March 18, 1947. S. H. McALLISTER ET AL 2,417,698

ISOMERIZING HYDROCARBONS

Filed May 16, 1942 2 Sheets-Sheet 1

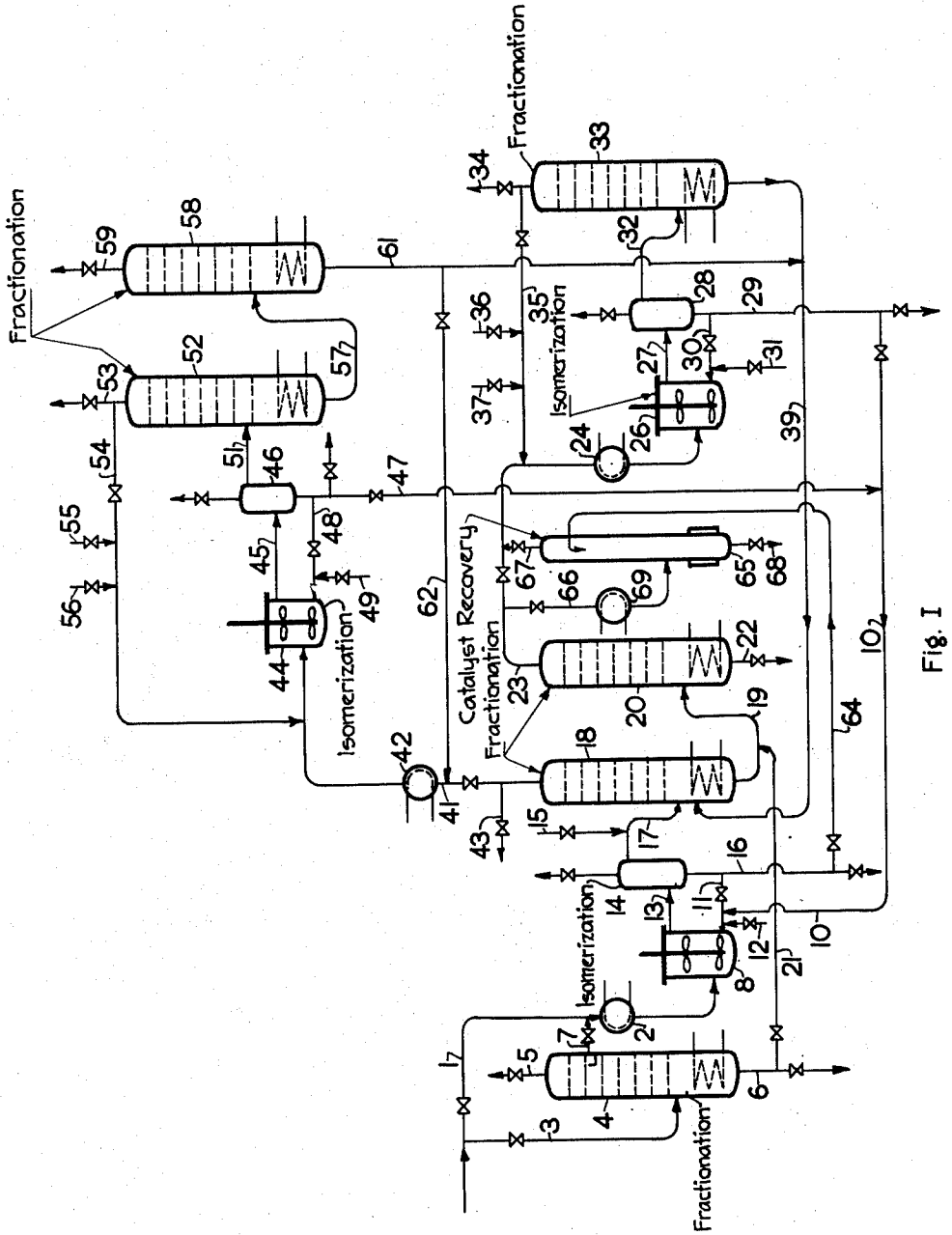


Fig. 1

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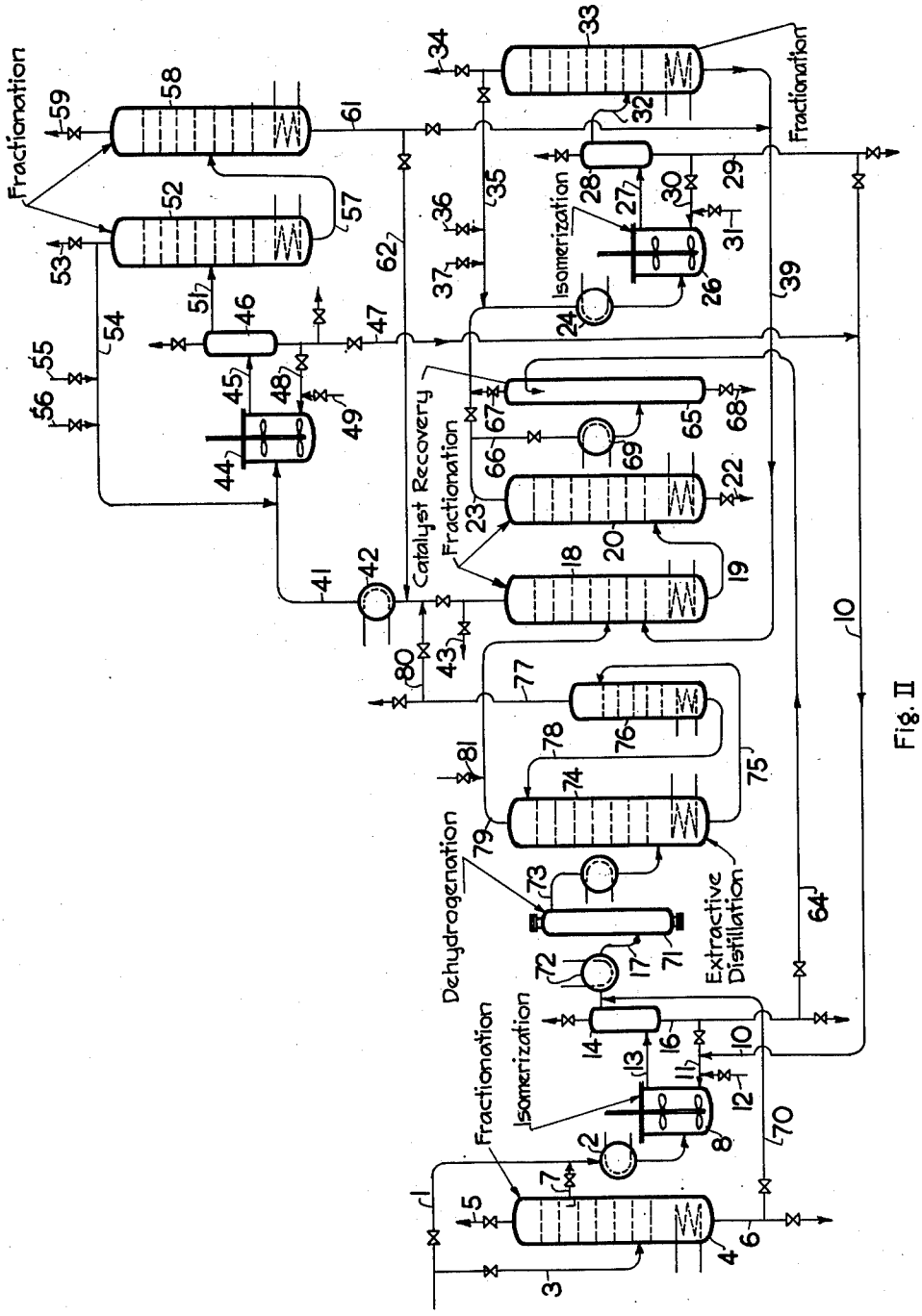


Fig. II

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ISOMERIZING HYDROCARBONS

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Application May 16, 1942, Serial No. 443,268

13 Claims. (Cl. 260—666)

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This invention relates to the production of high octane paraffinic hydrocarbon fractions from naphthenic petroleum fractions and relates more particularly to the production of multi-branched paraffin hydrocarbons from naturally occurring hydrocarbon mixtures.

