

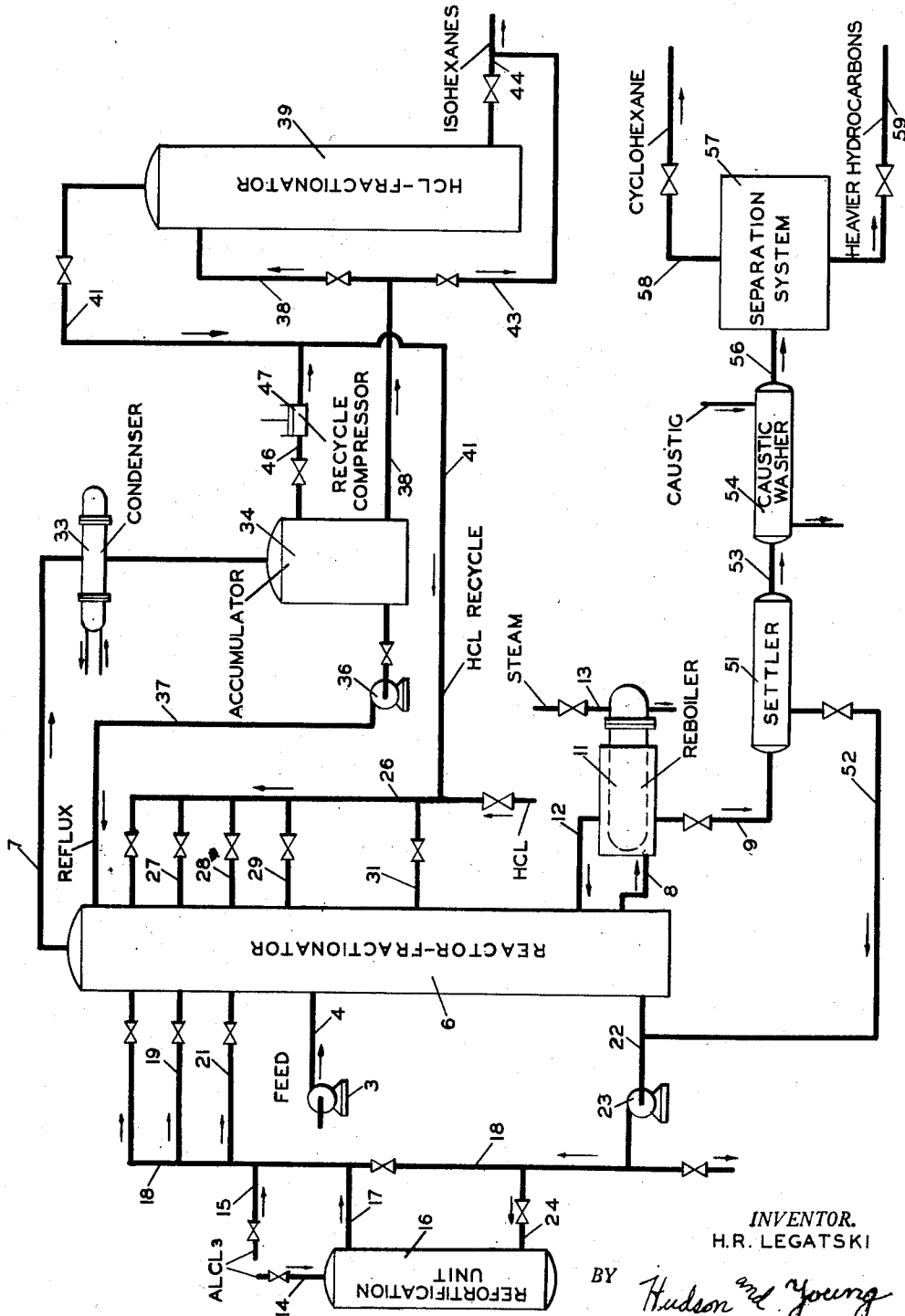
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ISOMERIZATION OF HYDROCARBONS

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ISOMERIZATION OF HYDROCARBONS

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This invention relates to the conversion of hydrocarbons. In one aspect this invention relates to isomerization of saturated normal paraffins and saturated mono-cycloparaffins. In a more particular aspect this invention relates to the isomerization of normal hexane and methylcyclopentane. In another aspect this invention relates to the separation of saturated normal paraffins and saturated mono-cycloparaffins having close boiling points.

The present application is a continuation-in-part of my copending application for the isomerization of a mixture of saturated normal paraffins and saturated mono-cycloparaffins, filed November 5, 1945, Serial Number 626,867, now Patent No. 2,440,751.

