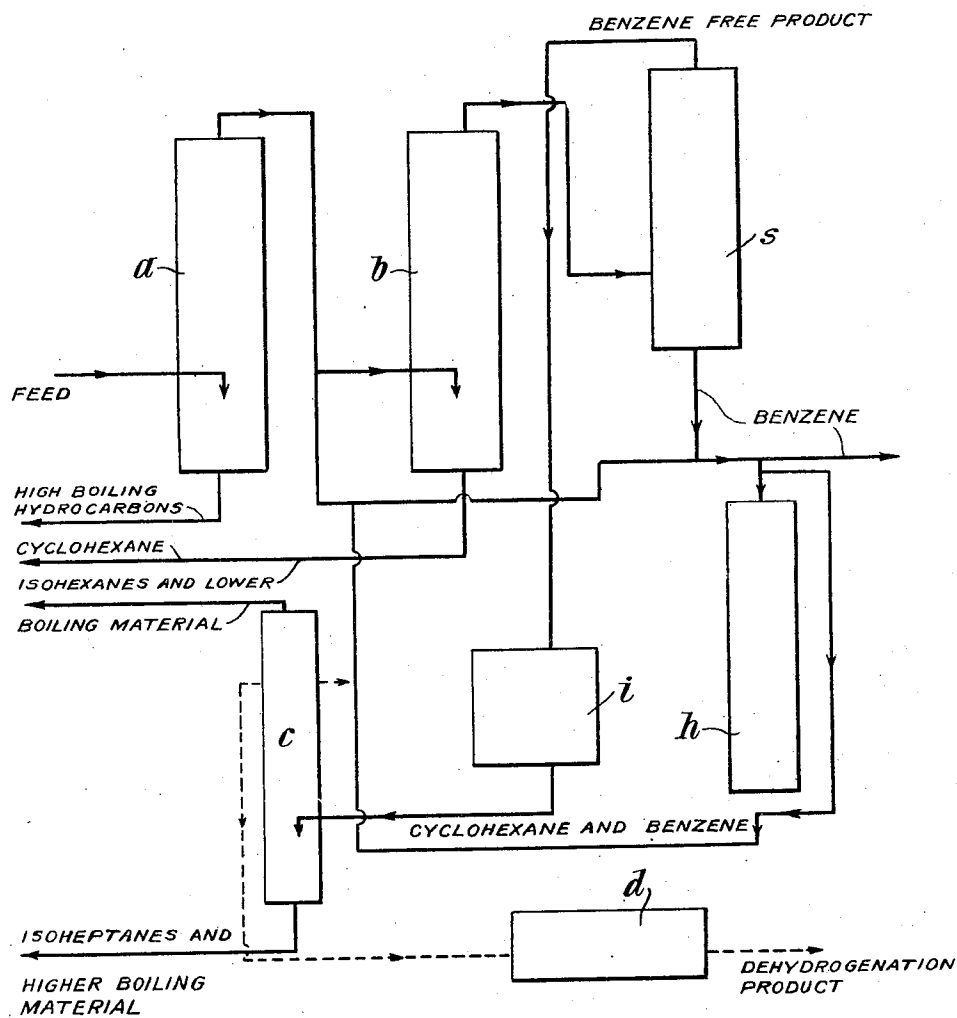


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FROM MIXTURES CONTAINING THEM
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THE INVENTORS

Stanley Francis Birch
John Habeshaw
Clarence Barnes Collis

By:

Robert N. Durham
Attorney.

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PREPARATION IN A CONDITION OF PURITY OF HYDROCARBONS FROM MIXTURES CONTAINING THEM

Stanley Francis Birch, John Habeshaw, and Clarence Barnes Collis, Sunbury-on-Thames, England, assignors to Anglo-Iranian Oil Company Limited, London, England, a British joint-stock corporation

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The invention relates to the preparation of hydrocarbons in a condition of purity from hydrocarbon mixtures containing them, and particularly with the preparation of pure cyclohexane and benzene in the utilisation of fractions consisting of or containing isomeric heptanes.

