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METHYLCYCLOPENTENE PRODUCTION

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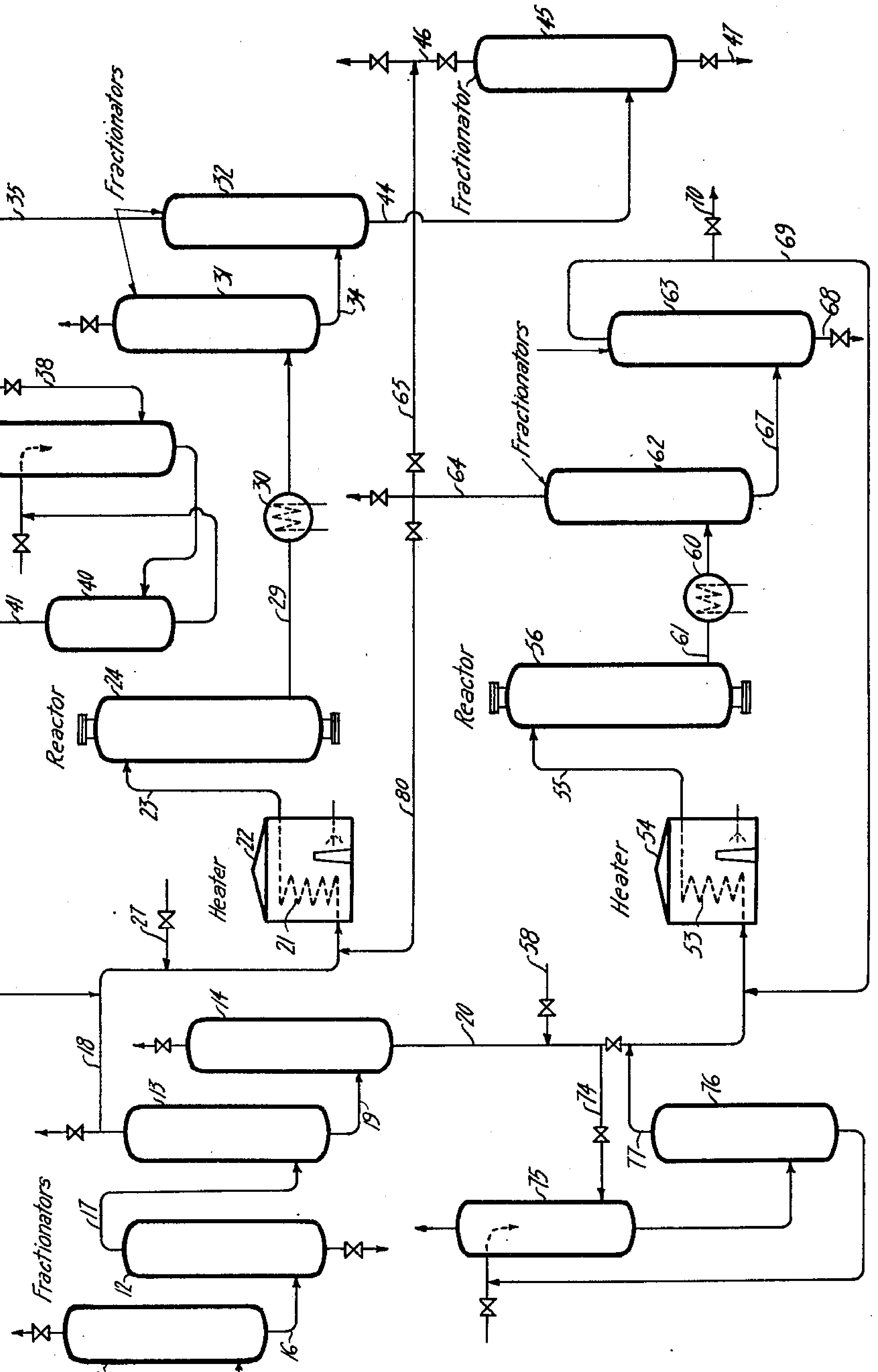

Inventors: George M. Good
Hervey H. Voge

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## METHYLCYCLOPENTENE PRODUCTION

George M. Good, Albany, and Hervey H. Voge, Berkeley, Calif., assignors to Shell Development Company, San Francisco, Calif., a corporation of Delaware

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This invention relates to the production of methylcyclopentenes of high purity. More particularly the invention relates to the production of methylcyclopentenes of high purity from complex hydrocarbon mixtures comprising methylcyclopentenes in admixture with close boiling hydrocarbons.

The methylcyclopentenes are valuable as intermediate and starting materials in the production of many valuable chemical derivatives. The need for these unsaturated cyclic compounds, in a state of relatively high purity, has rendered highly desirable suitable means enabling their more efficient production from readily available sources. Sources of the methylcyclopentenes comprise the olefinic hydrocarbon mixtures resulting from the thermal or catalytic treatment of naturally occurring or synthetically produced hydrocarbons or carbonaceous materials. The olefinic hydrocarbon mixtures boiling in the motor fuel boiling range obtained, for example, by the catalytic cracking of hydrocarbons, generally contain a substantial amount of methylcyclopentenes. The complexity of these hydrocarbon mixtures and the presence therein of a multiplicity of hydrocarbons boiling at temperatures in close proximity to the boiling temperatures of the methylcyclopentenes renders extremely difficult and often impossible the separation therefrom of these unsaturated cyclic hydrocarbons in a relatively high state of purity by methods available heretofore. The complexity of operative steps required, and in some cases the need for the use of catalysts or reagents of relatively high cost, to produce methylcyclopentene of a sufficient degree of purity by methods available heretofore, often render these processes highly impractical as a source of the desired unsaturated cyclic compounds. The difficulty of separating even a single one of the methylcyclopentene isomers from such hydrocarbon mixtures by methods available heretofore is made apparent by a realization of the multiplicity of hydrocarbons having closely approximating boiling temperatures generally present therein. Thus a hydrocarbon fraction consisting essentially of hydrocarbons having six carbon atoms to the molecule and having a boiling range of 65° C. to 69° C., separated from an olefinic cracked gasoline by fractionation will generally contain 3-methylcyclopentene in admixture with the close boiling hydrocarbons indicated in the following table:

