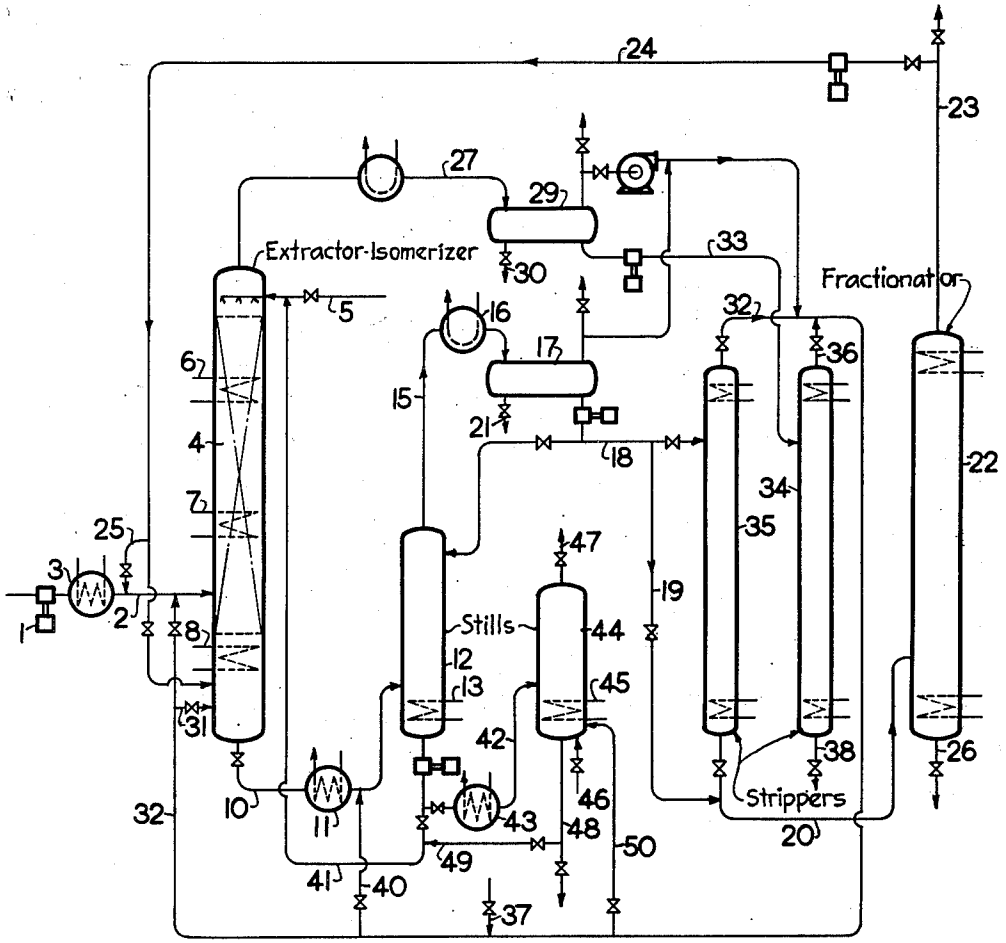
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CYCLOPARAFFIN PRODUCTION

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Inventors: William E. Ross
Philip Pezzaglia

By their Attorney: C. J. Ott

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CYCLOPARAFFIN PRODUCTION

William E. Ross, Berkeley, and Philip Pennaglia, Oakland, Calif., assignors to Shell Development Company, San Francisco, Calif., a corporation of Delaware

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This invention relates to an improved process for the separation of cycloparaffins from hydrocarbon mixtures comprising cycloparaffins in admixture with open chain paraffins. The invention relates more particularly to an improved process for the production of cycloparaffins of hydroaromatic structure from hydrocarbon fractions comprising open chain paraffins and cycloparaffins of non-hydroaromatic structure.

The cycloparaffins have become of exceeding importance as starting materials and intermediates in the production of a wide variety of organic products. The most fertile source of these highly desirable materials resides in the hydrocarbon mixtures obtained in the natural state as petroleum and in the products obtained in the thermal or catalytic treatment of petroleum or distillate fractions thereof, and in the thermal or catalytic treatment such as, for example, hydrogenation, of carbonaceous materials, etc. As is well known, the cycloparaffins in these readily available hydrocarbon mixtures are found therein in admixture with open chain paraffins. Realization of the full advantages inherent in the many chemical processes relying upon the cycloparaffins as starting or intermediate material has heretofore been seriously handicapped by the lack of a process enabling the efficient separation on a practical scale of the cycloparaffins from the open chain paraffins in admixture with which they are generally encountered. Thus, separation of the cycloparaffins from open chain paraffins having the same or approximately the same number of carbon atoms to the molecule by such methods as fractional distillation, if at all possible, is often rendered so complex and delicate an operation as to render it impractical.

