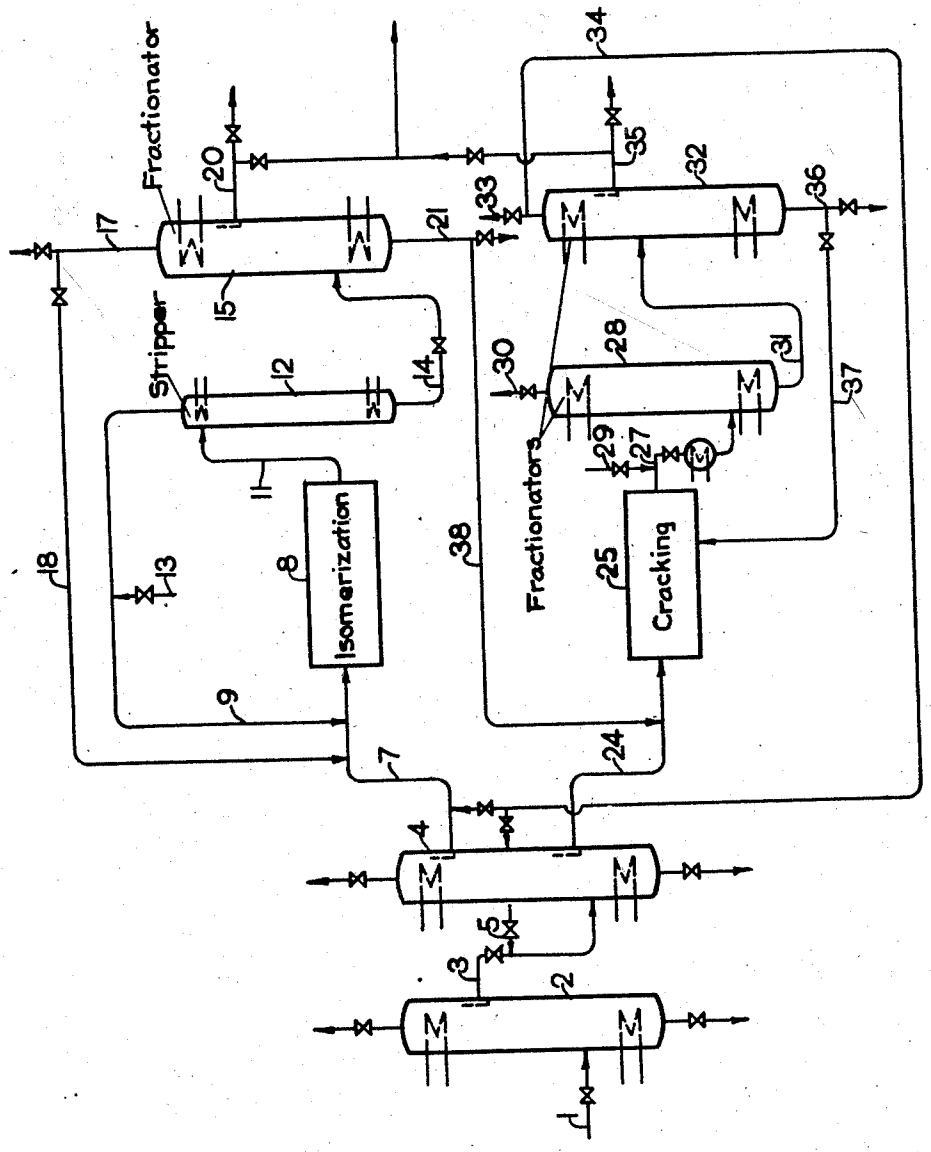
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CYCLOPARAFFIN PRODUCTION

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CYCLOPARAFFIN PRODUCTION

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This invention relates to the production of cycloparaffins of hydroaromatic structure from hydrocarbon mixtures of relatively wide boiling range such as naphthenic gasolines or fractions thereof comprising cycloparaffins of hydroaromatic and non-hydroaromatic structure in admixture with open chain paraffinic hydrocarbons. The invention relates more particularly to an improved process for the more efficient production of cyclohexane from naphthenic gasolines and fractions thereof comprising methylcyclopentane and cyclohexane.