It is among the objects of the invention to secure the desired amounts of either cyclohexane or benzene or both cyclohexane and benzene under conditions and at such a stage that the separation of pure products is simply and effectively carried out.

In carrying out such operations an important difficulty arises by reason of the presence of 2,4-dimethylpentane and 2,2-dimethylpentane in the fractions processed. We have now found that it is possible to convert these two paraffins into paraffins of higher boiling point, that may be separated from cyclohexane and benzene by distillation. The nature of the conversions may be more readily understood by reference to the following table in which the respective boiling points of the isomeric heptanes are set out:

TABLE 1

Boiling points of the isomeric heptanes

Hydrocarbon	Boiling Point at 760 mm., °C.
2,2,3-Trimethylbutane.....	80.88
2,2-Dimethylpentane.....	78.90
2,4-Dimethylpentane.....	80.65
3,3-Dimethylpentane.....	86.10
2-Methylhexane.....	89.67
2,3-Dimethylpentane.....	89.90
3-Methylhexane.....	91.88
3-Ethylpentane.....	93.74
n-Heptane.....	98.24

Of the hydrocarbons referred to in the preceding table, 2,2,3-trimethylbutane does not usually occur in hydrocarbon fractions, and is difficult to produce in a process of hydrocarbon conversion. The 2,4-dimethylpentane and 2,2-dimethylpentane are thus the principal hydrocarbons whose removal is advantageous, and of these the 2,4-dimethylpentane is generally present in greater proportion. The conversion of these two hydrocarbons into any of the other heptanes than 2,2,3-trimethylbutane would therefore permit of

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their separation from cyclohexane by a normal process of distillation. It is by such a conversion that according to the invention the separation of the heptane paraffins associated with cyclohexane is in part attained.

An object of the invention when cyclohexane is the product particularly required is thus to recover the cyclohexane and/or benzene present in the feedstock in a pure state, and to hydrogenate part or all of the benzene present to cyclohexane and to recover the cyclohexane so formed. When however benzene is the product particularly required, the object of the invention is to dehydrogenate part or all of the cyclohexane and to recover the benzene so formed in a pure state.

A further object of the invention is to convert the methylcyclopentane present to cyclohexane which may be recovered as such, or hydrogenated to yield benzene; and to convert the dimethylpentanes normally distilling with cyclohexane to paraffins of different boiling point, and if required to recover the paraffins so formed, thereby facilitating the recovery of pure benzene and pure cyclohexane.

Thus according to the invention a considerable amount of benzene and cyclohexane may be recovered pure, from feedstocks not formerly easily treated to yield these compounds in a pure state.

According to the invention a hydrocarbon fraction consisting essentially of n-hexane, benzene, methylcyclopentane, cyclohexane, and dimethylpentanes, is distilled, with or without the addition under known conditions of an azeotrope forming hydrocarbon, so that substantially pure cyclohexane is recovered as residual fraction, the overhead fraction comprising any cyclohexane not so removed, and all the other constituents of the fraction distilled being treated by a process of extractive distillation or azeotropic distillation or solvent extraction, whereby substantially the whole of the benzene present is recovered, the benzene-freed fraction being then passed to an isomerisation zone, where a substantial part of the methylcyclopentane content is converted to cyclohexane and a substantial part of the 2,2-dimethylpentane and 2,4-dimethylpentane to iso-heptanes of different boiling point, the product of this isomerisation being then fractionally distilled and a fraction, consisting of cyclohexane, unchanged methylcyclopentane, n-hexane and

dimethylpentanes recycled to the distillation zone for the recovery of cyclohexane with or without the further addition of benzene from the benzene recovery stage. The benzene from that stage may be partially or wholly hydrogenated and the cyclohexane so formed recovered in the distillation zone, and the aforesaid product of isomerisation or part of it, with or without the addition of cyclohexane formed in prior stages, may be dehydrogenated to benzene, which may be recovered separately or in the benzene recovery stage of the process.

