

March 18, 1947.

S. H. McALLISTER ET AL
METHOD FOR ISOMERIZING NAPHTHENES AND PARAFFINS
IN A HYDROCARBON MIXTURE
Filed May 16, 1942

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2 Sheets-Sheet 1

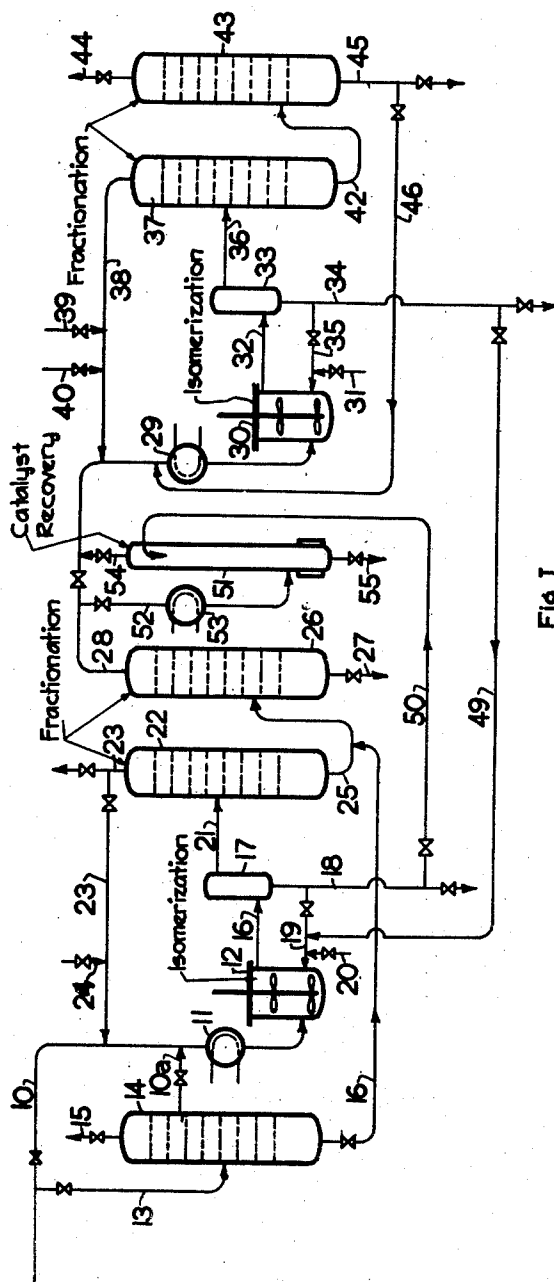


Fig. 1

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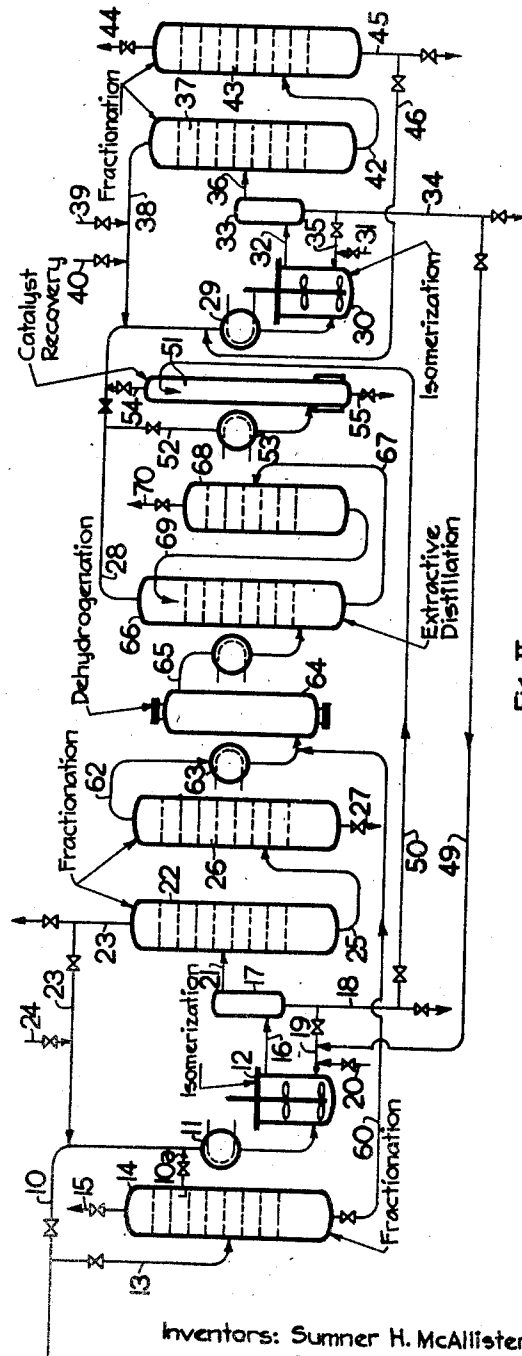