*Table A*

| | °C. |
|---|---|
| 2-ethylbutene-1 | 65 |
| 3-methylcyclopentene | 67 |
| 2-methylpentene-2 | 67 |
| 3-methylpentene-2 (trans) | 68 |
| Hexene-3 (cis) | 68 |
| Hexene-3 (trans) | 68 |
| Hexene-2 (cis and trans) | 68 |
| n-Hexane | 69 |

A fraction of such unsaturated cracked hydrocarbons boiling in the range of from 70° to 83° C. will generally contain 4-methylcyclopentene and 1-methylcyclopentene in admixture with the close boiling six carbon atom hydrocarbons indicated in the following table:

*Table B*

| | °C. |
|---|---|
| 3-methylpentene-2 (cis) | 71 |
| Methylcyclopentane | 72 |
| 2,3-dimethylbutene-2 | 73 |
| 4-methylcyclopentene | 75 |
| 1-methylcyclopentene | 76 |
| Methylenecyclopentane | 76 |
| Benzene | 80 |
| Cyclohexane | 81 |
| Cyclohexene | 83 |

Close boiling hydrocarbons other than the six carbon atom hydrocarbons are generally encountered which further complicates the problem of separation as evidenced from the following table of seven carbon atom aliphatic hydrocarbons boiling in the range of from 72° C. to 85° C. encountered in olefinic cracked gasolines.

*Table C*

| | °C. |
|---|---|
| 4,4-dimethylpentene-1 | 72 |
| 4,4-dimethylpentene-2 | 76 |
| 3,3-dimethylpentene-1 | 77 |
| 2,3,3-trimethylbutene-1 | 78 |
| 2,2-dimethylpentane | 79 |
| 2,4-dimethylpentane | 81 |
| 2,4-dimethylpentene-1 | 81 |
| 3,4-dimethylpentene-1 | 81 |
| 2,2,3-trimethylbutane | 81 |
| 2,4-dimethylpentene-2 | 82 |
| 3-methylhexene-1 | 84 |
| 2,3-dimethylpentene-1 | 85 |
| 3-ethylpentene-1 | 85 |
| 4-methylhexene-2 (trans) | 85 |

The relatively wide spread in boiling range of the three methylcyclopentene isomers and the fact that the practicality of a process for the production of relatively pure methylcyclopentenes is often dependent upon a recovery of at least the greater part of all three, renders the use of processes involving such steps as fractionation and olefin extraction, as utilized heretofore, highly unsatisfactory.

It is an object of the present invention to provide an improved process for the more efficient production of methylcyclopentenes in a relatively high state of purity from olefinic hydrocarbon mixtures comprising methylcyclopentene in admixture with close boiling hydrocarbons inseparable therefrom on a practical scale by methods available heretofore.

Another object of the invention is the provision of an improved process for the more efficient production of methylcyclopentene of high purity from olefinic cracked hydrocarbon distillates.

A more particular object of the invention is the provision of an improved process for the more efficient production of methylcyclopentenes consisting essentially of 1-methylcyclopentene and 4-methylcyclopentene of relatively high purity from olefinic hydrocarbon fractions comprising 3-methylcyclopentene.

A still more particular object of the invention is the provision of an improved process for the recovery of substantially all of the methylcyclopentenes comprised in a hydrocarbon mixture comprising 1-, 3-, and 4-methylcyclopentenes in admixture with close boiling open chain hydrocarbons in the form of 1- and 4-methylcyclopentenes of high purity.

Still another object of the invention is the provision of an improved process for the more efficient production of 3-methylcyclopentene of high purity from olefinic hydrocarbon fractions comprising 1-methylcyclopentene and 4-methylcyclopentene. Other objects and advantages of the invention will become apparent from the following detailed description thereof.

In accordance with the process of the invention methylcyclopentenes are produced from complex olefinic hydrocarbon mixtures comprising methylcyclopentenes in admixture with close boiling aliphatic hydrocarbons, with recovery of at least the greater part of said methylcyclopentenes in a high state of purity, by separating from said hydrocarbon mixture a hydrocarbon fraction comprising 3-methylcyclopentene and a hydrocarbon fraction comprising 1-methylcyclopentene and 4-methylcyclopentene, and separately treating said fractions under the conditions defined fully herein to recover at least a substantial part of the methylcyclopentene content therefrom.

The objects and advantages of the invention are obtained by fractionating a complex olefinic hydrocarbon mixture comprising methylcyclopentenes in admixture with close boiling aliphatic hydrocarbons from any suitable source, such as, for example, a catalytically cracked gasoline, to separate therefrom a lower boiling hydrocarbon fraction comprising 3-methylcyclopentene in admixture with close boiling aliphatic hydrocarbons having six carbon atoms to the molecule, and a higher boiling hydrocarbon fraction comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling aliphatic hydrocarbons having seven carbon atoms to the molecule. The lower boiling hydrocarbon fraction is subjected to olefin isomerizing conditions effecting the conversion of 3-methylcyclopentene to cyclic olefins comprising 1-methylcyclopentene and 4-methylcyclopentene. The higher boiling hydrocarbon fraction is separately subjected to olefin isomerizing conditions effecting the conversion of 1-methylcyclopentene and 4-methylcyclopentene to cyclic olefins comprising 3-methylcyclopentene. Methylcyclopentenes in a high state of purity are separated from the products of the isomerization operations.