The aluminum halides are applied successfully on a practical scale to the conversion of relatively pure paraffin hydrocarbons, particularly butane and pentane, to their respective branched chain isomers. The application of these processes to the treatment of paraffin hydrocarbons having more than five carbon atoms to the molecule is generally beset with difficulties, however, due to the difficulty of obtaining these hydrocarbons as relatively pure fractions. It is well known that the separation on a commercial scale of hydrocarbon fractions consisting essentially of only a single paraffin hydrocarbon from many readily available hydrocarbon mixtures, such as natural gas, petroleum, refinery products, etc., is often extremely impractical if not impossible. Thus a hexane or heptane fraction as obtained, for example, by the fractionation of natural gasoline, often comprises substantial amounts of other hydrocarbons, particularly naphthenes, which because of the proximity of their boiling points to those of paraffin hydrocarbons having the same number of carbon atoms cannot readily be separated therefrom by practical large scale fractionating methods. At least a substantial part of these naphthenes generally consist of naphthenes of non-hydroaromatic structure. The treatment of such fractions with aluminum halide catalysts in a single isomerization step in the absence of substantial hydrocarbon decomposition produces a relatively small rise in octane rating. Their treatment in accordance with methods disclosed heretofore furthermore generally produces only relatively small yields of the highly desirable multi-branched paraffin hydrocarbons, and attempts to increase the production in these processes of the multi-branched chain paraffins must generally be made at the expense of shortened catalyst life.

In co-pending application Serial No. 443,269, filed May 16, 1942, it has been shown that by the removal of naphthenes from the isomerization charge to at least a substantial degree, marked increase in the octane rating of the product is obtained with considerable increase in catalyst life. It has also been disclosed therein that in the treatment of hydrocarbons with aluminum halide catalysts the reaction rates and response to variations in catalyst activity and operating conditions of the naphthene and paraffin hydrocarbons differ considerably, and that by subjecting a mixture of these hydrocarbons to sufficiently mild isomerization conditions the naphthenes of non-hydroaromatic structure can be preferentially isomerized to naphthenes of hydroaromatic structure in which latter form they can be more readily removed from the admixed paraffins. This improved method, although superior to those disclosed heretofore for the production of high octane paraffin hydrocarbon fractions from naturally occurring hydrocarbon mixtures still does not enable the conversion of substantially all of the normal or single branched paraffins in the charge to the highly desired multi-branched chain paraffin isomers. By the term "hydroaromatic hydrocarbons" as used throughout this specification and claims is meant the naphthenes having a hexamethylene ring such as, for example, cyclohexane, the alkyl cyclohexanes, etc., to distinguish them from naphthenes of non-hydroaromatic structure comprising those having pentamethylene rings such as, for example, methyl cyclopentane, dimethyl cyclopentane, ethyl cyclopentane, etc.

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It is an object of the present invention to provide an improved process for the more efficient production of multi-branched chain paraffin hydrocarbons from naturally occurring hydrocarbon mixtures.

It is a further object of the invention to provide an improved process for the more efficient conversion of straight and singly branched chain paraffin hydrocarbons in admixture with naphthene hydrocarbons of non-hydroaromatic structure and having the same number of carbon atoms to the molecule to multi-branched chain paraffin hydrocarbons.

Another object of the invention is the provision of an improved process for the more efficient production of dimethyl butane from commercial hexane fractions obtained by the fractionation of naturally occurring hydrocarbon mixtures such as, for example, natural gasoline. Other objects and advantages of the invention will become apparent from the following detailed description thereof.

It has now been found that substantially increased yields of multi-branched chain paraffin hydrocarbons and much greater catalyst life are obtainable in the isomerization of saturated hydrocarbons when the mixture is subjected to isomerization conditions of progressively increased intensity. In a preferred embodiment of the invention the hydrocarbon mixture comprising, for example, paraffin and naphthene hydrocarbons of non-hydroaromatic structure, is subjected to mild isomerization conditions effective to convert naphthenes of non-hydroaromatic struc-

ture of naphthenes of hydroaromatic structure as the predominating reaction. Naphthenes are thereupon removed from the resulting products of the mild isomerization treatment and the remaining hydrocarbons are subjected to a more severe isomerization in a second conversion zone wherein the reaction variables are adjusted to produce predominantly single-branched paraffin hydrocarbons rather than multi-branched paraffin hydrocarbons. The resulting branched paraffin hydrocarbons are separated from the reaction products and subjected to isomerization conditions of preferably still greater intensity in a third conversion zone to convert less branched paraffin hydrocarbons to more highly branched chain paraffin hydrocarbons.

In order that the invention may be more readily understood it will be described herein with reference to the attached drawings forming part of this specification and wherein:

Figure I illustrates more or less diagrammatically one form of apparatus suitable for treating hydrocarbon fractions comprising paraffin hydrocarbons and naphthene hydrocarbons of non-hydroaromatic structure in accordance with the process of the invention and wherein the naphthenes are recovered as substantially pure hydroaromatic naphthene fractions, and

Figure II illustrates more or less diagrammatically a modified form of apparatus, wherein all parts of apparatus identical with those of Figure I are indicated with identical reference characters, suitable for the treatment of hydrocarbon fractions comprising paraffin hydrocarbons and naphthene hydrocarbons of non-hydroaromatic structure in accordance with the process of the invention, and wherein the naphthenes are recovered in the form of relatively pure aromatic hydrocarbon fractions.

A mixture of saturated hydrocarbons comprising straight chain paraffin hydrocarbons and naphthene hydrocarbons of non-hydroaromatic structure having the same number of carbon atoms to the molecule, such as a hexane fraction boiling, for example, within the range of from about 45° C. to about 85° C., comprising normal hexane, methyl cyclopentane and cyclohexane as obtained, for example, by fractionation of a natural gasoline, is passed through valved line 1, and heater 2, into a conversion zone. If the charge comprises substantial amounts of dimethyl butane and/or cyclohexane it may be subjected to a preliminary fractionation by passage through valved line 3 into a feed fractionator 4. Within fractionator 4 a light hydrocarbon fraction comprising substantial amounts of dimethyl butane may be separated as a vapor fraction and eliminated therefrom through valved line 5. If substantial amounts of cyclohexane are present in the charge a heavier fraction, for example, boiling above about 79° C. and comprising substantial amounts of the hydroaromatic naphthene hydrocarbon may be separated therefrom as a liquid fraction and withdrawn through valved line 6. The remainder of the charge comprising normal hexane and methyl cyclopentane, which because of the proximity of their boiling points cannot be readily separated, and some cyclohexane, is taken from fractionator 4 through valved line 7 and passed into line 1.

