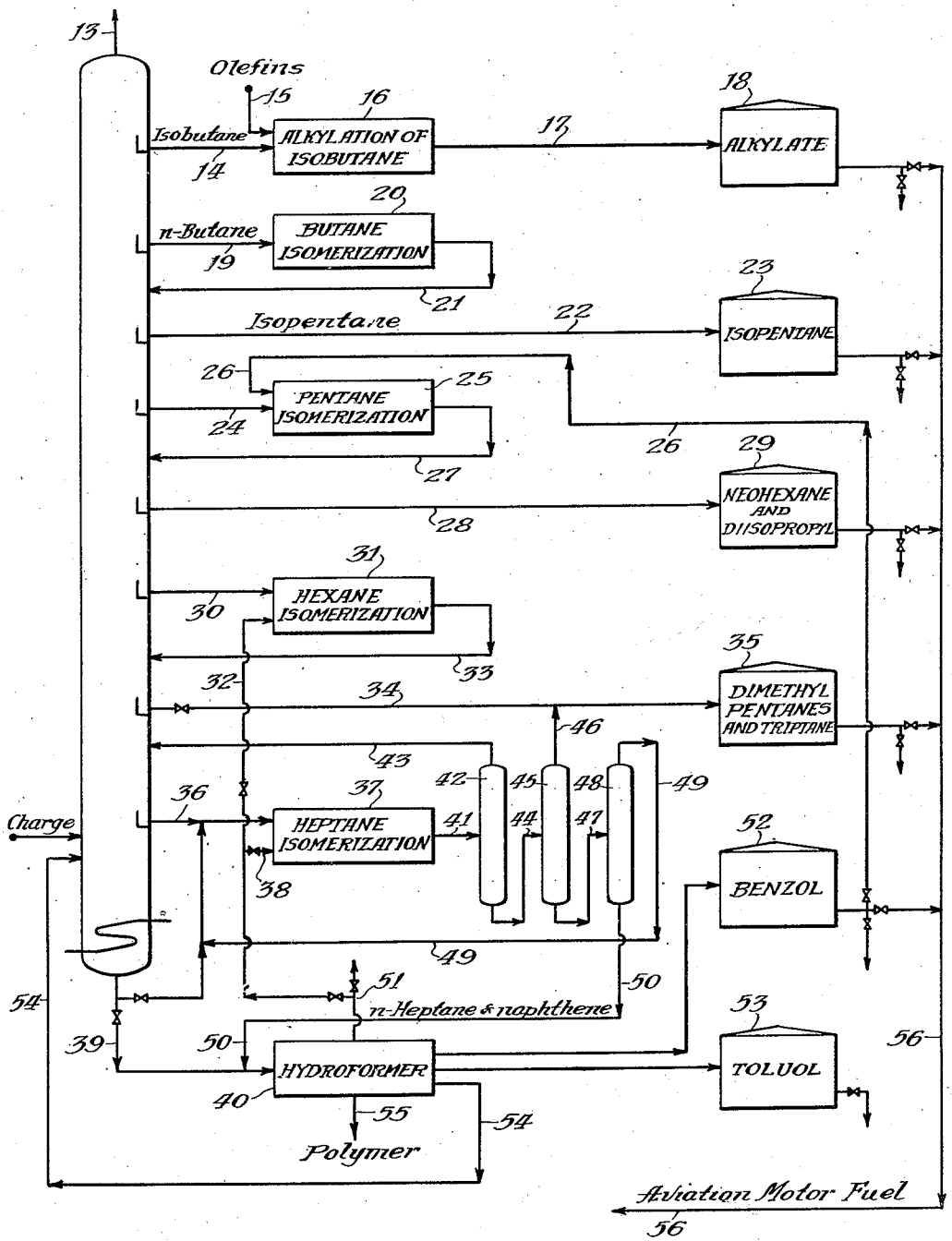


Fig. 1.