The conversion of the 2,2- and 2,4-dimethylpentanes to higher boiling heptanes is not accompanied by any significant formation of lower boiling hydrocarbons such as butanes. The following example illustrates the operation of the isomerisation:

A cyclohexane cut from Iranian isoheptane was extractively distilled using aniline as solvent, and from this extractive distillation a fraction of the following composition obtained (weight per cent.)

	Per cent
Methylcyclopentane + cyclohexane (equilibrium mixture at 80° C., see Table 2) ----	45.6
Paraffins, 2,2- and 2,4-dimethylpentane ----	54.4

The benzene was almost completely removed during the extractive distillation; being present in the above fraction to an extent less than 0.5 per cent. This product served as feedstock to the isomerisation.

520 g. of this feedstock was stirred for 2½ hours with 150 g. of aluminium chloride at 79° C., a slow stream of hydrogen chloride being passed through the reaction mixture. At the end of this time the reaction product was separated, soda and water washed and dried and fractionated in a 50-plate batch column. 13 per cent. by weight of the total product consisted of heptane paraffins boiling between 84° C. and 91° C., the remainder being distillate comprising methylcyclopentane and cyclohexane in proportions agreeing with the equilibrium compositions at the reaction temperature (79° C.) indicated in Table 2 and unchanged 2,2- and 2,4-dimethylpentanes. From these results 25 per cent. of the original 2,2- and 2,4-dimethylpentanes was converted to higher boiling heptanes and no significant formation of lower hydrocarbons such as butanes was detected.

The foregoing example illustrates the conversion of the 2,2- and 2,4-dimethylpentanes to higher boiling heptanes. The main heptanes formed were 2,3- and 3,3-dimethylpentanes, some methylhexanes but no ethylpentane being also detected.

The invention is hereinafter described with reference to the accompanying diagrammatic drawing.

In carrying the invention into effect as illustrated in the accompanying drawing any hydrocarbon fraction containing the compounds n-hexane, methylcyclopentane, cyclohexane, benzene and dimethylpentanes may serve as feedstock to the process. The presence of higher boiling constituents that is, above 81.1° C. is not important, since these may be removed in the initial fractionating zone *a*. It is however advantageous to remove lighter boiling hydrocarbons from the feedstocks if present in any large amount before subjection to the process of the invention.

A suitable feedstock to the process is for ex-

ample an "isoheptane" fraction from Iranian naphtha, which was fed to the fractionation zone *a* and gave an overhead fraction comprising 51 per cent. by weight of the total material. The overhead fraction had a boiling range of 68° C.-81.1° C. and the following composition (weight per cent):

n-Hexane -----	7.5
Methylcyclopentane -----	25.0
Benzene -----	10.6
Cyclohexane -----	46.1
C ₇ Paraffins (2,2-dimethylpentane and 2,4-dimethylpentane) -----	10.8

The overhead fraction was then passed to the second fractionation zone *b*, where by distillation in the presence of an azeotrope forming hydrocarbon, which may or may not be added to the fraction, a residual fraction was prepared comprising substantially pure cyclohexane, the remaining constituents of the charge together with any cyclohexane not removed in the residual fraction comprising the overhead fraction. The amount of cyclohexane taken off in this overhead fraction from the fractionating zone *b* depends on the efficiency of fractionation and on the composition of the charge passed to the second fractionating zone *b*.

The overhead fraction from the fractionation zone *b* passes to a zone *s* where by extractive distillation, azeotropic distillation, or solvent extraction, the benzene is recovered practically pure. The operation of an extractive distillation process of this character for the separation of aromatic hydrocarbons is described in the specification of the United States Patent No. 2,288,126. The application of azeotropic distillation is discussed in Research Paper RP. 1402 of the U. S. National Bureau of Standards. The use of solvent extraction in the zone *s* is also within the scope of the invention, either alone or when extractive distillation or azeotropic distillation is also employed. Benzene recovered in the zone *s* may be used as the added hydrocarbon azeotrope forming component in the distillation if such addition be required and the required amount may be passed from the zone *s* to the feed to the fractionating zone *b*.

