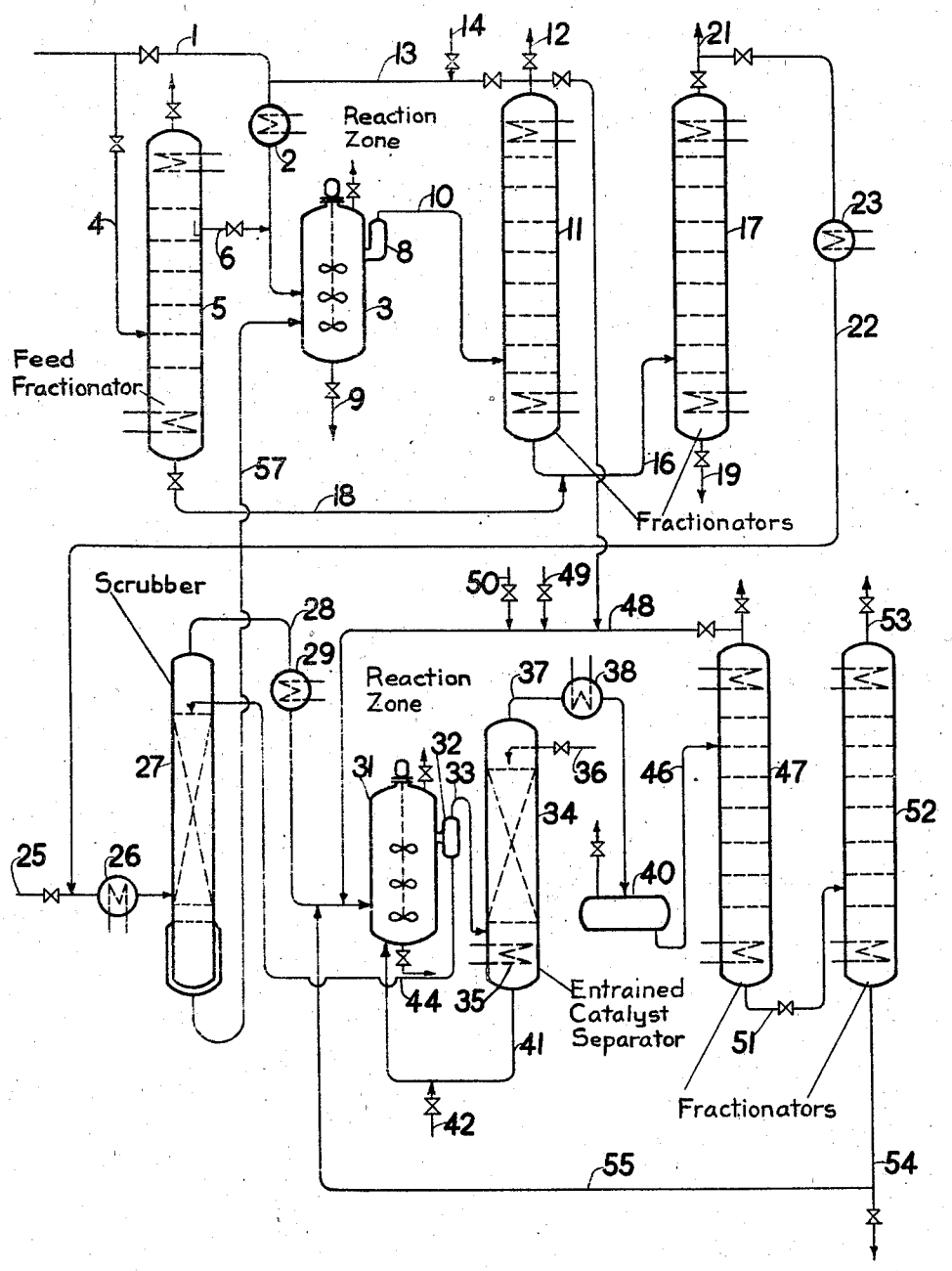
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ISOMERIZING HYDROCARBONS

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ISOMERIZING HYDROCARBONS

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This invention relates to the isomerization of hydrocarbons and relates more particularly to the catalytic treatment at isomerizing conditions of hydrocarbon mixtures comprising paraffinic and naphthenic hydrocarbons. A particular aspect of the invention relates to an improved process for the production of paraffinic hydrocarbon fractions comprising branched chain paraffins and hydrocarbon fractions comprising hydroaromatic naphthenes or aromatics from hydrocarbon mixtures comprising straight or less branched chain paraffins and naphthenes of non-hydroaromatic structure.