Natural and straight run gasolines are usually separated into their various components by fractional distillation and the components thus separated are utilized in various ways. Generally, natural and straight run gasolines are separated into about seven fractions. The lightest fraction comprises propane and lighter hydrocarbons. This fraction is further separated into propane which is marketed commercially as liquefied petroleum gas. The lighter hydrocarbons from this fraction may be used in the production of carbon black. The second fraction is a butane fraction comprising isobutane and normal butane. The two butanes are separated and the isobutane is usually alkylated with butylene to form octanes. The normal butane is marketed as liquefied petroleum gas, or may comprise a feed for the manufacture of butadiene, or may be used as a gasoline blending agent. A pentane fraction is also separated from the natural gasoline containing isopentane and normal pentane. The isopentane is a blending ingredient for both aviation and high octane motor fuels. Normal pentane is used as a solvent and as blending agent for motor fuels. A fourth fraction comprising isohexane and normal hexane is separated and the isohexane fraction is used in both aviation and motor fuels for increasing the octane quality of the product. The normal hexane fraction, which usually contains a large proportion of methylcyclopentane, is used in motor fuels and as a solvent. An isoheptane fraction separated from the natural or straight run gasoline is used as a component of 100 octane gasoline. Still another fraction separated from the natural and straight run gasoline is composed of normal heptane, isooctane and some cycloparaffins. This fraction is further separated into heptanes and octanes. The normal heptane has various uses, such as a solvent and as a feed for the manufacture of toluene. Isooctane is used as aviation fuel base stock and in high octane motor fuel. Usually the last fraction from the separation of the natural and straight run gasoline comprises normal octane and heavier hydrocarbons including

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some cycloparaffins which are used as a reforming feed stock.

The hexane fraction separated from the natural gasoline and straight run gasolines is of particular interest since the isohexanes have been found to be a valuable blending ingredient in super aviation fuels. Because of the more or less inability to isomerize both the normal hexane and the methylcyclopentane together to obtain a good yield of both cyclohexane and isohexanes simultaneously, this fraction has been used directly as a solvent or as a motor fuel blending agent without further treatment. It is also rather difficult to make a good separation of normal hexane and methylcyclopentane by fractional distillation in order that the hexanes may be isomerized separately, since their boiling points are only about 5° F. apart. It is highly desirable, therefore, to provide a method for isomerizing in a single reaction zone both normal hexane and methylcyclopentane simultaneously to isohexane and cyclohexane, respectively, without a preliminary separation of the hexanes preparatory for individual isomerization.

The object of this invention is to isomerize saturated normal paraffins and saturated monocycloparaffins in a single reaction zone.

It is an object of this invention to provide a method for isomerization of a normal hexane-methylcyclopentane fraction.

It is another object of this invention to provide a novel isomerization process for the production of isohexanes and cyclohexane.

Still another object of this invention is to provide a process for obtaining a high yield of cyclohexane in the isomerization of a hexane fraction containing normal hexane and methylcyclopentane.

It is another object of this invention to provide a method for simultaneously preparing a feed stock and isomerizing the prepared feed stock.

Other objects and advantages of the present invention will become apparent to those skilled in the art from the accompanying description and disclosure.

According to this invention a hydrocarbon fraction comprising a mixture of a saturated normal paraffin and a saturated monocycloparaffin is isomerized in a distillation zone in the presence of an isomerization catalyst. Conditions of temperature and pressure are maintained in the distillation zone suitable for the isomerization of a normal paraffin in the upper portion or rectifying section of the distillation zone and for the isomerization of a cycloparaffin in the lower portion or stripping section of the distillation zone. An overhead effluent comprising an isoparaffin is removed from the distillation zone as a product of the process and a bottom fraction comprising an isomeric cycloparaffin is simultaneously removed from the lower por-

tion of the distillation zone as a product of the process.

In the preferred embodiment of the present invention a hexane fraction boiling within the range between about 150 and about 160° F. obtained by the separation of the various components of natural or straight run gasoline is continuously passed to a fractional distillation column in the presence of an isomerization catalyst. Generally such a hexane fraction comprises between about 65 and about 80 weight per cent normal hexane and between about 20 and about 35 weight per cent methylcyclopentane. A typical hexane fraction separated from natural gasoline contains about 70 per cent normal hexane, 25 per cent methylcyclopentane and about 5 per cent isohexanes. The fractional distillation column may contain an appropriate number of bubble trays to obtain the required amount of separation between the isomeric products, namely, isohexanes and cyclohexane. If desired, the fractional distillation column may contain suitable contact material such as Raschig rings or Berl saddles made from ceramic, bauxite, silica gel, etc., rather than trays. Inasmuch as the isomerization catalyst such as an aluminum chloride-hydrocarbon complex commonly used may be corrosive, it is preferable that the fractional distillation column be packed with corrosion resistant contact material rather than with metal bubble trays. The hexane fraction to be isomerized is introduced into the fractional distillation zone in the normal manner at a point intermediate the upper and lower portion thereof.