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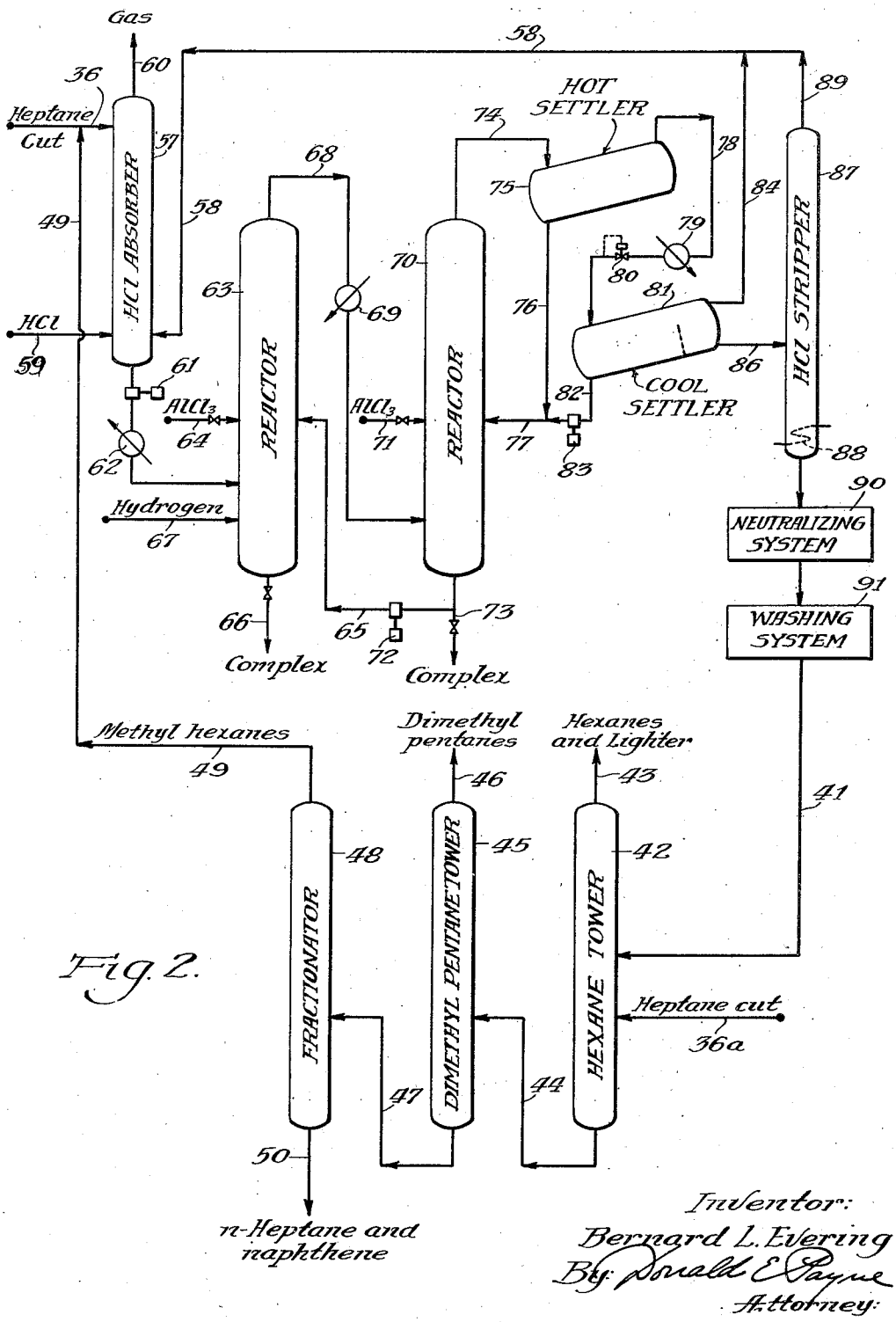


Fig. 2.

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2,443,607

HEPTANE ISOMERIZATION

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1 Claim. (Cl. 260—683.5)

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This invention relates to a light naphtha isomerization system and it pertains more particularly to an improved method and means for producing dimethyl pentanes and trimethylbutane (triptane) from a C_7 hydrocarbon fraction which is substantially free from olefins.