The conversion zone may comprise a reaction chamber 8 provided with suitable stirring means. Within reactor 8 the hydrocarbons are subjected to mild isomerization conditions whereby the non-hydroaromatic naphthene, methyl cyclopentane, is converted to the hydroaromatic naphthene, cyclohexane, as the predominant reaction. Suitable mild isomerization conditions are maintained within reactor 8 by the use of a catalyst of mild activity and/or a high ratio of hydrocarbon to catalyst, or a more active catalyst at a relatively low temperature with a high ratio of catalyst to hydrocarbon and short contact time. In a preferred method of operation the catalyst comprises a fluid catalyst of the molten salt type such as, for example, a molten mixture comprising aluminum chloride and antimony trichloride, the activity of which has been reduced by use in the treatment of paraffin hydrocarbons to a degree where the catalyst possesses but little if any ability to isomerize paraffin hydrocarbons. Thus it has been found that a catalyst of this type utilized in the isomerization of hexane to a degree where isomerization of hexane was no longer obtained, still possessed ability to isomerize naphthene hydrocarbons with equilibrium conversions. In the process of the invention, a catalyst comprising a molten mixture of aluminum chloride and antimony chloride which has been substantially spent in a paraffin isomerizing step of the process as described more fully below, is passed into reactor 8 through valved lines 10 and 11. When utilizing the molten salt catalyst of reduced activity a temperature below 80° C. and preferably not substantially above 75° C., and a phase ratio by volume of catalyst to hydrocarbon in the approximate range of 1:5 to 1:10 have been found suitable. It is to be pointed out that hydrogen halides are preferably present in only exceedingly small concentrations, for example, in amounts below about 0.5 per cent by weight of the hydrocarbon charge to the reaction zone. Under these mild conditions substantial conversion of methyl cyclopentane to cyclohexane is obtained as the predominating reaction, as shown by the following example.

Example I

A mixture of normal hexane and methyl cyclopentane consisting of 81.5% by weight of normal hexane and 18.5% by weight of methyl cyclopentane was treated at a temperature of 80° C. with a molten mixture of aluminum chloride and antimony chloride, the activity of which had been reduced by use in a previous hexane isomerization step until it had become substantially spent with respect to paraffin isomerization. A contact time of 7.5 minutes and a ratio of catalyst to hydrocarbon of 1:5 by volume was maintained. A conversion of methyl cyclopentane to cyclohexane of 50% was obtained in continuous single-pass operation, whereas the maximum conversion of normal hexane to methyl pentane attained only about 17.5%.

Although a catalyst comprising aluminum chloride and antimony chloride has been selected as a suitable catalyst, it is to be pointed out that other catalysts of the molten salt type, the activity of which has been reduced, such as, for example, $AlCl_3$—NaCl—KCl; $AlCl_3$—NaCl—$ZnCl_2$; $AlCl_3$—$ZnCl_2$—SO_2; $AlCl_3$—NaCl—KCl—$ZnCl_2$; etc., may be used. It is further to be understood that catalysts which are inherently relatively mild isomerization catalysts such as, for example, catalysts of the aluminum halide-hydrocarbon complex type obtained by the reaction of an aluminum halide such as aluminum chloride with a suitable hydrocarbon such as toluene, an unsaturated naphthene, and the like, or any other catalyst possessing mild isomerizing activity may be

used in the first conversions zone. It is to be noted that the aluminum halide-hydrocarbon complex type catalyst which may be used in reactor 8 contains no more aluminum halide than that in molecular combination with the hydrocarbon component of the catalyst and as such is devoid of any substantial amount of free aluminum halide. It has been found that the hydrocarbon-aluminum halide complex compound itself does not possess any appreciable ability to catalyze the isomerization of paraffin hydrocarbons, and that substantial paraffin isomerization is obtained only by the suspension of free aluminum halide therein. When using the aluminum chloride-hydrocarbon complex type catalyst, devoid of any substantial amounts of free $AlCl_3$, somewhat higher temperatures, for example, up to 100° C., preferably from about 60° C. to about 90° C., in the presence of small amounts of a hydrogen halide promoter, for example, below about 0.5% by weight of the charge, may be used. When a catalyst other than partially spent catalyst obtained in the process is used, such catalyst is introduced into the system through valved line 12. The criterion for proper operating conditions within the first conversion zone is the preferential conversion of non-hydroaromatic naphthenes to hydroaromatic naphthenes and the single factors comprising temperature, catalyst to hydrocarbon ratio and time of contact may vary within the scope of the invention to obtain the desired mild isomerization conditions. Thus a more active catalyst may be used with a lower temperature, or the use of a more active catalyst may be compensated for by the use of very low catalyst to hydrocarbon ratios as exemplified by the following example:

Example II

A mixture of normal hexane and methyl cyclopentane consisting of 81.5% by weight of normal hexane and 18.5% by weight of methyl cyclopentane was treated with a molten mixture of aluminum chloride and antimony chloride at a temperature of 75° C. with a contact time of 5 minutes and a ratio of catalyst to hydrocarbon of 1:18 by volume. A conversion of methyl cyclopentane to cyclohexane of 53% was obtained, whereas only 19% of the normal hexane was converted to methyl pentane.

Effluence from reactor 8 comprising normal hexane, cyclohexane, and entrained catalyst is passed through line 13 into separator 14 wherein separation of catalyst and hydrocarbons is effected. Separated catalyst is returned to reactor 8 through valved lines 16 and 11. After a period of time the catalyst will lose its activity even for naphthene isomerization. Spent catalyst is therefore withdrawn from the system regularly or intermittently through line 16. The separated hydrocarbons are passed through line 17 to a fractionator 18 wherein they are subjected to fractionation together with isomerized hexanes from a subsequent stage of the process. A liquid fraction comprising normal hexane and cyclohexane is passed from the lower part of fractionator 18, through line 19 into a second fractionator 20 wherein a hydrocarbon comprising cyclohexane is separated as a liquid fraction and removed therefrom through valved line 22 as a final product. If the charge to the system is subjected to prefractionation in feed fractionator 4, the heavier fraction removed through line 6 may be passed in part or in its entirety through line 21 into line 19. Hydrocarbons comprising normal hexane are passed overhead from fractionator 20 through line 23 and heater 24 into a second conversion zone.

Although but one reactor 8 is shown as constituting the first isomerizing zone a plurality of reactors connected in series or parallel may suitably be used. Additional fractionating means after the first conversion zone and between individual reactors thereof may be resorted to in order to effect the separation of cyclohexane as well as a lighter fraction comprising some hexanes and unconverted methyl cyclopentane which may be recycled. It is apparent that by such means substantially all of the non-hydroaromatic naphthenes are converted to the more readily removable hydroaromatic naphthenes.

Paraffin hydrocarbons consisting essentially of normal and single branched hexanes may be introduced from an outside source through valved line 15 into line 17 to be converted, together with the products emanating from separator 14, to multi-branched hexanes. This paraffin hydrocarbon stream may constitute at least a substantial part or even the total hydrocarbon charge to the process.

The second conversion zone may comprise a reactor 26 or a plurality of such reactors arranged in parallel or in series. Within the reactor 26 the hydrocarbons are subjected to conditions of isomerization which are more severe than those maintained within the first conversion zone. Heretofore the isomerization of such paraffin fractions for the production of high octane fractions has usually been effected under conditions most favorable to the formation of multi-branched chain paraffins. Such treatment in a single zone, it has been found, results not only in relatively shortened catalyst life but converts only relatively small amounts of the normal paraffins charged to the multi-branched chain isomers. In the process of the invention, conditions within reactor 26 are controlled to limit the formation of multi-branched paraffins and to produce primarily single branched paraffins. This is effected by maintaining isomerizing conditions of intermediate severity by selection of proper temperatures, contact time and catalyst to hydrocarbon ratio. A catalyst of high activity is used, however, in reactor 26. A particularly suitable catalyst comprises a molten mixture of aluminum chloride and antimony chloride. Other catalysts of the molten salt type such as

