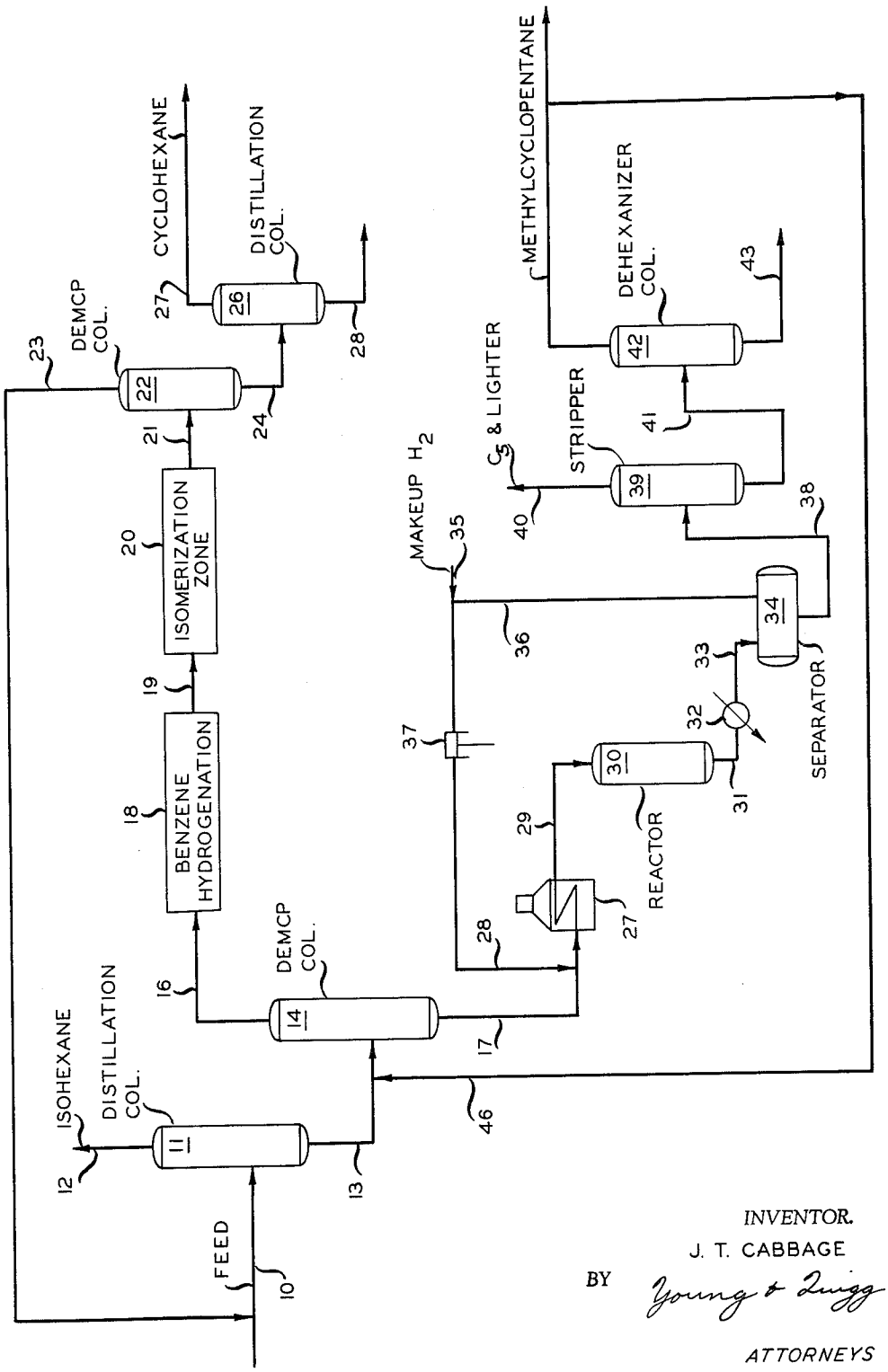
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ISOMERIZATION PROCESS

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ISOMERIZATION PROCESS

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This invention relates to an improved process for the isomerization of C_6 hydrocarbons. In one of its aspects, this invention relates to an improved process and apparatus for the production of high purity cyclohexane. In another one of its aspects, this invention relates to a process and apparatus for the isomerization of cyclohexane to methylcyclopentane.