Of the cycloparaffins, those of hydroaromatic structure are presently of particular value and find application in the production of an exceedingly wide range of valuable organic products. The production of the cycloparaffins of hydroaromatic structure in a state of required purity is rendered even more difficult since to the difficulty of their separation from open chain paraffins is added the often equally vexing problem of their separation from isomeric non-hydroaromatic cycloparaffins and other hydrocarbons of close boiling range or capable of forming azeotropes therewith. By the term "hydroaromatic cycloparaffins" as used throughout this specification and appended claims is meant the cycloparaffins having a hexamethylene ring such as, for example, cyclohexane and the alkyl cyclohexanes, to distinguish them from cycloparaffins of non-hydroaromatic structure comprising those having pentamethylene rings such as, for example, methylcyclopentane and the alkyl cyclopentanes.

It has been suggested heretofore to subject the hydrocarbon mixtures comprising open chain paraffins and cycloparaffins of non-hydroaromatic structure to isomerizing conditions effecting the conversion of non-hydroaromatic cycloparaffins to hydroaromatic cycloparaffins and thereafter subject the entire hydrocarbon mixture to fractionation to separate fractions comprising desired cycloparaffins. Although such a procedure enables the concentration on a practical scale of certain of the cycloparaffins such as, for example, cyclohexane, it still does not enable the attainment of desired yields in even such specific instances. It furthermore does not eliminate to a sufficient degree the difficulties of separation. Thus, for example, in the production of cyclohexane from hydrocarbon mixtures comprising C_6 paraffins and methylcyclopentane, the available raw material must first be subjected to a fractionation resulting in the production of a methylcyclopentane concentrate. In so doing, a considerable amount of valuable cyclohexane originally present in the available raw material as well as a certain amount of methylcyclopentane, is left in the higher boiling fraction from which the methylcyclopentane concentrate is separated. Such methods furthermore offer limited advantages in ony such specific cases. They do not provide a practical answer, for example, to the production of hydrocarbons predominating in methylcyclohexane from the readily available hydrocarbon mixtures comprising the non-hydroaromatic cycloparaffins having seven carbon atoms to the molecule in admixture with close boiling open chain paraffins having seven and eight carbon atoms to the molecule. In such case the problem of separation is in no wise overcome by isomerizing the mixture as a whole under conditions resorted to heretofore.

In its broadest aspect, the object of the present invention is to provide an improved process enabling the more efficient separation of cycloparaffins from hydrocarbon mixtures comprising cycloparaffins and open chain paraffins.

A more particular object of the invention is the provision of a process enabling the more efficient separation of cycloparaffins from hydrocarbon fractions comprising cycloparaffins and open chain paraffins having substantially the same number of carbon atoms to the molecule.

A further object of the invention is the provi-

sion of an improved process enabling the more efficient separation of cycloparaffins of non-hydroaromatic structure from hydrocarbon mixtures comprising cycloparaffins and open chain paraffins with simultaneous conversion, during the separation, of the non-hydroaromatic cycloparaffins to hydroaromatic cycloparaffins.

Another object of the invention is the provision of an improved process for the production of hydrocarbons predominating in cyclohexane from hydrocarbon fractions comprising open chain hexanes and methylcyclopentane.

Still another object of the invention is the provision of an improved process for the more efficient production of methylcyclohexane from hydrocarbon fractions comprising open chain paraffins and cycloparaffins of non-hydroaromatic structure having seven carbon atoms to the molecule. Other objects and advantages of the invention will become apparent from the following description thereof.

It is known that unsaturated hydrocarbons such as olefins and aromatic hydrocarbons which can react readily with an aluminum chloride, are removed from hydrocarbon mixtures containing them by treatment with aluminum chloride. It has now been found that saturated hydrocarbons of cyclic structure comprising the cycloparaffins can be separated efficiently by extraction under suitable conditions with a preformed complex obtained by the interaction of a metal halide of the Friedel-Crafts type and an organic compound. It has been found that by selection of suitable conditions, the cycloparaffins of non-hydroaromatic structure present in the hydrocarbon mixture treated are converted to, and separately recovered, as cycloparaffins of hydroaromatic structure.

In accordance with the process of the invention, the hydrocarbon charge comprising a mixture of cycloparaffins and open chain paraffins such as, for example, a naphthenic straight run gasoline fraction, optionally predominating in hydrocarbons having substantially the same number of carbon atoms to the molecule, such as a hexane or heptane fraction, is contacted with a preformed organo-metal halide complex, obtained by the interaction of a metal halide of the Friedel-Crafts type and an organic compound, in an extraction zone under suitable conditions resulting in the formation of a raffinate phase comprising paraffins and an extract phase comprising organo-metal halide complex and cycloparaffins. A suitable extraction zone comprises, for example, an enlarged chamber or a tower packed with a suitable packing material through which the hydrocarbon charge is passed counter-current to a descending stream of the organo-metal halide complex. The extract phase is passed into a complex separating zone wherein hydrocarbons comprising the cycloparaffins are separated from the organo-metal halide complex. The cycloparaffins eliminated from the complex separating zone are introduced into a product separating zone wherein separation of cycloparaffins into fractions predominating in cycloparaffins of particular composition is effected. A part of the cycloparaffins thus obtained is preferably recycled to the extraction zone and introduced therein at a point at, and preferably below, the point of introduction of the charge.