The cycloparaffins of hydroaromatic structure, particularly cyclohexane, are of great value as starting materials and intermediates in the production of a wide variety of organic products. A most fertile source of these highly desirable materials resides in the naturally occurring hydrocarbon mixtures of naphthenic character such as naphthenic, natural and straight run gasolines, etc. Other sources comprise hydrocarbon mixtures of naphthenic character, boiling in the gasoline boiling range obtained by fractionation of the products of many of the processes involving the catalytic or thermal treatment of hydrocarbons or carbonaceous materials. As is well known, these readily available hydrocarbons constitute highly complex mixtures of a plurality of individual hydrocarbons, many of which have similar or closely approximating boiling points and many of which are capable of forming azeotropes with one another during distillation. Realization of the full advantages inherent in the many chemical processes relying upon the cycloparaffins of hydroaromatic structure as starting or intermediate materials has been handicapped by the lack of a process enabling efficient production of the cycloparaffins of hydroaromatic structure on a practical scale from these available complex mixtures. Not only is it imperative that such cycloparaffins of hydroaromatic structures be produced with high yields, but it is essential that the product obtained be of a relatively high purity and yet involve the use of a minimum of operative steps.

Efficient production of a cycloparaffin of hydroaromatic structure such as, for example, cyclohexane from a readily available hydrocarbon mixture of naphthenic character involves not only the problem of recovering substantially all of the cyclohexane inherently present in such mixtures, but the simultaneous conversion of the cycloparaffins of non-hydroaromatic structure such as methylcyclopentane to cyclohexane. Separation of either or both of these cycloparaffins from the complex hydrocarbon mixtures in which they are generally encountered by such methods as fractional distillation, if at all possible, is often rendered so involved and delicate an operation as to render it highly impractical.

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Resort to such procedures as the initial separation of a fraction comprising both the methylcyclopentanes and cyclohexane, subjection of this fraction to isomerizing conditions effecting the conversion of methylcyclopentane to cyclohexane, and fractionation of this isomerizate has been found unsatisfactory In addition to other difficulties, such a method generally does not enable the production of cyclohexane of any substantial degree of purity. Thus, the isomerizate will contain hydrocarbons such as the open chain paraffin hydrocarbons having seven carbon atoms to the molecule including, for example, 2,2-dimethylpentane and 2,4-dimethylpentane, the boiling points of which are far too close to that of cyclohexane to enable separation by practical fractionating means. On the other hand, further separation of a methylcyclopentane concentrate and a higher boiling cyclohexane concentrate from this fraction and subjection of the methylcyclopentane concentrate separately to isomerizing conditions will result not only in the loss of methylcyclopentane in the cyclohexane concentrate, but will still present the difficulty of separating cyclohexane from admixture with C_7 open chain paraffins in the cyclohexane boiling range. 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 other alkyl cyclopentanes.

It is an object of the present invention to provide an improved process for the more efficient production of cycloparaffins of hydroaromatic structure from hydrocarbon mixtures of relatively wide boiling range such as naphthenic gasolines or fractions thereof comprising cycloparaffins of hydroaromatic and non-hydroaromatic structure in admixture with open chain paraffin hydrocarbons of substantially the same boiling range.

Another object of the invention is the provision of an improved process for the more efficient production of cyclohexane from hydrocarbon mixtures of relatively wide boiling range such as naphthenic gasolines.

Still another object of the invention is to provide an improved process for the more efficient production of cyclohexane from naphthenic gasoline fractions comprising methylcyclopentane and cyclohexane in admixture with open chain paraffinic hydrocarbons inseparable therefrom by fractionation. Other objects and advantages of the invention will become apparent from the following description thereof.

In accordance with the process of the invention

a hydrocarbon mixture of naphthenic character from any suitable source such as, for example, a naphthenic straight run gasoline is subjected to fractionation to separate a fraction comprising cycloparaffins of non-hydroaromatic structure such as, for example, methylcyclopentane and a fraction comprising cycloparaffins of hydroaromatic structure such as, for example, cyclohexane. The fraction comprising cycloparaffins of non-hydroaromatic structure is subjected to isomerizing conditions to effect the conversion of cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure. The fraction comprising cycloparaffins of hydroaromatic structure separated from the charge will unavoidably comprise some methylcyclopentane and open chain paraffins particularly branched chain heptanes inseparable from cyclohexane by such means as fractionation on a practical scale. The fraction comprising cyclohexane in admixture with open chain paraffins is subjected to thermal cracking conditions controlled to effect the substantially selective cracking of the open chain paraffin content of the mixture to lower boiling hydrocarbons readily separable from the cycloparaffins. The resulting cracked products are fractionated to separate therefrom cyclohexane of high purity free of any substantial amount of open chain paraffins and a fraction consisting essentially of the methylcyclopentanes originally present in the charge to the cracking zone. The fraction comprising the methylcyclopentane is recycled to the isomerization zone. As will be apparent from the following detailed description thereof, the invention not only provides for the production of cycloparaffins of hydroaromatic structure from natural gasolines with substantially improved efficiency on a practical scale, but enables the obtaining of the desired product on a large scale in a greater state of purity.