Of the methylcyclopentenes the tertiary cyclic olefin, 1-methylcyclopentene, is often of particular value as starting or intermediate material in the production of chemical derivatives therefrom. In a preferred modification of the invention substantially the entire methylcyclopentene content of the complex hydrocarbon mixture charged is recovered as methylcyclopentenes of high purity consisting essentially only of 1- and 4-methylcyclopentenes. In the modification of the invention the 3-methylcyclopentene produced in the treatment of the higher boiling 1- and 4-methylcyclopentene-containing fraction of the charge, now free of any substantial amount of open chain hydrocarbons, is combined with the lower boiling fraction of the charge to be subjected to the olefin isomerizing treatment therewith. In this wise the 3-methylcyclopentene emanating from the treatment of the higher boiling fraction of the charge is converted, together with the 3-methylcyclopentene content of the charge to the system, to 1- and 4-methylcyclopentenes of high purity free of any substantial amount of close boiling open chain hydrocarbons.

The process of the invention is applied to the separation of methylcyclopentenes in a high state of purity from complex hydrocarbon mixtures comprising them in admixture with close boiling aliphatic hydrocarbons obtained from any suitable source. Thus the charge to the system may comprise the methylcyclopentene-containing hydrocarbon mixtures obtained in the thermal or catalytic treatment of hydrocarbons, such as, for example, the methylcyclopentene-containing hydrocarbon mixtures obtained in the thermal and catalytic cracking, dehydrogenation, destructive dehydrogenation, reforming, and the like, of hydrocarbons.

In order to set forth more fully the nature of the invention, it will be described herein with reference to the attached drawing wherein the single figure represents a more or less diagrammatical elevational view of one form of apparatus suitable for executing the process of the invention.

Referring to the drawing, a complex olefinic hydrocarbon mixture comprising methylcyclopentenes in admixture with close boiling aliphatic hydrocarbons, such as, for example, a catalytically cracked gasoline, taken from an outside source is forced through valved line **10** into a feed fractionating zone. In the feed fractionating zone, the hydrocarbon charge is fractionated to separate therefrom a lower boiling fraction comprising 3-methylcyclopentene in admixture with close boiling aliphatic hydrocarbons, and a higher boiling fraction comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling aliphatic hydrocarbons. The feed fractionating zone is indicated in the drawing by fractionators **11**, **12**, **13** and **14**. Within fractionator **11** a vapor fraction comprising hydrocarbons boiling below about 66° C. is separated as a vapor fraction from a liquid fraction comprising hydrocarbons boiling above about 66° C. The liquid fraction is passed from fractionator **11** through line **16** into fractionator **12**. Within fractionator **12** a fraction comprising substantially all of the methylcyclopentene content of the charge, such as, for example, a fraction having a boiling range of from about 66° C. to about 77° C., is separated as a vapor fraction from a liquid fraction comprising hydrocarbons higher boiling than about 77° C. The vapor fraction comprising isomeric methylcyclopentenes in admixture with close boiling aliphatic hydrocarbons is passed from fractionator **12** by means of line **17** into a fractionator **13**. Within fractionator **13** a vapor fraction comprising 3-methylcyclopentene in admixture with close boiling hydrocarbons, such as, for example, a fraction boiling in the range of from about 66° C. to about 68° C. is separated as a vapor fraction from a liquid fraction comprising hydrocarbons boiling in the range of about 68° C. to about 77° C. The vapor fraction comprising 3-methylcyclopentene is taken overhead from fractionator **13** through line **18** and forms the charge to a first reaction zone.

The liquid fraction is passed from fractionator **13** through line **19** into fractionator **14**. Within fractionator **14** a vapor fraction comprising methylcyclopentane, such as, for example, a fraction boiling in the range of from about 68° C. to 74° C., is separated from a liquid fraction comprising substantially all of the 1-methylcyclopentene and 4-methylcyclopentene originally present in the charge in admixture with close boiling aliphatic hydrocarbons, such as, for example, a fraction boiling in the range of from about 74° C. to about 77° C. The liquid fraction comprising 1-methylcyclopentene and 4-methylcyclopentene is taken from fractionator **14** by means of line **20** and forms the charge to a second and separate reaction zone of the process.

The 3-methylcyclopentene-containing fraction flowing through line **18** will comprise a plurality of open chain olefinic hydrocarbons having six carbon atoms to the molecule boiling at, or close to, the boiling temperature of 3-methylcyclopentene and therefore inseparable therefrom on a practical scale by such expedients as fractionation.

The methylcyclopentene-containing fraction is passed from line **18** into a heating zone, such as, for example, an externally heated coil **21** positioned in a furnace structure **22**. From heating coil **21**, the heated 3-methylcyclopentene fraction is passed through line **23** into a suitable first reaction zone. The first reaction zone may comprise a reaction chamber **24**.

A hydrocarbon fraction consisting essentially of 3-methylcyclopentene in admixture with close-boiling aliphatic hydrocarbons may be introduced into line **18** from an outside source by means of valved line **27**. Such hydrocarbon fraction introduced into the system by means of line **27** may comprise a part or all of the 3-methylcyclopentene fraction introduced into the first reaction zone.

Within reaction chamber **24**, the 3-methylcyclopentene fraction is contacted with an olefin isomerization catalyst at olefin isomerizing conditions set forth fully below, effecting the conversion of 3-methylcyclopentene to unsaturated cyclic olefins consisting essentially of 1-methylcyclopentene, 4-methylcyclopentene and a minor amount of cyclohexene. Under the isomerizing conditions maintained in reactor **24** at least a substantial part of the six carbon atom open chain olefins are simultaneously converted to isomeric open chain olefins boiling below 66° C. Isomerization of the 3-methylcyclopentene fraction under these conditions is illustrated by the following example:

*Example I*

An olefinic hydrocarbon fraction having a boiling range of from about 66° C. to about 68° C., separated from a catalytically cracked gasoline by fractionation, and having a 3-methylcyclopentene content of 40% and an open chain $C_6$ olefine content of 55% is contacted with a bauxite catalyst at a temperature of 275° C. and atmospheric pressure. A conversion of 3-methylcyclopentene to 1-methylcyclopentene and 4-methylcyclopentene of 70%, and of open chain olefins to olefins boiling below 66° C. of 30% is obtained. Only about ½% of the 3-methylcyclopentene is converted to cyclohexene.

