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ISOMERIZING PARAFFINS AND NAPHTHENES IN A MIXED FEED

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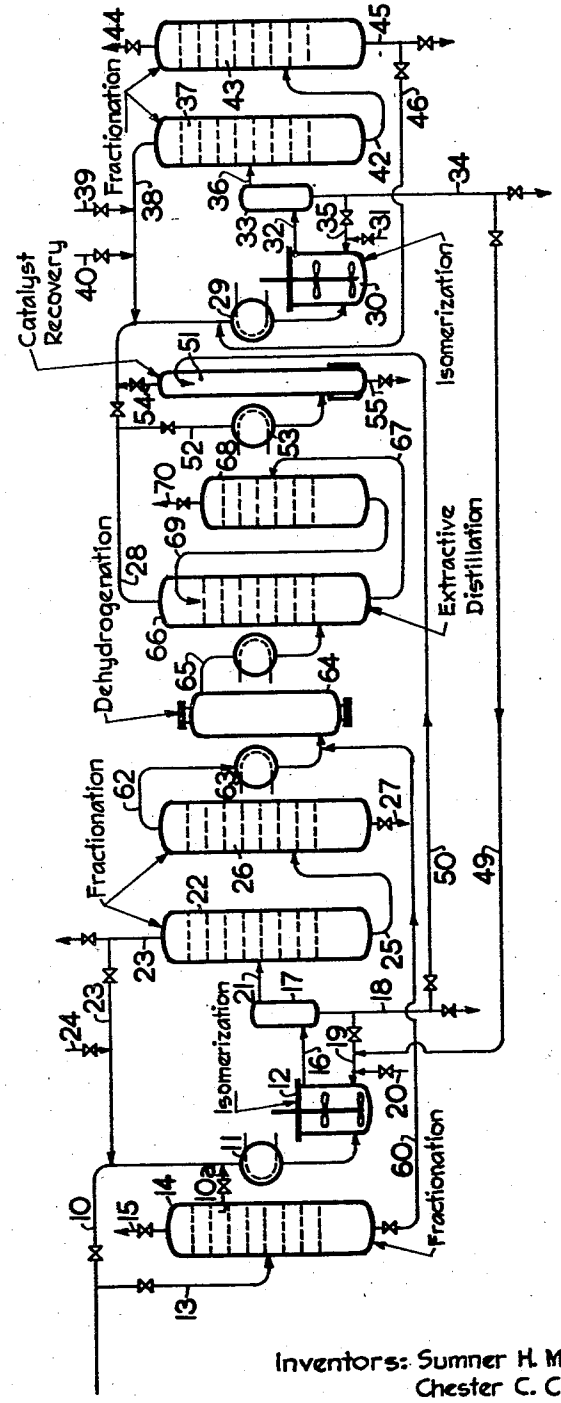

Inventors: Sumner H. McAllister
Chester C. Crawford

By their Attorney: C. J. Ott

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ISOMERIZING PARAFFINS AND NAPHTHENES IN A MIXED FEED

Sumner H. McAllister, Lafayette, Calif., and Chester C. Crawford, Bartlesville, Okla., assignors to Shell Development Company, San Francisco, Calif., a corporation of Delaware

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7 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 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 distillates obtainable from natural sources, renders the straightforward isomerization of these fractions, in accordance with methods disclosed heretofore, impractical. Laboratory experiments

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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 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 moderately elevated temperatures, as 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, hydroforming, 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 drawing illustrating more or less diagrammatically one form of apparatus suitable for the treatment of hydrocarbon mixtures comprising paraffin and naphthene hydrocarbons having more than six carbon atoms to the molecule.

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, and forced through heater 11 into a first reaction zone. The reaction zone may comprise, for example, a reactor 12 provided with suitable stirring means. If the charge contains 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 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 subjected to mild catalytic isomerization conditions to convert the non-hydroaromatic naphthenes comprising the methyl cyclopentanes and ethyl cyclopentanes to hydroaromatic naphthenes comprising methyl cyclohexanes as the predominating reaction.