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.

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 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. 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. 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" 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.

An object of the invention is to provide an improved and highly economical process for the more efficient substantially selective isomerization of naphthenes of non-hydroaromatic structure in admixture with paraffinic hydrocarbons to naphthenes of hydroaromatic structure.

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.

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.

Another 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. Other objects and advantages of the invention will become apparent from the following detailed description thereof.

It has been found that isomerization catalysts of the Friedel-Crafts type which have lost a substantial part of their activity in the isomerization of paraffinic hydrocarbons still possess ability to catalyze the isomerization of naphthenes. When such catalysts which are at least partly spent with regard to their ability to catalyze the paraffin isomerization are extracted or scrubbed with a suitable solvent, for example, a paraffinic hydrocarbon or hydrocarbon fraction, active catalyst components are removed therefrom by solution leaving a fluid catalyst residue. The resulting fluid catalyst residue, it has been found, though inactive with respect to its ability to catalyze the paraffin isomerization reaction possess the ability to catalyze the isomerization of naphthenes to a degree enabling the attainment of yields not only exceeding those obtainable with the partly spent catalyst from which it was produced but even those obtainable with freshly prepared catalysts of, for example, the hydrocarbon-aluminum halide complex type, heretofore often preferred in the isomerization of naphthenic hydrocarbons.

In accordance with the invention naphthenic hydrocarbons, optionally in the presence of other hydrocarbons capable or not of undergoing isomerization under conditions of execution of the process and/or inert gases are contacted with a fluid catalyst residue obtained by extracting with a suitable solvent, for example, a paraffinic hydrocarbon or hydrocarbon fraction, a catalyst comprising a metal halide of the Friedel-Crafts type previously used in the isomerization of paraffin hydrocarbons, thereby separating the catalyst into components active with respect to ability to promote the paraffin isomerization reaction and said catalyst residue. The reaction is preferably executed in the presence of a small amount of a suitable promoter and the amount of promoter, and isomerizing conditions of temperature, pressure and time are correlated to effect the isomerization of naphthenic hydrocarbons.

In one preferred embodiment 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 contacted in a first conversion zone with a catalyst residue, obtained within the system as described below, under isomerizing conditions of temperature and pressure to selectively convert non-hydroaromatic naphthenes to hydroaromatic naphthenes. 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 substantially paraffinic hydrocarbons are contacted with a catalyst comprising a metal halide of the Friedel-Crafts type, preferably a fluid-type catalyst, in a second conversion zone under paraffin isomerizing conditions. At least partly spent catalyst, drawn from the second conversion zone, is scrubbed with a suitable solvent, for example, at least a portion of the paraffinic charge to the second conversion zone, thereby removing from the catalyst active catalyst components by solution and leaving a fluid catalyst residue. The resulting fluid catalyst residue is passed into the first conversion zone as the naphthene isomerization catalyst used therein.

The discovery that the catalyst residue which is obtained after scrubbing out catalyst components which are still active for paraffin isomerization from an at least partly spent catalyst of the Friedel-Crafts type, and which heretofore has been discarded, enables the selective isomerization of naphthenes in the presence of paraffins therefore provides not only an unusually economical method for the efficient isomerization of naphthenes but enables the production of high octane paraffinic fractions and the simultaneous recovery of naphthenes as naphthenes of hydroaromatic structure or as aromatics from hydrocarbon mixtures comprising both paraffins and non-hydroaromatic naphthenes having the same number of carbon atoms to the molecule, with no greater catalyst consumption than heretofore required in the isomerization of only the paraffin portion of the feed.

In order that the invention may be more readily understood, it will be described herein with reference to the attached drawing forming a part of this specification and wherein the single figure illustrates more or less diagrammatically one form of apparatus suitable for the execution of the invention.

A mixture of saturated hydrocarbons consisting essentially of paraffins and naphthenes of non-hydroarmoatic 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 1 and heater 2 into a first reaction zone. The reaction zone may comprise, for example, a reactor 3 provided with suitable stirring means. It may at times be advantageous to subject the charge to a fractionation prior to its entry into reactor 3. 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 4 into a feed fractionating zone represented in the drawing by single fractionator 5. Within fractionator 5 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 6 into line 2 leading into reactor 3.