By maintaining suitable cycloparaffin isomerizing conditions within the extraction zone, comprising the introduction of hydrogen halide or a material affording a hydrogen halide, and the maintenance of temperature conditions defined more fully below, the isomerization of cycloparaffins such as, for example, the conversion of cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure is accomplished simultaneously with the extraction operation.

When the extraction zone is maintained under cycloparaffin isomerizing conditions, the raffinate phase eliminated therefrom and the cycloparaffins eliminated from the complex separating zone are passed in separate streams to separate stripping zones wherein the hydrogen halide admixed therewith is separated as gaseous fractions. The gaseous fractions comprising the hydrogen halide are recycled to the lower part of the extraction zone.

It is to be noted that in the process of the invention a raffinate phase comprising open chain paraffins and an extract phase comprising organo-metal halide complex in admixture with cycloparaffins are separately removed from the extraction zone, and that such operation in no wise approximates the practice resorted to heretofore in the isomerization of hydrocarbons wherein hydrocarbons and catalyst are drawn in single stream from the reaction zone and wherein hydrocarbons separated from catalyst drawn from the reaction zone are recombined with the total hydrocarbon effluence from the reaction zone before or during product separation.

In order to set forth more clearly the nature of the invention it will be described herein in detail with reference to the attached drawing in which the single figure represents a more or less diagrammatic elevational view of one form of apparatus suitable for executing the process of the invention.

A hydrocarbon mixture comprising open chain paraffins and cycloparaffins such as, for example, a naphthenic hexane fraction comprising open chain hexanes, methylcyclopentane and cyclohexane, is taken from an outside source and forced by means of pump 1 through line 2, containing suitable heating means such as an indirect heat exchanger 3, into an extraction zone. The extraction zone may comprise an elongated chamber or column 4 containing inert solid contact material such as, for example Raschig rings, crushed brick, silica stone, etc. The hydrocarbon charge is introduced into the column at an intermediate point along the length thereof.

A preformed fluid organo-metal halide complex is introduced into the top of the column by means of valved line 5. The fluid organo-metal halide complex is prepared by mixing a metal halide of the Friedel-Crafts type, for example, a halide of aluminum such as aluminum chloride and/or aluminum bromide, with an organic compound under suitable conditions resulting in the interaction of the metal halide with the organic compound and/or decomposition products thereof. Suitable organic compounds with which the metal halide may be combined under conditions resulting in the obtaining of a desired organo-metal halide complex comprise, for example, aromatic hydrocarbons such as benzene, toluene; hydrocarbon fractions, such as an aromatic kerosene extract; cyclic olefins, such as cyclohexene, cyclopentene, and alkyl derivatives thereof; paraffinic and olefinic hydrocarbons of straight or branched chain structure; phenols; organic acids; ethers, etc. Of the suitable organo-metal halide com-

plexes, those comprising aluminum chloride-hydrocarbon complex are somewhat preferred.

By means of heat exchanger 3, and optionally heating or cooling means, such as closed coils 6, 7 and 8 within column 4, the hydrocarbons and complex are maintained in the temperature range of from about 20° to about 140° C., and preferably from about 20° C. to about 70° C. Atmospheric or superatmospheric pressures are maintained within column 4. The pressure is, however, kept sufficiently high to maintain the hydrocarbons in the liquid phase. Under these conditions cycloparaffins, in the hydrocarbon mixture passing upward through the column, will be selectively removed from open chain paraffins resulting in the formation of a raffinate phase in the upper part of the column consisting essentially of paraffinic hydrocarbons, and an extract phase in the lower part of the column consisting essentially of complex and cycloparaffins.

The extract phase, comprising aluminum chloride-hydrocarbon complex and cycloparaffins, is passed from the lower part of column 4 through valved line 10, and heat exchanging means 11, into a complex separating zone. The complex separating zone may comprise a still 12. Within still 12, hydrocarbons comprising cycloparaffins are distilled from the extract phase. Vapors comprising methylcyclopentane and cyclohexane are passed from still 12 through line 15 and cooler 16 into an accumulator 17. Cycloparaffins may be removed from accumulator 17 through valved line 21 as a final product. A part of the cycloparaffins is, however, preferably passed through lines 18, 19 and 20 into a fractionator 22. Within fractionator 22 a vapor fraction comprising methylcyclopentane is separated from a liquid fraction comprising cyclohexane. The liquid fraction is eliminated from fractionator 22 through valved line 26 as a final product. The vapor fraction is eliminated from fractionator 22 through valved line 23, and a part thereof is preferably recycled through line 24 into extraction column 4 and introduced therein at a point below the introduction of the hydrocarbon charge. This, it has been found, aids materially in the separation of cycloparaffins from paraffins under the operating conditions. A by-pass 25 is provided for the introduction of recycled methylcyclopentane into charge line 2.

The raffinate phase comprising open chain hexanes is taken overhead from column 4 and passed through line 27 into accumulator 29.

Although separation of complex from the cycloparaffins contained in the extract phase is accomplished by distillation in the above illustrative description of the invention, other means of effecting the separation may be resorted to. The complex may be separated from cycloparaffins by scrubbing the extract phase with a suitable hydrocarbon such as, for example, a low boiling saturated hydrocarbon, such as butane or pentane, as disclosed in copending application, Serial No. 538,893, filed June 6, 1944.