Fig. II

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UNITED STATES PATENT OFFICE

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METHOD FOR ISOMERIZING NAPHTHENES
AND PARAFFINS IN A HYDROCARBON
MIXTURE

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9 Claims. (Cl. 260-666)

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This invention relates to the production of high octane paraffin hydrocarbon fractions from hydrocarbon mixtures comprising paraffin and naphthene hydrocarbons. The invention relates more particularly to the production of branched or more highly branched paraffin hydrocarbons from hydrocarbon mixtures comprising straight or less branched chain paraffin hydrocarbons in admixture with naphthene hydrocarbons having the same number of carbon atoms to the molecule.

In view of the great demand for branched chain paraffin hydrocarbons, valuable as components of high octane motor fuels as well as starting materials for the production of many organic compounds containing tertiary carbon atoms, much effort has been expended in attempts to provide practical methods for the conversion of the readily available straight chain paraffin hydrocarbons to their branched chain isomers. Processes have been disclosed heretofore for the conversion of substantially pure straight chain paraffin hydrocarbons, particularly butane and pentane, to their respective branched chain isomers. The application of these processes to the large scale conversion of paraffin hydrocarbons having at least six carbon atoms to the molecule to their respective branched chain isomers is, however, rendered highly impractical due to the difficulty of obtaining these hydrocarbons in sufficiently pure form from many of the available sources such as petroleum, natural gasoline, products of thermal and catalytic hydrocarbon treatments, etc. As is well known, the narrow boiling hydrocarbon fractions predominating in normally liquid hydrocarbons having the same number of carbon atoms to the molecule such as, for example, straight run hexane or heptane fractions, often comprise other hydrocarbons besides the paraffins, particularly naphthene hydrocarbons which, because of the proximity of their boiling points to those of the paraffins of equal number of carbon atoms, cannot be readily separated therefrom by practical fractionating methods.

It has been found that critical amounts of certain naphthenic hydrocarbons have the ability to suppress the degradation of paraffin hydrocarbons in the presence of aluminum chloride catalysts. The presence of the naphthenic hydrocarbons, however, particularly in the proportions generally found in straight run hydrocarbon dis-

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tillates obtainable from natural sources, renders the straightforward isomerization of these fractions, in accordance with methods disclosed heretofore, impractical. Laboratory experiments have shown, for example, that the straightforward isomerization of such fractions with aluminum chloride catalysts in the absence of any substantial amount of cracking generally results in but slight improvement in the octane rating of the treated mixture. It has further been found that substantial increase in active catalyst life can be obtained at the most favorable paraffin isomerization conditions when the naphthenes are removed to at least a substantial degree from the charge.

As stated above, the separation of the naphthenes from narrow boiling hydrocarbon fractions by such means as fractionation is generally impractical. Their elimination by subjecting the entire charge to an initial dehydrogenation treatment to convert them to aromatics is also impractical, since the dehydrogenating catalysts generally utilized heretofore such as, for example, chromium oxide on alumina, fail to convert the non-hydroaromatic naphthene hydrocarbons, which often comprise at least about one-half of the naphthenes in straight run naphthenic hydrocarbon fractions. A further disadvantage of first subjecting the entire charge to such dehydrogenating catalysts is the loss sustained due to the conversion of substantial amounts of the non-hydroaromatic naphthene hydrocarbons to undesired products as a result of side reactions which may comprise polymerization and degradation. It is essential to economical operation of any process treating such fractions that the naphthenes be recovered; and it is often desirable to recover them as substantially pure hydroaromatic naphthene or aromatic hydrocarbon fractions. By the term "hydroaromatic naphthenes" as used throughout this specification and claims is meant the naphthene hydrocarbons having a hexamethylene ring, such as cyclohexane and its alkyl derivatives, to distinguish them from the non-hydroaromatic naphthene hydrocarbons such as those comprising pentamethylene rings, for example, methyl cyclopentane and dimethyl cyclopentane.