Within reactor 3 the hydrocarbon stream is contacted at naphthene isomerizing conditions with a fluid catalyst residue obtained, as indicated in greater detail below in the treatment of paraffinic hydrocarbons with a metal halide catalyst of the Friedel-Crafts type, thereby effecting the selective conversion of non-hydroaromatic naphthenes comprising methyl cyclopentane to hydroaromatic naphthenes comprising cyclohexane. Temperatures in reactor 3 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 naphthene conversion, have been found suitable. Hydrogen halide promoters are preferably present in only small amounts, for example in quantities not exceeding about one per cent of the charge to reactor 3.

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 hydrocarbon fraction boiling in the range of from 63 to 90° C. and having the following composition:

	Percent
Normal hexane	41
Methyl cyclopentane	38
Cyclohexane	13
Benzene	8

was contacted at the naphthene isomerizing conditions indicated in the Table A below with a catalyst residue obtained by scrubbing with a paraffinic hydrocarbon, the spent catalyst produced in the isomerization of a paraffin with a catalyst melt consisting of $AlCl_3$ dissolved in molten $SbCl_3$ and separating the resulting residue.

Table A

Temperature	°C.	100
Catalyst residue to hydrocarbon feed ratio		1:1
Contact time	minutes	22
HCl added, percent of feed		0.87
Duration of run	hours	305

The results of the operation were as follows:

Cyclohexane in isomerizate as percentage of total naphthenes in feed	percent	65
Feed treated per pound of catalyst residue charged	gallons	71
Feed treated per pound of $AlCl_3$ in catalyst residue charged	do	116

Reaction products comprising normal hexane, cyclohexane, isohexanes originally present in the feed or formed in the process, and entrained catalyst are passed from reactor 3 into a catalyst separator 8, wherein entrained catalyst is separated. Separated catalyst is permitted to flow from separator 8 back into reactor 3. Spent catalyst is withdrawn from reactor 3 by means of valved line 9. Hydrocarbons are passed from separator 8 through line 10 into a fractionator 11.

Within fractionator 11 a lighter fraction comprising the hydrogen halide promoter is separated and passed therefrom through valved lines 12 and 13 into line 2. Hydrogen halide promoter, when needed, may be introduced into the system from an outside source by means of valved line 14 leading into line 13. If desired, a light hydrocarbon fraction comprising normal hexane and unconverted methyl cyclopentane may be separated in fractionator 11 and recycled with the promotor through lines 12, 13 and 2 into reactor 3.

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 11 and passed through line 16 into a fractionator 17. When the charge is subjected to a preliminary fractionation in feed fractionator 5 as described above, the bottoms therefrom comprising normal hexane and cyclohexane may be passed through line 18 into line 16. Within fractionator 17 a lighter fraction comprising normal hexane is separated from a heavier fraction consisting essentially of cyclohexane. The latter fraction is withdrawn from fractionator 17 through valved line 19 and eliminated from the system as a final product.

The lighter paraffinic fraction separated in fractionator 17 comprising largely normal hexane is passed, at least in part, through valved lines 21 and 22 and through indirect heat exchanger 23 into line 25, provided with heater 26 and leading into a scrubbing tower 27. Within scrubber 27 the hydrocarbon stream is contacted in the liquid phase with a portion of at least partly spent catalyst emanating from a second conversion zone described more fully below. The hydrocarbon stream comprising extracted catalyst components is passed from scrubber 27 through line 28 and indirect heat exchanger 29 into a second conversion zone. The second conversion zone may comprise, for example, a reactor 31 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 31 the hydrocarbon stream is subjected to isomerization conditions effecting the conversion of straight chain or branched chain paraffin hydrocarbons to branched and more highly branched chain paraffin hydrocarbons. The paraffin isomerization conditions are obtained by the use of an active isomerization catalyst comprising a metal halide of the Friedel-Crafts type, preferably of a fluid type. Suitable fluid 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—$ZnCl_2$, etc.

Other suitable paraffin isomerizing catalysts comprise: an aluminum halide suspended in a suitable organic solvent, such as for example, a portion of the charge; organo-metal halide complexes such as an aluminum halide-hydrocarbon complex comprising suspended free aluminum halide; etc. The temperature to be maintained within reactor 31 will vary with the nature of the particular catalysts used. When using the highly active 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 31 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
36	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	----
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 catalyst are passed from reactor 31 into catalyst separator 32.