Effluence from reactor **24** comprising 1-methylcyclopentene 4-methylcyclopentene, unconverted 3-methylcyclopentene, traces of cyclohexene, and the open chain isomerized and unisomerized six carbon atom olefins, is passed through line **29**, provided with suitable cooling means such as, for example, a heat exchanger **30**, into a product separating zone. Since the highest boiling non-cyclic $C_6$ olefin boils at 73° C., and 1-methylcyclopentene, 4-methylcyclopentene, and cyclohexene boil at 75°, 76° and 83° C., respectively, the 1- and 4-methylcyclopentenes along with the cyclohexene are readily separated from the reactor effluence by fractionation.

The product separating zone receiving reaction products from line **29** is depicted in the drawing by fractionators **31** and **32**. Within fractionator **31** a vapor fraction comprising isomerized open chain olefins boiling below 66° C. is separated from a liquid fraction comprising hydrocarbons boiling above 66° C. The liquid fraction is passed from fractionator **31** through line **34** into a fractionator **32**. Within fractionator **32** hydrocarbons comprising 1-methylcyclopentene, 4-methylcyclopentene as well as cyclohexene are separated as a liquid fraction from a vapor fraction having a boiling range of about 66° to about 74° C. comprising unconverted 3-methylcyclopentene in admixture with close boiling aliphatic olefins. At least a part of the vapor fraction is recycled from fractionator **32**, through line **35**, into line **18**. Valved line **36** is provided to enable the bleeding of a portion of the recycle stream from the system to avoid an accumulation of saturated hydrocarbons boiling in the boiling range of the recycled stream. Although such bleeding will generally suffice, a portion or all of the recycle stream may be bypassed through valved line **38** into suitable saturated hydrocarbon removing means such as, for example, an extraction zone depicted in the drawing by extraction column **39** and stripping column **40**. Within column **39** recycled hydrocarbons may be contacted with a suitable medium selectively absorbing the olefins. Absorbed olefins, comprising unconverted 3-methylcyclopentene are stripped from the fat absorbing medium in stripper **40** and returned therefrom through valved line **41** into line **35** discharging into line **18**.

The liquid fraction comprising 1- and 4-methylcyclopentenes and cyclohexene is passed from fractionator **32** through line **44** into a fractionator **45**. Within fractionator **45** a vapor fraction consisting essentially of 1-methylcyclopentene and 4-methylcyclopentene in a high state of purity is separated from a liquid fraction comprising cyclohexene formed in the system. The vapor fraction consisting essentially of 1-methylcyclopentene and 4-methylcyclopentene is taken from fractionator 45 through valved line 46 as a final product.

The hydrocarbon fraction comprising 1-methylcyclopentene and 4-methylcyclopentene separated from the charge, passing through line 20 will comprise close boiling heptenes inseparable from these methylcyclopentene isomers by ordinary fractionating means. In accordance with the invention, the hydrocarbon stream flowing through line 20 is passed into a heating zone, such as, for example, an externally heated coil 53, positioned in a furnace structure 54. From coil 53 the heated hydrocarbon stream is passed through line 55 to a second reaction zone of the process, such as, for example, a reaction chamber 56.

Additional hydrocarbons from an outside source consisting essentially of 1- and 4-methylcyclopentenes in admixture with close boiling open chain olefins having seven carbon atoms to the molecule may be introduced into the system by means of valved line 58. Such hydrocarbons additionally introduced through valved line 58 may constitute a part or all of the hydrocarbons comprising 1- and 4-methylcyclopentenes in admixture with close boiling aliphatic hydrocarbons introduced into the system.

Within reactor 56 the hydrocarbon stream is contacted with an olefin isomerizing catalyst at olefin isomerizing conditions effecting the conversion of 1-methylcyclopentene and 4-methylcyclopentene to cyclic olefins consisting of 3-methylcyclopentene and some cyclohexene.

Effluence from reactor 56 is passed through line 61, provided with siutable cooling means, such as, for example, a heat exchanger 60, into a product separating zone. The product separating zone receiving effluence from reactor 56 is depicted in the drawing by fractionators 62 and 63.

Since the boiling temperature of 3-methylcyclopentene is 67° C. and that of the lowest boiling heptene is 72° C., separation of the 3-methylcyclopentene from the reactor effluence is now easily accomplished by conventional fractionating means. Within fractionator 62 a vapor fraction comprising 3-methylcyclopentene is separated from liquid fraction comprising unconverted 1- and 4-methylcyclopentenes in admixture with close boiling heptenes and some cyclohexene.

The vapor fraction consisting essentially of 3-methylcyclopentene is taken overhead from fractionator 62 through valved line 64. The 3-methylcyclopentene thus passed through line 64 may be taken from the system in part or entirety as a final product, or may be passed through valved line 65 into line 46 to combine with the 1,- and 4-methylcyclopentenes flowing therethrough to obtain a single mixed methylcyclopentene product free of aliphatic hydrocarbon.

The liquid fraction is passed from fractionator 62 through line 67 into fractionator 63. Within fractionator 63 a vapor fraction comprising unconverted 1- and 4-methylcyclopentenes in admixture with close boiling heptenes and cyclohexene, such as, for example, a fraction boiling in the range of about 70° to 84° C., is separated as a vapor fraction from a liquid fraction boiling above about 84° C. comprising higher boiling materials including isomeric open chain $C_7$ olefins formed within the system. The liquid fraction is taken from fractionator 63 through valved line 68 and eliminated from the system. The vapor fraction is recycled from fractionator 63 by means of line 69 into line 20. A valved line 70 is provided for the bleeding of a part of the recycle stream from the system to avoid the accumulation of open chain hydrocarbons. Cyclohexene formed within the system will build up to an equilibrium value and its recycling with the stream flowing through line 69 will aid in the avoidance of its further formation in any substantial amount at the expense of the desired methylcyclopentenes in reactor 56.