It has been found that the reaction rates and response of naphthene and paraffin hydrocarbons

to changes in isomerization conditions vary greatly, thereby rendering the recovery of naphthenes as substantially pure non-hydroaromatic or aromatic hydrocarbon fractions difficult if not impossible in the isomerization of naphthenic fractions by processes disclosed heretofore. This discovery makes it possible to effect the isomerization of paraffin hydrocarbons in admixture with naphthene hydrocarbons, not only with improved efficiency, but with recovery of the naphthene hydrocarbons as substantially pure hydroaromatic or aromatic hydrocarbon fractions.

An object of the present invention is to provide an improved process for the more efficient production of high octane paraffin hydrocarbon fractions from hydrocarbon mixtures comprising paraffin and naphthene hydrocarbons such as naphthenic petroleum fractions.

Another object of the present invention is to provide an improved process for the more efficient production of branched or more highly branched chain paraffin hydrocarbons from hydrocarbon fractions comprising straight chain or less branched chain paraffin hydrocarbons in admixture with naphthene hydrocarbons of the same number of carbon atoms to the molecule.

Still another object of the invention is to provide an improved process for the more efficient production of branched or more highly branched chain paraffin hydrocarbons from hydrocarbon fractions comprising straight chain or less branched chain hydrocarbons in admixture with naphthene hydrocarbons, with simultaneous recovery of at least a substantial part of the naphthenes as hydroaromatic or aromatic hydrocarbons. Other objects and advantages of the invention will become apparent from the following detailed description thereof.

In accordance with the process of the invention a normally liquid hydrocarbon fraction comprising straight chain paraffin hydrocarbons in admixture with naphthene hydrocarbons such as, for example, a naphthenic hexane or heptane fraction obtained by the fractionation of natural gasoline, petroleum, or a distillate refinery product, is subjected to mild isomerization conditions in a first conversion zone effective to convert non-hydroaromatic naphthenes to hydroaromatic naphthenes as the predominant reaction. Preferential isomerization of the naphthenes in the first conversion zone is obtained by the maintenance therein of conditions comprising the use of an isomerization catalyst of mild activity and/or only moderately elevated temperatures, as is described more fully below. The resulting hydroaromatic hydrocarbons, together with those originally present in the charge, are removed from the reaction product from the first conversion zone by suitable means which may comprise, for example, fractionation, dehydrogenation, hydro-forming, solvent extraction, extractive distillation, or the like. The remaining hydrocarbons are subjected to more severe isomerization conditions more favorable to the conversion of straight chain or branched chain paraffin hydrocarbons to branched or 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 a part of this specification and wherein:

Figure I illustrates more or less diagrammatically one form of apparatus suitable for the treatment of hydrocarbon mixtures compris-

ing paraffin and naphthene hydrocarbons having six carbon atoms to the molecule.

Figure II illustrates more or less diagrammatically a modified form of apparatus suitable for the treatment of hydrocarbon mixtures comprising paraffin and naphthene hydrocarbons having more than six carbon atoms to the molecule, wherein all parts of apparatus which are the same as those shown in Figure I are indicated with like reference numbers.

A mixture of saturated hydrocarbons consisting essentially of paraffins and cycloparaffins of non-hydroaromatic and hydroaromatic structure having the same number of carbon atoms to the molecule such as, for example, a hexane fraction comprising normal hexane, methyl cyclopentane and cyclohexane, as obtained by fractionation of a naphthenic straight run gasoline, is drawn from an outside source and forced through valved line 10 and heater 11 into a first reaction zone. The reaction zone may comprise, for example, a reactor 12 provided with suitable stirring means. It may at times be advantageous to subject the charge to a fractionation prior to its entry into reactor 12. Thus, when treating a naphthenic hexane fraction boiling, for example, within the range of from about 45° C. to about 85° C., comprising substantial amounts of methyl pentanes and/or cyclohexane, all or part of the charge may be passed through valved line 13 into a feed fractionating zone represented in the drawing by the single fractionator 14. Within fractionator 14 the charge may be fractionated to separate a light fraction boiling, for example, below about 64° C. and comprising substantial amounts of methyl pentanes. If desired, a heavier fraction predominating in cyclohexane and boiling, for example, above about 79° C. may be withdrawn as a bottom fraction, while the remaining part of the charge comprising normal hexane and methyl cyclopentane is withdrawn as a side stream and passed through valved line 10a into line 10 leading into reactor 12.