Within separation chamber 32 a substantial degree of separation between catalyst melt and hydrocarbon will be effected. The supernatent hydrocarbon layer, which in general will comprise some admixed and dissolved catalyst, is withdrawn from separator 32 and passed through line 33 into a vaporizing zone. The vaporizing zone may suitably consist of the lower part of a column 34, an intermediate part of which is provided with suitable packing means, baffles, or the like. Within column 34 separation of hydrocarbons from entrained catalyst components is effected with the aid of heating coil 35. Since antimony chloride is relatively volatile, its separation from the hydrocarbon within column 34 is aided by the introduction of cold hydrocarbon reflux into the upper part of the column by means of valved line 36. Hydrocarbon vapors comprising hydrogen chloride promoter are passed from the upper part of column 34 through line 37 and cooler 38 into accumulator 40. Catalyst components consisting essentially of antimony chloride, separated out as a liquid fraction within column 34, are forced through line 41 into reactor 31. Additional aluminum chloride, required to maintain catalyst composition, is added to the catalyst flowing through line 41 by passing this stream through a suitable vessel containing anhydrous $AlCl_3$ or by the addition of the halide salt by means of valved conduit 42.

Hydrocarbons and hydrogen chloride are passed from accumulator 40 through line 46 into a fractionator 47. Within fractionator 47 a lighter fraction comprising hydrogen chloride is separated and recycled through line 48 to line 28. Make-up hydrogen chloride is introduced into line 48 through valved line 49. A valved line 50 leading into line 48 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 47 and passed through line 51 into a final fractionator 52. Within fractionator 52 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 53. A liquid fraction comprising normal hexane is withdrawn from the lower part of fractionator 52 and eliminated from the system through valved line 54. A part or all of the hydrocarbons passing through line 54 may be passed through valved line 55 into line 28 leading into reactor 31.

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 3 and 31.

The catalyst phase, separated out within separator 32, is forced through line 44 into the upper part of extraction column 27. The portion of catalyst thus introduced into extraction column 3 will pass countercurrent to the upflow of the liquid hydrocarbon. In its passage through column 27 active components comprising antimony chloride are dissolved in the hydrocarbon

stream and passed therewith to reactor 31. Another portion of the catalyst comprising components which are spent, or at least partly spent, with respect to their ability to catalyze the isomerization reaction, remains insoluble in the hydrocarbon stream and is separated therein as a heavier fluid catalyst residue. The hydrocarbon charge to scrubber 27 is preferably preheated, for example, with the aid of a suitable heat exchanger 26, to a temperature favorable to the extraction operation. This temperature will vary with the nature of the material being treated and the particular catalyst used. In the treatment of paraffinic hydrocarbons temperatures in the approximate range of from 50° C. to 125° C. and preferably from 50° C. to 100° C. are found suitable. The pressure within column 27 is always sufficiently high to maintain at least a substantial portion of the hydrocarbon stream passing therethrough in the liquid phase.

It has been found that the fluid catalyst residue separated within extractor 27 will comprise any hydrocarbon-aluminum chloride complex formed within reactor 31. It has also been found that this material is substantially insoluble in the hydrocarbon feed which contributed to its formation and will not undergo decomposition or disintegration to any substantial degree in the extraction zone, whereas the active antimony chloride-aluminum chloride catalyst components active for paraffin isomerization possess an appreciable degree of solubility in the hydrocarbon stream. The composition of the fluid catalyst residue separated within column 27 will vary to some degree with the nature of material treated and operating conditions used. The catalyst residue thus obtained as a by-product of the isomerization operation is found to possess appreciable fluidity and will maintain this fluidity at temperatures substantially below room temperatures. The lower part of column 27 may, however, be provided with a jacket for the passage of a heating medium therethrough to aid in maintaining the desired temperature conditions therein.

The rate at which catalyst is withdrawn from separating chamber 32 and passed to the upper part of extractor 27 may vary within the scope of the invention. As pointed out above, however, it is highly advantageous to effect the catalyst withdrawal at a rate sufficiently great to prevent the accumulation to any substantial degree of even partially spent catalyst within reactor 31.

The fluid catalyst residue separated within scrubber 27 is withdrawn therefrom and forced through line 57 to reactor 3. It is to be noted that the fluid catalyst residue 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 this hydrocarbon-aluminum halide complex 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.

It is to be stressed that not only is the addition of fresh aluminum chloride to the catalyst residue passing through line 57 into reactor 3 not required but is expressly to be avoided to maintain that peculiar quality of the resulting mixture which is imparted thereto by the inherent characteristics of the by-product catalyst residue emanating from scrubber 27.