$AlCl_3$—NaCl—KCl

$AlCl_3$—NaCl—$ZnCl_2$

$AlCl_3$—NaCl—KCl—$ZnCl_2$

$AlCl_3$—SO_2—$ZnCl_2$

and isomerization catalysts other than the molten salt type possessing high activity may, however, be used. The single factors comprising temperature, catalyst to hydrocarbon ratio, time of contact and promoter content may vary within the scope of the invention to obtain the isomerization conditions of intermediate severity the criterion of which is the conversion of normal paraffins to branched paraffins with a minimum production of multi-branched chain paraffin hydrocarbons. Suitable isomerizing conditions of intermediate severity when utilizing the molten salt type catalysts of high activity comprise temperatures in the range of from 80° C. to 90° C.; a catalyst to hydrocarbon ratio by volume from about 1:2 to about 1:5; a contact time in the range of from about 5 to about 15 minutes; and the pres-

ence of a hydrogen halide promoter such as hydrogen chloride, for example, in amounts ranging from about 2 to about 10% of the charge. By maintaining such conditions within the second conversion zone, hexane will be converted to methyl pentanes with substantially increased catalyst life in the absence of both substantial formation of dimethyl butane and any substantial hydrocarbon decomposition, as illustrated by the following example:

Example III

A hexane fraction consisting predominantly of normal hexane was treated with a catalyst consisting of a molten mixture of aluminum chloride and antimony chloride at 85° C. with a catalyst to hydrocarbon ratio of 1:1.7, contact time of 16 minutes and the addition of 4% hydrogen chloride to the charge. 210 pounds of isomerizate having an increase in octane rating of 20 units over the charge were obtained per pound of aluminum chloride in the catalyst, 23.3 pounds of neohexane being produced per pound of $AlCl_3$. A second portion of the same hexane fraction was treated with a molten mixture of aluminum chloride and antimony chloride under conditions minimizing the conversion of normal hexane to neohexane by reducing the temperature to 80° C., the catalyst to hydrocarbon ratio to 1:5, the contact time to 4.5 minutes, and the hydrogen chloride addition to 2% of the charge. 548 pounds of isomerizate, having an increase in octane rating of 21.5 units over that of the charge, were obtained per pound of aluminum chloride in the catalyst; only 13 pounds of neohexane being produced per pound of $AlCl_3$. An average conversion of normal hexane to methyl pentanes of 46% was obtained when continuing the operation under the less severe conditions to a final conversion of normal hexane to methyl pentane of 14%.

The disadvantage of attempting to isomerize naphthenic hydrocarbon fractions in a single conversion zone, and more particularly the advantage obtained by removing naphthenes from the charge to the second conversion zone of the process, is illustrated by the following examples showing the effect of increased naphthene concentrations in the charge upon the efficiency of the conversion operation in terms of increase in octane rating of the product over the charge.

Example IV

Mixtures of normal hexane and methyl cyclopentane were treated at a temperature of about 85° C. with a molten aluminum chloride-antimony chloride catalyst. The contact time was approximately 30 minutes and the ratio of catalyst to hydrocarbon about 1:5 by volume. Hydrogen chloride was added to the charge in the amount of 4% by weight of the hydrocarbon feed. The increase in octane number of the products over that of the feeds is given in the following table:

Weight per cent methyl cyclopentane in feed	Octane number increase of product
0	58
7	52
15	45
36	25

Effluence from reactor **26** comprising methyl pentane, unconverted hexane, hydrogen halide promoter and entrained catalyst is passed from reactor **26** through line **27** into separator **28** wherein separation of catalyst from hydrocarbons is effected. Separated catalyst is returned to reactor **26** through valved lines **29** and **30**. Fresh catalyst is introduced into reactor **26** from an external source by means of valved line **31**.

Hydrocarbon and promoter are passed from separator **28** through line **32** into a stripping column **33**. Within column **33** a lighter fraction comprising the hydrogen halide promoter is separated and eliminated overhead through valved line **34**. A part or all of the lighter fraction passing through line **34** is recycled through line **35** into line **23**. Make-up hydrogen halide promoter is introduced from an outside source into line **35** by means of valved line **36**. The conversion within the second conversion zone may be effected in the presence of diluent gases or agents such as hydrogen, isobutane or the like, capable of suppressing hydrocarbon decomposition. These may be introduced into line **35** from an outside source through valved line **37**.

A hydrocarbon fraction comprising methyl pentane and unconverted normal hexane is passed from the lower part of fractionator **33** through valved line **39** into fractionator **18** to be fractionated therein. A hydrocarbon fraction comprising methyl pentane is separated within fractionator **18** and passed therefrom through valved line **41**. If desired, a part or all of the products passing through line **41** may be removed from the system as a final product through valved line **43**. The methyl pentanes are, however, preferably passed through line **41** and heater **42** into a third conversion zone. The third conversion zone may comprise a reactor **44** provided with suitable stirring means, or a plurality of such reactors arranged in series or in parallel.

Within reactor **44** the methyl pentanes are subjected to catalytic isomerization conditions favorable to their conversion to dimethyl butane. Isomerization conditions of greater severity than those in the second conversion zone are preferably maintained within reactor **44**. Suitable catalysts comprise isomerization catalysts of high activity such as those described above for use in the second conversion zone. Proper conditions are obtained by increase in one or several of the factors comprising temperature, time of contact, catalyst to hydrocarbon ratio, or hydrogen chloride promoter content over those maintained in reactor **26**. The following example illustrates the efficient conversion of methyl pentane to neohexane obtained with a contact time of 30 minutes.

Example V

Methyl pentane was treated with a molten mixture comprising 92.5% by weight of $SbCl_3$ and 7.5% by weight of $AlCl_3$ at a temperature of 80° C. with a contact time of 30 minutes and a ratio of catalyst to hydrocarbon of 1:5 by volume. Hydrogen chloride and benzene in amounts of 2.5 and 1.1% by weight respectively of the methyl pentane charge were introduced into the reactor. A conversion of methyl pentane to dimethyl butane of 37.4% was obtained.

Excessively high temperatures at which substantial hydrocarbon decomposition is obtained are, however, avoided within reactor **44**. Thus when utilizing the molten salt type catalyst, temperatures in the range of from about 80° C. to about 125° C., and preferably from 80° C. to 95° C., are found suitable.

Effluence from reactor **44** comprising dimethyl butane, unconverted methyl pentane and hydro-

gen halide is passed through line 45 into separator 46 wherein separation of catalyst from hydrocarbons is effected. Separated catalyst is returned through valved lines 47 and 48 to reactor 44. Fresh catalyst is introduced into reactor 44 from an outside source by means of valved line 49. Hydrocarbons and promoter are passed from separator 49 through line 51 into a stripping column 52. Within column 52 a lighter fraction comprising hydrogen halide is separated and removed overhead through valved line 53. A part or all of the material passing through line 53 is recycled through line 54 into line 41. Make-up hydrogen halide is introduced into line 54 from an outside source through valved line 55. A diluent gas or an agent capable of suppressing hydrocarbon decomposition such as hydrogen, isobutane, benzene, etc., may be used in the third conversion zone, and is introduced into line 54 from an outside source through valved line 56. A hydrocarbon fraction comprising dimethyl butane and methyl pentane is passed from column 52 through line 57 into fractionator 58. Within fractionator 58 a hydrocarbon fraction comprising dimethyl butane is separated and removed overhead therefrom through valved line 59 as the final product. A liquid fraction comprising unreacted methyl pentane and some normal hexane formed within reactor 44 is separated within fractionator 58 and passed therefrom through valved line 61 into line 39 leading to fractionator 18. A part of the hydrocarbons flowing through line 61 may be recycled through valved line 62 to aid in suppressing the formation of normal hexane within reactor 44.