The practical isomerization of paraffinic hydrocarbons by Friedel-Crafts catalysts, exemplified by metal halide hydrocarbon complexes promoted by hydrogen halide activators, becomes increasingly difficult with hydrocarbon chains of increasing length. Butanes are readily isomerizable in the absence of hydrogen and cracking inhibitors. Pentanes are readily isomerizable in the presence of small amounts of cracking inhibitors and in the absence of hydrogen. Hexanes are isomerizable under suitable hydrogen pressures, preferably in the presence of cracking inhibitors such as critically small amounts of aromatics or naphthenes. Heptanes are more difficultly isomerizable and in the case of normal heptane even the use of cracking inhibitors and substantial hydrogen pressures fails to completely overcome the tendency toward cracking with resultant production of lower boiling products, rapid decrease in isomerization rate and relatively short catalyst life. I have discovered, however, that by eliminating normal heptane from a C_7 hydrocarbon fraction which is substantially free from olefins and which contains optimum amounts of aromatics or naphthenes the remainder of the C_7 fraction may be readily isomerized at a temperature within the approximate range of 100–300° F., preferably 150–180° F., under a hydrogen pressure within the range of 300–3000 pounds per square inch, for example about 1000 pounds per square inch.

An object of my invention is to convert paraffinic hydrocarbons of relatively low octane number, particularly C_7 hydrocarbons, into a valuable high octane number motor fuel component suitable for aviation gasolines. A further object is to provide a method and means for obtaining maximum yields of dimethyl pentanes and triptane from a C_7 paraffinic hydrocarbon fraction at minimum expense. A further object is to provide an improved method and means for increasing effective catalyst life and catalyst activity in a C_7 isomerization system and to produce a maximum amount of dimethyl pentanes and triptane with the minimum amount of catalyst. Other objects will be apparent as the detailed description of my invention proceeds.

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It has been known for years that heptanes could be isomerized by means of Friedel-Crafts catalysts and the most successful results to date have been obtained by aluminum halide-hydrocarbon complexes promoted by hydrogen halide activators with substantial hydrogen pressures under approximately the same conditions that hexanes are isomerized. The isomerization of heptanes, however, has been heretofore commercially unattractive because of the catalyst degradation which always occurred in the presence thereof and in hexane isomerization plants great pains have been taken to eliminate substantially all of the heptanes from the charging stock. In hexane isomerization, normal hexane is a desirable component of the charging stock along with methyl pentanes for the production of dimethyl butanes. I have discovered, however, that in the case of heptanes, normal heptane is unexpectedly and unexplainably detrimental when present in the charging stock in relatively large concentrations. By substantially eliminating normal heptane from the charging stock to a heptane isomerization system or by recycling a sufficiently large amount of methyl hexanes (which have been freed from normal heptane) so that the normal heptane concentration in the charging stock is below 10% and preferably below about 5%. I can convert C_7 hydrocarbons almost quantitatively into dimethyl pentanes and triptane which have a CFR–R octane number of about 90 and which are characterized by a remarkably favorable rich mixture performance in aviation engines. The isomerization with an aluminum chloride-hydrocarbon complex may be effected in simple tower reactors using about 2 to 20%, for example, about 6% by weight of hydrogen chloride based on charge, employing hydrogen at the rate of about 100 to 300 cubic feet per barrel of stock charged, for example about 200 cubic feet per barrel, employing a reaction temperature within the range of 100 to 300° F., preferably within the range of 150 to 180° F., employing a conversion pressure within the approximate range of 300 to 3000 pounds per

square inch, preferably about 1000 pounds to 1500 pounds per square inch and employing a space velocity within the approximate range of .3 to 3 volumes of liquid charging stock per hour per volume of complex in the reactors and a feed rate within the range of about 45 to 450 gallons of liquid feed per hour per square foot of cross sectional area of reactor. The charging stock should preferably contain a small amount of aromatics or naphthenes or both; aromatics should preferably be within the approximate range of .3 to 3%, and naphthenes in the approximate range of 2 to 20%. When a mixture of naphthenes and aromatics is present in the charging stock the amounts of each component may be correspondingly reduced.