If a packed column is used, the contact material may be impregnated with the isomerization catalyst such as aluminum chloride. Preferably, however, the isomerization catalyst comprises an aluminum chloride-hydrocarbon complex which is introduced into the upper portion of the fractional distillation column. This liquid complex introduced into the upper portion of the column flows downwardly over the contact material or trays and is removed from the lower portion of the column and recycled. A suitable hydrogen halide promoter, such as hydrogen chloride, is also introduced into a fractional distillation column at a multiplicity of points longitudinally along the column. The normal hexane in the feed is isomerized to isohexanes principally in the upper portion of the column, and the methylcyclopentane in the feed is isomerized to cyclohexane principally in the lower portion of the column. A vaporous overhead effluent containing the isohexanes formed by the isomerization of the normal hexane is withdrawn from the upper portion of the column and a liquid bottom fraction containing cyclohexane formed by the isomerization of methylcyclopentane is withdrawn from the lower portion of the column. The lower portion of the column is heated in conventional manner by indirect contact with steam or other means. A portion of the overhead effluent from the column is condensed and recycled as a liquid reflux to the upper portion of the fractional distillation column.

The effluents from the lower and upper portions of the column may be combined to form a high quality blending agent for motor fuels or may be separately treated and recovered as individual products of the process. The recovery of isohexanes and cyclohexanes from the effluents may be accomplished by fractional distillation,

crystallization, or other suitable method known in the art.

The present invention constitutes a novel process for the isomerization of a hexane fraction containing both normal hexane and methylcyclopentane in a single reaction zone. The use of a fractional distillation column as the reaction zone obviates the difficulties in simultaneously isomerizing normal hexane and methylcyclopentane in a single reaction zone and eliminates the necessity of separating the normal hexane and methylcyclopentane and separately isomerizing each component. Furthermore, the concentration of the hydrogen chloride promoter can easily be controlled in each isomerization zone of the column according to requirements. Since the isomerization of normal hexane requires more severe conditions than the isomerization of methylcyclopentane, a larger amount of hydrogen chloride is introduced into the upper portion of the column above the introduction of the feed where the normal hexane is isomerized than is introduced into the lower portion of the column. Furthermore, the present method enables a substantially better separation than could be obtained by individually separating normal hexane and methylcyclopentane since the normal hexane is converted to isohexane and the methylcyclopentane is converted to cyclopentane whose boiling points are between 35 and 45° F. apart.

In this invention there exists the novel situation wherein the isomerization is facilitated by the simultaneous fractionation of reaction products and also the fractionation itself is facilitated because of the isomerization which gives a greater spread in boiling points of the products. In another respect the present process has an advantage over a single isomerization zone for isomerizing methylcyclopentane since this isomer is removed from the lower portion of the fractional distillation column and by virtue thereof is substantially free from the promoter hydrogen chloride which is removed in the upper portion of the column. It is also known that the $AlCl_3$ complex has a preferential solubility for methylcyclopentane (naphthenes) and thus the simultaneous fractionation-isomerization results in an improved fractionating efficiency with respect to the initial feed stream and a greater yield of cyclohexane since the loss of methylcyclopentane to the overhead, other than required amount to inhibit disproportionation, is avoided.

This invention is applicable, generally, to the isomerization of saturated normal paraffins and saturated mono-cycloparaffins in admixture in various proportions. For example, a normal heptane fraction containing an appreciable amount of methylcyclohexane is isomerized under optimum reaction conditions in a fractional distillation column containing an isomerization catalyst. The normal heptane is isomerized to isohexanes which is withdrawn as an overhead fraction from the distillation column. The methylcyclohexane is isomerized principally to dimethylcyclopentane which is withdrawn as a kettle product from the distillation column. Both isomeric products are excellent blending agents for motor fuels and starting materials for the manufacture of various organic chemical compounds. This invention is also applicable to the isomerization of an octane fraction containing normal octane and a cycloparaffin such as methylcycloheptane, cyclooctane, etc.

The isomerization of the hexanes is carried out under appropriate conditions of temperature and

pressure. A preferred catalyst comprises a Friedel-Crafts metal halide in the form of a hydrocarbon complex or supported on suitable inorganic material. In all probability the isomerization reaction itself of both the normal hexane and the methylcyclopentane is effected in both the liquid and vapor phase since both liquid and vapor are present simultaneously in the fractionation zone. Such mixed phase isomerization is considered more advantageous than either type of single phase isomerization, i. e., vapor phase or liquid phase.

Among the solid inorganic catalyst supports suitable as packing material for the distillation zone in which the isomerization is effected are the mineral or mineral-like compounds, preferably nearly completely dehydrated, such as the kaolinites, Terrana, Floridin, pyrophyllite, apophyllite, meerschaum, serpentine, kieserite, bentonite, talc, bauxite, the permutites, the zeolites and the like, as well as the prepared hydrated materials such as the prepared permutites and zeolites, aluminum oxides, magnesium oxides, silica, and similar compounds prepared by partial dehydration of the hydroxides and the like. The contact material or support is in any suitable solid form as powder, pillules, pellets, granules, Raschig rings, Berl saddles, etc., of the desired size.

The above materials are employed in admixture or in combination with an active metal halide isomerization catalyst of the Friedel-Crafts or aluminum halide type. Preferred catalysts are those comprising aluminum chloride and aluminum bromide.

Isomerization, generally, is executed at a temperature not greater than about 450° F. At temperatures above 450° F. losses of material due to undesirable cracking reactions are prohibitive. The lower limit of temperature range is set by that temperature at which the desired isomerization will take place at a practical rate. Temperatures as low as about 150° F. may be used in some cases. A preferred practical operating range is from about 200° F. overhead temperature to about 425° F. kettle temperature in the distillation zone. A suitable temperature gradient within the above range is chosen for the operation of the fractional distillation column to provide a good separation between the isomeric products.