In order to set forth more fully the nature of the invention it will be described herein in detail in its application to the production of cyclohexane from hydrocarbon mixtures of naphthenic character in the gasoline boiling range, 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 of naphthenic character such as, for example, a naphthentic straight run gasoline is forced through valved line 1 into a feed fractionator 2. Within feed fractionator 2 a fraction comprising methylcyclopentane and cyclohexane is separated and forced through valved line 3 into a second fractionator 4. A naphthenic gasoline fraction comprising methylcyclopentane and cyclohexane from any other source may be separately introduced through valved line 5 into line 3 and may comprise a part or all of the charge to the system. The fraction passed into fractionator 4 is of sufficiently wide boiling range to comprise substantially all of the methylcyclopentane and cyclohexane originally present in the straight run gasoline. A fraction boiling in the range of from about 65° C. to about 85° C. has been found particularly desirable. Such a fraction will unavoidably comprise a number of other hydrocarbons besides methylcyclopentane and cyclohexane, particularly normal hexane and straight and branched chain heptanes and some benzene. Within fractionator 4 the hydrocarbon fraction is further fractionated to separate a fraction comprising methylcyclopentane and a fraction comprising cyclohexane. The fraction comprising methylcyclopentane will generally boil in the range of from about 65° C. to about 75° C. and will generally comprise some normal hexane and a small amount of benzene. The cyclohexane fraction will generally boil within the range of from about 75° C. to about 85° C. and will comprise beside the cyclohexane methylpentanes and some methylcyclopentane. Although it is preferred to select as the fraction passed into fractionator 4 a fraction boiling in the range of from about 65° C. to about 85° C. a fraction of somewhat wider boiling range may suitably be used. Under such conditions at least part of the material lighter boiling than methylcyclopentane may be eliminated overhead in fractionator 4, and hydrocarbons higher boiling than cyclohexane are eliminated as bottoms.

The methylcyclopentane fraction separated within fractionator 4 is forced through line 7 into a methylcyclopentane conversion zone 8. Within conversion zone 8 the methylcyclopentane fraction is contacted under cycloparaffin isomerizing conditions with an isomerization catalyst. Suitable catalysts comprise those containing a metal halide of the Friedel-Crafts type, particularly those comprising a halide of aluminum such as $AlCl_3$ and/or $AlBr_3$. Particularly suitable catalysts comprise the organo-aluminum halide complexes, preferably a preformed aluminum chloride hydrocarbon complex. Other suitable catalysts comprise those of the molten salt type containing the aluminum halide in admixture with one or more halide salts. The temperature in conversion zone 8 is maintained in the range of from about 20° C. to about 100° C. and preferably from about 50° C. to about 90° C. The particular temperature chosen within this specified temperature range will be governed to at least a substantial degree by the particular catalyst employed. When utilizing a preformed aluminum halide hydrocarbon complex as the catalyst a temperature in the range of from about 65° C. to about 85° C. is somewhat preferred. A hydrogen halide promoter such as, for example, hydrogen chloride is introduced into the conversion zone by means of line 9. The hydrogen chloride is added in an amount equal to from about 0.1 to about 3% and preferably from about 0.5 to about 2% by weight of the hydrocarbon charge to the conversion zone. Higher or lower concentrations of the hydrogen chloride may at times be desirable depending upon variation in operating conditions. Under these conditions methylcyclopentane will be converted to cyclohexane in conversion zone 8.