It has been found 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 paraffin fraction until it had lost substantially all of its ability to isomerize paraffins, when used to treat a naphthene fraction still enabled the attainment of equilibrium conversions of naphthenes of non-hydroaromatic structure to naphthenes of hydroaromatic structure. In accordance with the process of the invention partially spent molten salt catalyst obtained from a more severe paraffin isomerization step of the process 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 produced within the system as described below is passed through line 49 into line 19 leading to reactor 12. A temperature within reactor 12 of, 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. A hydrogen halide promoter, for example, hydrogen chloride, is 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.

The products from reactor 12 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. 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, 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. Hydrogen halide promoter, when needed, is introduced into the system from an outside source by means of valved line 24 leading into line 23.

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 which are to be further processed in accordance with the invention. 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.

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. 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.

Overhead from column 66 comprising paraffin C_7 hydrocarbons is passed through 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 chain paraffin hydrocarbons. The more severe isomerization conditions are obtained by the use of a more active isomerization catalyst, such as a catalyst of the molten salt type, 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 molten salt type catalysts 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. 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.

Reaction products comprising branched chain paraffin hydrocarbons having seven carbon atoms to the molecule and some unconverted normal heptane, hydrogen chloride and entrained catalyst are passed from reactor 30 through line 32 into separator 33 wherein separation of the entained catalyst is effected. Separated catalyst is withdrawn from separator 33 and passed through valved lines 34 and 35 into reactor 30. Fresh molten salt catalyst is introduced into line 35 from an outside source by means of valved line 31. 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. 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 branched chain heptanes and normal heptane 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 branched chain heptanes is separated as a vapor fraction and eliminated from the system as a final product through valved line 44. A liquid fraction comprising normal heptane 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.

After a period of time which will vary with the amount of non-hydroaromatic 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.

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.

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 excess 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.

This application is a division of application Serial No. 443,269, filed May 16, 1942.

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 heptane and dimethylcyclopentane which comprises contacting the hydrocarbon mixture in a first conversion zone at a temperature below about 80° C. in the presence of a hydrogen halide promoter added in an amount below about 0.5 per cent by weight of the hydrocarbon charge with a partially spent isomerization catalyst comprising an aluminum chloride-containing mixture of molten salts obtained within the system, thereby effecting the conversion of dimethylcyclopentane to methylcyclohexane as the predominating reaction, separating cycloparaffins comprising methylcyclohexane from the effluence of the first conversion zone, contacting the remaining hydrocarbons comprising normal heptane with an isomerization catalyst comprising an aluminum chloride-containing mixture of molten salts 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 heptanes, and pass-