Unless fairly high pressures are used, the catalyst may suffer loss of activity because of the sublimation of the metal halide therefrom. In practice the temperature and pressure are adjusted so that the isomerization and fractional distillation are carried out simultaneously. If the reaction is effected under moderately superatmospheric pressures of from about 25 to about 350 pounds per square inch gage, practicable conversion of the hexanes to the desired isomeric products can be effected at relatively lower temperatures than when the process is executed at atmospheric or lower pressures.

The presence in the reaction system of a hydrogen halide or substance capable of yielding a hydrogen halide under the conditions existing in the reaction system appears to have a beneficial effect upon the life and activity of the metal halide-containing catalyst, particularly those containing an aluminum halide. In many cases it is beneficial to the reaction to have relatively small amounts of hydrogen chloride added to the reactants and present during the reaction. As a substance capable of yielding a hydrogen halide, tertiary butyl chloride and the like halides which will decompose under reac-

tion conditions to yield the hydrogen halide, may be added to the system. The amount of hydrogen halide within the reaction or distillation zone at any time should not be more than 8 weight per cent for best results. Preferably, from about 5 to 8 weight per cent hydrogen chloride is maintained in the upper portion of the distillation column in which the normal hexane is isomerized and from about 1 to about 4 or to about 6 weight per cent hydrogen chloride in the lower portion of the column in which the methylcyclopentane is isomerized. If desired, the hydrogen chloride content in the lower portion of the column may be maintained less than about 1 per cent.

In effecting an isomerization according to this invention the usual requirement for accurate control and regulation of contact time of the reactants in the reaction zone is eliminated to a large extent if not entirely. The particular feature of this invention in this respect is that the isomeric products, such as isohexanes and cyclohexanes, are removed almost immediately upon forming while the reactants themselves, such as normal hexane and methylcyclopentane remain in the column until isomerized. The removal of the isomeric products as they form also shifts the equilibrium toward the formation of these isomeric products resulting in an increased yield. Of course, the condition within the distillation column may be so selected by trial that only the desired amount of unconverted reactants pass out of the column with the isomeric products, the remainder of the reactants remaining within the column until isomerized. It is also possible to adjust conditions of distillation such that the less desirable isomeric products remain within the distillation zone until converted to the more desirable isomerization products.

After a supported catalyst has suffered substantial deactivation because of use in the process, it can be restored to its initial activity by addition of an aluminum halide. The reactivation can be effected without removing the catalyst from the distillation column, even while the catalyst is functioning, but preferably after the catalyst has temporarily been taken out of use.

The preferred catalyst employed in the present isomerization process comprises essentially a Friedel-Crafts metal halide which will form a sludge complex with an olefinic polymer, kerosene, or an alkylate. This liquid metal halide-hydrocarbon complex having some free metal halide therein is a very active catalyst. The spent sludge may be withdrawn from the lower portion of the distillation column and recycled, or disposed of since it is relatively cheap, or it may be refortified for reuse. A liquid complex catalyst is especially adaptable for use in a fractional distillation column containing bubble trays.

Various other isomerization catalysts known to those skilled in the art may be used, which are suitable for isomerization of hexanes, such as hydrogen fluoride, boron trifluoride, mixtures of hydrogen fluoride and boron trifluoride, and sulfuric acid. Reaction conditions of isomerization and the catalyst used for the various isomerization steps may be altered and various modifications will become apparent to those skilled in the art without departing from the scope of this invention.

The drawing diagrammatically represents an arrangement of apparatus for effecting the

process of the present invention for the isomerization of a hexane fraction as hereinbefore described. In order to make this invention more easily understood and its applicability realized a brief description of a modification of the present invention will be made, as shown in the drawing. A hexane fraction having approximately the following composition: 70 per cent normal hexane; 25 per cent methylcyclopentane; and 5 per cent isohexanes, is introduced into reactor-fractionator 6 by means of pump 3 through line 4. In reactor-fractionator 6 normal hexane is isomerized to isohexanes and methylcyclopentane is isomerized to cyclohexane. The isohexanes and some of the light components of the feed pass upward through the fractional distillation column and are removed therefrom as a vaporous effluent through line 7. The cyclohexane and some of the heavy components of the feed pass downward through the reactor-fractionator 6 and are removed as a liquid therefrom through lines 8 and 9. A portion of the liquid hydrocarbon mixture accumulating in the lower portion of column 6 is passed into reboiler 11 and recycled back to the column through line 12. Steam is introduced into reboiler 11 through line 13 to provide the necessary heat.