Optionally a part or all of the fraction passing to reactor 56 may be subjected to a treatment effecting the removal of at least a part of the paraffins therefrom. To this effect a valved line 74 is provided for the passage of at least a part of the hydrocarbon stream from line 20 into a suitable saturated hydrocarbon removing zone, such as, for example, an extraction zone represented in the drawing by extraction column 75 and stripping column 76. Within column 75 the hydrocarbon stream is contacted with a medium having a selective solvent action for olefins. The olefinic constituents of the stream, comprising 1- and 4-methylcyclopentenes in admixture with close boiling heptenes are passed from stripper 76 through valved line 77 into line 20 leading to coil 53. When the hydrocarbon stream introduced into heating coil 53 comprises benzene in substantial amount, these aromatics may optionally be separated therefrom to at least a substantial degree by conventional means not shown in the drawing.

The manner of isomerization of the 1- and 4-methylcyclopentene-containing fraction to products comprising 3-methylcyclopentene in accordance with the process of the invention is illustrated by the following example:

### *Example II*

An olefinic hydrocarbon fraction, separated by fractionation from a catalytically cracked gasoline, boiling in the range of 74° C. to 77° C., having a 1- and 4-methylcyclopentene content of 70% and a heptene content of 25% is isomerized by contact with a bauxite catalyst at 275° C., atmospheric pressure, and a liquid hourly space velocity of 7. A conversion of 1- and 4-methylcyclopentenes to 3-methylcyclopentene of 30% is obtained.

Recovery of substantially the entire methylcyclopentene content of the complex hydrocarbon charge to the system as methylcyclopentenes consisting essentially only of 1- and 4-methylcyclopentenes is obtained by passing the 3-methylcyclopentene emanating from reaction chamber 56, from line 64, through valved line 80, into line 18. In this wise the 3-methylcyclopentene produced in reaction chamber 56 will again be converted to 1- and 4-methylcyclopentenes in reactor 24 and eliminated from the system free of any substantial amount of open chain hydrocarbons through valved line 46.

As indicated above the boiling range of the methylcyclopentene fractions introduced into the respective isomerizing zones may vary to some degree within the scope of the invention. Thus the higher boiling fraction separated from the charge through valved line 20 may optionally comprise at least a substantial part of the cyclohexene content of the hydrocarbon charge to the feed fractionating zone of the system. Under the conditions maintained in the reactor 56 at least a substantial part of the cyclohexene will undergo conversion therein to methylcyclopentenes thereby materially increasing the methylcyclopentene production of the process.

Catalysts employed in reactors 24 and 56 comprise any olefin isomerization catalyst of the solid type. Suitable solid olefin isomerization catalysts comprise, for example, the naturally occurring or synthetically prepared solid adsorptive aluminous materials such as: the aluminum oxides, activated alumina, bauxite, silica-alumina, etc. These catalytic materials may be subjected to a pretreatment before use. Such pretreatments comprise, for example, subjection to elevated temperatures, optionally in the presence of gaseous materials such as hydrogen, nitrogen, steam, gases comprising them, or the catalysts may be contacted with an inorganic mineral acid such as hydrochloric acid, sulfuric acid, carbamic acid, hydrofluoric acid, boric acid, etc. A particularly preferred type of catalyst comprises adsorptive aluminous materials containing substantial amounts of gamma alumina which has been pretreated with an acidic material. Although adsorptive materials are preferred as catalysts for the isomerization of the methylcyclopentenes, the invention is not necessarily limited thereto and other catalysts capable of activating the olefin isomerization reaction may be employed. Such catalysts comprise for example, catalysts of the type of naturally occurring siliceous materials such as clays, bentonites, or the like, alumina-silica compounds or mixtures thereof; zeolites; oxides of Be, Si, Ti, Th, V, Zr, Mn; etc. Other suitable catalysts are those comprising phosphoric acid and silica, as well as any acid of low volatility preferably on a solid oxide support material. Of the isomerization catalysts, those consisting essentially of alumina are somewhat preferred.

Temperatures within reactors 24 and 56 are maintained in the range of from about 150° to about 650° C., and preferably from about 200° to about 350° C. Temperature conditions in reactors 24 and 56 are controlled by the heat input into the hydrocarbon streams flowing through externally heated coils 21 and 53, respectively. The isomerization reactions are preferably executed in the vapor phase. Atmospheric, or superatmospheric pressures may be maintained within reactors 24 and 56. Pressures close to atmospheric have been found satisfactory. Throughput rates in terms of a liquid hourly space velocity of, for example, from about 0.5 to about 25 are employed.

Under the above-defined conditions 3-methylcyclopentene is converted to cyclic olefins consisting predominantly of 1- and 4-methylcyclopentenes in reactor 24; and 1- and 4-methylcyclopentenes are converted to cyclic olefins consisting essentially of 3-methylcyclopentene in reactor 56. Formation of undesirable by-products due to side reactions such as hydrocarbon degradation and polymerization are readily maintained at a minimum. Formation of the desired methylcyclopentenes with a minimum formation of cyclohexene is favored by the avoidance of relatively severe isomerization conditions in reactors 24 and 56. Mild isomerization conditions are obtained by the use of the lower temperatures within the prescribed temperature ranges and of the less active isomerization catalysts. Thus catalysts suitable for use under such mild isomerization conditions comprise such catalysts as phosphoric acid, and bauxite. Formation of cyclohexene in reactor 56 is further suppressed, as indicated above, by the recycling of cyclohexene to the reaction zone.

For the purpose of clarity, all parts of apparatus not essential to a complete description of the invention comprising, for example, pumps, condensers, complete fractionating systems, accumulators, etc., have been omitted from the drawing. It is to be understood that the apparatus shown may be modified as apparent to one skilled in the art without departing from the scope of the invention.

