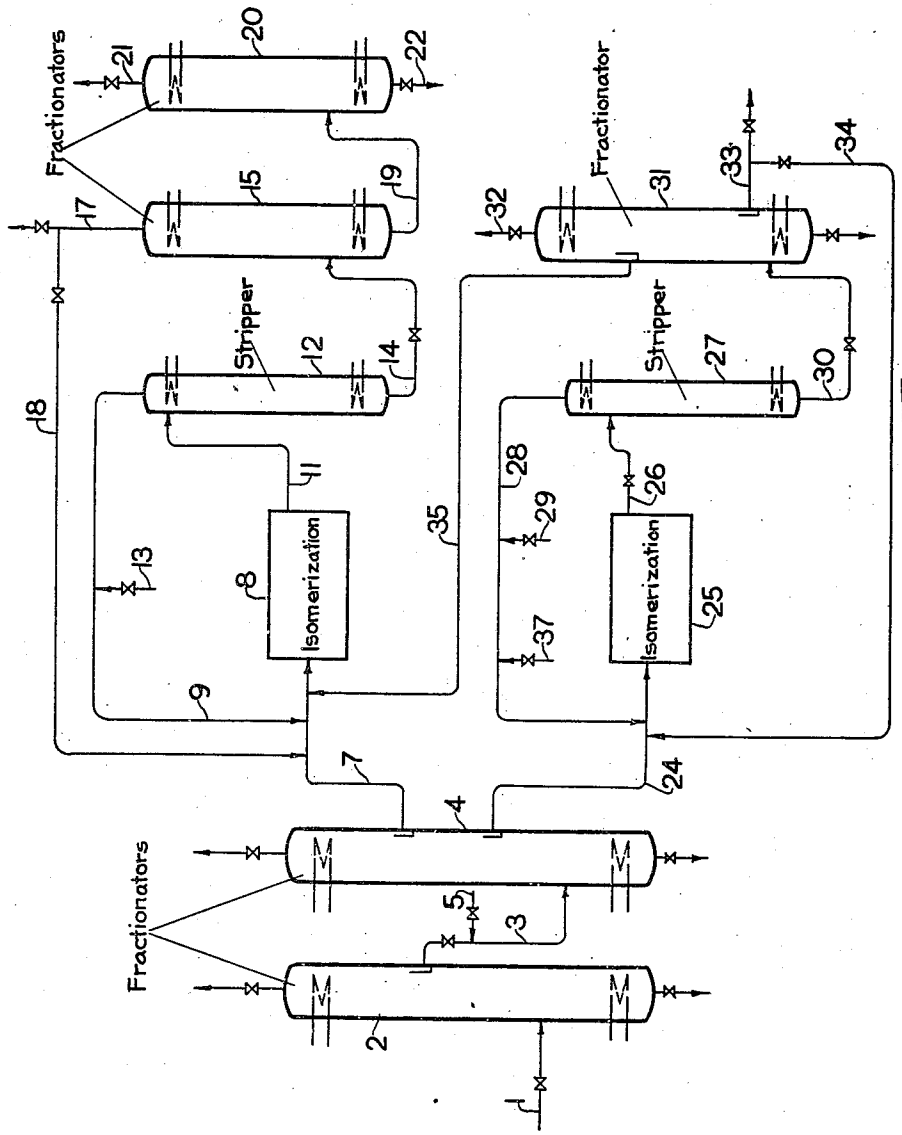
Aug. 14, 1945. W. E. ROSS ET AL 2,382,446

CYCLOPARAFFIN PRODUCTION

Filed June 21, 1944



Inventors: William E. Ross
Philip Pezzaglia

By their Attorney: C. J. Ott

Patented Aug. 14, 1945 2,382,446

UNITED STATES PATENT OFFICE

2,382,446

CYCLOPARAFFIN PRODUCTION

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

Application June 21, 1944, Serial No. 541,445

15 Claims. (Cl. 260—666)

This invention relates to 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. 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. 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 the 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 fraction separately to isomerizing conditions will result not only in the loss of methylcyclopentane in the cyclohexane concentrate, but still present the difficulty of separating cyclohexane from admixture with C_7 open chain paraffins of close boiling point. 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 close boiling open chain paraffin hydrocarbons.