Effluence from conversion zone 8 is passed through line 11 into a stripping zone 12 wherein a vapor fraction comprising the hydrogen chloride promoter is separated and recycled to the conversion zone 8 by means of line 9. Make-up hydrogen chloride is introduced into the system by means of valved line 13. Liquid hydrocarbons are passed from the stripper 12 and forced through line 14 into a product separating zone represented in the drawing by the single fractionator 15. Within fractionator 15 material lower boiling than cyclohexane and comprising unconverted methylcyclopentane is separated as a vapor fraction and recycled at least in part through lines 17 and 18 to the conversion zone. The stream thus recycled may be subjected to a fractionation to effect separation of hydrocarbons other than methylcyclopentane therefrom prior to passage to the conversion zone. Cyclohexane of a purity of 95% or better is separated as an intermediate product in

fractionator 15 and removed therefrom through valved line 20 as a final product. Material higher boiling than cyclohexane comprising some bicyclic compound formed during the isomerization operation is separated from column 15 as bottoms through valved line 21.

The efficiency with which methylcyclopentane in a straight run naphthenic gasoline fraction is converted to cyclohexane under these conditions is illustrated by the following example.

EXAMPLE I

A straight run naphthenic gasoline was fractionated to separate therefrom a methylcyclopentane-cyclohexane fraction boiling in the range of from 65° C. to 85° C. The composition of this fraction is given in Table I in column A. This fraction was then subjected to further fractionation to separate therefrom a methylcyclopentane concentrate having a boiling range of from 65° C. to 75° C. and a cyclohexane concentrate having a boiling range of from 75° C. to 85° C. The composition of the methylcyclopentane and cyclohexane concentrates is given in Table I in collumns B and C respectively. The methylcyclopentane concentrate was contacted with a preformed aluminum halide hydrocarbon complex at a temperature of 80° C. and a contact time of 30 minutes. HCl in an amount equal to 1% by weight of the charge was added to the conversion zone. A conversion of methylcyclopentane to cyclohexane of 75% of equilibrium was obtained. The composition of the isomerizate is given in column D of Table I. By further fractionation of the isomerizate a cyclohexane of a purity of 96% was obtained as indicated by the composition thereof shown in colume E of Table I.

	A	B	C	D Isomerizate	E Cyclohexane product
Boiling range, ° C.	65–85	65–75	75–85		
Composition, percent by volume:					
Methylpentanes	2.5	8		19	
n-Hexane	30	36		25	
Dimethylpentane	3		14		
Methylcyclopentane	37	48	1	12	
Cyclohexane	20.5		84	34	96
Benzene	7	8	1	8	2
Undetermined				2	2

The cyclohexane of high purity thus produced represents the greater part of the methylcyclopentane content originally present in the feed. It does, however not comprise the cyclohexane originally present in the feed nor the smaller amount of methylcyclopentane unavoidably comprised in the cyclohexane concentrate separated within fractionator 4. The cyclohexane concentrate separated in fractionator 4 will unavoidably comprise, beside the cyclohexane, a substantial amount of open chain heptanes, certain isomers of which cannot be separated from the cyclohexane by such means as fractionation on a practical scale. However, in accordance with the process of the invention substantially all of the cyclohexane and methylcyclopentane comprised in the cyclohexane fraction is ultimately recovered as cyclohexane of a purity of at least 95% or better.

In accordance with the process of the invention the cyclohexane concentrate separated within fractionator 4 is passed through line 24 to a thermal cracking zone 25. The thermal cracking zone may comprise any suitable type of apparatus such as, for example, an externally heated coil positioned in a furnace structure and optionally followed by a zone of enlarged cross-sectional area such as a reaction chamber. Prior to passage of the cyclohexane concentrate into the thermal cracking zone it is preferably subjected to a treatment to effect the removal of aromatic hydrocarbons therefrom by means not shown in the drawing. Thus the benzene contained in the cyclohexane concentrate flowing through line 24 may be removed therefrom by such means as treatment with sulfuric acid or a selective solvent for aromatic hydrocarbons. Within conversion zone 25 the cyclohexane concentrate is subjected to an elevated temperature in the range of from about 500° C. to about 700° C. and preferably from about 550° C. to about 650° C. for a period of time ranging from about 5 to about 30 seconds and preferably from about 10 to about 20 seconds. A pressure in the range of from atmospheric to slightly elevated pressures for example not substantially in excess of about 500 pounds have been found suitable. Higher pressures may, however, be employed. Under these conditions open chain paraffins admixed with the cyclohexane are selectively converted to hydrocarbons readily separable from the cycloparaffins.