An important feature of my invention is the avoidance of large amounts of normal heptane in the charging stock introduced into the conversion system. Normal heptanes may be utilized if they are admixed with enough methyl hexanes so that the total amount of normal heptanes in the charging stock is less than about 10% or preferably less than about 5%. By effecting only a small amount of isomerization in each pass and recycling a large amount of methyl hexanes I can utilize at least a substantial portion of the normal heptane content of a charging stock without exceeding the stated maximum normal heptane concentration in the conversion zone itself. The recycle stream in the preferred example of my invention is three tenths to five times the volume of the charging stock stream which is introduced from an external source. For converting pure normal heptane into dimethyl pentanes and triptane it may, however, be necessary to recycle five to twenty five volumes or even more of methyl hexanes for each volume of normal heptane introduced from an outside source.

The invention will be more clearly understood from the following detailed description read in conjunction with the accompanying drawings which form a part of this specification and in which

Figure 1 is a schematic flow sheet diagrammatically illustrating a system for isomerizing light naphtha components with maximum efficiency for the production of aviation gasoline, this figure bringing out the relationship between a heptane isomerization step with other isomerizing and refining steps, and

Figure 2 is a schematic flow diagram of a heptane isomerization system per se.

The charging stock for the manufacture of aviation gasoline may be a virgin light naphtha or any other hydrocarbon mixture of similar constitution and boiling range providing that the mixture is substantially free from olefins and free from excessive amounts of aromatics and naphthenes. It is desirable, however, that the charge contain about .3 to 3% of aromatics or about 2 to 20% of naphthenes or a correspondingly diminishing amount of each if both are present, the higher concentrations being most desirable in the upper temperature range and the lower concentrations in the lower temperature range. Usually a crude virgin light naphtha will contain sufficient aromatics or naphthenes for C_7 isomerization and the important consideration is the removal of effective amounts of such aromatics or naphthenes from material which is recycled to the heptane isomerization unit.

Referring to Figure 1, a crude light naphtha boiling up to about 200 to 250° F. may be charged through line 11 to a fractionation system schematically illustrated as tower 12. In practice a series of towers will be employed instead of a single column. Propane and lighter hydrocarbons and gases may be taken overhead through line 13. Isobutane may be withdrawn through line 14 and introduced together with olefins from line 15 to alkylation system 16 to form an alkylate introduced by line 17 to storage tank 18. Normal butane may be withdrawn through line 19 to isomerizer system 20 and the product stream from the isomerizer may be returned to the fractionation system through line 21. Isopentane may be withdrawn through line 22 to storage tank 23. Normal pentane may be withdrawn through line 24 to pentane isomerizer 25 together with about .5 to 2% of aromatics from line 26. The isomerization products are returned by line 27 to fractionation system 12.

A fraction boiling between about 110° and about 135° F. and consisting chiefly of dimethyl butanes is withdrawn through line 28 to storage tank 29. A fraction boiling predominantly within the range of about 135° F. to about 165° F. is withdrawn by line 30 to hexane isomerization system 31 into which hydrogen is introduced through line 32. This stream will usually contain the desired amount of naphthenes or aromatics for inhibiting cracking. The product stream from the hexane isomerizer may be returned to the fractionation system through line 33.

A fraction boiling within the approximate range of about 165 to 185° F. may be withdrawn through line 34 to dimethyl pentane storage tank 35; this line may be unnecessary, however, when a separate fractionation system is employed in the heptane isomerization step per se. A fraction boiling within the approximate range of about 185° F. to about 205° F. is introduced by line 36 to heptane isomerization system 37 into which hydrogen is introduced through line 38. If dimethyl pentanes and triptane are not previously removed from the charging stock, then the boiling range of the fraction removed through line 36 may be about 165 to 205° F. Hydrocarbons boiling above 205° F. are withdrawn from the base of the fractionation system through line 39 to hydroformer 40. Here again, however, the heptane isomerization system itself may be employed to segregate the hydroformer charge in which case the end point of the fraction withdrawn through line 36 may be 215° F. or higher, i. e., at least high enough to include substantially all of the normal heptane. When normal heptane is thus included in the charge to line 36 there must, however, be sufficient recycle of methyl hexanes so that the normal heptane content of the charging stock which is actually introduced into the conversion zone will not exceed 10% and will preferably be below 5%.