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, cyclohexane, and close boiling open chain paraffinic hydrocarbons. 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 in a first conversion zone 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 is subjected to isomerizing conditions in a second conversion zone to effect the conversion of cycloparaffins of hydroaromatic structure to cycloparaffins of non-hydroaromatic structure. Hydrocarbons comprising cycloparaffins of non-hydroaromatic structure are separated from the effluence of the second conversion zone and passed to the inlet of the first conversion zone. Effluence from the first conversion zone is passed into a product separating zone to effect the separation therein of cycloparaffins of hydroaromatic structure in a high state of purity. As will be apparent from the following detailed description thereof, the invention enables not only a substantial increase in the total production of cycloparaffins of hydroaromatic structure from natural gasolines 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 napthenic 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 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 sufficently 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 unavoidably comprise beside cyclohexane, dimethylpentanes and a small amount of 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 a part of the material lower boiling than methylcyclopentane preferably will be eliminated overhead from the fractionator 4, and hydrocarbons higher boiling than cyclohexane will be 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 other 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 fractionator 15. Within fractionator 15 material lower boiling than cyclohexane and comprising unconverted methylcyclopentane is separated as a vapor fraction and re-

cycled at least in part through line 18 to the conversion zone. The stream thus recycled may be subjected to fractionation to effect separation of hydrocarbons other than methylcyclopentane therefrom prior to passage to the conversion zone. Liquid bottoms comprising cyclohexane and higher boiling materials are withdrawn from fractionator 15 and passed through line 19 into a fractionator 20. Within fractionator 20 cyclohexane of a purity of at least 95% is separated and eliminated from the system as a final product 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 columns 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% 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 column E of Table I.

Table I

	A	B	C	D	E
Boiling range, °C	65–85	65–75	75–85	(1)	(2)
Composition per cent by volume:					
Methylpentanes	2.5	8		19	
n-Hexane	30.0	36		25	
Dimethylpentanes	3.0		14		
Methylcyclopentane	37.0	48	1	12	
Cyclohexane	20.5		84	34	96
Benzene	7.0	8	1	8	2
Undetermined				2	2

[1] Isomerizate.
[2] Cyclohexane product.

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 methylcylopentane comprised in the cyclohexane fraction is ultimately recovered as cyclohexane of a purity of at least 95%.

In accordance with the process of the invention the cyclohexane concentrate separated within fractionator 4 is passed through line 24 to cyclohexane conversion zone 25. Within conversion zone 25 the hydrocarbons are contacted with isomerization catalysts of the Friedel-Crafts type such as used in conversion zone 8. Temperature conditions maintained in conversion zone 25 are, however, maintained at a substantially higher level than those within conversion zone 8. Thus, the temperature in conversion zone 25 is maintained in the range of from about 110° C. to about 200° C. and preferably from about 130° C. to about 170° C. The particular temperature selected within this temperature range will vary to some extent with the type of catalyst used. When utilizing a catalyst of the aluminum halide hydrocarbon complex type, a temperature in the range of from about 140° C. to about 150° C. has been found particularly advantageous. A hydrogen halide promoter, for example, hydrogen chloride is introduced into the conversion zone by means of line 28. The hydrogen chloride is added in an amount ranging from about 0.1 to about 3% and preferably from about 0.5 to about 2% of the hydrocarbon charge to the conversion zone. Somewhat higher or lower hydrogen chloride concentrations may, however, be employed. Make-up hydrogen chloride is introduced into conversion zone 25 by means of line 29.

Under these conditions there is attained not only a conversion of cyclohexane to methylcyclopentane, which latter hydrocarbon is readily separable in relatively pure form by simple fractionating means from the isomerizate, but there is effected a simultaneous conversion of dimethylpentanes to higher boiling materials. This has the very advantageous result of reducing the amount of dimethylpentanes admixed with the remaining unconverted cyclohexane in the isomerizate and enables the recycling of this mixture with ultimate substantially complete conversion of cyclohexane to methylcyclopentane.

Effluence from conversion zone 25 is passed through valved line 26 to a stripping column 27. Within stripping column 27 a vapor fraction comprising the hydrogen chloride promoter is separated and passed through line 28 to the conversion zone. Liquid hydrocarbons are passed from the lower part of stripping column 27 through a valved line 30 into a product separating zone. The product separating zone is depicted in the drawing by means of the single fractionator 31. In fractionator 31 material lighter boiling than methylcyclopentane is separated and eliminated through valved line 32. The remaining isomerizate is separated therein into a relatively pure methylcyclopentane, a cyclohexane fraction and liquid bottoms comprising material higher boiling than cyclohexane. The cyclohexane fraction comprising some dimethylpentane not separable therefrom is taken from fractionator 31 through line 33 and recycled at least in part to the conversion zone by means of line 34. Relatively pure methylcyclopentane is taken from fractionator 31 and passed through line 35 to conversion zone 8 to be converted therein to cyclohexane.