Within reactor 12 the hydrocarbon stream is subjected to mild catalytic isomerization conditions. Suitable conditions are obtained by the use of a mild isomerization catalyst and controlling the temperature, time of contact and catalyst to hydrocarbon ratio effective to convert the non-hydroaromatic naphthenes comprising methyl cyclopentane to hydroaromatic naphthenes comprising cyclohexane as the predominating reaction. Suitable mild isomerization catalysts comprise catalysts of the aluminum halide-hydrocarbon complex type, such as the complex formed by the reaction of aluminum chloride with an aromatic hydrocarbon, for example, toluene. It is to be noted that the complex catalyst as used in the reactor 12 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. With the use of this catalyst, free of any substantial amounts of free aluminum halide, temperatures in the range of from about 50° C. to about 100° C. and preferably from about 60° C. to about 90° C. with a contact time not exceeding the period of time required to obtain equilibrium

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naphthene conversion, have been found suitable. Hydrogen halide promoters are preferably present in only exceedingly small amounts, for example, in quantities not exceeding about 0.5 per cent of the charge to reactor 12.

The preferential isomerization of non-hydroaromatic naphthenes contained in a naphthenic hexane fraction to hydroaromatic naphthenes in accordance with the process of the invention is shown by the following example:

Example I

A naphthenic hexane fraction obtained by fractionation of a naphthenic straight run gasoline and having the following composition:

	Per cent
Benzene	5
Methyl cyclopentane.....	52
Paraffins predominating in normal hexane...	43

was treated with an AlCl_3 -toluene complex catalyst at 65° C. with a catalyst to hydrocarbon ratio of 1:2. Sixty per cent of the methyl cyclopentane was converted to cyclohexane whereas the conversion of paraffins to isoparaffins did not exceed 5 per cent.

Reaction products comprising normal hexane, cyclohexane, isohexanes originally present in the feed or formed in the process, and entrained catalyst are passed from reactor 12 through line 16 to a separator 17, wherein entrained catalyst is separated. Separated catalyst is withdrawn from separator 17 and returned to the reactor 12 through valved lines 18 and 19. Fresh catalyst is introduced into line 19 by means of valved line 20. The hydrocarbons are passed from separator 17 through line 21 into a fractionator 22.

Within fractionator 22 a lighter fraction comprising the hydrogen halide promoter is separated and passed therefrom through valved line 23 into line 10. Hydrogen halide promoter, when needed, may be introduced into the system from an outside source by means of valved line 24 leading into line 23. If desired, a light hydrocarbon fraction comprising normal hexane and unconverted methyl cyclopentane may be separated in fractionator 22 and recycled with the promoter through line 23 to reactor 12.

Although but one converter is shown in the drawing as constituting the naphthene isomerizing zone, it is to be understood that a plurality of such converters may be used and fractionation be resorted to between the individual converters to effect the removal of fractions predominating in normal hexane and cyclohexane which are to be further processed in accordance with the invention as described below. It is readily apparent that by such recycling and, if desired, the use of a plurality of converters, substantially all of the non-hydroaromatic naphthenes in the charge can be converted to hydroaromatic hydrocarbons.

A liquid fraction comprising normal hexane and cyclohexane is withdrawn from the lower part of fractionator 22 and passed through line 25 into a fractionator 26. When the charge is subjected to a preliminary fractionation in feed fractionator 14 as described above, the bottoms therefrom comprising normal hexane and cyclohexane may be passed through line 16 into line 25. Within fractionator 26 a lighter fraction comprising normal hexane is separated from a heavier fraction consisting essentially of cyclohexane. The latter fraction is withdrawn from fractionator 26 through valved line 27 and eliminated from the system as a final product.