A particular advantage of the invention resides in the ability to recover the naphthenic hydrocarbons of non-hydroaromatic structure, originally present in the charge, in the form of naphthenic hydrocarbons of hydroaromatic structure. Thus, in the treatment of a naphthenic hexane fraction containing methylcyclopentane, maintenance of suitable cycloparaffin isomerizing conditions within column 4 enables the conversion of the methylcyclopentane to cyclohexane during the extraction operation. To attain these objectives the temperature within column 4 is maintained within the range of, for example, from about 30° to about 140° C. and preferably from about 70° to about 100° C. A hydrogen halide promoter such as, for example, hydrogen chloride, or a material affording the hydrogen halide under the conditions maintained in column 4, is introduced into the lower part of the column through valved line 31 at a point below the introduction of the charge. A part of the hydrogen halide may be introduced directly into charge line 2 from line 32. The hydrogen halide promoter is introduced at such a rate as to maintain a concentration of the hydrogen halide in the column in the range of from about 0.1 to about 2.0 and preferably from about 0.1 to about 0.5 per cent by weight of the hydrocarbon in the column.

When thus maintaining cycloparaffin isomerizing conditions within column 4, the raffinate phase passing through line 27, as well as the cycloparaffins emanating from still 12 through line 15, will comprise hydrogen chloride. The hydrocarbons comprising hydrogen chloride within accumulator 29 are forced through line 33 into a stripping column 34. Hydrocarbons comprising cycloparaffins containing hydrogen chloride are taken from accumulator 17, and forced through line 18 into a separate stripping column 35. Within stripping columns 34 and 35 conditions are maintained to effect the removal of the hydrogen chloride as a vapor overhead from the hydrocarbons. The hydrogen chloride thus separated in columns 34 and 35 is passed therefrom through lines 36, 32 and 31 into column 4. Make-up HCl is introduced into the system as required by means of valved line 37. Paraffinic hydrocarbons comprising open chain hexanes are eliminated from the lower part of stripping column 34, through valved line 38, as a final product. Cycloparaffins comprising cyclohexane and unconverted methylcyclopentane are passed from stripping column 35, through valved line 28, into fractionator 22.

Although the above-detailed description of the invention has been directed to the treatment of a naphthenic hexane fraction, it is to be understood that the invention is in no wise limited to the treatment of this particular naphthenic hydrocarbon mixture and may be applied to any hydrocarbon mixture comprising open chain paraffins in admixture with cycloparaffins. Thus, the invention may be applied with advantage to the treatment of naphthenic heptane fractions comprising dimethylcyclopentane, ethylcyclopentane, and methylcyclohexane, in addition to open chain heptanes, under conditions effecting separation of cycloparaffins from paraffins, optionally with simultaneous conversion of the dimethylcyclopentane, and ethylcyclopentane to methylcyclohexane. The charge to the system need not necessarily comprise only hydrocarbons having substantially the same number of carbon atoms to the molecule, and hydrocarbon mixtures comprising cycloparaffins and paraffins of relatively wide boiling range such as straight run naphthenic gasolines, straight run naphthenic naphthas, etc. may be charged directly to the system.

It is apparent from the foregoing that the invention obviates in a simple and a highly efficient manner the difficulties heretofore encountered in effecting the separation of cycloparaffins from paraffins and enables the attainment of such separation with the simultaneous isomerization of the cycloparaffins.

The following examples are indicative of the degree to which isomerization of cycloparaffins is accomplished, with simultaneous separation of cycloparaffins from admixture with open chain paraffins in accordance with the process of the invention.

Example I

A methylcyclopentane concentrate having the following composition

	Per cent volume
Methyl pentane	4.5
Normal hexane	40.0
Methylcyclopentane	55.0
Undetermined	0.5

was contacted in a single stage operation with an aluminum chloride-hydrocarbon complex under the following conditions:

Ratio of complex to hydrocarbon	2:1
Time of contact, minutes	30
Temperature, °C.	70

Hydrogen chloride was bubbled through the liquid throughout the operation to maintain a concentration of HCl equal to 0.1% of the hydrocarbons charged. A raffinate phase and an extract phase were separately withdrawn. The raffinate phase contained 70% by volume of the hydrocarbons charged whereas the extract phase contained 30% of the hydrocarbons charged. A conversion of methylcyclopentane to cyclohexane of 40% was obtained. The degree of separation of cycloparaffins from open chain paraffins is exemplified by the following ratios of naphthenes to paraffins:

Ratio of naphthenes to paraffins in charge	1.25
Ratio of naphthenes to paraffins in raffinate	1.06
Ratio of naphthenes to paraffins in extract	1.62

Example II

A methylcyclopentane concentrate having the following composition

	Per cent volume
Methyl pentane	4.0
Normal hexane	37.0
Methylcyclopentane	51.0
Benzene	8.0

was contacted in a single stage operation with an aluminum chloride hydrocarbon complex under the following conditions.