Aluminum chloride is passed to refortification unit 16 through line 14 where aluminum chloride-hydrocarbon complex is refortified. Liquid complex passes through line 17, line 18 and introduced into the upper portion of fractionator 6 through lines 18, 19 and 21. The hydrocarbon complex passes downward counter-currently to upward flowing vapor and concurrent to downward flowing liquid in fractionator 6. Fractionator 6 contains suitable bubble trays and/or contact material such as Raschig rings, etc. The catalyst complex separates as a liquid phase at the bottom of fractionator 6 distinct from the liquid hydrocarbon mixture. This liquid catalyst phase is withdrawn from the bottom of fractionator 6 through line 22 and is passed by means of pump 23 through line 18 back to the upper portion of the fractionator 6. A portion of the hydrocarbon complex may be by-passed from line 19 through line 24 to catalyst refortification unit 16. Excess and spent catalyst complex may be withdrawn from the system through line 18. Make-up aluminum chloride complex may be added to the system through line 15.

Hydrogen chloride as a promoter is introduced in appropriate amounts into fractionator 6 through lines 26, 27, 28, 29, and 31. Usually the concentration of hydrogen chloride below the point of introduction of the feed is from about 1 to about 6 weight per cent and above the point of introduction of the feed from about 5 to about 8 weight per cent.

The conditions prevailing in reaction-fractionator 6, preferably, are such that at least 1 to about 12 weight per cent or more methylcyclopentane is present in the upper portion or normal hexane isomerization section of fractionator 6. Usually from about 25 to about 40 weight per cent methylcyclopentane is present adjacent to feed entrance into fractionator 6 and from about 1 to about 12 weight per cent is present at the top of fractionator 6. The methylcyclopentane acts as an inhibitor to disproportionation reactions of normal hexane within reactor-fractionator 6.

The aluminum chloride-hydrocarbon complex contains between about 10 and about 80 weight per cent aluminum chloride. Generally, the liquid

complex introduced into the upper portion of fractionator 6 contains between about 50 to about 70 weight per cent aluminum chloride. As the complex flows downward through the column it becomes somewhat diluted and may contain between about 40 and about 60 weight per cent or less aluminum chloride when it is finally removed. Slight dilution of the liquid complex is not harmful to the isomerization reaction since isomerization of methylcyclopentane which is present in the lower portion of the column may be effected under less severe conditions than required for isomerization of normal hexane which is in the upper portion of the column. The dilution of the liquid complex is also partially or entirely compensated for by progressively increased temperature from top to bottom of reactor-fractionator 6.

The preferred conditions of temperature and pressure for the operation of reactor-fractionator 6 for the conversion of normal hexane and methylcyclopentane to isohexanes and cyclohexane are approximately as follows:

Pressure=about 50 to about 225 p. s. i. g.

Top temperature=about 210 to about 375° F.

Kettle temperature=about 285 to about 425° F.

The overhead effluent from fractionator 6 comprising isohexanes and a small amount of unconverted normal hexane, generally less than about 20 weight per cent, is passed through line 7, through condenser 33 to accumulator 34. Condensate collected in accumulator 34 is recycled by means of pump 35 and line 37 as reflux to the upper portion of fractionator 6. A reflux ratio (liquid reflux to liquid product) between about 5/1 and about 20/1 is appropriate. When total condensation of the effluent is effected in condenser 33, liquid hydrocarbons containing dissolved hydrogen chloride are removed from accumulator 34 through line 38 and passed to hydrogen chloride fractionator 39. In hydrogen chloride fractionator 39 hydrogen chloride is removed as an overhead fraction and recycled to fractionator 6 through lines 41 and 26. If desired, a portion or all of the liquid hydrocarbons from accumulator 34 may be recovered directly as a product of the process without passing through fractionator 39, for example passing the liquid hydrocarbons directly through lines 43 to line 44. When hydrogen chloride fractionator 39 is used, isohexanes and any unconverted normal hexane are removed from the lower portion of the fractionator 39 through line 44 as a product of the process.

In case partial condensation is effected in condenser 33, a vapor phase comprising essentially hydrogen chloride will exist in accumulator 34. The vapor is passed from accumulator 34 through line 46, compressor 47 and recycled to fractionator 6 through lines 41 and 26. Liquid hydrocarbons in the lower portion of accumulator 34 are passed therefrom through line 38 either through fractionator 39, if necessary, or directly to line 44 through line 43.

The liquid bottom product from fractionator 6 is removed therefrom through lines 8 and 9 and passed to settler 51. Since this liquid bottom fraction may contain both dissolved and entrained aluminum chloride-hydrocarbon complex, it is essential that a phase separation be effected, which phase separation between liquid hydrocarbons and the heavier liquid complex is accomplished in settler 51. The hydrocarbon complex settles to the lower portion of settler 51 as a liquid phase and is recycled as a catalyst to

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reactor-fractionator 6 through lines 52, 22 and 18. The liquid hydrocarbon phase from settler 51 is passed to caustic washing unit 54 through line 53. In caustic washing unit 54 dissolved aluminum chloride in the liquid hydrocarbon phase from settler 51 is neutralized. Liquid hydrocarbons substantially free from aluminum chloride are passed from caustic washer 54 through line 56 to separation system 57. In separation system 57, which may comprise one or a series of fractional distillation columns, cyclohexane is separated from other hydrocarbons. Any suitable method for separating cyclohexane from other hydrocarbons, such as crystallization, may be employed without departing from the scope of this invention. Cyclohexane is withdrawn from separation system 57 through line 58. Other hydrocarbons, such as normal hexane, etc., are withdrawn from the system through line 59.