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The lighter fraction separated in fractionator 26 comprising normal hexane is passed through a valved line 28 and heater 29 into a second conversion zone. The second conversion zone may comprise, for example, a reactor 30 provided with suitable stirring means. Although but one such reactor is shown in the drawing, it is to be understood that a plurality of reactors connected in series or in parallel may be used. Within reactor 30 the hydrocarbon stream is subjected to more severe isomerization conditions than those maintained in reactor 12, in order to effect the conversion of straight chain or branched chain paraffin hydrocarbons to branched and more highly branched paraffin hydrocarbons. The more severe isomerization conditions are obtained by the use of a more active isomerization catalyst and/or a higher temperature, longer contact time and a greater catalyst to hydrocarbon ratio. Suitable more active isomerization catalysts comprise catalysts of the molten salt type such as, for example, a molten salt mixture comprising aluminum chloride dissolved in antimony trichloride. Although a fluid melt comprising aluminum chloride and antimony trichloride has been chosen as a suitable more active isomerization catalyst, it is to be understood that other catalysts of high isomerization activity may be used, such as molten salt mixtures comprising an excess of aluminum chloride and/or aluminum bromide and the halide of at least one or more alkali metals, for example, AlCl_3 - NaCl - KCl , AlCl_3 - NaCl - ZnCl_2 , or a melt comprising AlCl_3 , SO_2 and ZnCl_2 , etc. The temperature to be maintained within reactor 30 will vary with the nature of the particular catalysts used. When using catalysts of the molten salt type, temperatures of from about 80° C. to about 125° C., preferably from about 85° C. to about 100° C., have been found suitable. The paraffin conversion step is effected in the presence of a hydrogen halide promoter. The promoter, for example, hydrogen chloride, is introduced into reactor 30 in an amount ranging from about 0.5 per cent to about 10 per cent of the hydrocarbons charged to this conversion zone.

The advantage of the removal of the naphthenes from the charge to the second conversion zone is illustrated by the following examples showing the effect of increase in naphthene concentration upon catalyst life and the octane rating of the resulting product.

Example II

Mixtures of normal hexane and increased amounts of methyl cyclopentane were treated at a temperature of about 85° C. with a fluid catalyst melt consisting of 92.5 per cent by weight of SbCl_3 and 7.5 per cent by weight of AlCl_3 . The contact time was approximately 30 minutes and the ratio of catalyst to hydrocarbon charge about 1:5 by volume. Hydrogen chloride was added to the charge in the amount of 4 per cent by weight of the hydrocarbon feed. The increase in octane number of the product 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
30	25

Example III

Mixtures of normal hexane and methyl cyclopentane were treated under the conditions of Example II. The life of the catalyst in terms of pounds of dimethyl butane produced per pound of aluminum chloride in the catalyst is shown in column A of the following table. The figures in column B show the length of catalyst life in terms of per cent of normal hexane converted to dimethyl butane at a yield of 80 pounds of isomerizate per pound of $AlCl_3$ in the catalyst.

Weight per cent methyl cyclopentane in feed	A	B
0	36	16
18.5	22	16
42.5	11	7.5
47.0	7	6.8

The above examples, which demonstrate the deleterious effect of the naphthenes upon catalyst life and the octane rating of the hydrocarbon product, clearly show the advantages obtained by the removal of at least a substantial amount of the naphthenes from the charge to the paraffin isomerizing zone.

Reaction products comprising methyl pentane, dimethyl butane, some unconverted normal hexane, hydrogen chloride and entrained catalyst are passed from reactor 30 through line 32 into separator 33 wherein separation of the entrained catalyst is effected. Separated catalyst is withdrawn from separator 33 and passed through valved lines 34 and 35 into reactor 30. Fresh catalyst is introduced into line 35 from an outside source by means of valved line 31. Hydrocarbons and hydrogen chloride are passed from separator 33 through line 36 into a fractionator 37. Within fractionator 37 a lighter fraction comprising hydrogen chloride is separated and recycled through line 38 to line 28. Make-up hydrogen chloride is introduced into line 38 through valved line 39. A valved line 40 leading into line 38 is provided for the introduction of hydrogen, isobutane, or any other suitable paraffin degradation suppressor or gaseous diluent into the system.

A liquid hydrocarbon fraction comprising isohexanes and normal hexane is withdrawn from the lower part of fractionator 37 and passed through line 42 into a final fractionator 43. Within fractionator 43 a lighter fraction comprising methyl pentanes and substantial amounts of the highly desirable dimethyl butane, is separated as a vapor fraction and eliminated from the system as a final product through valved line 44. A liquid fraction comprising normal hexane is withdrawn from the lower part of fractionator 43 and eliminated from the system through valved line 45. A part or all of the hydrocarbons passing through line 45 may be passed through valved line 46 into line 29 leading into reactor 30.