Ratio of complex to hydrocarbon	1:1
Time of contact, minutes	30
Temperature, °C.	70

Hydrogen chloride was bubbled through the liquid throughout the operation to maintain a concentration of HCl equal to 0.1% of hydrocarbons charged. A raffinate phase and an extract phase were separately withdrawn. The raffinate phase contained 70% by volume of the hydrocarbons charged whereas the extract phase contained 30% of the hydrocarbons charged. A conversion of methylcyclopentane to cyclohexane of 35% was obtained. The separation of cycloparaffins from open chain paraffins is exemplified by the following ratios of naphthenes to paraffins:

Ratio of naphthenes to paraffins in charge	1.24
Ratio of naphthenes to paraffins in raffinate	0.84
Ratio of naphthenes to paraffins in extract	1.64

It is to be pointed out that the above examples are single stage extraction operations wherein the complex and hydrocarbons are contacted with one another in a single operation. After equilibrium is established the two phases are separated from each other and withdrawn from the contacting zone. As such they are indicative of the substantially complete separation of cycloparaffins from admixed open chain paraffins obtainable when operating in a multiple stage or continuous flow operation. It is also evident from the foregoing examples that high conversions of the non-hydroaromatic cycloparaffin to hydroaromatic cycloparaffin is accomplished during the execution of the process within the specified conditions.

Separation of the complex from the raffinate, it has been found, may be facilitated by effecting the separation in the presence of additionally introduced hydrogen halide into the still. A valved line 40 is therefore provided enabling the passage of hydrogen chloride from line 32 into line 10 carrying the extract phase into still 12. In a further modification of the invention hydrogen halide, for example, hydrogen chloride, is introduced into still 12 through line 40, but no hydrogen halide is introduced into column 4. Column 4 will then function as described above to effect the separation of cycloparaffins from paraffins in the absence of any substantial cycloparaffin isomerization, whereas in still 12 isomerization of cycloparaffins, for example, conversion of cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure will take place. Under these conditions still 12 will function as a cycloparaffin isomerizing zone.

Aluminum chloride-hydrocarbon complex, substantially free of cycloparaffins, is eliminated from still 12 through valved line 41 and introduced into line 5, passing into the top of column 4.

Hydrocarbon mixtures comprising naphthenic hydrocarbons often contain, in addition to open chain paraffins, a certain amount of aromatic hydrocarbons. Thus, the naphthenic hexane and/or heptane fractions will generally comprise a certain amount of benzene and/or toluene. This material may be removed from the charge by suitable pretreatments prior to introduction into column 4. The aluminum chloride hydrocarbon complex, it has been found, however, is far more selective as a solvent for aromatic hydrocarbons than for naphthenic hydrocarbons. Distillation of the extract under conditions effecting the separation of cycloparaffins from the complex will generally result in a retention in the complex of at least a substantial amount of the aromatics originally present in the charge. In a modification of the invention, when the charge to the system comprises aromatic hydrocarbons, at least a part of the complex eliminated from still 12 is passed through line 42, containing heat exchanging means 43, into a second distillation zone comprising, for example, still 44. Within still 44 the complex, substantially free of cycloparaffins but still containing aromatic hydrocarbons, which in the treatment of naphthenic hexane fractions will comprise benzene, is subjected to more drastic distillation conditions to effect the separation of substantially all of the benzene. The more drastic conditions may be obtained by distillation at a higher temperature by means of heat input into heating means 43 and closed heating coil 45, by prolonged residence

time in still 44, by use of subatmospheric pressure, by the introduction of stripping gases such as hydrogen, methane, ethane, nitrogen, etc., through valved line 46 or HCl through line 50, or by any two or more of these expedients. Vapors comprising benzene are eliminated from still 44 through valved line 47. Aluminum chloride-hydrocarbon complex, now free of any substantial amount of benzene, is passed from still 44 through valved line 48, and is recycled at least in part through lines 49, 41 and 5 into the upper part of column 4.

The degree to which aromatic hydrocarbons can be separately recovered in the process of the invention is exemplified by the following example.

Example III

The complex remaining after subjecting the extract phase in Example II to distillation at a temperature of 90° C. and atmospheric pressure to separate the extracted cycloparaffins therefrom, was subjected to a second distillation in a separate zone at a temperature of 70° C., under a subatmospheric pressure of 150 mm. for a period of 2 hours. The resulting vapors were condensed and recovered. Upon analysis 33% by volume of the distillate was found to be aromatic hydrocarbon.

Example IV

A hydrocarbon fraction boiling in the range of from 65° C. to 85° C., containing normal hexane, methylcyclopentane, cyclohexane and 7% by weight of benzene was contacted countercurrently in continuous operation with an $AlCl_3$ hydrocarbon complex thereby forming a paraffinic raffinate phase and an extract phase containing the complex, cycloparaffins and benzene. The extract phase was stripped at 90° to 110° C. and atmospheric pressure for 30 minutes to remove extracted cycloparaffins therefrom. The remaining complex was thereafter subjected to further stripping, with the aid of hydrogen chloride, at a temperature of 90° to 100° C. for a period of one hour. Properties of the distillate product from the second stripping operation indicated it to contain above 90% of benzene.