In a conventional isomerization process for the production of high purity cyclohexane from a C_6 hydrocarbon feed, isohexane is separated by fractionation from the C_6 hydrocarbon feed. The substantially isohexane-free hydrocarbon mixture is further fractionated to produce a normal hexane-methylcyclopentane fraction (containing limited quantities of higher boiling materials) for isomerization to isohexane and cyclohexane, respectively. High purity cyclohexane is then easily fractionated from the isomerized material because of the limited quantities of heavy materials in the feed and the large spread in boiling points between methylcyclopentane and cyclohexane. Naturally occurring cyclohexane may be present in the raw C_6 hydrocarbon feed in concentrations near 6 L.V. percent. Most of this material must be rejected from the isomerization feed in order to remove the intermediate boiling 2,2- and 2,4-dimethylpentane impurities. This substantially reduces the ultimate recovery of high purity cyclohexane from the raw feed.

Accordingly, an object of my invention is to provide an isomerization process and apparatus for the maximum recovery of cyclohexane from a C_6 hydrocarbon feed.

Another object of my invention is to provide a process for the recovery of cyclohexane from a hydrocarbon feed containing said cyclohexane and 2,2- and 2,4-dimethylpentane.

Another object of my invention is to provide a process and apparatus for the isomerization of cyclohexane.

Another object of my invention is to provide a process and apparatus for the production of high purity methylcyclopentane.

Other objects, advantages and features of my invention will be readily apparent from the following description and the appended claims.

By my invention I provide an isomerization process for the maximum recovery of cyclohexane from a C_6 hydrocarbon feed mixture comprising the steps of (1) separating an isohexane fraction from said C_6 hydrocarbon feed mixture, (2) fractionating the remainder of said C_6 hydrocarbon mixture into a methylcyclopentane fraction and a residual hydrocarbon fraction, (3) passing said residual hydrocarbon fraction to an isomerization process step whereby the cyclohexane contained therein is isomerized to methylcyclopentane, (4) combining said methylcyclopentane fraction and the methylcyclopentane produced from the isomerization step, and (5) isomerizing the combined methylcyclopentane fractions to cyclohexane.

The drawing is a schematic representation of one embodiment of the inventive process.

A better understanding of the inventive process can be obtained by referring to the drawing. A C_6 hydrocarbon feed normally comprising n-hexane, isohexane, methylcyclopentane, benzene, cyclohexane, isoheptanes and minor proportions of isobutane, normal butane, isopentane and heavy residual hydrocarbons is passed via conduit means 10 to a distillation column 11. Within distillation column 11, isohexane and lighter hydrocarbons are separated from the hydrocarbon feed mixture and withdrawn from distillation column 11 via conduit means 12. Typical operating conditions within distillation column 11 are a temperature in the range of 220° F. to 257° F. and a pressure in the range of 55 p.s.i.a. to 63 p.s.i.a., respectively. A substantially isohexane-free hydrocarbon stream is withdrawn from distillation column 11 via conduit means 13 and passed to a demethylcyclopentanizer column 14.

Within demethylcyclopentanizer column 14 a methylcyclopentane fraction is separated from the hydrocarbon feed mixture and withdrawn from column 14 via conduit means 16. A hydrocarbon residual fraction containing isoheptanes, 2,2- and 2,4-dimethylpentane and cyclohexane is withdrawn from column 14 via conduit means 17. Operating temperatures and pressures within column 14 are maintained typically within the range of 249° F. to 289° F. and in the range of 55 p.s.i.a. to 64 p.s.i.a., respectively.