Although the detailed illustrative description of the invention has been directed to the treatment of hydrocarbon mixtures consisting essentially of naphthenes and paraffins having six carbon atoms to the molecule, it is in no wise intended to limit the application of the invention to any particular naphthene-paraffin mixture and may be applied to hydrocarbon mixtures comprising naphthenes and paraffins of more than six carbon atoms to the molecule.

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.

The high efficiency with which naphthenic hydrocarbons of non-hydroaromatic structure, having more than six carbon atoms to the molecule, are selectively converted to naphthenes of hydroaromatic structure in the presence of paraffinic hydrocarbons is exemplified by the following example:

EXAMPLE IV

A dimethylcyclopentane concentrate having the following composition:

	Per cent
Dimethylcyclopentanes	55
Cyclohexane and methylcyclohexane	20
Paraffins predominating in heptane	24

was contacted at the naphthene isomerizing conditions indicated in Table B below with a catalyst residue having the following composition:

	Per cent by weight
$AlCl_3$	62.8
$SbCl_3$	5.5
Carbon as CH_2	26.2
Cl as HCl	4.8

The catalyst residue was obtained by scrubbing with a paraffinic hydrocarbon, the spent catalyst obtained in the isomerization of a paraffinic hydrocarbon with a catalyst melt consisting of aluminum chloride dissolved in molten antimony trichloride and separating the resulting residue.

Table B

Temperature, °C.	100
Cat. residue to hydrocarbon feed ratio	1:1
Contact time, minutes	18
Vol. of feed/vol. of catalyst residue/hr.	3.4
HCl added percent of feed	0.24
Duration of operation, hours	500

Results of the operation were as follows:

Conversion of dimethylcyclopentane to methylcyclohexane, per cent	67
Paraffins converted (percent of feed), per cent	Less than 3
Feed treated per pound of catalyst residue, gallons	150
Feed treated per pound of $AlCl_3$ in catalyst residue, gallons	240
Potential toluene production per pound of catalyst residue, gallons	46
Potential toluene production per pound of $AlCl_3$ in catalyst residue, gallons	73

In a parallel operation under substantially identical operating conditions but utilizing a fresh $AlCl_3$-hydrocarbon complex prepared from $AlCl_3$ and an aromatic kerosene extract having a boiling range of 150° C.–200° C. the following results were obtained:

Conversion of dimethylcyclopentane to methylcyclohexane ----------per cent--	65
Feed treated per pound of $AlCl_3$ in catalyst ----------gallons--	80
Potential toluene production per pound of $AlCl_3$ in catalyst ----------gallons--	25

The highly advantageous aspect of the invention is readily apparent from the foregoing example wherein it is shown that the catalyst residue, which already has functioned to exhaustion in the isomerization of paraffins was still able to catalyze naphthene isomerization with yields considerably in excess of a freshly prepared $AlCl_3$-hydrocarbon complex catalyst heretofore generally preferred in large scale operations involving naphthene isomerization.

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.

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.

We claim as our invention:

1. The process for isomerizing naphthenic hydrocarbons having at least six carbon atoms to the molecule and containing at least five carbon atoms in the ring to isomeric naphthenic hydrocarbons having at least six carbon atoms to the molecule and containing at least five carbon atoms in the ring which comprises contacting hydrocarbons consisting essentially of paraffinic hydrocarbons with a liquid catalyst comprising a metal halide of the Friedel-Crafts type at paraffin isomerizing conditions until said catalyst is at least partly spent with regard to ability to promote the paraffin isomerization reaction, separating at least partly spent catalyst from hydrocarbon reactants, extracting said separated catalyst with a substantially paraffinic hydrocarbon solvent, thereby separating said catalyst by solution into catalyst components soluble in said solvent and a liquid catalyst residue, and contacting hydrocarbons comprising said naphthenic hydrocarbons with said catalyst residue at naphthene isomerizing conditions thereby selectively converting naphthenic hydrocarbons having at least six carbon atoms to the molecule and containing at least five carbon atoms in the ring to isomeric naphthenic hydrocarbons having at least six carbon atoms to the molecule and containing at least five carbon atoms in the ring.