The invention claimed is:

1. The process for the production of methylcyclopentenes in a relatively high state of purity from complex hydrocarbon mixtures comprising 1-methylcyclopentene, 3-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons having six and seven carbon atoms to the molecule inseparable therefrom by fractionation on a practical scale, which comprises separating a lower boiling fraction comprising 3-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons having six carbon atoms to the molecule and a higher boiling fraction comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons having seven carbon atoms to the molecule from said hydrocarbons mixture, contacting said lower boiling fraction with a solid adsorptive aluminous material under olefin isomerizing conditions at a temperature of from about 200° C. to about 350° C. and a liquid hourly space velocity of from about 0.5 to about 25 thereby effecting the conversion of 3-methylcyclopentene to 1-methylcyclopentene and 4-methylcyclopentene in a first reaction zone, separately contacting said higher boiling fraction with a solid adsorptive aluminous material under olefin isomerizing conditions at a temperature of from about 200° C. to about 350° C. and a liquid hourly space velocity of from about 0.5 to about 25 thereby effecting the conversion of 1-methylcyclopentene and 4-methylcyclopentene to 3-methylcyclopentene in a second reaction zone, fractionating 1-methylcyclopentene and 4-methylcyclopentene free of any substantial amount of open chain aliphatic hydrocarbons from the effluence of the first reaction zone, fractionating 3-methylcyclopentene free of any substantial amount of open chain aliphatic hydrocarbons from the effluence of the second reaction zone, and combining said 3-methylcyclopentene fractionated from the effluence of said second reaction zone with said 1- and 4-methylcyclopentenes fractionated from the effluence of said first reaction zone to obtain a mixture of isomeric methylcyclopentenes of high purity.

2. The process for the production of methylcyclopentenes in a relatively high state of purity from complex hydrocarbon mixtures comprising 1-methylcyclopentene, 3-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons having six and seven carbon atoms to the molecule inseparable therefrom by fractionation on a practical scale, which comprises separating a lower boiling fraction comprising 3-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons having six carbon atoms to the molecule and a higher boiling fraction comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons having seven carbon atoms to the molecule from said hydrocarbon mixture, contacting said lower boiling fraction with a solid isomerization catalyst comprising adsorptive alumina under olefin isomerizing con-

ditions at a temperature of from about 200° C. to about 350° C. and a liquid hourly space velocity of from about 0.5 to about 25 thereby effecting the conversion of 3-methylcyclopentene to 1-methylcyclopentene and 4-methylcyclopentene in a first reaction zone, separately contacting said higher boiling fraction with a solid isomerization catalyst comprising adsorptive alumina under olefin isomerizing conditions at a temperature of from about 200° C. to about 350° C. and a liquid hourly space velocity of from about 0.5 to about 25 thereby effecting the conversion of 1-methylcyclopentene and 4-methylcyclopentene to 3-methylcyclopentene in a second reaction zone, fractionating 1-methylcyclopentene and 4-methylcyclopentene free of any substantial amount of open chain aliphatic hydrocarbons from the effluence of the first reaction zone, fractionating 3-methylcyclopentene free of any substantial amount of open chain aliphatic hydrocarbons from the effluence of the second reaction zone, and combining said 3-methylcyclopentene fractionated from the effluence of said second reaction zone with said 1- and 4-methylcyclopentenes fractionated from the effluence of said first reaction zone to obtain a mixture of isomeric methylcyclopentenes of high purity.

3. The process for the production of methylcyclopentenes in a relatively high state of purity from complex hydrocarbon mixtures comprising 1-methylcyclopentene, 3-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons having six and seven carbon atoms to the molecule inseparable therefrom by fractionation on a practical scale which comprises separating a lower boiling fraction comprising 3-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons having six carbon atoms to the molecule and a higher boiling fraction comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons having seven carbon atoms to the molecule from said hydrocarbon mixture, contacting said lower boiling fraction with a solid olefin isomerizing catalyst under olefin isomerizing conditions at a temperature of from about 150° C. to about 650° C. and a liquid hourly space velocity of from about 0.5 to about 25 thereby effecting the conversion of 3-methylcyclopentene to 1-methylcyclopentene and 4-methylcyclopentene in a first reaction zone, separately contacting said higher boiling fraction with a solid olefin isomerizing catalyst under olefin isomerizing conditions at a temperature of from about 150° C. to about 650° C. and a liquid hourly space velocity of from about 0.5 to about 25 thereby effecting the conversion of 1-methylcyclopentene and 4-methylcyclopentene to 3-methylcyclopentene in a second reaction zone, fractionating 1-methylcyclopentene and 4-methylcyclopentene free of any substantial amount of open chain aliphatic hydrocarbons from the effluence of the first reaction zone, fractionating 3-methylcyclopentene free of any substantial amount of open chain aliphatic hydrocarbons from the effluence of the second reaction zone, and combining said 3-methylcyclopentene fractionated from the effluence of said second reaction zone with said 1- and 4-methylcyclopentenes fractionated from the effluence of said first reaction zone to obtain a mixture of isomeric methylcyclopentenes of high purity.