The products from the heptane isomerization system are introduced through line 41 to the C_6 tower 42, the overhead from which it is returned by line 43 to fractionation system 12. The bottoms from tower 42 are introduced by line 44 to dimethyl pentane tower 45 the overhead stream from which it is introduced by line 46 to dimethyl pentane storage tank 35. The overhead stream from line 46 should boil within the approximate range of about 165° F. to about 185° F. and should consist essentially of dimethyl pentanes and triptane along with cyclohexane and benzene. This particular fraction boiling between 165 and 185° F. has been found to have a remarkably high octane number and what is still more important

is that it has the property of unusually high rich-mixture performance which makes it a valuable component for aviation gasoline.

The bottoms from line 46 are introduced into line 47 to fractionating column 48. Methyl hexanes together with dimethyl cyclopentanes, ethyl pentane, etc., i. e., the fraction boiling from about 185 to about 205° F., is removed as an overhead stream through line 49, condensed and recycled to line 36 for further isomerization in heptane isomerizer 37. It should be particularly pointed out that this recycle stream is substantially free from normal heptane as well as from naphthenes boiling above about 205° F.

The bottoms from fractionator column 48 are withdrawn through line 50 for introduction into hydroformer 40. This hydroformer or dehydroaromatization unit is preferably of the type employing a VIth group metal oxide on active alumina and it is operated under such conditions as to convert the charging stock to aromatics with a net production of hydrogen. Such units are well known in the art and no detailed description thereof is therefore necessary. Hydrogen from the hydroformer may supply lines 32 and 38 and any excess may be withdrawn through line 51. Aromatics may be separated and separately stored, e. g., in benzol tank 52, toluene tank 53, etc., and any unconverted or separated paraffinic hydrocarbons may be recycled by line 54 to fractionation system 12. It may be desirable to remove residual olefins from this predominantly paraffinic fraction before recycling by line 54 to fractionation system 12. This may be accomplished by subjecting the fraction to a sulfuric acid treating step or to a spent aluminum chloride catalyst complex treating step. As an alternate method the olefins in this fraction may be conserved by hydrogenation or alkylation with isoparaffin.

It will be noted from the above description that the lighter or heavier components formed in any of the isomerization or treating systems are automatically fractionated to provide charging stocks for other systems, all of the propane and lighter gases being withdrawn through line 13 and all of the heavier products being withdrawn as "polymer" through line 55 to the hydroformer. The dimethyl pentanes and triptane from tank 35 may be blended with the desired amounts of neohexanes from tank 29, isopentane from tank 23, alkylate from tank 18 and benzol from tank 52 for making an aviation gasoline of any desired volatility, octane number and rich mixture performance. The benzol from tank 52 may be alkylated for making isopropyl benzol, or other alkyl benzols which may be desirable for use in aviation fuels. As indicated in Figure 1, the various isomerization products, etc. may be blended to form aviation motor fuel which may be withdrawn from the system through line 56 or each fraction may be separately withdrawn for other specific purposes.

Figure 1 graphically illustrates the fact that the difficulty of isomerization increases with the length of the hydrocarbon chain to be isomerized it being understood, of course, that a Friedel-Crafts catalyst, preferably an aluminum halide-hydrocarbon complex, is employed for effecting the isomerization in each of these steps. Butane may be isomerized without addition of cracking inhibitors or hydrogen. Pentane does not require hydrogen but does require a cracking inhibitor which in this case is a small amount of aromatics supplied from benzol tank 52 via line

26. Hexane requires hydrogen for prolonging catalyst life and catalyst activity and if the charging stock to this system is deficient of aromatics or naphthenes such components should likewise be added to the charge. Normal hexane in large amounts is desirable in the charging stock to the hexane isomerization system.