The separate removal of the aromatics from the recycled complex is resorted to not only to maintain the efficiency of the aluminum chloride hydrocarbon complex as extracting medium and/or isomerization catalyst, but also, to separately recover the aromatic hydrocarbons originally present in the charge as a valuable by-product of the process.

The invention as described is capable of modifications without departing from the spirit and scope thereof. Thus, though a packed column has been chosen as a preferred extraction or extraction-isomerizing zone, other types of apparatus enabling intimate contact between the hydrocarbon charge and the organo-metal halide complex, resulting in the formation of an extract phase, and a raffinate phase may suitably be used. Thus, column 4 may be replaced by a plurality of chambers connected in series and provided with suitable stirring means, through which the hydrocarbon charge is passed, and in which operation raffinate may be removed from one or more of the chambers.

We claim as our invention:

1. The process for the production of cyclohexane from a hydrocarbon mixture comprising open chain hexanes and methylcyclopentane which comprises, subjecting said hydrocarbon mixture and a hydrocarbon-aluminum chloride complex to continuous countercurrent contact in the presence of added hydrogen chloride in a contacting zone at a temperature of from about 70° C. to about 100° C. to effect the conversion of methylcyclopentane to cyclohexane while forming a raffinate phase comprising open chain hexanes and an extract phase comprising said complex, cyclohexane and unconverted methylcyclopentane, removing the raffinate phase from one end of said contacting zone, separately removing said extract phase from the opposite end of said contacting zone, and separating cycloparaffins comprising cyclohexane from said extract phase.

2. The process for the production of cyclohexane from a hydrocarbon mixture comprising open chain hexanes and methylcyclopentane which comprises, subjecting said hydrocarbon mixture and a hydrocarbon-aluminum halide complex to continuous countercurrent contact in the presence of an added promoter affording a hydrogen halide in a contacting zone at a temperature of from about 30° C. to about 140° C. to effect the conversion of methylcyclopentane to cyclohexane while forming a raffinate phase comprising open chain hexanes and an extract phase comprising said complex, cyclohexane and unconverted methylcyclopentane, removing the raffinate phase from one end of said contacting zone, separately removing said extract phase from the opposite end of said contacting zone, and separating cycloparaffins comprising cyclohexane from said extract phase.

3. The process for the production of cycloparaffins of hydroaromatic structure from a hydrocarbon mixture comprising open chain paraffins and cycloparaffins of non-hydroaromatic structure which comprises, subjecting said hydrocarbon mixture and a hydrocarbon-aluminum halide complex to continuous countercurrent contact in the presence of an added hydrogen halide in a contacting zone at a temperature of from about 70° C. to about 100° C. to effect the conversion of cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure while forming a raffinate phase comprising open chain paraffins and an extract phase comprising said complex and cycloparaffins of hydroaromatic structure, removing the raffinate phase from one end of said contacting zone, separately removing said extract phase from the opposite end of said contacting zone, and separating cycloparaffins of hydroaromatic structure from said extract phase.

4. The process for the production of cycloparaffins of hydroaromatic structure from a hydrocarbon mixture comprising open chain paraffins and cycloparaffins of non-hydroaromatic structure which comprises, subjecting said hydrocarbon mixture and an organo-aluminum halide complex to continuous countercurrent contact in the presence of an added hydrogen halide in a contacting zone at a temperature of from about 30° C. to about 140° C. to effect the conversion of cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure while forming a raffinate phase comprising open chain paraffins and an extract phase comprising said complex and cycloparaffins of hydroaromatic structure, removing the raffinate phase from one end of said contacting zone, separately removing said extract phase from the opposite end of said contacting zone, and separating cycloparaffins of hydroaromatic structure from said extract phase.

5. The process for the production of cycloparaffins of hydroaromatic structure from a hydrocarbon mixture comprising open chain paraffins and cycloparaffins of non-hydroaromatic structure which comprises, subjecting said hydrocarbon mixture and an organo-metal halide complex to continuous countercurrent contact in the presence of an added promoter affording a hydrogen halide in a contacting zone at a temperature of from about 30° C. to about 140° C. to effect the conversion of cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure while forming a raffinate phase comprising open chain paraffins and an extract phase comprising said complex and cycloparaffins of hydroaromatic structure, separately removing the raffinate phase and extract phase from said contacting zone, and separating cycloparaffins of hydroaromatic structure from said extract phase.

6. The process for the production of cycloparaffins of hydroaromatic structure from a hydrocarbon mixture comprising open chain paraffins and cycloparaffins of non-hydroaromatic structure which comprises, subjecting said hydrocarbon mixture and an organo-metal halide complex to continuous countercurrent contact in the presence of an added promoter affording a hydrogen halide in a contacting zone at cycloparaffin isomerizing conditions to effect the conversion of cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure while forming a raffinate phase comprising open chain paraffins and an extract phase comprising said complex and cycloparaffins of hydroaromatic structure, separately removing the raffinate phase and extract phase from said contacting zone, passing said extract phase into a complex separating zone, separating cycloparaffins of hydroaromatic structure from complex in said complex separating zone, and passing complex free of any substantial amount of cycloparaffins from said complex separating zone to said contacting zone.