2. The process for the conversion of naphthenic hydrocarbons of nonhydroaromatic structure having at least six carbon atoms to the molecule to naphthenes of hydroaromatic structure which comprises contacting hydrocarbons consisting essentially of paraffinic hydrocarbons with a liquid catalyst comprising a metal halide of the Friedel-Crafts type at paraffin isomerizing conditions until said catalyst is at least partly spent with regard to ability to promote the paraffin isomerization reaction, separating at least partly spent catalyst from hydrocarbon reactants, extracting said separated catalyst with a substantially paraffinic hydrocarbon solvent, thereby separating said catalyst by solution into catalyst components soluble in said solvent and a liquid catalyst residue, and contacting hydrocarbons comprising said naphthenic hydrocarbons with said catalyst residue at naphthene isomerizing conditions, thereby selectively converting naphthenes of non-hydroaromatic structure to naphthenes of hydroaromatic structure.

3. The process for selectively isomerizing naphthenes of nonhydroaromatic structure having at least six carbon atoms to the molecule in admixture with isomerizable paraffinic hydrocarbons to naphthenes of hydroaromatic structure which comprises contacting hydrocarbons consisting essentially of paraffinic hydrocarbons with a liquid catalyst comprising a metal halide of the Friedel-Crafts type at paraffin isomerizing conditions until said catalyst is at least partly spent with regard to ability to promote the paraffin isomerization reaction, separating at least partly spent catalyst from hydrocarbon reactants, extracting said separated catalyst with a substantially paraffinic hydrocarbon solvent, thereby separating said catalyst by solution into catalyst components soluble in said solvent and a liquid catalyst residue, and contacting hydrocarbons comprising said naphthenic hydrocarbons with said catalyst residue at naphthene isomerizing conditions, thereby selectively isomerizing naphthenes of nonhydroaromatic structure to naphthenes of hydroaromatic structure.

4. The process for selectively isomerizing naphthenes of nonhydroaromatic structure having at least six carbon atoms to the molecule in admixture with isomerizable paraffinic hydrocarbons to naphthenes of hydroaromatic structure which comprises contacting hydrocarbons consisting essentially of paraffinic hydrocarbons with a liquid catalyst comprising a halide of aluminum at paraffin isomerizing conditions until said catalyst is at least partly spent with regard to ability to promote the paraffin isomerization reaction, separating at least partly spent catalyst from hydrocarbon reactants, extracting said separated catalyst with a substantially paraffinic hydrocarbon solvent, thereby separating said catalyst by solution into catalyst components soluble in said solvent and a liquid catalyst residue, and contacting hydrocarbons comprising said naphthenic hydrocarbons with said catalyst residue at naphthene isomerizing conditions, thereby selectively isomerizing naphthenes of

nonhydroaromatic structure to naphthenes of hydroaromatic structure.

5. The process for selectively isomerizing naphthenes of nonhydroaromatic structure having at least six carbon atoms to the molecule in admixture with isomerizable paraffinic hydrocarbons to naphthenes of hydroaromatic structure which comprises contacting hydrocarbons consisting essentially of paraffinic hydrocarbons with a liquid catalyst comprising aluminum chloride at paraffin isomerizing conditions until said catalyst is at least partly spent with regard to ability to promote the paraffin isomerization reaction, separating at least partly spent catalyst from hydrocarbon reactants, extracting said separated catalyst with a substantially paraffinic hydrocarbon solvent, thereby separating said catalyst by solution into catalyst components soluble in said solvent and a liquid catalyst residue, and contacting hydrocarbons comprising said naphthenic hydrocarbons with said catalyst residue at naphthene isomerizing conditions, thereby selectively isomerizing naphthenes of nonhydroaromatic structure to naphthenes of hydroaromatic structure.

6. The process for selectively isomerizing naphthenes of nonhydroaromatic structure having at least six carbon atoms to the molecule in admixture with isomerizable paraffinic hydrocarbons to naphthenes of hydroaromatic structure which comprises contacting hydrocarbons consisting essentially of paraffinic hydrocarbons with a liquid catalyst melt comprising a halide of antimony and a halide of aluminum at paraffin isomerizing conditions until said catalyst is at least partly spent with regard to ability to promote the paraffin isomerization reaction, separating at least partly spent catalyst from hydrocarbon reactants, extracting said separated catalyst with a substantially paraffinic hydrocarbon solvent, thereby separating said catalyst by solution into catalyst components soluble in said solvent and a liquid catalyst residue, and contacting hydrocarbons comprising said naphthenic hydrocarbons with said catalyst residue at naphthene isomerizing conditions, thereby selectively isomerizing naphthenes of nonhydroaromatic structure to naphthenes of hydroaromatic structure.