Effluence from cracking zone 25 is passed through valved line 27 into a fractionator 28. A valved line 29 is provided for the introduction of a quenching medium such as, for example, hydrocarbon material higher or lower boiling than cyclohexane into line 27. Within column 28 material lower boiling than methylcyclopentane is eliminated overhead through valved line 30. Liquid hydrocarbons are eliminated from fractionator 28 as bottoms and passed through line 31 into a fractionating zone represented in the drawing by the single fractionator 32.

Within fractionator 32 material lower boiling than cyclohexane and comprising the methylcyclopentane originally present in the charge to the cracking zone is separated overhead through line 33 and recycled at least in part through lines 34 and 7 to the isomerization zone 8. Cyclohexane, comprising a substantially reduced dimethylpentane content is taken as an intermediate product from fractionator 32 through valved line 35. Material higher boiling than cyclohexane is eliminated as a bottom product from fractionator 32 by means of valved line 36. The material thus eliminated as bottoms through line 36 may be recycled in part to an intermediate section of the cracking zone and is preferably introduced in the final portion of the cracking zone to dilute the hydrocarbon stream flowing therethrough, thereby increasing rate of flow, facilitating temperature control therein, and enabling more efficient selectivity of cracking. Products resulting from the cracking of the open chain paraffins will comprise unsaturated hydrocarbons, for example, of olefinic structure. The cyclohexane taken off through valved line 35 (optionally the entire effluence of cracking zone 25) is preferably subjected to any suitable olefin removal treatment comprising, for example, scrubbing with a selective solvent or acid such as sulfuric acid, by means not shown in the drawing to assure the removal of unsaturated hydrocarbons therefrom.

A part or all of the material eliminated as a bottom product in fractionator 15 may be passed from line 21 through line 38 to the inlet of cracking zone 25.

The separation of open chain paraffins from admixed cycloparaffins, inseparably by fractiona-

tion means, is exemplified by the following example.

EXAMPLE II

A cyclohexane concentrate containing 88% by volume of cyclohexane and 7% by weight of dimethylpentanes was subjected to selective paraffin cracking at a temperature of 600° C. and a contact time of from 9 to 12 seconds. 43% of the dimethylpentane present in the charge to the cracking zone was converted to material substantially lower boiling than cyclohexane and readily separable therefrom. Distillation and acid treatment of the products from the cracking zone yielded a cyclohexane of better than 95% purity.

The following example is given to illustrate the signal advantages attained by effecting the production of cyclohexane from naphthenic hydrocarbon mixtures in accordance with the invention over methods involving the isomerization of a single fraction comprising both methylcyclopentane and cyclohexane originally present in the charge.

EXAMPLE III

A portion of the methylcyclopentane-cyclohexane fraction boiling in the range of from 65° C. to 85° C. separated from the naphthenic gasoline charge in Example I, the composition of which is given in column A of Table I, was isomerized by contact with a preformed aluminum chloride hydrocarbon complex at a temperature of 80° C. with a contact time of 26 minutes. Hydrogen chloride in an amount equal to 1% by weight of the charge was added. The isomerizate had the following composition:

	Per cent
Methylpentanes	13
Normal hexane	20
Dimethylpentane	3
Methylcyclopentane	15
Cyclohexane	40
Benzene	7
Higher boiling material	2

The isomerizate was distilled to effect the separation of cyclohexane therefrom. The cyclohexane cut thus produced contained only 88% by volume of cyclohexane. The rest of the hexane cut consisted of benzene, 5%, and dimethylpentane, 7%. Such a proportion of dimethylpentane is substantially above that tolerated in many of the processes wherein cyclohexane is utilized as starting or intermediate material. Reduction of the paraffinic content of such a fraction on a large scale would be so costly as to render the process economically unfeasible. The process of the invention on the other hand, not only enables the recovery of substantially all of the available methylcyclopentane and cyclohexane in readily available naphthenic hydrocarbon mixtures, but enables their recovery as a cyclohexane of a purity of 95% or better.

A particular advantage of the process of the invention resides in the passage to the selective paraffin cracking zone of a material consisting predominantly of cyclohexane and the open chain paraffins difficult to separate therefrom by fractionating means. There is thus assured the passage of a minimum of material through the cracking zone facilitating not only selectivity in cracking but avoiding the subjection of methylcyclopentane to the cracking conditions. It furthermore avoids the passage into the cracking zone, and consequent conversion to less valuable materials, of desirable open chain hexanes generally unavoidably in admixture with any methylcyclopentane separated from the charge.