The following example is illustrative of the efficiency with which the cyclohexane originally present in the straight run gasoline and not separable from paraffinic components thereof by fractionation is converted to methylcyclopentane and recovered as relatively pure methylcyclopentane suitable for conversion to cyclohexane of a high

purity in the methylcyclopentane conversion zone of the system.

EXAMPLE II

The cyclohexane concentrate boiling in the range of from 75° C. to 85° C. separated from the naphthenic gasoline charge in Example I, the composition of which is given in column C of Table I, was contacted with a preformed aluminum chloride hydrocarbon complex at a temperature of 140° C. and a contact time of 15 minutes. Hydrogen chloride in an amount of 0.5% by weight of the hydrocarbon charge was added. A conversion of cyclohexane to methylcyclopentane of 40% was obtained. The composition of the isomerizate was as follows:

	Percent by volume
Methylcyclopentane	33
Cyclohexane	47
Dimethylpentanes	7
Material higher boiling than cyclohexane	9
Material boiling below 65° C.	4

The isomerizate was fractionated to separate therefrom relatively pure methylcyclopentane for recycling to the methylcyclopentane conversion zone and a cyclohexane fraction for recycling to the cyclohexane conversion zone.

Conditions to be maintained within conversion zone **25** are not limited to the use of catalysts of the Friedel-Crafts type at a temperature below 200° C. Substantial advantages are obtained by the utilization of a solid isomerization catalyst such as, for example, a heavy metal sulfide isomerization catalyst; in particular the sulfides of the metals of the left hand side of Group VI of the Periodic System. Molybdenum sulfide and/or tungsten sulfide are particularly suitable catalysts. These catalysts may be used as such or in combination with suitable inert, solid diluent or support material. When utilizing isomerization catalysts of the heavy metal sulfide type in conversion zone **25**, temperatures in the range of from about 300° C. to about 600° C. and preferably from about 350° C. to about 400° C. are employed. Hydrogen is added to the charge in sufficient amount to maintain a hydrogen pressure in the range of, for example, from about 50 to about 200 atmospheres and higher. A line **37** is provided for the introduction of hydrogen into the system. When thus operating, the conversion zone **25** at the higher temperatures in the presence of hydrogen, stripping column **27** is replaced by suitable means for separating hydrogen from the isomerizate.

EXAMPLE III

A cyclohexane concentrate boiling in the range of from 75° C. to 85° C. was separated by fractionation from a naphthenic straight run gasoline fraction. The cyclohexane concentrate had the following composition:

	Percent by volume
Dimethylpentanes	12
Methycyclopentane	7
Cyclohexane	79
Benzene	1
Dimethylcyclopentane	1

The cyclohexane concentrate was passed over a molybdenum sulfide catalyst at a temperature of 400° C. and a liquid hourly space velocity of 0.2. Hydrogen was added to the charge to maintain a hydrogen pressure of approximately 660 pounds throughout the operation. Under these conditions a 70% conversion of cyclohexane to methylcyclopentane was attained. The isomerizate was fractionated to separate relatively pure methylcyclopentane therefrom for passage to the methylcyclopentane conversion zone.

The following example is given to illustrate the signal advantages attained by effecting the production of cyclohexane from napthenic 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 IV

A portion of the methylcyclopentane-cyclohexane fraction boiling in the range of from 65° C. to 85° C. separated from the napthenic gasoline charge in Example I, the composition of which is given in column A of Table I, was isomerized by contact with a preferred 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:

	Percent
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.

Although the detailed illustrative description of the invention has been directed to the production of cyclohexane, the invention is not 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 hydroaromatic structure is passed to conversion zone **25** maintained at the higher temperature to effect the conversion of cycloparaffins of hydroaromatic structure to cycloparaffins of non-hydroaromatic structure therein. The cycloparaffins of non-hydroaromatic structure

are separated from the isomerizate, combined with the fraction comprising cycloparaffins of non-hydroaromatic structure separated from the gasoline charge, and the combined streams passed into conversion zone 8 maintained at lower temperature. Within conversion zone 8 cycloparaffins of non-hydroaromatic structure are converted to cycloparaffins of hydroaromatic structure, which are separated as a final product from the system.