4. The process for the production of methylcyclopentenes in a relatively high state of purity

from complex hydrocarbon fractions comprising 1-methylcyclopentene, 3-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons having six and seven carbon atoms to the molecule inseparable therefrom by fractionation on a practical scale, which comprises separating a lower boiling fraction comprising 3-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons having six carbon atoms to the molecule and a higher boiling fraction comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons having seven carbon atoms to the molecule from said hydrocarbon fractions, contacting said lower boiling fraction with a solid isomerization catalyst comprising adsorptive alumina under olefin isomerizing conditions at a temperature of from about 150° C. to about 650° C. and a liquid hourly space velocity of from about 0.5 to about 25 thereby effecting the conversion of 3-methylcyclopentene to [illegible]-methylcyclopentene and 4-methylcyclopentene in a first reaction zone, separately contacting said higher boiling fraction with a solid isomerization catalyst comprising adsorptive alumina under olefin isomerizing conditions at a temperature of from about 150° C. to about 650° C. and a liquid hourly space velocity of from about 0.5 to about 25 thereby effecting the conversion of 1-methylcyclopentene and 4-methylcyclopentene to 3-methylcyclopentene in a second reaction zone, fractionating 1-methylcyclopentene and 4-methylcyclopentene free of any substantial amount of open chain aliphatic hydrocarbons from the effluence of the first reaction zone, fractionating 3-methylcyclopentene free of any substantial amount of open chain aliphatic hydrocarbons from the effluence of the second reaction zone, and combining said 3-methylcyclopentene fractionated from the effluence of said second reaction zone with said 1- and 4-methylcyclopentenes fractionated from the effluence of said first reaction zone to obtain a mixture of isomeric methylcyclopentenes of high purity.

5. The process for the production of methylcyclopentenes in a relatively high state of purity from cracked gasoline comprising 1-methylcyclopentene, 3-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons having six and seven carbon atoms to the molecule inseparable therefrom by fractionation on a practical scale, which comprises separating a lower boiling fraction comprising 3-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons having six carbon atoms to the molecule and a higher boiling fraction comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons having seven carbon atoms to the molecule from said cracked gasoline, contacting said lower boiling fraction with a solid isomerization catalyst comprising adsorptive alumina under olefin isomerizing conditions at a temperature of from about 150° C. to about 650° C. and a liquid hourly space velocity of from about 0.5 to about 25 thereby effecting the conversion of 3-methylcyclopentene to 1-methylcyclopentene and 4-methylcyclopentene in a first reaction zone, separately contacting [illegible] boiling fraction with a solid isomerization catalyst comprising adsorptive alumina under olefin isomerizing conditions at a temperature of from about 150° C. to about 650° C. and a liquid hourly

space velocity of from about 0.5 to about 25 thereby effecting the conversion of 1-methylcyclopentene and 4-methylcyclopentene to 3-methylcyclopentene in a second reaction zone, fractionating 1-methylcyclopentene and 4-methylcyclopentene free of any substantial amount of open chain aliphatic hydrocarbons from the effluence of the first reaction zone, fractionating 3-methylcyclopentene free of any substantial amount of open chain aliphatic hydrocarbons from the effluence of the second reaction zone, and combining said 3-methylcyclopentene fractionated from the effluence of said second reaction zone with said 1- and 4-methylcyclopentenes fractionated from the effluence of said first reaction zone to obtain a mixture of isomeric methylcyclopentenes of high purity.

6. The process for the production of methylcyclopentenes in a relatively high state of purity from cracked gasolines comprising 1-methylcyclopentene, 3-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons having six and seven carbon atoms to the molecule inseparable therefrom by fractionation on a practical scale, which comprises separating a methylcyclopentene-containing fraction having a boiling range of from about 66° C. to about 77° C. from said gasoline, separating a lower boiling fraction boiling in the range of from about 66° C. to about 68° C. comprising 3-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons having six carbon atoms to the molecule and a higher boiling fraction having a boiling range of from about 74° C. to about 77° C. comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons having seven carbon atoms to the molecule from said methylcyclopentene-containing fraction, contacting said lower boiling fraction with a solid olefin isomerizing catalyst under olefin isomerizing conditions at a temperature of from about 200° C. to about 350° C. and a liquid hourly space velocity of from about 0.5 to about 25 thereby effecting the conversion of 3-methylcyclopentene to 1-methylcyclopentene and 4-methylcyclopentene in a first reaction zone, separately contacting said higher boiling fraction with a solid olefin isomerizing catalyst under olefin isomerizing conditions at a temperature of from about 200° C. to about 350° C. and a liquid hourly space velocity of from about 0.5 to about 25 thereby effecting the conversion of 1-methylcyclopentene and 4-methylcyclopentene to 3-methylcyclopentene in a second reaction zone, fractionating 1-methylcyclopentene and 4-methylcyclopentene free of any substantial amount of open chain aliphatic hydrocarbons from the effluence of the first reaction zone, fractionating 3-methylcyclopentene free of any substantial amount of open chain aliphatic hydrocarbons from the effluence of the second reaction zone, and combining said 3-methylcyclopentene fractionated from the effluence of said second reaction zone with said 1- and 4-methylcyclopentenes fractionated from the effluence of said first reaction zone to obtain a mixture of isomeric methylcyclopentenes of high purity.

7. The process for the production of methylcyclopentenes consisting essentially only of 1- and 4-methylcyclopentenes in a relatively high state of purity from complex hydrocarbon mixtures comprising 1-methylcyclopentene, 3-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons having six and seven carbon atoms to the molecule inseparable therefrom by fractionation on a practical scale which comprises separating a lower boiling fraction comprising 3-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons having six carbon atoms to the molecule and a higher boiling fraction comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons having seven carbon atoms to the molecule from said hydrocarbon mixture, contacting said lower boiling fraction with a solid olefin isomerizing catalyst under olefin isomerizing conditions at a temperature of from about 150° C. to about 650° C. and a liquid hourly space velocity of from about 0.5 to about 25 thereby effecting the conversion of 3-methylcyclopentene to 1-methylcyclopentene and 4-methylcyclopentene in a first reaction zone, separately contacting said higher boiling fraction with a solid olefin isomerizing catalyst under olefin isomerizing conditions at a temperature of from about 150° C. to about 650° C. and a liquid hourly space velocity of from about 0.5 to about 25 thereby effecting the conversion of 1-methylcyclopentene and 4-methylcyclopentene to 3-methylcyclopentene in a second reaction zone, fractionating 3-methylcyclopentene free of any substantial amount of open chain aliphatic hydrocarbons from the effluence of the second reaction zone, passing said 3-methylcyclopentenes fractionated from the effluence of the second reaction zone to said first reaction zone, and fractionating 1-methylcyclopentene and 4-methylcyclopentene free of any substantial amount of open chain aliphatic hydrocarbons from the effluence of the first reaction zone.