Although the detailed illustrative description of the invention has been directed to the production of cyclohexane, the invention is not necessarily limited to the production of only this cycloparaffin and may be applied with advantage to the production of other cycloparaffins of hydroaromatic structure from complex naphthenic hydrocarbon mixtures. Thus the process of the invention is applied to the production of methylcyclohexane from a naphthenic gasoline by separation therefrom of a fraction comprising cycloparaffins of non-hydroaromatic structure having seven carbon atoms to the molecule such as dimethylcyclopentane and a fraction comprising cycloparaffins of hydroaromatic structure having seven carbon atoms to the molecule such as methylcyclohexane and the paraffinic hydrocarbons of close boiling range inseparable therefrom by fractionation on a practical scale. The fraction comprising the cycloparaffin of non-hydroaromatic structure is passed to the isomerization zone 8 whereas the fraction comprising the cycloparaffin of hydroaromatic structure in admixture with open chain paraffins is passed to the selective paraffin cracking zone 25. Cycloparaffins of hydroaromatic structure of high purity are separated from the products of the isomerization and selective cracking zones.

For the purpose of simplicity parts of apparatus such as pumps, separators, coolers, condensers and detailed showing of reactors, etc., not essential to a complete understanding of the invention have been omitted from the drawing. Similarly fractionating zones depicted in the drawing by single fractionators will in actual practice comprise the use of more than one fractionator to effect the indicated separations.

We claim as our invention:

1. Process for the production of cyclohexane from a hydrocarbon mixture comprising methylcyclopentane, cyclohexane and open chain paraffins having six and seven carbon atoms to the molecule, which comprises separating a lower boiling fraction comprising methylcyclopentane and a higher boiling fraction comprising cyclohexane, methyl cyclopentane and open chain paraffins having seven carbon atoms to the molecule from said hydrocarbon mixture, contacting said lower boiling fraction with an aluminum chloride isomerization catalyst at methylcyclopentane isomerizing conditions in an isomerization zone, thereby converting methylcyclopentane to cyclohexane, subjecting said higher boiling fraction to thermal cracking at a temperature of from about 550° C. to about 650° C. for a period of time from about 10 to about 20 seconds in a thermal cracking zone, thereby converting open chain paraffins to lower boiling hydrocarbons, fractionally distilling hydrocarbons comprising cyclohexane and hydrocarbons comprising methylcyclopentane from the effluence of said isomerization and said cracking zones, and recycling said hydrocarbons comprising methylcyclopentane to said isomerization zone.

2. Process for the production of cyclohexane from a hydrocarbon mixture comprising methylcyclopentane, cyclohexane and open chain paraffins having six and seven carbon atoms to the molecule, which comprises separating a lower boiling fraction comprising methylcyclopentane and a higher boiling fraction comprising cyclohexane, methylcyclopentane and open chain par-

affins having seven carbon atoms to the molecule from said hydrocarbon mixture, contacting said lower boiling fraction with an aluminum halide isomerization catalyst at methylcyclopentane isomerizing conditions in an isomerization zone, thereby converting methylcyclopentane to cyclohexane, subjecting said higher boiling fraction to thermal cracking at a temperature of from about 500° C. to about 700° C. for a period of time of from about 5 to about 30 seconds in a thermal cracking zone, thereby converting open chain paraffins to lower boiling hydrocarbons, fractionally distilling hydrocarbons comprising cyclohexane and hydrocarbons comprising methylcyclopentane from the effluence of said isomerization and said cracking zones, and recycling said hydrocarbons comprising methylcyclopentane to said isomerization zone.

3. Process for the production of cyclohexane from a hydrocarbon mixture comprising methylcyclopentane, cyclohexane and open chain paraffins having six and seven carbon atoms to the molecule, which comprises separating a lower boiling fraction comprising methylcyclopentane and a higher boiling fraction comprising cyclohexane, methylcyclopentane and open chain paraffins having seven carbon atoms to the molecule from said hydrocarbon mixture, contacting said lower boiling fraction with an isomerization catalyst comprising a metal halide of the Friedel-Crafts type at methylcyclopentane isomerizing conditions in an isomerization zone, thereby converting methylcyclopentane to cyclohexane, subjecting said higher boiling fraction to thermal selective paraffin cracking conditions at a temperature of from about 500° C. to about 700° C. for a period of from about 5 to about 30 seconds in a thermal cracking zone, thereby converting open chain paraffins to lower boiling hydrocarbons, fractionally distilling hydrocarbons comprising cyclohexane and hydrocarbons comprising methylcyclopentane from the effluence of said isomerization and said cracking zones, and recycying said hydrocarbons comprising methylcyclopentane to said isomerization zone.