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 reactors 12 and 30.

Although the invention has been described with the use of a mild isomerization catalyst of the $AlCl_3$ -hydrocarbon complex type in the first conversion zone, it is to be pointed out that the invention is in no wise limited to the use of this particular catalyst. It has been found, for example, that a catalyst of the molten salt type

which is spent to a degree where it no longer possesses the ability to isomerize paraffin hydrocarbons is still able to effectively isomerize naphthene hydrocarbons. Thus, a molten salt catalyst comprising aluminum chloride dissolved in antimony trichloride which had been used in the isomerization of a hexane fraction until it had lost substantially all of its ability to isomerize paraffins, when used to treat a hexane fraction comprising 81.5% normal hexane and 18.5% methyl cyclopentane still enabled the attainment of equilibrium conversions of the methyl cyclopentane to cyclohexane. In a preferred modification of the process of the invention the partially spent molten salt catalyst from the more severe paraffin isomerization step is used as the catalyst for the first or milder isomerization step. In accordance with this mode of operation, at least a part of the spent catalyst eliminated from reactor 30 through valved line 34 is passed through line 49 into line 19 leading to reactor 12. When utilizing a molten salt catalyst of reduced activity in reactor 12 a temperature, for example, below about 80° C., and a ratio of catalyst to hydrocarbon in the approximate range of from about 1:5 to about 1:10 have been found to be suitable. As stated above, hydrogen halide promoters should be used in only exceedingly small amounts, for example, not in excess of about 0.5 per cent by weight of the hydrocarbon charge to reactor 12.

After a period of time which will vary with the amount of nonhydroaromatic naphthenes in the charge, the molten salt catalyst will lose its activity even for the isomerization of naphthene hydrocarbons. A part of the molten salt catalyst eliminated from separator 17 through line 18 is therefore continuously passed through valved line 50 into the upper part of an extraction column 51. Within extractor 51 the spent catalyst is scrubbed with a part or all of the paraffin hydrocarbon charge to reactor 30. A valved line 52 provided with heat exchanger 53 is provided, leading from line 28 to an intermediate part of extractor 51. Within extractor 51 the more soluble components of the spent catalyst, which in this illustrative example of the invention will comprise antimony trichloride, is dissolved in the hydrocarbon stream and passed therewith through valved lines 54 and 28 into reactor 30. Spent catalyst consisting of a carbonaceous aluminum chloride sludge is eliminated from the lower part of extractor 51 through valved line 55. The temperature to be maintained within scrubber 51 will vary in accordance with the nature of the spent catalyst introduced into the extractor. A temperature of from about 80° C. to about 90° C. has been found to be suitable. The temperature is maintained therein by passing a suitable indirect heat exchange medium, which may comprise one of the available streams of the process, through heat exchanger 53.

This modification of the invention utilizing the flow of the molten salt catalyst consecutively through the more severe and mild isomerizing zones and thereafter through the catalyst scrubber results in a highly efficient operation, realizing substantial saving in catalyst cost, thereby furthering the efficiency of the process.

It is to be noted that one or several of the single factors comprising catalyst activity, temperature, contact time, catalyst to hydrocarbon ratio, and amount of promoter, which co-operate to produce the mild isomerization conditions in

reactor 12, may vary within the scope of the invention, and that the sole criterion of suitable mild isomerization conditions is the ability to effect the preferential isomerization of the naphthene hydrocarbons. Thus a more active catalyst may be used in the first conversion zone with a substantial decrease in temperature and/or catalyst to hydrocarbon ratio and/or contact time. The following example illustrates the preferential isomerization of the naphthene content of a hexane charge wherein a short contact time and a low ratio of catalyst to hydrocarbon is used to offset the greater activity of the catalyst.

Example IV

A mixture of normal hexane and methyl cyclopentane consisting of 81.5 per cent by weight of normal hexane and 18.5 per cent by weight of methyl cyclopentane was treated with a fresh molten catalyst consisting of aluminum chloride dissolved in antimony trichloride 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 per cent was obtained, whereas only 19 per cent of the normal hexane was converted to methyl pentane.