Benzene contained in the methylcyclopentane fraction withdrawn from column 14 via conduit means 16 is hydrogenated to cyclohexane by passing the methylcyclopentane fraction to a conventional benzene hydrogenation zone 18. Within benzene hydrogenation zone 18 the methylcyclopentane fraction is contacted with hydrogen in the presence of a hydrogenation catalyst such as nickel at a temperature in the range of 350° F. to 500° F. A benzene-free hydrocarbon effluent is withdrawn from benzene hydrogenation zone 18 via conduit means 19.

The hydrocarbon effluent from benzene hydrogenation zone 18 is passed via conduit means 19 to a liquid isomerization zone 20 wherein the methylcyclopentane within the hydrocarbon feed mixture is isomerized to cyclohexane by contacting the hydrocarbon feed with a conventional isomerization catalyst such as an HCl promoted aluminum halide complex-type catalyst. When employing an aluminum halide complex-type catalyst, the temperature and pressure of the isomerization zone is preferably maintained typically in the range of 100° F. to 160° F. and in the range of 100 p.s.i.a. to 250 p.s.i.a., respectively. The isomerization zone effluent is separated from the catalyst and promoter by conventional means and withdrawn from isomerization zone 20 via conduit means 21.

The isomerization zone effluent withdrawn from isomerization zone 20 via conduit means 21 is passed to a demethylcyclopentanizer column 22 wherein methylcyclopentane and lighter hydrocarbons are separated from the hydrocarbon feed mixture and withdrawn from column 22 via conduit means 23. It is within the scope of this invention to condense and recycle the methylcyclopentane and lighter hydrocarbon fraction withdrawn from column 22 via conduit means 23 to distillation column 11, thereby recovering the methylcyclopentane not isomerized in isomerization zone 20 and recycling the recovered methylcyclopentane to isomerization zone 20. A hydrocarbon

mixture comprising cyclohexane and heavier hydrocarbons is withdrawn from column **22** via conduit means **24**. The temperature and pressure of column **22** is maintained typically in the range of 237° F. to 285° F. and in the range of 55 p.s.i.a. to 63 p.s.i.a. respectively.

The hydrocarbon mixture withdrawn from column **22** via conduit means **24** is passed to a conventional distillation column **26** wherein cyclohexane is separated from the hydrocarbon feed mixture and withdrawn from distillation column **26** via conduit means **27**. A residual hydrocarbon fraction is withdrawn from distillation column **26** via conduit means **28** and removed from the isomerization process. Distillation column **26** is operated at a temperature in the range of, for example, 250° F. to 260° F. and a pressure in the range of 45 p.s.i.a. to 50 p.s.i.a.

It is considered to be within the skill of the art to provide means for heating and refluxing columns **11**, **22** and **26** and to provide conventional means of fluid transmission and process control not herein illustrated. It is also considered to be within the skill of the art to provide means for heating and cooling process streams. Such heating and cooling means except where herein illustrated are considered to be conventional and within the skill of the art.

The isomerization of the cyclohexane contained in the residual hydrocarbon fraction withdrawn from column **14** to methylcyclopentane will hereinafter be discussed as applied to the isomerization of cyclohexane in the presence of a platinum-type catalyst, such as Penex catalyst described in U.S. Patent 2,900,425, August 18, 1959. Other isomerization catalysts usually comprising alumina containing minor amounts of a metal of the platinum group, such as ruthenium, rhodium, palladium, osmium, iridium and platinum, promoted by a minor amount of combined halogen can, of course, be employed. The residual hydrocarbon fraction is combined with hydrogen passed to conduit means **17** via conduit means **28** and the combined mixture passed to a heat exchange means, such as a furnace **27**, wherein the combined mixture is heated. The heated mixture is passed from furnace **27** via conduit means **29** to an isomerization reactor **30**. The feed mixture is heated to a temperature within furnace **27** such that the temperature within reactor **30** is maintained in the range of 650–750° F.