ing 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 heptane and dimethylcyclopentane which comprises contacting the hydrocarbon mixture in a first conversion zone at a temperature below about 80° C. in the presence of a hydrogen halide promoter added in an amount below about 0.5 per cent by weight of the hydrocarbon charge with a partially spent isomerization catalyst comprising a mixture of molten salts obtained within the system, thereby effecting the conversion of dimethylcyclopentane to methylcyclohexane as the predominating reaction, separating cycloparaffins comprising methylcyclohexane from the effluence of the first conversion zone, contacting the remaining hydrocarbons comprising normal heptane with an isomerization catalyst comprising an aluminum chloride-containing mixture of molten salts 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 heptanes, 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 mixture of saturated hydrocarbons comprising normal heptane and dimethylcyclopentane which comprises contacting the hydrocarbon mixture in a first conversion zone at a temperature below about 80° C. in the presence of a hydrogen halide promoter added in an amount below about 0.5 per cent by weight of the hydrocarbon charge with a partially spent isomerization catalyst comprising an aluminum halide-containing mixture of molten salts obtained within the sytem, thereby effecting the conversion of dimethylcyclopentane to methylcyclohexane as the predominating reaction, separating cycloparaffins comprising methylcyclohexane from the effluence of the first conversion zone, contacting the remaining hydrocarbons comprising normal heptane with an isomerization catalyst comprising an aluminum halide-containing mixture of molten salts 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 heptanes, 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 heptane and dimethylcyclopentane which comprises contacting the hydrocarbon mixture in a first conversion zone at a temperature below about 80° C. in the presence of an added hydrogen halide promoter with a partially spent isomerization catalyst comprising an aluminum halide-containing mixture of molten salts obtained within the system, thereby effecting the conversion of dimethylcyclopentane to methylcyclohexane as the predominating reaction, separating cycloparaffins comprising methylcyclohexane from the effluence of the first conversion zone, contacting the remaining hydrocarbons comprising normal heptane with an isomerization catalyst comprising an aluminum halide-containing mixture of molten salts 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 heptanes, 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 portion 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 normally liquid saturated hydrocarbons boiling in the gasoline boiling range comprising straight chain paraffinic hydrocarbons having at least seven carbon atoms to the molecule and naphthenic hydrocarbons of non-hydroaromatic structure having the same number of carbon atoms to the molecule as said paraffins which comprises contacting the hydrocarbon mixture in a first conversion zone at a temperature below about 80° C. in the presence of a hydrogen halide promoter added in an amount below about 0.5 per cent by weight of the hydrocarbon charge, with a partially spent isomerization catalyst comprising an aluminum chloride-containing mixture of molten salts obtained within the system, thereby effecting 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 an isomerization catalyst comprising an aluminum chloride-containing mixture of molten salts 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 paraffins, and passing partially spent catalyst from the second conversion zone to the first conversion zone.

6. The process for the production of a high octane paraffinic hydrocarbon fraction from a mixture of normally liquid saturated hydrocarbons boiling in the gasoline boiling range comprising straight chain paraffinic hydrocarbons having at least seven carbon atoms to the molecule and naphthenic hydrocarbons of non-hydroaromatic structure having the same number of carbon atoms to the molecule as said paraffins which comprises contacting the hydrocarbon mixture in a first conversion zone at a temperature below about 80° C. in the presence of a hydrogen halide promoter added in an amount below about 0.5 per cent by weight of the hydrocarbon charge, with a partially spent isomerization catalyst comprising an aluminum halide-containing mixture of molten salts obtained within the system, thereby effecting 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 an isomerization catalyst comprising an aluminum halide-containing mixture of molten salts at a temperature of from about 85° 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 paraffins, and passing partially spent catalyst from the second conversion zone to the first conversion zone.

7. The process for the production of a high octane paraffinic hydrocarbon fraction from a mixture of normally liquid saturated hydrocarbons boiling in the gasoline boiling range comprising straight chain paraffinic hydrocarbons having at least seven carbon atoms to the molecule and naphthenic hydrocarbons of non-hydroaromatic structure having the same number of carbon atoms to the molecule as said paraffins which comprises contacting the hydrocarbon mixture in a first conversion zone at a temperature below about 80° C. in the presence of a hydrogen halide promoter with a partially spent isomerization catalyst comprising an aluminum halide-containing mixture of molten salts obtained within the system, thereby effecting 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 an isomerization catalyst comprising an

aluminum halide-containing mixture of molten salts at a temperature of from about 85° C. to about 125° C. in the presence of an added hydrogen halide in a second conversion zone, thereby converting the remaining hydrocarbons to a high octane paraffinic hydrocarbon fraction comprising branched chain paraffins, passing partially spent catalyst from the second conversion zone to the first conversion zone, and countercurrently contacting spent catalyst drawn from the first conversion zone as a scrubbing zone with at least a portion of the hydrocarbon charge to the second conversion zone in the liquid phase.

SUMNER H. McALLISTER.
CHESTER C. CRAWFORD.

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