The particular steps by which naphthenes comprising hydroaromatic naphthenes are separated from the products emanating from the first conversion zone may vary within the scope of the invention. Whereas in the treatment of a naphthenic hexane fraction, fractionation is found to be 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 10. 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 14 to separate a heavier fraction

predominating in methyl cyclohexane as a bottom fraction, which is withdrawn through line 60. The remainder of the charge comprising substantially all of the normal heptane and dimethyl cyclopentanes is passed as a side stream from fractionator 14 through lines 10a and 10 into reactor 12. Within reactor 12 the hydrocarbons are treated as described above to convert the non-hydroaromatic naphthenes comprising the methyl cyclopentanes and ethyl cyclopentanes to hydroaromatic naphthenes comprising methyl cyclohexanes as the predominating reaction. The products from reactor 12 are passed to fractionator 22 wherein a light fraction comprising the hydrogen halide promoter, if used, and if desired a certain amount of hydrocarbons comprising unconverted non-hydroaromatic naphthenes, is removed overhead and recycled in part or in its entirety through line 23 to line 10. Bottoms from fractionator 22 comprising normal heptane and methyl cyclohexanes are passed through line 25 into the fractionator 26. Within fractionator 26 hydrocarbon material of more than seven carbon atoms to the molecule which may have been introduced therein is eliminated from the bottom thereof through line 27. A lighter fraction comprising normal heptane and methyl cyclohexanes is taken overhead from fractionator 26 and passed through line 62 and heater 63 into a dehydrogenating zone. If a heavier fraction has been removed from the fractionator 14 through line 60, this is combined with the hydrocarbon stream flowing through line 62.

The dehydrogenating zone may comprise a reactor 64 or a plurality of reactors connected in series or in parallel. Within reactor 64 the hydrocarbon stream is contacted with a catalyst under conditions at which the hydroaromatic naphthenes 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 is, however, 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 64 by means of heater 63 and if desired by other means not shown in the drawing, for supplying heat from an outside source.

Products from reactor 64 comprising paraffin and aromatic hydrocarbons including, for example, normal heptane and toluene, are passed through line 65 to an extractive distillation column 66 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. Overhead from column 66 comprising paraffin C₇ hydrocarbons is passed through line 28 to the reactor 30 to be subjected to the more severe paraffin isomerization conditions as described above. The resulting products of the paraffin isomerization are fractionated in fractionators 37 and 43 to obtain

a high octane paraffinic fraction comprising branched and multi-branched chain paraffin hydrocarbons having seven carbon atoms to the molecule, which is removed from the system through line 44 as a final product. Bottoms from column 66 comprising solvent and aromatic hydrocarbons are passed through line 67 to distillation column 68 wherein aromatic hydrocarbons comprising toluene are separated from the solvent. Aromatic hydrocarbons comprising toluene are removed as overhead from column 68 through valved line 70 as a final product of the process. The lean solvent is returned from column 68 to the upper part of column 66 by means of line 69.

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. The invention is, however, not necessarily limited thereto. 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, now substantially free of non-hydroaromatic hydrocarbons, 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 hydroaromatic naphthenes from the paraffins. The resulting paraffin fractions may then be subjected separately or combined to the second conversion step 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 comprising, 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 11, 29 and 63 may consist of 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 17 and 33 are preferably subjected to a fractionating step by means not shown in the drawing to remove entrained or dissolved catalyst components therefrom prior to passing to columns 22 and 37 respectively.

Due to the elimination of naphthenes from the hydrocarbon charge, made possible by the process of the invention, the more severe isomerizing conditions within the second conversion zone may be maintained with substantial increase in catalyst life over periods of time substantially in ex-

cess of those possible when treating the original charge with its total or only slightly modified naphthene content. It is to be noted that not only is catalyst life increased, but a paraffinic product is obtained with a substantially increased octane rating over that possible when treating straight run naphthenic fractions with less effective removal of naphthene hydrocarbons prior to the paraffin isomerization step. It is thus seen that the process presents not only a substantially improved method for obtaining paraffinic hydrocarbon fractions of substantially increased octane rating, suitable as blending agents for motor fuels and eminently suited as stocks for the alkylation of olefins and aromatics, but enables the recovery of the naphthene content of the charge as substantially pure hydroaromatic or aromatic hydrocarbon fractions.