For the purpose of simplicity parts of apparatus such as pumps, separators, coolers, condensers and detailed showing of reactors, catalyst separators, accumulators, etc., not essential to complete and adequate description of the invention have been omitted from the drawing. Similarly, fractionating zones depicted in the drawing by the single fractionators 2, 4 and 31 will, in actual practice, comprise the use of more than one fractionator to effect the indicated separations.

We claim as our invention:

1. The 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 and open chain paraffins having seven carbon atoms to the molecule from said hydrocarbon mixture, contacting said higher boiling fraction with an aluminum chloride isomerization catalyst at cyclohexane isomerizing conditions in a cyclohexane conversion zone thereby converting cyclohexane to methylcyclopentane, separating hydrocarbons comprising methylcyclopentane from the effluence of said cyclohexane conversion zone, contacting said hydrocarbons comprising methylcyclopentane in admixture with said lower boiling hydrocarbon fraction with an aluminum chloride isomerization catalyst at methylcyclopentane isomerizing conditions in a methylcyclopentane conversion zone thereby converting methylcyclopentane to cyclohexane, and separating hydrocarbons comprising cyclohexane from the effluence of said methylcyclopentane conversion zone.

2. The 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 and open chain paraffins having seven carbon atoms to the molecule from said hydrocarbon mixture, contacting said higher boiling fraction with an aluminum chloride isomerization catalyst at a temperature of from about 130° C. to about 170° C. in a cyclohexane conversion zone thereby converting cyclohexane to methylcyclopentane, separating hydrocarbons comprising methylcyclopentane from the effluence of said cyclohexane conversion zone, contacting said hydrocarbons comprising methylcyclopentane in admixture with said lower boiling hydrocarbon fraction with an aluminum chloride isomerization catalyst at a temperature of from about 50°C to about 90° C. in a methylcyclopentane conversion zone thereby converting methylcyclopentane to cyclohexane, and separating hydrocarbons comprising cyclohexane from the effluence of said methylcyclopentane conversion zone.

3. The 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 and open chain paraffins having seven carbon atoms to the molecule from said hydrocarbon mixture, contacting said higher boiling fraction with an aluminum halide isomerization catalyst at cyclohexane isomerizing conditions in a cyclohexane conversion zone thereby converting cyclohexane to methylcyclopentane, separating hydrocarbons comprising methylcyclopentane from the effluence of said cyclohexane conversion zone, contacting said hydrocarbons comprising methylcyclopentane in admixture with said lower boiling hydrocarbon fraction with an aluminum halide isomerization catalyst at methylcyclopentane isomerizing conditions in a methylcyclopentane conversion zone thereby converting methylcyclopentane to cyclohexane, and separating hydrocarbons comprising cyclohexane from the effluence of said methylcyclopentane conversion zone.

4. The 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 and open chain paraffins having seven carbon atoms to the molecule from said hydrocarbon mixture, contacting said higher boiling fraction with an aluminum halide isomerization catalyst at a temperature of from about 110° C. to about 200° C. in a cyclohexane conversion zone thereby converting cyclohexane to methylcyclopentane, separating hydrocarbons comprising methylcyclopentane from the effluence of said cyclohexane conversion zone, contacting said hydrocarbons comprising methylcyclopentane in admixture with said lower boiling hydrocarbon fraction with an aluminum halide isomerization catalyst at a temperature of from about 20° C. to about 100° C. in a methylcyclopentane conversion zone thereby converting methylcyclopentane to cyclohexane, and separating hydrocarbons comprising cyclohexane from the effluence of said methylcyclopentane conversion zone.

5. The 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 and open chain paraffins having seven carbon atoms to the molecule from said hydrocarbon mixture, contacting said higher boiling fraction with an isomerization catalyst comprising a metal halide of the Friedel-Crafts type at cyclohexane isomerizing conditions in a cyclohexane conversion zone thereby converting cyclohexane to methylcyclopentane, separating hydrocarbons comprising methylcyclopentane from the effluence of said cyclohexane conversion zone, contacting said hydrocarbons comprising methylcyclopentane in admixture with said lower boiling hydrocarbon fraction with an isomerization catalyst comprising a metal halide of the Friedel-Crafts type at methylcyclopentane isomerizing conditions in a methylcyclopentane conversion zone thereby converting methylcyclopentane to cyclohexane, and separating hydrocar-

bons comprising cyclohexane from the effluence of said methylcyclopentane conversion zone.