7. The process for the conversion of naphthenic hydrocarbons of nonhydroaromatic structure having at least six carbon atoms to the molecule to naphthenes of hydroaromatic structure which comprises contacting hydrocarbons consisting essentially of paraffinic hydrocarbons with a liquid catalyst melt comprising aluminum chloride and antimony chloride at paraffin isomerizing conditions until said catalyst is at least partly spent with regard to ability to promote the paraffin isomerization reaction, separating at least partly spent catalyst from hydrocarbon reactants, extracting said separated catalyst with a substantially paraffinic hydrocarbon solvent, thereby separating said catalyst by solution into catalyst components soluble in said solvent and a liquid catalyst residue, and contacting hydrocarbons comprising said naphthenic hydrocarbons with said catalyst residue at naphthene isomerizing conditions, thereby selectively converting naphthenes of non-hydroaromatic structure to naphthenes of hydroaromatic structure.

8. The process for catalytically isomerizing hydrocarbons comprised in a hydrocarbon mixture consisting essentially of isomerizable straight chain paraffin hydrocarbons and naphthene hydrocarbons of non-hydroaromatic structure having at least 6 carbon atoms to the molecule which comprises contacting said hydrocarbon mixture at isomerizing conditions in a first conversion zone with selective naphthene isomerization catalyst comprising a catalyst residue obtained within the system, thereby selectively converting naphthenes of non-hydroaromatic structure to naphthenes of hydroaromatic structure, separating naphthenes comprising naphthenes of hydroaromatic structure from the effluence from the first conversion zone, contacting the remaining paraffinic hydrocarbons with a liquid type catalyst comprising a metal halide of the Friedel-Crafts type at isomerizing conditions in a second conversion zone, thereby effecting the conversion of straight chain paraffins to branched chain paraffins, withdrawing a portion of at least partly spent catalyst from said second conversion zone, scrubbing said portion of catalyst with said paraffinic hydrocarbons passing to the second conversion zone thereby separating active catalyst components by solution from a liquid catalyst residue, and passing said catalyst residue to said first conversion zone to be used therein as said selective naphthene isomerization catalyst.

9. The process for catalytically isomerizing hydrocarbons comprised in a hydrocarbon mixture consisting essentially of isomerizable straight chain paraffin hydrocarbons and naphthene hydrocarbons of non-hydroaromatic structure having at least 6 carbon atoms to the molecule which comprises contacting said hydrocarbon mixture at isomerizing conditions in a first conversion zone with selective naphthene isomerization catalyst comprising a catalyst residue obtained within the system, thereby selectively converting naphthenes of non-hydroaromatic structure to naphthenes of hydroaromatic structure, separating naphthenes comprising naphthenes of hydroaromatic structure from the effluence from the first conversion zone, contacting the remaining paraffinic hydrocarbons with a liquid type catalyst comprising halide of aluminum at isomerizing conditions in a second conversion zone, thereby effecting the conversion of straight chain paraffins to branched chain paraffins, withdrawing a portion of at least partly spent catalyst from said second conversion zone, scrubbing said portion of catalyst with said paraffinic hydrocarbons passing to the second conversion zone thereby separating active catalyst components by solution from a liquid catalyst residue, and passing said catalyst residue to said first conversion zone, to be used therein as said selective naphthene isomerization catalyst.

10. The process for catalytically isomerizing hydrocarbons comprised in a hydrocarbon mixture consisting essentially of isomerizable straight chain paraffin hydrocarbons and naphthene hydrocarbons of non-hydroaromatic structure having at least 6 carbon atoms to the molecule which comprises contacting said hydrocarbon mixture at isomerizing conditions in a first conversion zone with selective naphthene isomerization catalyst comprising a catalyst residue obtained within the system, thereby selectively converting naphthenes of non-hydroaromatic structure to naphthenes of hydroaromatic structure, separating naphthenes comprising naphthenes of hydroaromatic structure from the effluence from the first conversion zone, contacting the remaining paraffinic hydrocarbons with a liquid type catalyst comprising aluminum chloride at isomerizing conditions in a second conversion zone, thereby effecting the conversion of straight

chain paraffins to branched chain paraffins, withdrawing a portion of at least partly spent catalyst from said second conversion zone, scrubbing said portion of catalyst with said paraffinic hydrocarbons passing to the second conversion zone thereby separating active catalyst components by solution from a liquid catalyst residue, and passing said catalyst residue to said first conversion zone to be used therein as said selective naphthene isomerization catalyst.