Reactor **30** contains a platinum-type isomerization catalyst such as Penex catalyst. As previously noted, the temperature within reactor **30** is maintained in the range of 650–750° F. The pressure within reactor **30** is maintained in the range of 400–500 p.s.i.g. The mol ratio of hydrogen to hydrocarbon in the feed mixture passed to reactor **30** is maintained in the range of 1:1 to 5:1.

An effluent mixture is withdrawn from reactor **30** via conduit means **31** and passed to a heat exchange means **32** whereby the hydrocarbon fraction in the reactor effluent is condensed. The temperature of the vaporous and liquid mixture withdrawn from heat exchange means **32** is maintained at about 100° F. The vaporous and liquid mixture is passed from heat exchange means **32** via conduit means **3** to a separator **34**. Hydrogen is withdrawn from separator **34** via conduit means **36**, compressed via compressor means **37** and passed via conduit means **28** to conduit means **17** in the heretofore described manner. Makeup H_2, as required, is passed to conduit **36** via conduit means **35**.

A liquid hydrocarbon mixture is withdrawn from separator **34** via conduit means **38** and passed to a stripper **39**. Within stripper **39**, the C_5 hydrocarbon and lighter fraction is separated from the feed mixture and withdrawn from stripper **39** via conduit means **40**. The hydrocarbon mixture comprising C_6 and heavier hydrocarbons is withdrawn from stripper **39** via conduit means **41** and passed to a dehexanizer column **42**. The temperature and pressure of stripper **39** is typically maintained in the range of 270° F. to 340° F. and in the range of 135 p.s.i.a. to 140 p.s.i.a, respectively.

Within dehexanizer column **42**, a C_7 hydrocarbon fraction is separated from the hydrocarbon feed mixture and withdrawn from dehexanizer column **42** via conduit means **43**. A vaporous methylcyclopentane portion containing cyclohexane is withdrawn from dehexanizer column **42** via conduit means **44** and condensed by a means not herein illustrated.

Column **42** can be operated as a dehexanizer column, as herein illustrated, or it can be operated to produce a high purity methylcyclopentane product having a purity of at least 95 volume percent. When producing a high purity methylcyclopentane product, column **42** is operated so as to produce a residual fraction containing cyclohexane not isomerized in reactor **30**, 2,2- and 2,4-dimethylpentane not converted in reactor **30**, and heavier hydrocarbons. This residual fraction can be further fractionated to produce a cyclohexane fraction for recycle to reactor **30** and a second residual fraction.

As in the case of columns **11**, **14**, **22** and **26**, it is within the skill of the art to provide means for heating and refluxing columns **39** and **42**, not herein illustrated.

In isomerizing cyclohexane to methylcyclopentane at a temperature in the range of 650–750° F. the formation of benzene—a process problem of high temperature prior art processes—in the isomerization zone has been substantially eliminated. This enables the recovery of a high purity methylcyclopentane product having a product purity of at least 95 weight percent.

The methylcyclopentane can be recovered as a product in the illustrated manner or it can be recycled via conduit means **46** to demethylcyclopentanizer column **14**. Although either the high purity methylcyclopentane fraction or the methylcyclopentane fraction containing cyclohexane can be recycled, it is preferred for reasons of economy that the recycle methylcyclopentane stream be the product obtained when column **42** is operated as a dehexanizer.

By recycling the methylcyclopentane to column **14**, the recycle methylcyclopentane is added to the methylcyclopentane in the original feed and the combined methylcyclopentane fraction passed to isomerization zone **20** wherein the methyblcyclopentane is isomerized to cyclohexane. This recycle process provides a method of recovering a maximum quantity of cyclohexane from a C_6 hydrocarbon feed mixture.

An advantage of the cyclohexane to methylcyclopentane isomerization is that this proces converts 2,2- and 2,4-dimethylpentane to 2-methylhexane, 3-methylhexane and other hydrocarbons boiling higher than cyclohexane. These materials can be removed in stream **43** with minimum methylcyclopentane-cyclohexane loss from the process.