Coming to heptane, however, I have discovered that the amount of normal heptane in the charging stock entering the isomerization system must be maintained within the critically small limits or entirely eliminated if catalyst life and catalyst activity are to be such as to make the process commercially feasible. The conversion conditions for heptane isomerization are somewhat milder than in the case of hexane isomerization, more hydrogen is required with higher operating pressures and cracking inhibitors should be employed. By eliminating normal heptane from the recycle stream and employing relatively large amounts of recycle stream as compared with incoming fresh feed I can effectively keep the normal heptane concentration in isomerizer 37 below 10% or even below 5% and by this means I can obtain almost quantitative conversion of heptanes to dimethyl pentanes and triptane.

It may be desirable to include in the feed to the heptane isomerization step sufficient paraffinic hydrocarbons of lower molecular weight than heptanes to further decrease the degeneration of the heptanes to these lighter products. This may be accomplished by closing valves (not shown) in the C_4, C_5, C_6 and the 165–185° F. fraction draw-off lines from fractionator 12. (See Figure 1.) The total drawoff which is thereby made by line 36 is sent to heptane isomerizer 37 and the product is sent to the heptane fractionation system from which the C_4, C_5 and C_6 is withdrawn as an overhead stream which is fractionated in a separate fractionating system (not shown) to supply separate C_4, C_5 and C_6 isomerization feed streams described above.

The heptane isomerization system itself is illustrated in more detail in Figure 2. The charging stock stream from line 36 is introduced at the upper part of hydrogen chloride absorber 57 which may be operated at a pressure of about 300 pounds per square inch and a temperature of about 100° F. Gases containing hydrogen chloride may be introduced at the base of the absorber through line 58 and make-up hydrogen chloride may be introduced through line 59. Unabsorbed gases are discharged from the top of the absorber through line 60. The charging stock which may contain about 6% of dissolved hydrogen chloride is then pumped by pump 61 through heater 62 to a low point in tower 63 which is about one-half to two-thirds full of an aluminum chloride-hydrocarbon complex. This complex may be made by the action of aluminum chloride on the charging stock itself in the presence of hydrogen chloride or it may be made from other hydrocarbons but it should not be made from olefins or aromatics, the best results being obtainable by complexes made from paraffins, particularly isoparaffins. Such complexes are already well known to those skilled in the art and will require no further detailed description.

Make-up aluminum chloride may be introduced through line 64 but I would preferably replenish the complex in this tower by introducing complex through line 65 from another tower as will be hereinafter described. Spent complex may be withdrawn from the base of the tower through

line 66. Hydrogen may be introduced through line 67 at the rate of about 200 cubic feet per barrel of stock charged.

The charging stock is passed upwardly through tower 63 at a space velocity of about .3 to 3, e. g., one volume of liquid feed per volume of catalyst in the tower per hour and at a feed rate within the range of about 45 to 450 gallons per hour per square foot of cross sectional area of reactor, the tower being maintained at a temperature of about 150 to 200° F., e. g., 175° F. and under a pressure within the range of about 300 to 3000 pounds per square inch, e. g., 1000 pounds per square inch. The product stream leaving tower 63 may pass through line 68 and cooler 69 to tower 70 which is likewise about one-half to three-fourths full of liquid complex and into which make-up aluminum chloride may be introduced through line 71 either as a slurry in oil or complex or as a solution in a light hydrocarbon or a portion of the charging stock or in any other suitable manner. About .2 to 2 pounds of aluminum chloride may be employed per barrel of stock charged. The relatively inactive catalyst from the base of tower 70 is preferably returned by pump 72 through line 65 for introduction into tower 63 although catalyst may be removed from the base of tower 70 through line 73. Tower 70 may be operated under substantially the same conditions as tower 63 but preferably at a temperature which is at least 25 degrees lower and which in this case may be about 150° F.

The overhead stream from tower 70 may be introduced by line 74 to hot settler 75 operating at substantially conversion temperature and pressure. Settled complex may be returned directly by lines 76 and 77 to tower 70. The product stream from hot settler 75 passes through line 78 to cooler 79 and pressure reducing valve 80 to cold settler 81 which may operate at about atmospheric temperature or about 100° F. and at a pressure slightly higher than the pressure maintained on absorber 57. Settled catalyst material may be withdrawn as a liquid or slurry through line 82 and returned by pump 83 to line 77 and tower 70. Hydrogen, hydrogen chloride and light gases leave the top of settler 81 through line 84 and are returned by line 58 to absorber 57. The liquid product flows over weir 85 and is withdrawn through line 86 to hydrogen chloride stripper 87 which is provided with a suitable heater 88 at its base. The stripped hydrogen chloride is returned via lines 89 and 58 to absorber 57.