8. The process for the production of methylcyclopentenes consisting essentially of 1-methylcyclopentene and 4-methylcyclopentene in a relatively high state of purity from cracked gasoline comprising 1-methylcyclopentene, 3-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons inseparable therefrom by fractionation on a practical scale, which comprises separating from said gasoline a fraction comprising 3-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons, contacting said fraction comprising 3-methylcyclopentene with a solid adsorptive aluminous material under olefin isomerizing conditions at a temperature of from about 200° C. to about 350° C. and a liquid hourly space velocity of from about 0.5 to about 25 thereby effecting the conversion of 3-methylcyclopentene to methylcyclopentenes consisting essentially of 1-methylcyclopentene and 4-methylcyclopentene in reaction zone, and fractionating methylcyclopentenes consisting essentially of 1-methylcyclopentene and 4-methylcyclopentene free of any substantial amount of open chain aliphatic hydrocarbons from the effluence of said reaction zone.

9. The process for the production of methylcyclopentenes consisting essentially of 1-methylcyclopentene and 4-methylcyclopentene in a relatively high state of purity from a cracked gasoline fraction comprising 1-methylcyclopentene, 3-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons inseparable therefrom by fractionation on a practical scale, which comprises separating from said cracked gasoline fraction, a fraction comprising 3-methylcyclopentene in admixture with close boiling open chain aliphatic hydro-

carbons, contacting said fraction comprising 3-methylcyclopentene with a solid olefin isomerizing catalyst consisting essentially of adsorptive alumina under olefin isomerizing conditions at a temperature of from about 150° C. to about 650° C. and a liquid hourly space velocity of from about 0.5 to about 25 thereby effecting the conversion of 3-methylcyclopentene to methylcyclopentenes consisting essentially of 1-methylcyclopentene and 4-methylcyclopentene in a reaction zone, and fractionating methylcyclopentenes consisting essentially of 1-methylcyclopentene and 4-methylcyclopentene free of any substantial amount of open chain aliphatic hydrocarbons from the effluence of said reaction zone.

10. The process for the production of methylcyclopentenes consisting essentially of 1-methylcyclopentene and 4-methylcyclopentene in a relatively high state of purity from a hydrocarbon mixture comprising 1-methylcyclopentene, 3-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons inseparable therefrom by fractionation on a practical scale, which comprises separating from said hydrocarbon mixture a fraction comprising 3-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons, contacting said fraction comprising 3-methylcyclopentene with a solid olefin isomerizing catalyst under olefin isomerizing conditions at a temperature of from about 150° C. to about 650° C. and a liquid hourly space velocity of from about 0.5 to about 25 thereby effecting the conversion of 3-methylcyclopentene to methylcyclopentenes consisting essentially of 1-methylcyclopentene and 4-methylcyclopentene in a reaction zone, and fractionating methylcyclopentenes consisting essentially of 1-methylcyclopentene and 4-methylcyclopentene free of any substantial amount of open chain aliphatic hydrocarbons from the effluence of said reaction zone.

11. The process for the production of 3-methylcyclopentene in a relatively high state of purity from cracked gasoline comprising 3-methylcyclopentene, 4-methylcyclopentene and 1-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons inseparable therefrom on a practical scale by fractionation, which comprises separating from said gasoline a fraction comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons, contacting said fraction with a solid adsorptive aluminous material under olefin isomerizing conditions at a temperature of from about 200° C. to about 350° C. and a liquid hourly space velocity of from about 0.5 to about 25 thereby effecting the conversion of 1-methylcyclopentene and 4-methylcyclopentene to 3-methylcyclopentene in a reaction zone, and fractionating 3-methylcyclopentene free of any substantial amount of open chain aliphatic hydrocarbons from the effluence of said reaction zone.

12. The process for the production of 3-methylcyclopentene in a relatively high state of purity from a cracked gasoline fraction comprising 3-methylcyclopentene, 4-methylcyclopentene and 1-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons inseparable therefrom on a practical scale by fractionation, which comprises separating from said gasoline fraction, a fraction comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons, contacting said fraction comprising 1-methylcyclopentene and 4-methylcyclopentene with a solid olefin isomerizing catalyst consisting essentially of adsorptive alumina under olefin isomerizing conditions at a temperature of from about 150° C. to about 650° C. and a liquid hourly space velocity of from about 0.5 to about 25 thereby effecting the conversion of 1-methylcyclopentene and 4-methylcyclopentene to 3-methylcyclopentene in a reaction zone, and fractionating 3-methylcyclopentene free of any substantial amount of open chain aliphatic hydrocarbons from the effluence of said reaction zone.

13. The process for the production of 3-methylcyclopentene in a relatively high state of purity from a hydrocarbon mixture comprising 3-methylcyclopentene, 4-methylcyclopentene and 1-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons inseparable therefrom on a practical scale by fractionation, which comprises separating from said hydrocarbon mixture a fraction comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling open chain aliphatic hydrocarbons, contacting said fraction with a solid olefin isomerizing catalyst under olefin isomerizing conditions at a temperature of from about 150° C. to about 650° C. and a liquid hourly space velocity of from about 0.5 to about 25 thereby effecting the conversion of 1-methylcyclopentene and 4-methylcyclopentene to 3-methylcyclopentene in a reaction zone, and fractionating 3-methylcyclopentene free of any substantial amount of open chain aliphatic hydrocarbons from the effluence of said reaction zone.

GEORGE M. GOOD.
HERVEY H. VOGE.

## REFERENCES CITED

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

Plate, J. Gen. Chem. (U. S. S. R.) 15, 156–64 (1945).

Arbuzov et al., Compt. Rend. (U. S. S. R.) 30, 717–20 (1941).