A further advantage of recycling the methylcyclopentane fraction to column **14** is that a higher purity methylcyclopentane can be obtained and the conversion of cyclohexane to methylcyclopentane increased. 2,2- and 2,4-dimethylpentane present in the recycle methylcyclopentane fraction is converted to 2-methylhexane, 3-methylhexane and other hydrocarbons boiling higher than cyclohexane in the cyclohexane to methylcyclopentane isomerization process as previously described. These converted hydrocarbons can easily and effectively be separated from the methylcyclopentane-cyclohexane fraction in column **42** and withdrawn from the process via conduit **43**. Benzene present in the recycle methylcyclopentane stream is withdrawn from column **14** via conduit means **16** and hydrogenated to cyclohexane within benzene hydrogenation zone **18**.

To illustrate the effectiveness of the inventive process the following example is presented. It is not intended that the invention should be limited thereto.

Example

A hydrocarbon feed mixture having the following composition:

	Weight percent
2,2- and 2,4-dimethylpentane	8.4
Triptane	0.9
Methylcyclopentane	0.1
3,3-dimethylpentane	0.4
2-methylhexane	1.1
2,3-dimethylpentane	0.5
3-methylhexane	0.5
Cyclohexane	87.6
Residue	0.5

was admixed with hydrogen in the proportion of 2.5 mols hydrogen per mol hydrocarbon feed. The hydrogen and hydrocarbon mixture was contacted with I–3 Penex catalyst. The temperature of the contact zone was 707° F. and the pressure within the contact zone was 500 p.s.i.g. A LHSV through the Penex catalyst of 2.0 was maintained.

Hydrogen was separated from the contact zone effluent and analysis of the hydrocarbon fraction of the contact zone effluent provided the following results:

	Weight percent
Hydrogen	0.01
Propane	0.43
Isobutane	0.62
Normal butane	0.30
Isopentane	0.11
Neohexane	0.11
2-methylpentane	1.48
3-methylpentane	0.89
Normal hexane	0.89
2,2- and 2,4-dimethylpentane	1.58
Methylcyclopentane	72.08
2-methylhexane	2.28
3-methylhexane	3.37
Cyclohexane	12.48
Normal heptane and/or DMCP's	1.88
Benzene	1.29
Residue	0.20
	100.00

The cyclohexane conversion as measured by the following equation:

$$C_yC_6 \text{ Conversion} = 100 \times \frac{C_yC_6 \text{ in feed} - C_yC_6 \text{ in product}}{C_yC_6 \text{ in feed}}$$

was equal to 85.75 percent. The process efficiency as determined by the following equation:

$$\text{Process efficiency} = 100 \times \frac{\text{MCP in product} - \text{MCP in feed}}{C_yC_6 \text{ in feed} - C_yC_6 \text{ in product}}$$

was equal to 95.82 percent. It is noted that the above highly effective process for the isomerization of cyclohexane to methylcyclopentane was conducted with a formation of only 1.29 weight percent of benzene. This is particularly significant when it is desired to yield a high purity methylcyclopentane product. Benzene production can be further reduced by operating at lower temperatures and resulting lower conversion of cyclohexane to methylcyclopentane. The process problem of hydrogenating the benzene in the methylcyclopentane feed has been substantially minimized in comparison with prior art processes for the production of methylcyclopentane and cyclohexane.

As will be evident to those skilled in the art, various modification of this invention can be made, or followed, in the light of the foregoing disclosure and discussion without departing from the spirit or the scope thereof.