When molten salt type catalysts are used in reactors 26 and 44 and a molten salt type catalyst of reduced activity is used as the catalyst in reactor 8 the catalyst which has become at least partially spent with respect to paraffin isomerization and which is withdrawn from separators 28 and 46 through lines 29 and 47, respectively, is passed in part or in its entirety through valved lines 10 and 11 into reactor 8. After a period of use in reactor 8 the molten salt catalyst will become inactive even for the isomerization of the non-hydroaromatic naphthenes. Such spent catalyst is removed from separator 14 through valved line 16. In a preferred method of executing the process of the invention, at least a part of the spent catalyst passing through line 16 is passed through valved line 64 into the upper part of a scrubber 65. Within scrubber 65 the spent catalyst is contacted countercurrently with a part or all of the hydrocarbon stream, in the liquid state, flowing through line 23. To this effect a valved line is provided leading from line 66 into an intermediate part of scrubber 65. Within scrubber 65 the more soluble catalyst components, which in the case of the $AlCl_3$—$SbCl_3$ catalyst will comprise $SbCl_3$, is recovered from the spent catalyst by solution in the hydrocarbon. The hydrocarbon stream comprising dissolved catalyst components is passed from scrubber 65 through valved line 67 back into line 23. Spent catalyst consisting essentially of a carbonaceous aluminum chloride-containing material settles to the lower part of scrubber 65 and is removed therefrom through valved line 68. The temperature to be maintained within scrubber 65 will depend upon the nature of the spent catalyst introduced therein. In general, a temperature in the range of from 80° C. to 90° C. has been found suitable and may be maintained therein by use of a suitable heat exchanger 69.

The particular steps by which the hydroaromatic naphthene hydrocarbons are removed from the products emanating from the first conversion zone may vary within the scope of the invention. Thus this phase of the process may comprise, besides fractionation, one or more of such steps as dehydrogenation, solvent extraction, extractive distillation, hydroforming, etc. Whereas in the treatment of a naphthenic hexane fraction, fractionation is found to be highly suitable, this method is often rendered impractical with hydrocarbon fractions comprising hydrocarbons of more than six carbon atoms to the molecule, due to the complexity of the hydrocarbon mixture and the proximity of the boiling points of certain of the hydroaromatic naphthene hydrocarbons to those of the paraffin constituents. Thus, in the treatment of a naphthenic hydrocarbon fraction comprising hydrocarbons having, for example, seven carbon atoms to the molecule, the products of the first conversion zone comprise the hydroaromatic naphthene, methyl cyclohexane, the boiling point of which differs by only about two degrees from that of the normal heptane admixed therewith.

When treating a naphthenic hydrocarbon fraction comprising hydrocarbons having more than six carbon atoms to the molecule, the removal of the hydroaromatic naphthenes from the products emanating from the naphthene isomerizing zone may comprise such steps as the conversion of the hydroaromatic naphthenes to aromatic hydrocarbons, and the separation of the resulting aromatics by solvent extraction, extractive distillation, or other suitable methods. Thus, referring to Figure II, a mixture of saturated hydrocarbons consisting essentially of paraffins and cycloparaffins of non-hydroaromatic and hydroaromatic structure having more than six carbon atoms to the molecule such as, for example, a heptane fraction having a boiling range from about 85° C. to about 105° C., comprising normal heptane, dimethyl cyclopentane, ethyl cyclopentane and methyl cyclohexane, as obtained by fractionation of a naphthenic straight run gasoline, is introduced into the system through line 1. If the charge contain but a minor amount of ethyl cyclopentane and substantial amounts of methyl cyclohexane, it may be desirable to subject the charge to a preliminary fractionation in fractionator 4 to separate a heavier fraction predominating in methyl cyclohexane as a bottom fraction, which is withdrawn through line 6. The remainder of the charge comprising substantially all of the normal heptane and dimethyl cyclopentanes is passed as a side stream from fractionator 4 through lines 7 and 1 into reactor 8. Within reactor 8 the hydrocarbons are treated as described above to selectively convert the non-hydroaromatic naphthenes comprising the methyl cyclopentanes and ethyl cyclopentanes to hydroaromatic naphthenes comprising methyl cyclohexanes. The products from reactor 8 comprising normal heptane and methyl cyclohexane are passed through line 17 into a dehydrogenating zone. If the charge to the system is subjected to a pre-fractionation in feed fractionator 4, the heavier fraction removed through line 6 may be passed in part or in its entirety through line 70 into line 17.

The dehydrogenating zone may comprise a reactor 71 or a plurality of reactors connected in series or in parallel. Within reactor 71 the hydrocarbon stream is contacted with a catalyst under conditions at which the hydroaromatic naph-

thenes will be converted to aromatic hydrocarbons. It is preferred to use a catalyst of the nickel-tungsten-sulfur type, which it has recently been found is particularly effective in selectively converting hydroaromatic naphthenes to aromatic hydrocarbons. The invention, however, is not limited to the use of this preferred type of catalyst, and other dehydrogenation catalysts comprising, for example, chromium oxide or molybdenum oxide on alumina or zirconia may be used. The dehydrogenation is effected at a temperature in the range of, for example, from about 400° C. to about 550° C., preferably at elevated pressures, for example, above about 350 pounds, in the presence of added hydrogen. The desired temperature conditions are maintained within reactor 71 by means of heater 72 and if desired by other means, not shown in the drawing, for supplying heat from an outside source.

Products from reactor 71 comprising paraffin and aromatic hydrocarbons including, for example, normal heptane and toluene, are passed through line 73 to an extractive distillation column 74 wherein they are extractively distilled in the presence of a suitable solvent having preferential solvent power for the aromatic hydrocarbons. Suitable solvents comprise, for example, one or a mixture of the following: phenol, cresylic acids, alkyl phenol mixtures, etc. Bottoms from column 74 comprising solvent and aromatic hydrocarbons are passed through line 75 to a distillation column 76 wherein aromatic hydrocarbons comprising toluene are separated from the solvent. Aromatic hydrocarbons comprising toluene are removed as overhead from column 76 through valved line 77 as a final product. The lean solvent is returned from column 76 to the upper part of column 74 by means of line 78.

Overhead from column 74 comprising paraffinic C_7 hydrocarbons is passed through line 79 into fractionator 18. Thence the paraffinic hydrocarbons are treated as described above at isomerizing conditions of progressively increased intensity to obtain multi-branched paraffin hydrocarbons having seven carbon atoms to the molecule as the final product. Paraffin hydrocarbons consisting essentially of normal and singly branched heptanes may be introduced into line 79 through valved line 81 to be converted, together with the products emanating from fractionator 74, to multi-branched chain heptanes. Such paraffinic hydrocarbon fractions may constitute at least a substantial part or even the total hydrocarbon charge to the process.

It has been found that the presence of minor amounts of aromatic hydrocarbons such as benzene, toluene, etc., in the third conversion zone has the ability to suppress decomposition of the branched chain paraffins. Addition in amounts of, for example, from about 1% to about 3% by weight of the charge to reactor 44 have been found suitable. Higher or lower concentrations may, however, be used. The aromatic hydrocarbons may be introduced into the system through line 56. When aromatics are obtained within the system as in the method illustrated in Figure II, a part of such aromatics may be passed through valved line 80 directly into line 41 carrying the charge to the third conversion zone.

The process of the invention is preferably executed in the liquid phase. Pressures sufficiently high to maintain at least a substantial part of the hydrocarbons being treated in the liquid phase are therefore maintained within the conversion zones.

The invention can be applied with particular advantage to the treatment of hydrocarbon mixtures predominating in paraffin and naphthene hydrocarbons having the same number of carbon atoms to the molecule, such as the fractions of relatively narrow boiling range readily obtained by fractionation on a practical scale of naturally occurring naphthenic hydrocarbon mixtures, although it is to be pointed out that the invention is not necessarily limited thereto. Thus it is within the scope of the invention to treat naphthenic hydrocarbon fractions of relatively wider boiling range such as, for example, a fraction comprising the paraffin and naphthene hydrocarbons of both six and seven carbon atoms to the molecule. The wider boiling fraction may be subjected to the first conversion step of the process and the resulting hydrocarbon mixture subjected to a plurality of steps, not shown in the drawing, which may comprise one or more such treatments as fractionation, solvent extraction, dehydrogenation, extractive distillation, etc., to effect the separation of naphthenes from the paraffins. The resulting paraffin fractions may then be subjected separately or combined to the other conversion steps of the process for the production of high octane paraffin fractions predominating in branched chain hydrocarbons. Olefins, aromatic hydrocarbons and impurities which are deleterious to catalyst life are preferably removed to at least a substantial degree from the charge by pretreatment which may comprise one or more of such steps as treatment with mineral acid, adsorbent clays, spent isomerization catalysts, etc.