7. The process for the production of cyclohexane from a hydrocarbon mixture comprising open chain hexanes and methylcyclopentane which comprises subjecting said hydrocarbon mixture and a hydrocarbon-aluminum halide complex to continuous countercurrent contact in the presence of an added hydrogen halide in a contacting zone at a temperature of from about 70° C. to about 100° C. to effect the conversion of methylcyclopentane to cyclohexane while forming a raffinate phase comprising open chain hexanes and hydrogen halide and an extract phase comprising said complex, cyclohexane, methylcyclopentane and hydrogen halide, passing the raffinate phase from one end of said contacting zone into a stripping zone, passing said extract phase from the opposite end of said contacting zone into a complex separating zone, separating cycloparaffins in admixture with hydrogen halide from complex in said complex separating zone, passing said cycloparaffins in admixture with hydrogen halide from said complex separating zone to a separate stripping zone, separating a gaseous fraction comprising hydrogen halide in each of said stripping zones, and recycling said gaseous fractions from said stripping zones to said contacting zone.

8. The process for the production of cycloparaffins of hydroaromatic structure from a hydrocarbon mixture comprising open chain paraffins and cycloparaffins of non-hydroaromatic structure which comprises, subjecting said hydrocarbon mixture and an organo-metal halide complex to continuous countercurrent contact in the presence of an added promoter affording a hydrogen halide in a contacting zone at cycloparaffin isomerizing conditions to effect the conversion of cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure while forming a raffinate phase comprising open chain paraffins and hydrogen halide and an extract phase comprising said complex, cycloparaffins of hydroaromatic structure and hydrogen halide, passing said raffinate phase into a stripping zone, passing said extract phase to a complex separating zone, separating cycloparaffins in admixture with hydrogen halide from complex in said complex separating zone, passing said cycloparaffins in admixture with hydrogen halide from said complex separating zone to a separate stripping zone, separating a gaseous fraction comprising hydrogen halide in each of said stripping zones, and passing said gaseous fractions from said stripping zones to said contacting zone.

9. The process for the production of cyclohexane from a hydrocarbon mixture comprising open chain hexanes, methylcyclopentane and benzene, which comprises, subjecting said hydrocarbon mixture and a hydrocarbon-aluminum halide complex to continuous countercurrent contact in the presence of an added promoter affording a hydrogen halide in a contacting zone at a temperature of from about 70° C. to about 100° C. to effect the conversion of methylcyclopentane to cyclohexane while forming a raffinate phase comprising open chain hexanes and an extract phase comprising said complex, cyclohexane, methylcyclopentane and benzene, removing the raffinate phase from one end of the contacting zone, separately removing the extract phase from the opposite end of the contacting zone, passing said extract phase into a first distillation zone, separating hydrocarbons comprising cyclohexane and methylcyclopentane as a vapor fraction from a liquid fraction comprising complex containing benzene in said first distillation zone, passing said liquid fraction into a second distillation zone, separating hydrocarbons comprising aromatic hydrocarbons as a vapor from a liquid fraction comprising complex in said second distillation zone, and recycling said liquid fraction comprising complex from said second distillation zone to said contacting zone.

10. The process for the production of cycloparaffins of hydroaromatic structure from a hydrocarbon mixture comprising open chain paraffins, cycloparaffins of non-hydroaromatic structure and aromatic hydrocarbons, which comprises, subjecting said hydrocarbon mixture and an organo-metal halide complex to continuous countercurrent contact in the presence of an added promoter affording a hydrogen halide in a contacting zone at cycloparaffin isomerizing conditions to effect the conversion of cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure while forming a raffinate phase comprising open chain paraffins and an extract phase comprising said complex, cycloparaffins and aromatic hydrocarbons, separately removing the raffinate phase and extract phase from said contacting zone, passing said extract phase into a first distillation zone, separating hydrocarbons comprising cycloparaffins as a vapor fraction from a liquid fraction comprising complex containing aromatic hydro-

carbons in said first distillation zone, passing said liquid fraction into a second distillation zone, separating hydrocarbons comprising aromatic hydrocarbons as a vapor from a liquid fraction comprising complex in said second distillation zone, and recycling said liquid fraction comprising complex from said second distillation zone to said contacting zone.

11. The process for the production of cyclohexane from a hydrocarbon mixture comprising open chain hexanes and methylcyclopentane which comprises, subjecting said hydrocarbon mixture and a hydrocarbon-aluminum chloride complex to continuous countercurrent contact in a contacting zone at a temperature of from about 20° C. to about 70° C. to form a raffinate phase comprising open chain hexanes and an extract phase comprising said complex and methylcyclopentane, separately removing said raffinate and extract phases from the contacting zone, passing said extract phase and hydrogen chloride into a cycloparaffin isomerizing zone maintained at cycloparaffin isomerizing conditions, thereby effecting the conversion of methylcyclopentane to cyclohexane, and separately withdrawing hydrocarbons comprising cyclohexane and complex from said isomerizing zone.