The benzene-freed product from the zone *s* passes to the catalytic isomerisation zone *i*. Here it is subjected to catalytic conversion whereby a substantial proportion of the methylcyclopentane is converted to cyclohexane, and a substantial proportion of the 2,4-dimethylpentane and 2,2-dimethylpentane, to hydrocarbons of different boiling point, and especially to isoheptanes of higher boiling point. The catalyst used in the catalytic isomerisation zone *i* is preferably of the Friedel-Crafts type, aluminum chloride and catalysts prepared from or containing aluminum chloride being especially suitable. Minor proportions of hydrogen halides may be added as catalyst activators as is usual in conversions of the type using Friedel-Crafts catalysts, particularly halides of aluminum. Although such Friedel-Crafts catalysts are preferred, the use of other catalysts in the isomerisation zone is within the scope of the invention, and may in fact be advantageous when the benzene separated in the zone *s* is hydrogenated. Some hydrogenation catalysts are known to have activity in conversions such as those indicated. The oxides and sulphides of metals as catalysts in the zone *s* may therefore be used.

There are a number of known conditions in which isomerisation may be carried out in the catalytic isomerisation stage *i* of the process. Thus the benzene-free product from the zone *s* may be fractionated into two fractions, the lower boiling fraction containing the bulk of the methylcyclopentane, and the higher boiling fraction substantially the whole of the cyclohexane and dimethylpentanes. The lower boiling fraction contains normal hexane and methylcyclopentane, and possibly minor proportions of isohexanes. The two fractions may be isomerised separately. The isomerisation of the lower boiling fraction is readily carried out with substantial conversion of the methylcyclopentane to cyclohexane, and partial conversion of the normal hexane to isohexane. The isomerisation product of this fraction may be passed to the distillation zone *a*, or to the fractionating zone *b* after removal by separate fractionation of the higher boiling products of side reactions. The higher boiling fraction from the fractionating zone *s*, containing some methylcyclopentane, cyclohexane, 2,4-dimethylpentane and 2,2-dimethylpentane is passed to a separate isomerisation zone, operated under conditions whereby a substantial proportion of the 2,4- and 2,2-dimethylpentanes are converted to hydrocarbons of different boiling point, especially to higher boiling iso-heptanes. In order to avoid isomerisation of the cyclohexane to methylcyclopentane in the zone *i*, it is advantageous that this higher boiling fraction be so prepared that the methylcyclopentane and cyclohexane are present in the proportions corresponding to the equilibrium mixture of these isomers at the temperature of isomerisation. These equilibrium compositions are indicated in the following Table 2:

TABLE 2

Equilibrium concentrations of methylcyclopentane and cyclohexane

Temperature, °C.	Mole per cent, Methylcyclopentane	Mole per cent, Cyclohexane
25	12.5	87.5
35	14.5	85.5
45	16.2	83.8
55	19.2	80.8
65	21.4	78.6
77.4	25.6	74.4
140	50	50

(Glasebrook and Lovell, J. Amer. Chem. Soc., 61, 1717 (1939), Schmit, Hoog, and Verhues, Rec. Trav. Chim., 59, 793-810 (1940))

The isomerisation product of this higher boiling fraction may then be passed to the fractionation zone *a*, where high boiling constituents are removed. Sufficient additional benzene from the zone *s* should be passed with the feed to the fractionation-zone *b* to ensure the removal of the unchanged dimethylpentanes passed to the fractionation zone *a* from the isomerisation zone *i*. Or alternatively this isomerisation product may be separately fractionated to remove the high and low boiling conversion products formed in the isomerisation zone *i*, the remaining mixture of cyclohexane, methylcyclopentane and unchanged dimethylpentanes being passed straight to the fractionation zone *b* together with any additional benzene required as hereinbefore described.