6. The 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 and open chain paraffins having seven carbon atoms to the molecule from said hydrocarbon mixture, contacting said higher boiling fraction with a molybdenum sulfide isomerization catalyst at cyclohexane isomerizing conditions in a cyclohexane conversion zone thereby converting cyclohexane to methylcyclopentane, separating hydrocarbons comprising methylcyclopentane from the effluence of said cyclohexane conversion zone, contacting said hydrocarbons comprising methylcyclopentane in admixture with said lower boiling hydrocarbon fraction with an aluminum chloride isomerization catalyst at methylcyclopentane isomerizing conditions in a methylcyclopentane conversion zone thereby converting methylcyclopentane to cyclohexane, and separating hydrocarbons comprising cyclohexane from the effluence of said methylcyclopentane conversion zone.

7. The 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 and open chain paraffins having seven carbon atoms to the molecule from said hydrocarbon mixture, contacting said higher boiling fraction with a heavy metal sulfide isomerization catalyst at cyclohexane isomerizing conditions in a cyclohexane conversion zone thereby converting cyclohexane to methylcyclopentane, separating hydrocarbons comprising methylcyclopentane from the effluence of said cyclohexane conversion zone, contacting said hydrocarbons comprising methylcyclopentane in admixture with said lower boiling hydrocarbon fraction with an aluminum halide isomerization catalyst at methylcyclopentane isomerizing conditions in a methylcyclopentane conversion zone thereby converting methylcyclopentane to cyclohexane, and separating hydrocarbons comprising cyclohexane from the effluence of said methylcyclopentane conversion zone.

8. The 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 and open chain paraffins having seven carbon atoms to the molecule from said hydrocarbon mixture, contacting said higher boiling fraction with an isomerization catalyst at cyclohexane isomerizing conditions in a cyclohexane conversion zone thereby converting cyclohexane to methylcyclopentane, separating hydrocarbons comprising methylcyclopentane from the effluence of said cyclohexane conversion zone, contacting said hydrocarbons comprising methylcyclopentane in admixture with said lower boiling hydrocarbon fraction with an isomerization catalyst at methylcyclopentane isomerizing conditions in a methylcyclopentane conversion zone thereby converting methylcyclopentane to cyclohexane, and separating hydrocarbons comprising cyclohexane from the effluence of said methylcyclopentane conversion zone.

9. 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 having a maximum boiling point of about 85° C. from said gasoline, contacting said higher boiling fraction with an aluminum halide isomerization catalyst at cyclohexane isomerizing conditions in a cyclohexane conversion zone thereby converting cyclohexane to methylcyclopentane, separating hydrocarbons comprising methylcyclopentane from the effluence of said cyclohexane conversion zone, contacting said hydrocarbons comprising methylcyclopentane in admixture with said lower boiling fraction with an aluminum halide-isomerization catalyst at methylcyclopentane isomerizing conditions in a methylcyclopentane conversion zone, thereby converting methylcyclopentane to cyclohexane, and separating cyclohexane from the effluence of said methylcyclopentane conversion zone.

10. 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 having a maximum boiling point of about 85° C. from said gasoline, contacting said higher boiling fraction with an isomerization catalyst comprising a metal halide of the Friedel-Crafts type at cyclohexane isomerizing conditions in a cyclohexane conversion zone thereby converting cyclohexane to methylcyclopentane, separating hydrocarbons comprising methylcyclopentane from the effluence of said cyclohexane conversion zone, contacting said hydrocarbons comprising methylcyclopentane in admixture with said lower boiling fraction with an isomerization catalyst comprising a metal halide of the Friedel-Crafts type at methylcyclopentane isomerizing conditions in a methylcyclopentane conversion zone, thereby converting methylcyclopentane to cyclohexane, and separating cyclohexane from the effluence of said methylcyclopentane conversion zone.

11. 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 having a maximum boiling point of about 85° C. from said gasoline, contacting said higher boiling fraction with a molybdenum sulfide isomerization catalyst at cyclohexane isomerizing conditions in a cyclohexane conversion zone thereby converting cyclohexane to methylcyclopentane, separating hydrocarbons comprising methylcyclopentane from the effluence of said cyclohexane conversion zone, contacting said hydrocarbons comprising methylcyclopentane in admixture with said lower boiling fraction with an aluminum halide-isomerization catalyst at methylcyclopentane isomerizing conditions in a methylcyclopentane conversion zone, thereby converting methylcyclopentane to cyclohexane, and separating cyclohexane from the effluence of said methylcyclopentane conversion zone.