12. The process for the production of cyclohexane from a hydrocarbon mixture comprising open chain hexanes and methylcyclopentane which comprises, subjecting said hydrocarbon mixture and an organo-aluminum halide complex to continuous countercurrent contact in a contacting zone at a temperature of from about 20° C. to about 70° C. to form a raffinate phase comprising open chain hexanes and an extract phase comprising said complex and methylcyclopentane, separately removing said raffinate and extract phases from the contacting zone, passing said extract phase and a hydrogen halide into a cycloparaffin isomerizing zone maintained at cycloparaffin isomerizing conditions, thereby effecting the conversion of methylcyclopentane to cyclohexane, and separately withdrawing hydrocarbons comprising cyclohexane and complex from said isomerizing zone.

13. The process for the production of cycloparaffins of hydroaromatic structure from a hydrocarbon mixture comprising open chain paraffins and cycloparaffins of non-hydroaromatic structure which comprises, subjecting said hydrocarbon mixture and a hydrocarbon-aluminum halide complex to continuous countercurrent contact in a contacting zone at a temperature of from about 20° C. to about 140° C. to form a raffinate phase comprising open chain paraffins and an extract phase comprising said complex and cycloparaffins of non-hydroaromatic structure, separately removing said raffinate phase and said extract phase from the contacting zone, passing said extract phase and a hydrogen halide into a cycloparaffin isomerizing zone maintained at cycloparaffin isomerizing conditions, thereby effecting the conversion of cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure, and separately removing hydrocarbons comprising cycloparaffins of hydroaromatic structure and complex from said isomerizing zone.

14. The process for the production of cycloparaffins of hydroaromatic structure from a hydrocarbon mixture comprising open chain paraffins and cycloparaffins of non-hydroaromatic structure which comprises, subjecting said hydrocarbon mixture and a hydrocarbon-aluminum halide complex to continuous countercurrent contact in a contacting zone to form a raffinate phase comprising open chain paraffins and an extract phase comprising said complex and cycloparaffins of non-hydroaromatic structure, separately removing said raffinate phase and said extract phase from the contacting zone and subjecting said extract phase in the presence of an added hydrogen halide to cycloparaffin isomerizing conditions thereby effecting the conversion of cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure.

15. The process for the production of cycloparaffins from a hydrocarbon mixture comprising cycloparaffins in admixture with open chain paraffins and aromatic hydrocarbons which comprises, subjecting said hydrocarbon mixture and an organo-metal halide complex to continuous countercurrent contact in a contacting zone at a temperature of from about 20° C. to about 140° C. to form a raffinate phase comprising open chain paraffins and an extract phase comprising said complex, cycloparaffins and aromatic hydrocarbons, removing the raffinate phase from one end of said contacting zone, separately removing said extract phase from the opposite end of said contacting zone, passing said extract phase into a first distillation zone, separating hydrocarbons comprising cycloparaffins as a vapor fraction from a liquid fraction comprising complex containing aromatic hydrocarbons in said first distillation zone, passing said liquid fraction into a second distillation zone, separating hydrocarbons comprising aromatic hydrocarbons as a vapor from a liquid fraction comprising complex in said second distillation zone, and recycling said liquid fraction comprising complex from said second distillation zone to said contacting zone.

16. The process for the separation of cycloparaffins from a hydrocarbon mixture comprising an isomerizable cycloparaffin having at least six carbon atoms to the molecule and containing at least five carbon atoms in the ring in admixture with open chain paraffins while simultaneously isomerizing said cycloparaffin, which comprises subjecting said hydrocarbon mixture and a hydrocarbon aluminum chloride complex to continuous counter current contact in the presence of an added promoter affording a hydrogen halide in a contacting zone at a temperature of from about 30° C. to about 140° C., thereby effecting the isomerization of said cycloparaffin having at least six carbon atoms to the molecule and containing at least five carbon atoms in the ring to a cycloparaffin having at least six carbon atoms to the molecule and containing at least five carbon atoms in the ring while forming a raffinate phase comprising open chain paraffins and an extract phase comprising said complex and isomerized cycloparaffin, separately removing the raffinate phase from one end of said contacting zone, separately removing said extract phase from the opposite end of said contacting zone, and separating said isomerized cycloparaffin from said extract phase.

17. The process for the separation of cycloparaffins from a hydrocarbon mixture comprising an isomerizable cycloparaffin having at least six carbon atoms to the molecule and containing at least five carbon atoms in the ring in admixture with open chain paraffins, which comprises subjecting said hydrocarbon mixture and an organo-metal halide complex to continuous counter current contact in the presence of an added

promoter affording a hydrogen halide in a contacting zone at cycloparaffin isomerizing conditions to effect the isomerization of said isomerizable cycloparaffin having at least six carbon atoms to the molecule and at least five carbon atoms in the ring to a cycloparaffin having at least six carbon atoms to the molecule and at least five carbon atoms in the ring while forming a raffinate phase comprising open chain paraffins, and an extract phase containing said complex and cycloparaffins comprising said isomerized cycloparaffin, separately removing the raffinate phase and extract phase from said contacting zone, and separating cycloparaffins comprising said isomerized cycloparaffin from said extract phase.

WILLIAM E. ROSS.
PHILIP PEZZAGLIA.