As an alternative to such separation of the benzene-free product from the zone *s* into two fractions, the whole product may be passed without prior fractionation to the isomerisation zone

i, and there subjected to catalytic conversion in one or more stages, as hereinbefore described. The product from this conversion is then passed to the fractionating zone *c*, where the higher boiling paraffins, especially branched-chain heptanes are recovered, and any lighter boiling conversion products (principally isohexanes) are removed, the remainder of the product, comprising unchanged *n*-hexane, dimethylpentanes, methylcyclopentane and cyclohexane being then passed to the fractionation zone *b*.

In the operation of the fractionation stage in zone *b*, and its co-relation with conditions of operation in other stages of the process, it is important that the amount of benzene fed from the zone *s* to the fractionation zone *b* be adjusted to allow for the amount of paraffins recycled to the fractionation zone *b* from the isomerisation zone *i* as hereinbefore described. It is also important, whether the benzene-free product be passed in two fractions or as a whole, that all processing conditions comprising catalyst volume, contact time and temperature be regulated so that the amount of 2,4- and 2,2-dimethylpentane converted to hydrocarbons of different boiling point, be at least equivalent to the amount of those paraffins introduced into the system in the feed to the fractionation zone *a*, otherwise the amount of those paraffins in the system will increase and ultimately may interfere with the operation in other stages of the process, particularly with that of the fractionation zone *b*.

If it be required to produce a large yield of benzene, the product from the isomerisation zone *i* may be passed to the dehydrogenation zone *d*, whereby in the catalytic dehydrogenation, the cyclohexane present may be converted to benzene, which may be recovered in the zone *s* or separately.

A preferred method of operating in the manner immediately before described is to pass to the dehydrogenating zone *d* the product of isomerisation of higher boiling fraction of the benzene-free product from the zone *s*, after removal of the higher boiling heptanes as hereinbefore described, the benzene being recovered separately from the products of dehydrogenation. Obviously also cyclohexane formed in preceding zones, as in the fractionation zone *b* may advantageously be dehydrogenated to benzene in known manner in the zone *d*, if the main product required is benzene.

Processes of dehydrogenation for the production of benzene from cyclohexane and the course of reaction with paraffins are described in the following prior literature, viz: British Patent No. 563,555, United States Patent No. 2,357,694, German Patent No. 516,251, German Patent No. 626,273, German Patent No. 629,838, by Maihle, Marty and Gaudry, Comp. Rend. 194, 1947 (1932), and by Taylor and Jones, Bull. Soc. Chim. Belg. 46, 241-252 (1937).

The dehydrogenation may be effected with oxides or sulphides of metals as isomerisation catalysts, either alone or on porous supports, approximately in the temperature range 200-600° C.

The ease with which the benzene formed by dehydrogenation may be separated from the paraffins present as compared with the relative difficulty of separating these paraffins from cyclohexane is one of the advantages following from the operation of the dehydrogenation stage in the manner indicated. Alternatively, if the production of cyclohexane is the main object intended, part or whole of the benzene recovered

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in the zone *s* may be hydrogenated to cyclohexane in the hydrogenation zone *h*. A disadvantage of such hydrogenation under known conditions is that the last traces of benzene are difficult to remove from the treated stock and thus the cyclohexane produced is impure. In the process of the invention sufficient benzene is left unhydrogenated in the zone *h*, either by by-passing part of the benzene from the zone *s* past the zone *h* or by regulation of the conditions in the zone *h* to ensure that when the total material from the zone *h* is passed with the isomerisation product from the zone *c* to the fractionation zone *a* or *b*, sufficient benzene is present in the total feed to the fractionation zone *b* to ensure that all the dimethylpentanes are removed overhead and substantially pure cyclohexane left as the residual fraction. Thus the cyclohexane present in the feed, that produced in the isomerisation zone *i* and that produced by the hydrogenation of the benzene, are all recovered in the fractionation zone *b*. In this way the benzene may be used in the separation of the cyclohexane and later converted to cyclohexane, it being understood that the presence of unchanged benzene in the hydrogenation product has no effect on the substantial purity of the cyclohexane product.