4. Process for the production of cyclohexane from a naphthenic gasoline fraction having a maximum boiling point below the boiling point of normal heptane and comprising methylcyclopentane, cyclohexane and open chain paraffins having six and seven carbon atoms to the molecule, which comprises separating a lower boiling fraction comprising methylcyclopentane and a higher boiling fraction comprising cyclohexane, methylcyclopentane and open chain paraffins having seven carbon atoms to the molecule from said hydrocarbon mixture, contacting said lower boiling fraction with an aluminum halide isomerization catalyst at methylcyclopentane isomerizing conditions in an isomerization zone, thereby converting methylcyclopentane to cyclohexane, subjecting said higher boiling fraction to selective paraffin cracking conditions at a temperature of from about 500° C. to about 700° C. for a period of time of from about 5 to about 30 seconds in a thermal cracking zone, thereby converting open chain paraffins to lower boiling hydrocarbons, fractionally distilling hydrocarbons comprising cyclohexane and hydrocarbons comprising methylcyclopentane from the effluence of said isomerization and said cracking zones, and recycling said hydrocarbons comprising methylcyclopentane to said isomerization zone.

5. The process for the production of cyclohexane from naphthenic gasoline, which comprises separating a lower boiling fraction comprising methylcyclopentane having a maximum boiling point of about 75° C. and a higher boiling fraction comprising cyclohexane, methylcyclopentane and open chain paraffins having a maximum boiling range of about 85° C. from said gasoline, contacting said lower boiling fraction with an aluminum halide isomerization catalyst at methylcyclopentane isomerizing conditions in an isomerization zone, thereby converting methylcyclopentane to cyclohexane, subjecting said higher boiling fraction to thermal cracking at a temperature of from about 550° C. to about 650° C. for a period of time of from about 10 to about 20 seconds in a thermal cracking zone, thereby converting open chain paraffins to lower boiling hydrocarbons, fractionally distilling hydrocarbons comprising cyclohexane and hydrocarbons comprising methylcyclopentane from the effluence of said isomerization and said cracking zones, and recycling said hydrocarbons comprising methylcyclopentane to said isomerization zone.

6. The process for the production of cyclohexane from naphthenic gasoline, which comprises separating a lower boiling fraction comprising methylcyclopentane having a maximum boiling point of about 75° C. and a higher boiling fraction comprising cyclohexane, methylcyclopentane and open chain paraffins having a maximum boiling range of about 85° C. from said gasoline, contacting said lower boiling fraction with an aluminum halide isomerization catalyst at methylcyclopentane isomerizing conditions in an isomerization zone, thereby converting methylcyclopentane to cyclohexane, subjecting said higher boiling fraction to thermal cracking at a temperature of from about 500° C. to about 700° C. for a period of from about 5 to about 30 seconds in a thermal cracking zone, thereby converting open chain paraffins to lower boiling hydrocarbons, fractionally distilling hydrocarbons comprising cyclohexane and hydrocarbons comprising methylcyclopentane from the effluence of said isomerization and said cracking zones, and recycling said hydrocarbons comprising methylcyclopentane to said isomerization zone.

7. The process for the production of cyclohexane from naphthenic gasoline, which comprises separating a lower boiling fraction comprising methylcyclopentane having a maximum boiling point of about 75° C. and a higher boiling fraction comprising cyclohexane, methylcyclopentane and open chain paraffins having a maximum boiling range of about 85° C. from said gasoline, contacting said lower boiling fraction with an isomerization catalyst comprising a metal halide of the Friedel-Crafts type at methylcyclopentane isomerizing conditions in an isomerization zone, thereby converting methylcyclopentane to cyclohexane, subjecting said higher boiling fraction to selective paraffin cracking conditions at a temperature of from about 500° C. to about 700° C. for a period of time of from about 5 to about 30 seconds in a thermal cracking zone, thereby converting open chain paraffins to lower boiling hydrocarbons, fractionally distilling hydrocarbons comprising cyclohexane and hydrocarbons comprising methylcyclopentane from the effluence of said isomerization and said cracking zones, and recycling said hydrocarbons comprising methylcyclopentane to said isomerization zone.

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