For the purpose of clarity, all parts of apparatus not essential to a complete description of the invention such as, for example, pumps, condensers, accumulators, and the like, have been omitted from the drawing. It is to be understood that the apparatus shown may be modified as apparent to one skilled in the art without departing from the scope of the invention. Thus, for example, heaters 2, 24, 42 and 72 may consist of any suitable indirect heat exchanging means, fluid heaters comprising externally heated elongated coils positioned in furnace structures, or the like. In practical operation of the process of the invention, the hydrocarbon streams withdrawn from separators 14, 28 and 46 are preferably subjected to a fractionating step, by means not shown in the drawing, to remove entrained or dissolved catalyst components therefrom prior to their passage to any subsequent part of the system.

We claim as our invention:

1. Process for the production of dimethylbutane from hydrocarbon mixtures comprising normal hexane and methylcyclopentane which comprises contacting the hydrocarbon mixture with a partially spent aluminum chloride-containing isomerization catalyst of the molten salt type in a first conversion zone at a temperature not substantially in excess of about 80° C. in the presence of an added hydrogen halide promoter not substantially in excess of about 0.5 per cent by weight of the hydrocarbon charge, thereby effecting the conversion of methylcyclopentane to cyclohexane as the predominating reaction, separating naphthenes comprising cyclohexane from the effluence of the first conversion zone, contacting the remaining hydrocarbons comprising normal hexane with an aluminum chloride-containing isomerization catalyst of the molten salt type in the presence of an added hydrogen halide promoter in

a second conversion zone at a temperature in the range of from about 80° C. to about 90° C. and a correlated contact time of from about 5 to about 15 minutes so as to effect the conversion of normal hexane to methylpentane with a minimum formation of dimethylbutane, separating a hydrocarbon fraction predominating in methylpentane from the effluence of the second conversion zone, contacting said methylpentane fraction in admixture with a hydrogen halide promoter with an aluminum chloride-containing isomerization catalyst of the molten salt type in a third conversion zone at a temperature in the range of from about 80° C. to about 125° C. and a time of contact sufficiently long to effect the conversion of methylpentane to dimethylbutane as the predominant reaction, passing partially spent catalyst from the second and third conversion zones to the first conversion zone, and maintaining an increase in at least one of the isomerizing conditions of temperature, catalyst activity and time of contact in each of said conversion zones over that maintained in each preceding conversion zone, thereby maintaining isomerizing conditions of progressively increased intensity through said conversion zones.

2. Process for the production of multi-branched paraffin hydrocarbons from hydrocarbon mixtures comprising straight chain paraffin hydrocarbons having at least six carbon atoms to the molecule and naphthene hydrocarbons of non-hydroaromatic structure having the same number of carbon atoms to the molecule which comprises contacting the hydrocarbon mixture with a partially spent aluminum chloride-containing isomerization catalyst of the molten salt type in a first conversion zone at a temperature not substantially in excess of about 80° C. in the presence of an added hydrogen halide promoter not substantially in excess of about 0.5 per cent by weight of the hydrocarbon charge, thereby effecting the conversion of naphthenes of non-hydroaromatic structure to naphthenes of hydroaromatic structure as the predominant reaction, separating naphthenes comprising naphthenes of hydroaromatic structure from the effluence of the first conversion zone, contacting the remaining hydrocarbons comprising straight chain paraffins with an aluminum chloride-containing isomerization catalyst of the molten salt type in the presence of an added hydrogen halide promoter in a second conversion zone at a temperature in the range of from about 80° C. to about 90° C. and a correlated contact time of from about 5 to about 15 minutes so as to effect the conversion of straight chain paraffins to single-branched paraffins with a minimum formation of multi-branched paraffins, separating a hydrocarbon fraction predominating in single-branched paraffins from the effluence of the second conversion zone, and contacting said fraction predominating in single-branched paraffins in admixture with a hydrogen halide promoter with an aluminum chloride-containing isomerization catalyst of the molten salt type in a third conversion zone at a temperature in the range of from about 80° C. to about 125° C. and a time of contact sufficiently long to effect the conversion of single-branched paraffins to multi-branched paraffins as the predominant reaction, passing partially spent catalyst from the second and third conversion zones to the first conversion zone, and maintaining an increase in at least one of the isomerizing conditions of temperature, catalyst activity and time of contact in each of said conversion zones over that maintained in each preceding conversion zone, thereby maintaining isomerizing conditions of progressively increased intensity through said conversion zones.

3. Process for the production of multi-branched paraffin hydrocarbons from hydrocarbon mixtures comprising straight chain paraffin hydrocarbons having at least six carbon atoms to the molecule and naphthene hydrocarbons of non-hydroaromatic structure having the same number of carbon atoms to the molecule, which comprises contacting the hydrocarbon mixture with a partially spent aluminum halide-containing isomerization catalyst of the molten salt type in a first conversion zone at a temperature not substantially in excess of about 80° C. in the presence of an added hydrogen halide promoter, thereby effecting the conversion of naphthenes of non-hydroaromatic structure to naphthenes of hydroaromatic structure as the predominant reaction, separating naphthenes comprising naphthenes of hydroaromatic structure from the effluence of the first conversion zone, contacting the remaining hydrocarbons comprising straight chain paraffins with an aluminum halide-containing isomerization catalyst of the molten salt type in the presence of a hydrogen halide promoter in a second conversion zone at a temperature in the range of from about 80° C. to about 90° C., limiting the time of contact of hydrocarbons and catalyst in the second conversion zone so as to effect the conversion of straight chain paraffins to single-branched paraffins with a minimum formation of multi-branched paraffins, separating a fraction predominating in single-branched paraffins from the effluence of the second conversion zone, contacting said fraction predominating in single-branched paraffins in admixture with a hydrogen halide promoter with an aluminum halide-containing isomerization catalyst of the molten salt type in a third conversion zone at a temperature in the range of from about 80° C. to about 125° C. and a time of contact sufficiently long to effect the conversion of single-branched paraffins to multi-branched paraffins as the predominant reaction, passing partially spent catalyst from the second and third conversion zones to the first conversion zone, and maintaining an increase in at least one of the isomerizing conditions of temperature, catalyst activity and time of contact in each of said conversion zones over that maintained in each preceding conversion zone, thereby maintaining isomerizing conditions of progressively increased intensity through said conversion zones.

4. Process for the production of multi-branched paraffin hydrocarbons from hydrocarbon mixtures comprising straight chain paraffin hydrocarbons having at least six carbon atoms to the molecule and naphthene hydrocarbons of non-hydroaromatic structure having the same number of carbon atoms to the molecule, which comprises contacting the hydrocarbon mixture with a partially spent aluminum halide-containing isomerization catalyst of the molten salt type in a first conversion zone at a temperature not substantially in excess of about 80° C. in the presence of an added hydrogen halide promoter, thereby effecting the conversion of naphthenes of non-hydroaromatic structure to naphthenes of hydroaromatic structure as the predominant reaction, separating naphthenes comprising naphthenes of hydroaromatic structure from the effluence of the first conversion zone, contacting

the remaining hydrocarbons comprising straight chain paraffins with an aluminum halide-containing isomerization catalyst of the molten salt type in the presence of a hydrogen halide promoter in a second conversion zone at a temperature in the range of from about 80° C. to about 90° C., limiting the time of contact of hydrocarbons and catalyst in the second conversion zone so as to effect the conversion of straight chain paraffins to single-branched paraffins with a minimum formation of multi-branched paraffins, separating a fraction predominating in single-branched paraffins from the effluence of the second conversion zone, contacting said fraction predominating in single-branched paraffins in admixture with a hydrogen halide promoter with an aluminum halide-containing isomerization catalyst of the molten salt type in a third conversion zone at a temperature in the range of from about 80° C. to about 125° C. and a time of contact sufficiently long to effect the conversion of single-branched paraffins to multi-branched paraffins as the predominant reaction, passing partially spent catalyst from the second and third conversion zones to the first conversion zone, contacting spent catalyst drawn from the first conversion zone with at least a portion of the charge to the second conversion zone, and maintaining an increase in at least one of the isomerizing conditions of temperature, catalyst activity and time of contact in each of said conversion zones over that maintained in each preceding conversion zone, thereby maintaining isomerizing conditions of progressively increased intensity through said conversion zones.