If desired the column operating conditions may be established so that neohehexane is the predominant overhead product, the other isohexanes remaining within the column until isomerized to neohehexane.

It should be understood that column size and design (number of trays and holdup); column operating conditions of temperature, pressure and reflux ratio; and aluminum chloride complex content and promoter effect may be varied over wide ranges as required by the depth or degree of conversion and products desired. For instance, it is possible to create a normal hexane to isohexane (predominantly 2-methylpentane) conversion zone in one part of the rectification section of the distillation column by selecting the proper point of catalyst introduction and column reflux ratio such that normal hexane is not allowed to progress above this zone.

The following examples illustrate the utility and applicability of the present invention.

EXAMPLE I

A normal hexane fraction was isomerized under optimum conditions in the presence of an aluminum chloride isomerization catalyst. The following is the approximate feed and effluent compositions of a conventional isomerization process in single reaction zone.

Feed Composition, Weight Percent	Effluent Composition, Weight Percent
Pentanes and lighter-----	4.8
Isohexanes-----	52.9
Methylcyclopentane-----	9.8
Cyclohexane-----	7.2
Normal hexane-----	19.2
Heavier hydrocarbons-----	6.1
100	100.0

Normal hexane conversion=70% or more
Isohexane yield per normal hexane reacted=94.1%

Methylcyclopentane reacted=53.8%
Cyclohexane yield per methylcyclopentane reacted=29.8%

In order to recover and separate the isohexanes and cyclohexanes a second separation step, such as fractional distillation, must be used.

EXAMPLE II

A normal hexane fraction is fed to a fractional distillation zone in the presence of an aluminum

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chloride-hydrocarbon complex under optimum conditions.

Feed composition, weight per cent

Isohexanes-----	5
Normal hexane-----	70
Methylcyclopentane-----	25
100	

Approximate composition of isohexane fraction of overhead effluent from distillation column.

Weight per cent

Neohexane-----	18
Diisopropyl-----	15
2-methylpentane-----	50
3-methylpentane-----	17
100	

Normal hexane conversion=70% or more

Isohexane yield per normal hexane converted=89%

Methylcyclopentane conversion=50% or more

Cyclohexane yield per methylcyclopentane converted=85%

It is evident from a comparison of Examples I and II that the process of this invention, represented, by Example II, yields a high quality and quantity isohexane fraction as an overhead product. Furthermore, Example II indicates a large increase in yield of cyclohexane as compared to the yield of cyclohexane in the conventional process illustrated in Example I. A particular advantage of the present process is the fact that only one item of equipment is needed to prepare the feed, effect the isomerization, and separate the isomeric products. In the process of Example I on the other hand an additional fractionation unit must be used to separate the isomeric products from the isomerization effluent.

Various items of equipment, such as heat exchangers, liquid level controls, heaters, and coolers, have been omitted from the drawing as a matter of convenience. Other modifications of the present invention and various changes may become apparent to those skilled in the art without departing from the scope of this invention. Essentially, in its broad aspect, this invention comprises isomerizing two or more reactants in a single reaction zone to form two or more isomeric products, the separation of which products is effected within the reaction zone itself.

Although the reactor-fractionator of this invention has been described as a column containing more or less a continuous series of bubble trays or continuously packed with contact material, contact material may be limited to the intermediate section of the column with bubble trays positioned both above and below the intermediate section containing the contact material. In such case, the hydrocarbon feed mixture is fed, as a liquid or liquid-vapor mixture, into the section containing the contact material. Various other arrangements of contact material and bubble trays or baffles, such as positioning the bubble trays in the intermediate section and the contact material above and below the intermediate section, may be practiced without departing from the scope of this invention.

I claim:

1. A process for isomerizing a hexane fraction containing between about 65 and about 85 weight per cent normal hexane and between about 20 and about 35 weight per cent methylcyclopentane in the presence of an isomerization catalyst com-

prising an aluminum chloride-hydrocarbon complex, which comprises passing said hexane fraction into a fractional distillation zone having a rectifying section and a stripping section, isomerizing normal hexane to isohexanes principally in said rectifying section and methylcyclopentane to cyclohexane principally in said stripping section, introducing an aluminum chloride-hydrocarbon complex catalyst into the upper portion of said fractional distillation zone, removing aluminum chloride-hydrocarbon complex catalyst from the lower portion of said fractional distillation zone and recycling at least a portion of same to the upper portion of said distillation zone, maintaining an overhead temperature between about 210 and about 375° F., maintaining a kettle temperature between about 285 and about 425° F., maintaining a pressure within said fractional distillation zone between about 50 and about 225 pounds per square inch gage independently, introducing hydrogen chloride into said fractional distillation zone at a point above the hexane fraction feed as a promoter for said isomerization of n-hexane and independently at a point below said feed for said isomerization of methylcyclopentane, maintaining the concentration of hydrogen chloride in said rectifying section between about 5 and about 3 weight per cent and in said stripping section between about 1 and about 4 weight per cent, maintaining between about 1 and about 12 weight per cent methylcyclopentane at the top of said rectifying section, withdrawing a vaporous overhead fraction from said distillation zone comprising isohexanes and hydrogen chloride, cooling and condensing said overhead fraction, recycling at least a portion of the resulting condensate to the upper portion of said distillation zone as reflux therefor, separately recovering hydrogen chloride and isohexanes from said overhead fraction, said isohexanes being a product of the process, recycling separated hydrogen chloride to said distillation zone, withdrawing a liquid bottom fraction from said distillation zone comprising cyclohexane, and separating cyclohexane therefrom as a product of the process.