It will be understood that the invention is not confined to the sequence of operations hereinbefore described by way of example.

We claim:

1. A process for the preparation of a pure hydrocarbon from a feedstock consisting essentially of *n*-hexane, benzene, methylcyclopentane, cyclohexane and 2,2- and 2,4-dimethylpentanes, which comprises the distillation of the feedstock in an initial distillation zone to remove a primary fraction distilling at a temperature not above 81.1° C., the primary fraction being distilled in a second distillation zone in the presence of sufficient azeotrope-forming hydrocarbon, such as benzene, to ensure the recovery of pure cyclohexane as a residual fraction, an overhead fraction also being taken, comprising any cyclohexane not retained in the residue fraction, together with azeotropic mixtures comprising methylcyclopentane and dimethylpentanes with benzene and any other azeotrope-forming hydrocarbon present, together with all other constituents of the feedstock to the second distillation zone, the overhead fraction then being subjected to extractive distillation whereby substantially the whole of the benzene in the overhead fraction is recovered in association with the extraction medium and a benzene-freed fraction produced, the said benzene-freed fraction being then passed to an isomerization zone in which a substantial part of its methylcyclopentane content is converted into cyclohexane, and a substantial part of the 2,2-dimethylpentane and 2,4-dimethylpentane converted to hydrocarbons of different boiling point.

2. A process for the preparation of a pure hydrocarbon as specified in claim 1 in which benzene is separated from the extraction medium, as by distillation and is recycled to the second distillation zone.

3. A process for the preparation of a pure hydrocarbon, as specified in claim 1 in which benzene is separated from the extraction medium as by distillation and hydrogenated and the cyclohexane so formed recycled to the second distillation zone.

4. A process for the preparation of a pure hydrocarbon as specified in claim 1, in which the

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product of isomerization is subjected to distillation and a fraction containing cyclohexane, unchanged methylcyclopentane, normal hexane and iso-heptane is recycled to the second distillation zone.

5. A process for the preparation of a pure hydrocarbon as specified in claim 1 in which the product of isomerization is subjected to distillation to take overhead a fraction containing methylcyclopentane and hexanes, a middle fraction containing *n*-hexane, dimethylpentanes, methylcyclopentane and cyclohexane being recovered and recycled to the second distillation zone and higher boiling paraffins recovered as a bottoms product.

6. A process for the preparation of a pure hydrocarbon as specified in claim 1, in which at least a part of the isomerization product is dehydrogenated to benzene and the benzene recycled to the second distillation zone.

7. A process for the preparation of a pure hydrocarbon as specified in claim 1, in which the fraction obtained in the initial fractional distillation and subjected to distillation in the second distillation zone has a boiling range of 69–81° C. and contains the whole of the methylcyclopentane, cyclohexane and benzene present in the feedstock.

8. A process for the preparation of a pure hydrocarbon as specified in claim 1, in which the benzene-freed product from the extractive distillation zone is fractionally distilled to separate a methylcyclopentane-enriched fraction from an iso-heptane-enriched fraction, the methylcyclopentane-enriched fraction passed to an isomerisation zone in which a substantial amount of its methylcyclopentane content is converted to cyclohexane and at least part of the isomerisation product passed to the second distillation zone.

9. A process for the preparation of a pure hydrocarbon as specified in claim 1, in which an azeotrope-forming hydrocarbon is added to the feedstock to the second distillation zone.

10. A process for the preparation of a pure hydrocarbon as specified in claim 1 in which benzene is added to the feedstock to the second distillation zone.