We claim as our invention:

1. The process for the production of a high octane paraffinic hydrocarbon fraction from a mixture of saturated hydrocarbons 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 at a temperature of from about 85° C. to about 100° C., in the presence of an added hydrogen halide promoter in a second conversion zone, thereby converting the remaining hydrocarbons to a high octane paraffinic hydrocarbon fraction comprising branched chain hexanes, and passing partially spent catalyst from the second conversion zone to the first conversion zone.

2. The process for the production of a high octane paraffinic hydrocarbon fraction from a mixture of saturated hydrocarbons 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 at a temperature of from about 80° C. to about 125° C. in the presence of an added hydrogen halide promoter in a second conversion zone, thereby converting the remaining hydrocarbons to a high octane paraffinic hydrocarbon fraction comprising branched chain hexanes, and passing partially spent catalyst from the second conversion zone to the first conversion zone.

3. The process for the production of a high octane paraffinic hydrocarbon fraction from a mix-

ture of saturated hydrocarbons comprising normal hexane and methylcyclopentane 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 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 halide-containing isomerization catalyst of the molten salt type at paraffin isomerizing conditions in a second conversion zone, thereby converting the remaining hydrocarbons to a high octane paraffinic hydrocarbon fraction comprising branched chain hexanes, and passing partially spent catalyst from the second conversion zone to the first conversion zone.

4. The process for the production of a high octane paraffinic hydrocarbon fraction from a mixture of saturated hydrocarbons comprising normal hexane and methylcyclopentane 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 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 halide-containing isomerization catalyst of the molten salt type at paraffin isomerizing conditions in a second conversion zone, thereby converting the remaining hydrocarbons to a high octane paraffinic hydrocarbon fraction comprising branched chain hexanes, passing partially spent catalyst from the second conversion zone to the first conversion zone, and contacting spent catalyst drawn from the first conversion zone with at least a part of the charge to the second conversion zone.

5. The process for the production of a high octane paraffinic hydrocarbon fraction from a mixture of saturated hydrocarbons 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, and contacting the remaining hydrocarbons comprising normal hexane with an aluminum chloride-containing isomerization catalyst of the molten salt type in a second conversion zone in the presence of an added hydrogen halide promoter at a temperature of from about 85° to about 100° C., thereby converting the remaining hydrocarbons

to a high octane paraffinic hydrocarbon fraction comprising branched chain hexanes.

6. The process for the production of a high octane paraffinic hydrocarbon fraction from a mixture of saturated hydrocarbons 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 50° C. to about 100° 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, and contacting the remaining hydrocarbons comprising normal hexane with an aluminum chloride-containing isomerization catalyst of the molten salt type in a second conversion zone in the presence of an added hydrogen halide promoter at a temperature of from about 80° C. to about 125° C., thereby converting the remaining hydrocarbons to a high octane paraffinic hydrocarbon fraction comprising branched chain hexanes.

7. The process for the production of a high octane paraffinic hydrocarbon fraction from a mixture of saturated hydrocarbons 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 at a temperature of from about 50° C. to about 100° 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, and contacting the remaining hydrocarbons comprising normal hexane with an aluminum halide-containing isomerization catalyst of the molten salt type in a second conversion zone under paraffin isomerizing conditions thereby converting the remaining hydrocarbons to a high octane paraffinic hydrocarbon fraction comprising branched chain hexanes.

8. The process for the production of a high octane paraffinic hydrocarbon fraction from a mixture of saturated hydrocarbons 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, and contacting the remaining hydrocarbons comprising normal hexane with an aluminum halide-containing isomerization catalyst of the molten salt type in a second conversion zone under paraffin isomerizing conditions, thereby converting the remaining hydrocarbons to a high octane paraffinic hydrocarbon fraction comprising branched chain hexanes.

9. The process for the production of a high octane paraffinic hydrocarbon fraction from a mixture of saturated hydrocarbons comprising

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normal hexane and methylcyclopentane 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 methylcyclopentane to cyclohexane as the predominating reaction, separating naphthenes comprising cyclohexane from the hydrocarbon mixture after the mild isomerization treatment, and contacting the remaining hydrocarbons comprising normal hexane with a more active aluminum halide-containing isomerization catalyst in a second conversion zone under paraffin isomerizing conditions, thereby converting the remaining hydrocarbons to a high octane paraffinic hydrocarbon fraction comprising branched chain hexanes.

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