2. A process for isomerizing a hexane fraction containing between about 65 and about 85 weight per cent normal hexane and between about 20 and about 35 weight per cent methylcyclopentane in the presence of an isomerization catalyst comprising an aluminum chloride-hydrocarbon complex, which comprises passing said hexane fraction into a fractional distillation zone having a rectifying section and a stripping section, isomerizing normal hexane to isohexanes principally in said rectifying section and methylcyclopentane to cyclohexane principally in said stripping section, introducing an aluminum chloride-hydrocarbon complex catalyst into the upper portion of said fractional distillation zone, removing aluminum chloride-hydrocarbon complex catalyst from the lower portion of said fractional distillation zone and recycling same, maintaining an overhead temperature between about 210 and about 375° F., maintaining a kettle temperature between about 285 and about 425° F., maintaining a pressure within said fractional distillation zone between about 50 and about 225 pounds per square inch gage, introducing above the hexane fraction feed hydrogen chloride independently into said rectifying section and independently below said feed to said stripping section as a promoter for said isomerization so as to maintain a higher

concentration of hydrogen chloride in the rectifying section than in the stripping section, withdrawing a vaporous overhead fraction from said distillation zone comprising isohexanes, cooling and condensing said overhead fraction, recycling at least a portion of the resulting condensate to the upper portion of said distillation zone as reflux therefor, recovering isohexanes as a product of the process from said overhead fraction, withdrawing a bottom fraction from said distillation zone comprising cyclohexane, and separating cyclohexane therefrom as a product of the process.

3. A process for isomerizing a hexane fraction containing between about 65 and about 85 weight per cent normal hexane and between about 20 and about 35 weight per cent methylcyclopentane in the presence of an isomerization catalyst, which comprises passing said hexane fraction into a fractional distillation zone having a rectifying section and a stripping section, isomerizing normal hexane to isohexanes principally in said rectifying section and methylcyclopentane to cyclohexane principally in said stripping section, introducing above the hexane fraction feed hydrogen chloride independently into said rectifying section and independently below said feed to said stripping section so as to maintain a higher concentration of hydrogen chloride in the rectifying section than in the stripping section maintaining an overhead temperature between about 210 and about 375° F., maintaining a kettle temperature between about 285 and about 425° F., maintaining a pressure within said fractional distillation zone between about 50 and about 225 pounds per square inch gage, withdrawing a vaporous overhead fraction from said distillation zone comprising isohexanes, cooling and condensing said overhead fraction, recycling at least a portion of the resulting condensate to the upper portion of said distillation zone as reflux therefor, recovering isohexanes as a product of the process from said overhead fraction, withdrawing a bottom fraction from said distillation zone comprising cyclohexane, and separating cyclohexane therefrom as a product of the process.

4. A process for isomerizing a hexane fraction containing normal hexane and methylcyclopentane in the presence of an isomerization catalyst comprising an aluminum chloride-hydrocarbon complex, which comprises passing said hexane fraction into a fractional distillation zone having a rectifying section and a stripping section, isomerizing normal hexane to isohexanes principally in said rectifying section and methylcyclopentane to cyclohexane principally in said stripping section, introducing an aluminum chloride-hydrocarbon complex catalyst containing between about 50 and about 70 weight per cent aluminum chloride into the upper portion of said fractional distillation zone, removing aluminum chloride-hydrocarbon complex catalyst from the lower portion of said fractional distillation zone and recycling at least a portion of same, regulating the temperature and pressure in said distillation zone to cause the isohexanes to pass upward in the vaporous state and cyclohexane to pass downward in the liquid state in said distillation zone whereby the isomeric products leave the distillation zone substantially as soon as formed, introducing hydrogen chloride at vertically spaced points along said fractional distillation zone above the point of feed of said hexane fraction as a promoter for said isomerization of normal hexane and independently at a point below said feed for

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said isomerization of methylcyclopentane so as to maintain the concentration of hydrogen chloride in said rectifying section between about 5 and about 8 weight per cent and in said stripping section between about 1 and about 4 weight per cent, withdrawing a vaporous overhead fraction from said distillation zone comprising isohexanes, hydrogen chloride and between about 1 and about 12 weight per cent methylcyclopentane, cooling and condensing said overhead fraction, recycling at least a portion of the resulting condensate to the upper portion of said distillation zone as reflux therefor, separately recovering hydrogen chloride and isohexanes from said overhead fraction, said isohexanes being a product of the process, recycling separated hydrogen chloride to said distillation zone, withdrawing a liquid bottom fraction from said distillation zone comprising cyclohexane, and separating cyclohexane therefrom as a product of the process.