The stripped product may be scrubbed with caustic in neutralizing system 90, washed with water in washing system 91 and then introduced by line 41 to hexane tower 42 from the top of which hexanes and lighter materials are withdrawn through line 43. The C_7 hydrocarbons are withdrawn from the base of tower 42 through line 44 and introduced into dimethyl pentane tower 45, the dimethyl pentane-triptane stream being withdrawn overhead through line 46 (165 to 185° F.). Methyl hexanes, normal heptane and high boiling naphthenes are withdrawn from the base of tower 45 through line 47 and introduced into fractionating column 48. The methyl hexanes are taken overhead through line 49, condensed and returned as recycle to line 36.

Any unconverted normal heptane is withdrawn from the system through line 50 together with methyl cyclohexane and higher boiling naphthenes. As above pointed out, this particular stock is a particularly valuable charge for dehydroaromatization to produce aromatics. Any paraffinic hydrocarbons separated from the aromatic products of dehydroaromatization may be returned for isomerization after suitable treatment to remove olefins if present in excess.

While I have described in detail a specific embodiment of my invention it should be understood that my invention is not limited thereto. The conversion conditions may vary throughout the ranges earlier set forth in the specification. Any number of towers may be employed in the conversion system and in fact the invention is applicable to heptane isomerization with other types of Friedel-Crafts catalysts in stirred reaction vessels or in reaction vessels containing supported catalysts. With other types of catalyst other conversion conditions may be desirable, for example, with hydrogen fluoride or an aqueous hydrogen fluoride boron fluoride catalyst higher temperatures may be employed than are desirable for the aluminum chloride-hydrocarbon complex.

If desired the neutralization and washing may be limited to the unrecycled product streams, i. e., to streams which are not returned to an aluminum halide or Friedel-Crafts conversion zone. The product fractionator may likewise serve as a feed stock fractionator by introducing the heptane charge through line 36*a* directly into hexane tower 42. In this system as well as in Figure 1 advantages are obtained by removing desired products from the original feed whereby the conversion zone itself might be operated more effectively. There are many other alternative arrangements and modifications which will be apparent from the above description to those skilled in the art.

I claim:

The method of producing heptanes having a plurality of branched chains from a hydrocarbon charging stock boiling within the light naphtha boiling range which charging stock contains more than 10% by volume of normal heptane and large amounts of methyl hexanes and cyclic hydrocarbons, the latter being of the class consisting of naphthenes and aromatic hydrocarbons, but which charging stock is substantially free from olefins and from hydrocarbons higher boiling than normal heptane, which method comprises diluting said charging stock with a recycle stream hereinafter defined in such amounts that the normal heptane content of the diluted charging stock is less than 5% by volume, contacting said diluted charging stock with an aluminum chloride-hydrocarbon complex isomerization catalyst promoted by hydrogen chloride in a conversion zone at a temperature in the range of 100 to 300° F., at a pressure within the range of 300 to 3000 pounds per square inch in the presence of added hydrogen, at a space velocity within the approximate range of .3 to 3 volumes of liquid charging stock per hour per volume of complex in the conversion zone and at a feed rate within the range of 45 to 450 gallons of liquid feed per hour per square foot of cross sectional conversion zone area, removing catalyst and activator from product effluent leaving the conversion zone, then fractionating said product effluent to obtain a fraction of heptanes having a plurality of branched chains and a methyl hexane fraction boiling chiefly within the range of 185° F. to 205° F. and substantially free from normal heptane and higher boiling hydrocarbons, recycling at least a part of said methyl hexane fraction for diluting charging stock as hereinabove set forth and withdrawing from the sys-

tem components of the product effluent which are higher boiling than said methyl hexane fraction.

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