11. A process for the preparation of a pure hydrocarbon from a feedstock consisting essentially of *n*-hexane, benzene, methylcyclopentane, cyclohexane and 2,2- and 2,4-dimethylpentanes, which comprises the distillation of the feedstock in an initial distillation zone to remove a primary fraction distilling at a temperature not above 81.1° C., the primary fraction being distilled in a second distillation zone in the presence of sufficient azeotrope forming hydrocarbon, such as benzene, to ensure the recovery of pure cyclohexane as a residual fraction, an overhead fraction also being taken, comprising any cyclohexane not retained in the residue fraction, together with azeotropic mixtures comprising methylcyclopentane and dimethylpentanes with benzene and any other azeotrope-forming hydrocarbon present, together with all other constituents of the feedstock to the second distillation zone, the overhead fraction then being subjected to solvent extraction whereby substantially the whole of the benzene in the overhead fraction is recovered in association with the solvent extraction medium and a benzene-freed fraction produced, the said benzene-freed fraction being then passed to an isomerisation zone in which a substantial part of its methylcyclopentane content is con-

verted into cyclohexane, and a substantial part of the 2,2-dimethylpentane and 2,4-dimethylpentane converted to hydrocarbons of different boiling point.

12. A process for the preparation of a pure hydrocarbon as specified in claim 11 in which benzene is separated from the solvent extraction medium, as by distillation and is recycled to the second distillation zone.

13. A process for the preparation of a pure hydrocarbon as specified in claim 11 in which benzene is separated from the extraction medium as by distillation and hydrogenated and the cyclohexane so formed recycled to the second distillation zone.

14. A process for the preparation of a pure hydrocarbon as specified in claim 11 in which the product of isomerisation is subjected to distillation and a fraction containing cyclohexane, unchanged methylcyclopentane, normal hexane and iso-heptane is recycled to the second distillation zone.

15. A process for the preparation of a pure hydrocarbon as specified in claim 11 in which the product of isomerisation is subjected to distillation to take overhead a fraction containing methylcyclopentane and hexanes, a middle fraction containing n-hexane, dimethylpentanes, methylcyclopentane and cyclohexane being recovered and recycled to the second distillation zone and higher boiling paraffins recovered as a bottoms product.

16. A process for the preparation of a pure hydrocarbon as specified in claim 11 in which at least part of the isomerisation product is dehydrogenated to benzene and the benzene recycled to the second distillation zone.

17. A process for the preparation of a pure hydrocarbon as specified in claim 11, in which the fraction obtained in the initial fractional distillation and subjected to distillation in a second distillation zone has a boiling range of 69-81° C. and contains the whole of the methylcyclopentane, cyclohexane and benzene present in the feedstock.

18. A process for the preparation of a pure hydrocarbon as specified in claim 11 in which the benzene-freed product from the solvent extraction zone is fractionally distilled to separate a methylcyclopentane-enriched fraction from an isoheptane-enriched fraction, the methylcyclopentane-enriched fraction passed to an isomerisation zone in which a substantial amount of its methylcyclopentane content is converted to cyclohexane and at least part of the isomerisation product passed to the second distillation zone.

19. A process for the preparation of a pure hydrocarbon as specified in claim 11 in which an azeotrope-forming hydrocarbon is added to the feedstock to the second distillation zone.

20. A process for the preparation of a pure hydrocarbon as specified in claim 11 in which benzene is added to the feedstock to the second distillation zone.

21. A process for the preparation of pure hydrocarbon from a feed stock consisting essentially of n-hexane, benzene, methylcyclopentane, cyclohexane and 2,2- and 2,4-dimethylpentanes, which comprises the distillation of the feedstock in an initial distillation zone to remove a primary fraction distilling at a temperature not above 81.1° C., the primary fraction being distilled in a second distillation zone in the presence of sufficient azeotrope forming hydrocarbons, such as

benzene, to ensure the recovery of pure cyclohexane as a residual fraction, an overhead fraction also being taken, comprising any cyclohexane not retained in the residue fraction, together with azeotropic mixtures comprising methylcyclopentane and dimethylpentanes with benzene and any other azeotrope-forming hydrocarbon present, together with all other constituents of the feedstock to the second distillation zone, the overhead fraction then being subjected to azeotropic distillation whereby substantially the whole of the benzene in the overhead fraction is recovered and a benzene-freed fraction produced, the said benzene-freed fraction being then passed to an isomerisation zone in which a substantial part of its methylcyclopentane content is converted into cyclohexane, and a substantial part of the 2,2-dimethylpentane and 2,4-dimethylpentane converted to hydrocarbons of different boiling point.