12. The process for the production of cyclo-

hexane 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 having a maximum boiling point of about 85° C. from said gasoline, contacting said higher boiling fraction with an isomerization catalyst at cyclohexane isomerizing conditions in a cyclohexane conversion zone thereby converting cyclohexane to methylcyclopentane, separating hydrocarbons comprising methylcyclopentane from the effluence of said cyclohexane conversion zone, contacting said hydrocarbons comprising methylcyclopentane in admixture with said lower boiling fraction with an isomerization catalyst at methylcyclopentane isomerizing conditions in a methylcyclopentane conversion zone, thereby converting methylcyclopentane to cyclohexane, and separating cyclohexane from the effluence of said methylcyclopentane conversion zone.

13. The process for the production of cycloparaffins of hydroaromatic structure from hydrocarbon mixtures comprising cycloparaffins of hydroaromatic and non-hydroaromatic structure and hydrocarbons difficult to separate by fractionating means from said cycloparaffins of hydroaromatic structure, which comprises separating a fraction comprising cycloparaffins of non-hydroaromatic structure and a fraction comprising cycloparaffins of hydroaromatic structure in admixture with hydrocarbons difficultly separable therefrom by fractionation from said mixture, contacting said fraction comprising hydrocarbons of hydroaromatic structure with an aluminum halide isomerization catalyst at cycloparaffin isomerizing conditions, thereby effecting the conversion of cycloparaffins of hydroaromatic structure to cycloparaffins of non-hydroaromatic structure, separating hydrocarbons comprising said cycloparaffins of non-hydroaromatic structure from the resulting isomerization products, contacting said cycloparaffins of non-hydroaromatic structure so produced in admixture with said fraction comprising cycloparaffins of non-hydroaromatic structure separated from the charge with an aluminum halide isomerization catalyst at cycloparaffin isomerizing conditions, thereby converting cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure, and separating cycloparaffins of hydroaromatic structure from the resulting isomerization products.

14. The process for the production of cycloparaffins of hydroaromatic structure from hydrocarbon mixtures comprising cycloparaffins of hydroaromatic and non-hydroaromatic structure and hydrocarbons difficult to separate by fractionating means from said cycloparaffins of hydroaromatic structure, which comprises separating a fraction comprising cycloparaffins of non-hydroaromatic structure and a fraction comprising cycloparaffins of hydroaromatic structure in admixture with hydrocarbons difficultly separable therefrom by fractionation from said mixture, contacting said fraction comprising hydrocarbons of hydroaromatic structure with a heavy metal sulfide isomerization catalyst at cycloparaffin isomerizing conditions, thereby effecting the conversion of cycloparaffins of hydroaromatic structure to cycloparaffins of non-hydroaromatic structure, separating hydrocarbons comprising said cycloparaffins of non-hydroaromatic structure from the resulting isomerization products, contacting said cycloparaffins of non-hydroaromatic structure so produced in admixture with said fraction comprising cycloparaffins of non-hydroaromatic structure separated from the charge with an isomerization catalyst comprising a metal halide of the Friedel-Crafts type at cycloparaffin isomerizing conditions, thereby converting cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure, and separating cycloparaffins of hydroaromatic structure from the resulting isomerization products.

15. The process for the production of cycloparaffins of hydroaromatic structure from hydrocarbon mixtures comprising cycloparaffins of hydroaromatic and non-hydroaromatic structure and hydrocarbons difficult to separate by fractionating means from said cycloparaffins of hydroaromatic structure, which comprises separating a fraction comprising cycloparaffins of non-hydroaromatic structure and a fraction comprising cycloparaffins of hydroaromatic structure in admixture with hydrocarbons difficultly separable therefrom by fractionation from said mixture, contacting said fraction comprising hydrocarbons of hydroaromatic structure with an isomerization catalyst at cycloparaffin isomerizing conditions, thereby effecting the conversion of cycloparaffins of hydroaromatic structure to cycloparaffins of non-hydroaromatic structure, separating hydrocarbons comprising said cycloparaffins of non-hydroaromatic structure from the resulting isomerization products, contacting said cycloparaffins of non-hydroaromatic structure so produced in admixture with said fraction comprising cycloparaffins of non-hydroaromatic structure separated from the charge with an isomerization catalyst at cycloparaffin isomerizing conditions, thereby converting cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure, and separating cycloparaffins of hydroaromatic structure from the resulting isomerization products.

WILLIAM E. ROSS.
PHILIP PEZZAGLIA.