5. Process for the production of dimethylbutane from hydrocarbon mixtures comprising normal hexane and methylcyclopentane, which comprises contacting the hydrocarbon mixture with an aluminum chloride-hydrocarbon complex catalyst substantially free of free aluminum chloride in a first conversion zone at a temperature of from about 60° C. to about 90° C. in the presence of an added hydrogen halide promoter not substantially in excess of about 0.5 per cent by weight of the hydrocarbon charge, thereby effecting the conversion of methylcyclopentane to cyclohexane as the predominating reaction, separating naphthenes comprising cyclohexane from the effluence of the first conversion zone, contacting the remaining hydrocarbons comprising normal hexane with an aluminum chloride-containing isomerization catalyst of the molten salt type in the presence of a hydrogen halide promoter in a second conversion zone at a temperature in the range of from about 80° C. to about 90° C. and a correlated contact time of from about 5 to about 15 minutes so as to effect the conversion of normal hexane to methylpentane with a minimum formation of dimethylbutane, separating a hydrocarbon fraction predominating in methylpentane from the effluence of the second conversion zone, contacting said methylpentane fraction in admixture with a hydrogen halide promoter with an aluminum chloride-containing isomerization catalyst of the molten salt type in a third conversion zone at a temperature in the range of from about 80° C. to about 125° C. and a time of contact sufficiently long to effect the conversion of methylpentane to dimethylbutane as the predominating reaction, and maintaining an increase in at least one of the isomerizing conditions of temperature, catalyst activity and time of contact in each of said conversion zones over that maintained in each preceding conversion zone, thereby maintaining isomerizing conditions of progressively increased intensity through said conversion zones.

6. Process for the production of dimethylbutane from hydrocarbon mixtures comprising normal hexane and methylcyclopentane, which comprises contacting the hydrocarbon mixture with an aluminum chloride-hydrocarbon complex catalyst substantially free of free aluminum chloride in a first conversion zone at a temperature of from about 60° C. to about 90° C. in the presence of an added hydrogen halide promoter not substantially in excess of about 0.5 per cent by weight of the hydrocarbon charge, thereby effecting the conversion of methylcyclopentane to cyclohexane as the predominating reaction, separating naphthenes comprising cyclohexane from the effluence of the first conversion zone, contacting the remaining hydrocarbons comprising normal hexane with an aluminum chloride-containing isomerization catalyst of the molten salt type in the presence of a hydrogen halide promoter in a second conversion zone at a temperature in the range of from about 80° C. to about 90° C., limiting the time of contact of hydrocarbons and catalyst in the second conversion zone so as to effect the conversion of normal hexane to methylpentane with a minimum formation of dimethylbutane, separating a fraction predominating in methylpentane from the effluence of the second conversion zone, contacting said fraction comprising methylpentane in admixture with a hydrogen halide promoter with an aluminum chloride-containing isomerization catalyst of the molten salt type in a third conversion zone at a temperature in the range of from about 80° C. to about 125° C. and a time of contact sufficiently long to effect the conversion of methylpentane to dimethylbutane as the predominating reaction, and maintaining an increase in at least one of the isomerizing conditions of temperature, catalyst activity and time of contact in each of said conversion zones over that maintained in each preceding conversion zone, thereby maintaining isomerizing conditions of progressively increased intensity through said conversion zones.

7. Process for the production of multi-branched paraffin hydrocarbons from hydrocarbon mixtures comprising straight chain paraffins having at least six carbon atoms to the molecule and naphthene hydrocarbons of non-hydroaromatic structure having the same number of carbon atoms to the molecule, which comprises contacting the hydrocarbon mixture with an aluminum halide-hydrocarbon complex catalyst substantially free of free aluminum halide in a first conversion zone at a temperature of from about 50° C. to about 100° C. in the presence of a hydrogen halide promoter, thereby effecting the conversion of naphthenes of non-hydroaromatic structure to naphthenes of hydroaromatic structure as the predominant reaction, separating naphthenes comprising naphthenes of hydroaromatic structure from the effluence of the first conversion zone, contacting the remaining hydrocarbons comprising straight chain paraffins with an aluminum halide-containing isomerization catalyst of the molten salt type in the presence of a hydrogen halide promoter in a second conversion zone at a temperature in the range of from about 80° C. to about 90° C., limiting the time of contact of hydrocarbons and catalyst in the second conversion zone so as to effect the conversion of straight chain paraffins to single-branched paraffins with a minimum formation

of multi-branched paraffins, separating a fraction predominating in single-branched paraffins from the effluence of the second conversion zone, contacting said fraction predominating in single-branched paraffins in admixture with a hydrogen halide promoter with an aluminum halide-containing isomerization catalyst of the molten salt type in a third conversion zone at a temperature in the range of from about 80° C. to about 125° C. and a time of contact sufficiently long to effect the conversion of single-branched paraffins to multi-branched paraffins as the predominant reaction, and maintaining an increase in at least one of the isomerizing conditions of temperature, catalyst activity and time of contact in each of said conversion zones over that maintained in each preceding conversion zone, thereby maintaining isomerizing conditions of progressively increased intensity through said conversion zones.

8. Process for the production of multi-branched paraffin hydrocarbons from hydrocarbon mixtures comprising straight chain paraffins having at least six carbon atoms to the molecule and naphthene hydrocarbons of non-hydroaromatic structure having the same number of carbon atoms to the molecule, which comprises contacting the hydrocarbon mixture with an aluminum halide-hydrocarbon complex catalyst substantially free of free aluminum halide in a first conversion zone at a temperature of from about 50° C. to about 100° C. in the presence of a hydrogen halide promoter not substantially in excess of about 0.5 per cent by weight of the hydrocarbon charge, thereby effecting the conversion of naphthenes of non-hydroaromatic structure to hydrocarbons of hydroaromatic structure as the predominant reaction, separating naphthenes comprising naphthenes of hydroaromatic structure from the effluence of the first conversion zone, contacting the remaining hydrocarbons comprising straight chain paraffins with an aluminum halide-containing isomerization catalyst of the molten salt type in the presence of a hydrogen halide promoter in a second conversion zone at a paraffin isomerizing temperature below about 90° C., limiting the time of contact of hydrocarbons and catalyst in the second conversion zone to effect the conversion of straight chain paraffins to single-branched paraffins with a minimum formation of multi-branched paraffins, separating a hydrocarbon fraction predominating in multi-branched paraffins from the effluence of the second reaction zone, contacting said fraction comprising multi-branched hydrocarbons in admixture with a hydrogen halide promoter with an aluminum halide-containing isomerization catalyst of the molten salt type in a third conversion zone at a temperature in the range of from about 80° C. to about 125° C. and a time of contact sufficiently long to effect the conversion of single-branched paraffins to multi-branched paraffins as the predominant reaction, and maintaining an increase in at least one of the isomerizing conditions of temperature, catalyst activity and time of contact in each of said conversion zones over that maintained in each preceding conversion zone, thereby maintaining isomerizing conditions of progressively increased intensity through said conversion zones.