22. A process for the preparation of a pure hydrocarbon as specified in claim 21 in which benzene recovered in the azeotropic distillation is recycled to the second distillation zone.

23. A process for the preparation of a pure hydrocarbon as specified in claim 21 in which benzene recovered in the azeotropic distillation is hydrogenated and the cyclohexane so formed recycled to the second distillation zone.

24. A process for the preparation of a pure hydrocarbon as specified in claim 21 in which the product of isomerisation is subjected to distillation and a fraction containing cyclohexane, unchanged methylcyclopentane, normal hexane and isoheptane is recycled to the second distillation zone.

25. A process for the preparation of a pure hydrocarbon as specified in claim 21 in which the product of isomerisation is subjected to distillation to take overhead a fraction containing methylcyclopentane and hexanes, a middle fraction containing n-hexane, dimethylpentanes, methylcyclopentane and cyclohexane being recovered and recycled to the second distillation zone and higher boiling paraffins recovered as a bottoms product.

26. A process for the preparation of a pure hydrocarbon as specified in claim 21 in which at least part of the isomerisation product is dehydrogenated to benzene and the benzene recycled to the second distillation zone.

27. A process for the preparation of a pure hydrocarbon as specified in claim 21 in which the fraction obtained in the initial fractional distillation and subjected to distillation in a second distillation zone has a boiling range of 69-81° C. and contains the whole of the methylcyclopentane, cyclohexane and benzene present in the feedstock.

28. A process for the preparation of a pure hydrocarbon as specified in claim 21 in which the benzene-freed product from the azeotropic distillation zone is fractionally distilled to separate a methylcyclopentane-enriched fraction from an isoheptane-enriched fraction, the methylcyclopentane-enriched fraction passed to an isomerisation zone in which a substantial amount of its methylcyclopentane content is converted to cyclohexane and at least part of the isomerisation product passed to the second distillation zone.

29. A process for the preparation of a pure hydrocarbon as specified in claim 21 in which an azeotrope-forming hydrocarbon is added to the feedstock to the second distillation zone.

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30. A process for the preparation of a pure hydrocarbon as specified in claim 21 in which benzene is added to the feedstock to the second distillation zone.

31. A process for the preparation of a pure hydrocarbon from a feedstock consisting essentially of n-hexane, benzene, methylcyclopentane, cyclohexane and 2,2- and 2,4-dimethylpentanes, which comprises the distillation of the feedstock in an initial distillation zone to remove a primary fraction distilling at a temperature not above 81.1° C., the primary fraction being distilled in a second distillation zone in the presence of sufficient azeotrope-forming hydrocarbon, such as benzene, to ensure the recovery of pure cyclohexane as a residual fraction, an overhead fraction also being taken, comprising any cyclohexane not retained in the residue fraction, together with azeotropic mixtures comprising methylcyclopentane and dimethylpentanes with benzene and any other azeotrope-forming hydrocarbon present, together with all other constituents of the feedstock to the second distillation zone, the overhead fraction then being treated for the recovery of substantially the whole of the benzene in the

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overhead fraction and the production of a benzene-freed fraction, the said benzene-freed fraction being then passed to an isomerisation zone in which a substantial part of its methylcyclopentane content is converted into cyclohexane, and a substantial part of the 2,2-dimethylpentane and 2,4-dimethylpentane converted to hydrocarbons of different boiling point.

STANLEY FRANCIS BIRCH.
JOHN HABESHAW.
CLARENCE BARNES COLLIS.

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