I claim:

1. A process which comprises passing a hydrocarbon feed containing cyclohexane to an isomerization zone, said isomerization zone containing an isomerization catalyst, passing hydrogen to said isomerization zone, maintaining the temperature of said isomerization zone in the range of 650–750° F., maintaining a pressure in said isomerization zone in the range of 400–500 p.s.i.g., withdrawing an effluent containing methylcyclopentane from said isomerization zone, partially condensing said effluent withdrawn from said isomerization zone, passing said partially condensed effluent to a separation zone, withdrawing hydrogen from said separation zone, passing a liquid hydrocarbon mixture from said separation zone to a stripping zone, withdrawing a C_5 hydrocarbon and lighter fraction from said stripping zone, passing a hydrocarbon mixture from said stripping zone to a distillation zone, withdrawing a methylcyclopentane product from said distillation zone, and withdrawing from said distillation zone a residual hydrocarbon fraction.

2. A process which comprises passing a C_6 hydrocarbon feed containing isohexane, methylcyclopentane, cyclohexane and isoheptanes to a first distillation zone, withdrawing an isohexane vaporous fraction from said first distillation zone, passing a liquid hydrocarbon from said first distillation zone to a second distillation zone, withdrawing from said second distillation zone a methylcyclopentane fraction, passing a residual hydrocarbon fraction from said second distillation zone to an isomerization zone, said isomerization zone containing an isomerization catalyst, passing hydrogen to said isomerization zone, maintaining the temperature of said isomerization zone in the range of 650–750° F., maintaining the pressure in said isomerization zone in the range of 400–500 p.s.i.g., withdrawing an effluent containing methylcyclopentane from said isomerization zone, partially condensing said effluent withdrawn from said isomerization zone, passing said partially condensed effluent to a separation zone, withdrawing hydrogen from said separation zone, passing a liquid hydrocarbon from said separation zone to a stripping zone, withdrawing a C_5 hydrocarbon and lighter fraction from said stripping zone, passing a hydrocarbon from said stripping zone to a third distillation zone, withdrawing methylcyclopentane from said third distillation zone, and withdrawing from said third distillation zone a residual hydrocarbon fraction.

3. The process of claim 2 wherein at least a portion of the methylcyclopentane withdrawn from said third distillation zone is recycled to said second distillation zone.

4. A process which comprises passing a C_6 hydrocarbon feed containing isohexane, methylcyclopentane, benzene, cyclohexane and isoheptanes to a first distillation zone, withdrawing from said first distillation zone an isohexane vaporous fraction, passing a liquid hydrocarbon from said first distillation zone to a second distillation zone, withdrawing a methylcyclopentane fraction from said second distillation zone, passing a liquid hydrocarbon containing cyclohexane from said second distillation zone to an isomerization zone, passing hydrogen to said isomerization zone, withdrawing an effluent containing methylcyclopentane from said isomerization zone, partially condensing said effluent, passing said partially condensed effluent to a separation zone, withdrawing hydrogen from said separation zone, passing a liquid from said separation zone to a stripping zone, withdrawing a vaporous fraction comprising C_5 hydrocarbons and lighter from said stripping zone, passing a liquid from said stripping zone to a third distillation zone, withdrawing methylcyclopentane from said third distillation zone, withdrawing a residual hydrocarbon fraction from said third distillation zone, passing at least a portion of the methylcyclopentane withdrawn from said third distillation zone to said second distillation zone, passing a methylcyclopentane fraction withdrawn from said second distillation zone to a benzene hydrogenation zone, with-

drawing a benzene-free effluent from said benzene hydrogenation zone, passing said benzene-free effluent to a second isomerization zone, withdrawing an effluent containing cyclohexane from said second isomerization zone, passing said effluent containing cyclohexane to a fourth distillation zone, passing a methylcyclopentane and lighter constituent fraction withdrawn from said fourth distillation zone to said first distillation zone, passing a liquid from said fourth distillation zone to a fifth distillation zone, withdrawing cyclohexane from said fifth distillation zone, and withdrawing a residual hydrocarbon fraction from said fifth distillation zone.

5. The process of claim 4 wherein the isomerization catalyst contained within said first isomerization zone is a platinum-containing catalyst.

6. The process of claim 5 wherein the temperature and pressure of said second distillation zone is maintained in the range of 249 to 289° F. and in the range of 55 to 64 p.s.i.a., respectively.

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