9. Process for the production of dimethylbutane from hydrocarbon mixtures comprising normal hexane and methylcyclopentane which comprises contacting the hydrocarbon mixture with an aluminum halide-hydrocarbon complex catalyst substantially free of free aluminum halide in a first conversion zone under sufficiently mild isomerization conditions to effect the conversion of methylcyclopentane to cyclohexane as the predominating reaction, separating naphthenes comprising cyclohexane from the hydrocarbon mixture after the mild isomerization treatment, contacting the remaining hydrocarbons comprising normal hexane in admixture with a hydrogen halide promoter with an aluminum halide-containing isomerization catalyst of the molten salt type in a second conversion zone at a paraffin isomerizing temperature below about 90° C., limiting the time of contact of hydrocarbons with the catalyst in the second conversion zone to effect the conversion of normal hexane to methylpentane with a minimum formation of dimethylbutane, separating a fraction predominating in methylpentane from the effluence of the second conversion zone, contacting said fraction comprising methylpentane in admixture with hydrogen halide with an aluminum halide-containing isomerization catalyst of the molten salt type in a third conversion zone at a temperature in the range of from about 80° C. to about 125° C. and a time of contact sufficiently long to effect the conversion of methylpentane to dimethylbutane as the predominant reaction, and maintaining an increase in at least one of the isomerizing conditions of temperature, catalyst activity and time of contact in each of said conversion zones over that maintained in each preceding conversion zone, thereby maintaining isomerizing conditions of progressively increased intensity through said conversion zones.

10. Process for the production of multi-branched paraffin hydrocarbons from hydrocarbone mixtures comprising straight chain paraffins having at least six carbon atoms to the molecule and naphthene hydrocarbons of non-hydroaromatic structure having the same number of carbon atoms to the molecule, which comprises contacting the hydrocarbon mixture with a mild isomerization catalyst comprising an aluminum halide in a first conversion zone under sufficiently mild isomerization conditions to effect the conversion of naphthenes of non-hydroaromatic structure to naphthenes of hydroaromatic structure as the predominant reaction, separating naphthenes comprising naphthenes of hydroaromatic structure from the effluence of the first conversion zone, contacting the remaining hydrocarbons comprising straight chain paraffins with a more active aluminum halide-containing isomerization catalyst in the presence of a hydrogen halide promoter in a second conversion zone at a paraffin isomerization temperature not substantially in excess of about 90° C., limiting the time of contact of hydrocarbons and catalyst in the second conversion zone so as to effect the conversion of straight chain paraffins to single-branched chain paraffins with a minimum formation of multi-branched chain paraffins, separating a fraction predominating in single-branched paraffins from the effluence of the second conversion zone, contacting said fraction comprising single-branched paraffins in admixture with a hydrogen halide promoter with a separate portion of said more active aluminum halide-containing isomerization catalyst in a third conversion zone at a temperature of from about 80° C. to about 125° C. and a time of contact sufficiently long to effect the conversion of single-branched paraffins to multi-branched paraffins as the predominant reaction, and maintaining an increase in

at least one of the isomerizing conditions of temperature, catalyst activity and time of contact in each of said conversion zones over that maintained in each preceding conversion zone, thereby maintaining isomerizing conditions of progressively increased intensity through said conversion zones.

11. Process for the production of multi-branched paraffin hydrocarbons from hydrocarbon mixtures comprising straight chain paraffins having at least six carbon atoms to the molecule and naphthene hydrocarbons of non-hydroaromatic structure having the same number of carbon atoms to the molecule, which comprises contacting the hydrocarbon mixture with a mild isomerization catalyst comprising aluminum halide in a first conversion zone under sufficiently mild isomerization conditions to effect the conversion of naphthenes of non-hydroaromatic structure to naphthenes of hydroaromatic structure as the predominating reaction, separating naphthenes comprising naphthenes of hydroaromatic structure from the effluence of the first conversion zone, contacting the remaining hydrocarbons comprising straight chain paraffins with a more active aluminum halide-containing isomerization catalyst in a second conversion zone under paraffin isomerizing conditions, limiting the time of contact of hydrocarbons and catalyst in the second conversion zone to effect the conversion of straight chain paraffins to single-branched paraffins with a minimum formation of multi-branched paraffins, separating a fraction predominating in single-branched paraffins from the effluence of the second conversion zone, contacting said fraction comprising single-branched paraffins with a separate portion of said more active isomerization catalyst under paraffin isomerizing conditions in a third conversion zone, maintaining a time of contact in said third conversion zone sufficiently long to effect the conversion of single-branched paraffins to multi-branched paraffins as the predominant reaction, and maintaining an increase in at least one of the isomerizing conditions of temperature, catalyst activity and time of contact in each of said conversion zones over that maintained in each preceding conversion zone, thereby maintaining isomerizing conditions of progressively increased intensity through said conversion zones.

12. Process for the production of dimethylbutane from saturated hydrocarbons comprising normal hexane which comprises contacting said hydrocarbons in admixture with a hydrogen halide promoter in a first conversion zone with an isomerization catalyst comprising an aluminum halide at a temperature in the range of from about 80° C. to about 90° C. and a correlated contact time of from 5 to about 15 minutes so as to effect the conversion of normal hexane to methylpentane with a minimum formation of dimethylbutane, separating a hydrocarbon fraction predominating in methylpentane from the effluence of the first conversion zone, contacting said methylpentane fraction in admixture with a hydrogen halide promoter with an isomerization catalyst comprising an aluminum halide in a second conversion zone at a temperature in the range of from about 80° C. to about 125° C. and

a time of contact sufficiently long to effect the conversion of methylpentane to dimethylbutane as the predominant reaction, and maintaining an increase in at least one of the isomerizing conditions of temperature, catalyst activity and time of contact in said second conversion zone over that maintained in the first conversion zone, thereby maintaining isomerizing conditions of progressively increased intensity through said conversion zones.

13. Process for the production of multi-branched paraffin hydrocarbons from saturated hydrocarbons comprising straight chain paraffins having at least six carbon atoms to the molecule which comprises contacting said hydrocarbons in admixture with a promoter affording a hydrogen halide in a first conversion zone with an isomerization catalyst comprising an aluminum halide at a paraffin isomerizing temperature below about 90° C. and a correlated contact time of from about 5 to about 15 minutes so as to effect the conversion of straight chain paraffins to single-branched paraffins with a minimum formation of multi-branched paraffins, separating a hydrocarbon fraction predominating in single-branched paraffins from the effluence of the first conversion zone, contacting said fraction predominating in single-branched paraffins in admixture with a promoter affording a hydrogen halide with an isomerization catalyst comprising an aluminum halide in a second conversion zone at a temperature in the range of from about 80° C. to about 125° C. and a time of contact sufficiently long to effect the conversion of single-branched paraffins to multi-branched paraffins as the predominant reaction, and maintaining an increase in at least one of the isomerizing conditions of temperature, catalyst activity and time of contact in said second conversion zone over that maintained in the first conversion zone, thereby maintaining isomerizing conditions of progressively increased intensity through said conversion zones.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,202,081	McAfee	Oct. 24, 1916
2,299,716	Van Peski	Oct. 20, 1942
2,266,012	d'Ouville et al.	Dec. 16, 1941
2,278,934	Lee	Apr. 7, 1942
2,265,870	Schuit	Dec. 9, 1941
2,288,866	Hoog	July 7, 1942
2,306,253	McMillan	Dec. 22, 1942
2,249,337	Visser et al.	July 15, 1941
2,350,834	Sensel et al.	June 6, 1944

OTHER REFERENCES

Schuit et al., Rec. Trav. Chem., vol. 59, 793–810 (1940).

Turova-Poliak et al., Comptes Rendus (Doklady) de l'Acad. des Sciences de l'URSS (1941), vol. XXXII, No. 8, 551–4.