11. The process for catalytically isomerizing hydrocarbons comprised in a hydrocarbon mixture consisting essentially of isomerizable straight chain paraffin hydrocarbons and naphthene hydrocarbons of non-hydroaromatic structure having at least 6 carbon atoms to the molecule which comprises contacting said hydrocarbon mixture at isomerizing conditions in a first conversion zone with selective naphthene isomerization catalyst comprising a catalyst residue obtained within the system, thereby selectively converting naphthenes of non-hydroaromatic structure to naphthenes of hydroaromatic structure, separating naphthenes comprising naphthenes of hydroaromatic structure from the effluence from the first conversion zone, contacting the remaining paraffinic hydrocarbons with a liquid catalyst melt comprising antimony trichloride and aluminum chloride at isomerizing conditions in a second conversion zone, thereby effecting the conversion of straight chain paraffins to branched chain paraffins, withdrawing a portion of at least partly spent catalyst from said second conversion zone, scrubbing said portion of catalyst with said paraffinic hydrocarbons passing to the second conversion zone thereby separating active catalyst components by solution from a liquid catalyst residue, and passing said catalyst residue to said first conversion zone to be used therein as said selective naphthene isomerization catalyst.

12. The process for the production of a high octane paraffin hydrocarbon fraction from a mixture of saturated hydrocarbons comprising straight chain paraffin hydrocarbons having at least 6 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 at isomerization conditions in a first conversion zone with a selective naphthene isomerization catalyst comprising a catalyst residue obtained within the system, thereby effecting the selective conversion of naphthenes of non-hydroaromatic structure to naphthenes of hydroaromatic structure, separating naphthenes comprising naphthenes of hydroaromatic structure from the effluence from the first conversion zone, contacting the remaining hydrocarbons with a liquid type catalyst comprising a metal halide of the Friedel-Crafts type at isomerization conditions in a second conversion zone, thereby converting said remaining hydrocarbons to a high octane paraffin hydrocarbon fraction comprising branched chain paraffins, withdrawing a portion of at least partly spent catalyst from said second conversion zone, contacting said portion of catalyst with at least a part of the hydrocarbon charge to the second conversion zone, thereby separating said catalyst into soluble active catalyst components and a liquid catalyst residue, and utilizing said liquid catalyst residue as said selective naphthene isomerization catalyst in said first conversion zone.

13. The process for the production of a high octane paraffin hydrocarbon fraction from a mixture of saturated hydrocarbons comprising straight chain paraffin hydrocarbons having at least 6 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 at isomerization conditions in a first conversion zone with a selective naphthene isomerization catalyst comprising a catalyst residue obtained within the system, thereby effecting the selective conversion of naphthenes of non-hydroaromatic structure to naphthenes of hydroaromatic structure, separating naphthenes comprising naphthenes of hydroaromatic structure from the effluence from the first conversion zone, contacting the remaining hydrocarbons with a liquid type catalyst comprising a halide of aluminum at isomerization conditions in a second conversion zone, thereby converting said remaining hydrocarbons to a high octane paraffin hydrocarbon fraction comprising branched chain paraffins, withdrawing a portion of at least partly spent catalyst from said second conversion zone, contacting said portion of catalyst with at least a part of the hydrocarbon charge to the second conversion zone, thereby separating said catalyst into soluble active catalyst components and a liquid catalyst residue, and utilizing said liquid catalyst residue as said selective naphthene isomerization catalyst in said first conversion zone.

14. The process for the production of a high octane paraffin hydrocarbon fraction from a mixture of saturated hydrocarbons comprising straight chain paraffin hydrocarbons having at least 6 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 at isomerization conditions in a first conversion zone with a selective naphthene isomerization catalyst comprising a catalyst residue obtained within the system, thereby effecting the selective conversion of naphthenes of non-hydroaromatic structure to naphthenes of hydroaromatic structure, separating naphthenes comprising naphthenes of hydroaromatic structure from the hydrocarbon mixture after the naphthene treatment, contacting the remaining hydrocarbons with a liquid catalyst melt comprising antimony trichloride and aluminum chloride at isomerization conditions in a second conversion zone, thereby converting said remaining hydrocarbons to a high octane paraffin hydrocarbon fraction comprising branched chain paraffins, withdrawing a portion of at least partly spent catalyst from said second conversion zone, contacting said portion of catalyst with at least a part of the hydrocarbon charge to the second conversion zone, thereby separating said catalyst into soluble active catalyst components and a liquid catalyst residue, and utilizing said liquid catalyst residue as said selective naphthene isomerization catalyst in said first conversion zone.

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