5. A process for isomerizing a hexane fraction containing normal hexane and methylcyclopentane in the presence of an isomerization catalyst, which comprises passing said hexane fraction into a fractional distillation zone having a rectifying section and a stripping section, isomerizing normal hexane to isohexane principally in said rectifying section and methylcyclopentane to cyclohexane principally in said stripping section, introducing above the point of feed of said hexane fraction hydrogen chloride independently into said rectifying section and independently below said feed to said stripping section as a promoter for said isomerization so as to maintain a higher concentration of hydrogen chloride in the rectifying section than in the stripping section, regulating the temperature and pressure in said distillation zone to cause the isohexane to pass upward as soon as formed and cyclohexane to move downward in said distillation zone as soon as formed, withdrawing a vaporous overhead fraction from said distillation zone comprising isohexane, cooling and condensing said overhead fraction, recycling at least a portion of the resulting condensate to the upper portion of said distillation zone as reflux therefor, recovering isohexane as a product of the process from said overhead fraction, withdrawing a bottom fraction from said distillation zone comprising cyclohexane, and separating cyclohexane therefrom as a product of the process.

6. The process according to claim 5 in which said isohexane is neohehexane.

7. A process for isomerizing a hexane fraction containing normal hexane and methylcyclopentane in the presence of an isomerization catalyst, which comprises passing said hexane fraction into a fractional distillation zone having a rectifying section and a stripping section, isomerizing normal hexane to isohexanes and methylcyclopentane to cyclohexane, introducing above the point of feed of said hexane fraction hydrogen chloride independently into said rectifying section and independently below said feed to said stripping section as a promoter for said isomerization so as to maintain a higher concentration of hydrogen chloride in the rectifying section than in the stripping section, regulating the temperature and pressure in said distillation zone to cause the isohexanes to pass upward in the vaporous state as soon as formed and cyclohexane to pass downward in the liquid state in said distillation zone as soon as formed, recovering isohexanes as an overhead product, and recovering cyclohexane as a bottom product from said distillation zone.

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8. The process for isomerizing a hydrocarbon fraction containing a saturated normal paraffin and a saturated monocycloparaffin whose separation by fractionation is difficult because of their closely adjacent boiling points, which comprises passing said hydrocarbon fraction into a distillation zone having a rectifying section and a stripping section, isomerizing normal paraffin to an isoparaffin and cycloparaffin to an isomeric cycloparaffin in the presence of an isomerization catalyst comprising a Friedel-Crafts metal halide, introducing above the point of feed of said hydrocarbon fraction into said rectifying section independently a promoting amount of hydrogen chloride and independently below said feed to said stripping section a promoting amount of hydrogen chloride and maintaining a higher concentration of hydrogen chloride in said rectifying section than in said stripping section, maintaining a temperature in said distillation zone between about 150 and about 450° F., maintaining a pressure in said distillation zone between about 25 and about 350 pounds per square inch gage, passing isoparaffin upward in the vaporous state and isomeric cycloparaffin downward in the liquid state, recovering isoparaffin as an overhead product, and recovering isomeric cycloparaffin as a bottom product from said distillation zone.

9. The process for isomerizing a hydrocarbon fraction containing a saturated normal paraffin and a saturated monocycloparaffin, whose separation by fractionation is difficult because of their closely adjacent boiling points, which comprises passing said hydrocarbon fraction into a distillation zone having a rectifying section and a stripping section, simultaneously isomerizing normal paraffin to an isoparaffin and cycloparaffin to an isomeric cycloparaffin in the presence of an isomerization catalyst and introducing above the point of feed of said hydrocarbon fraction hydrogen chloride independently into said rectifying section and independently below said point of feed to said stripping section and maintaining a higher concentration of hydrogen chloride in said rectifying section than in said stripping section, simultaneously fractionating the isomeric products of said isomerization by passing isoparaffin upward in the vaporous state and isomeric cycloparaffin downward in the liquid state, recovering isoparaffin as an overhead product, and recovering isomeric cycloparaffin as a bottom product from said distillation zone.

10. The process of claim 9 in which said hydrocarbon fraction is a normal heptane fraction, said normal paraffin is normal heptane, said monocycloparaffin is methylcyclohexane, said isoparaffin is isoheptane, and said isomeric cycloparaffin is dimethylcyclopentane.

11. The process of claim 9 in which said hydrocarbon fraction is an octane fraction.

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

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Certificate of Correction

Patent No. 2,562,926

August 7, 1951

HAROLD R. LEGATSKI

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 5, lines 58 and 59, for "conversation" read *conversion*; column 9, Example I, line 62, for "70% or more" read 72.4%; column 14, line 3, after "monocycloparaffin" insert a comma;

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 18th day of December, A. D. 1951.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.