

Feb. 6, 1951

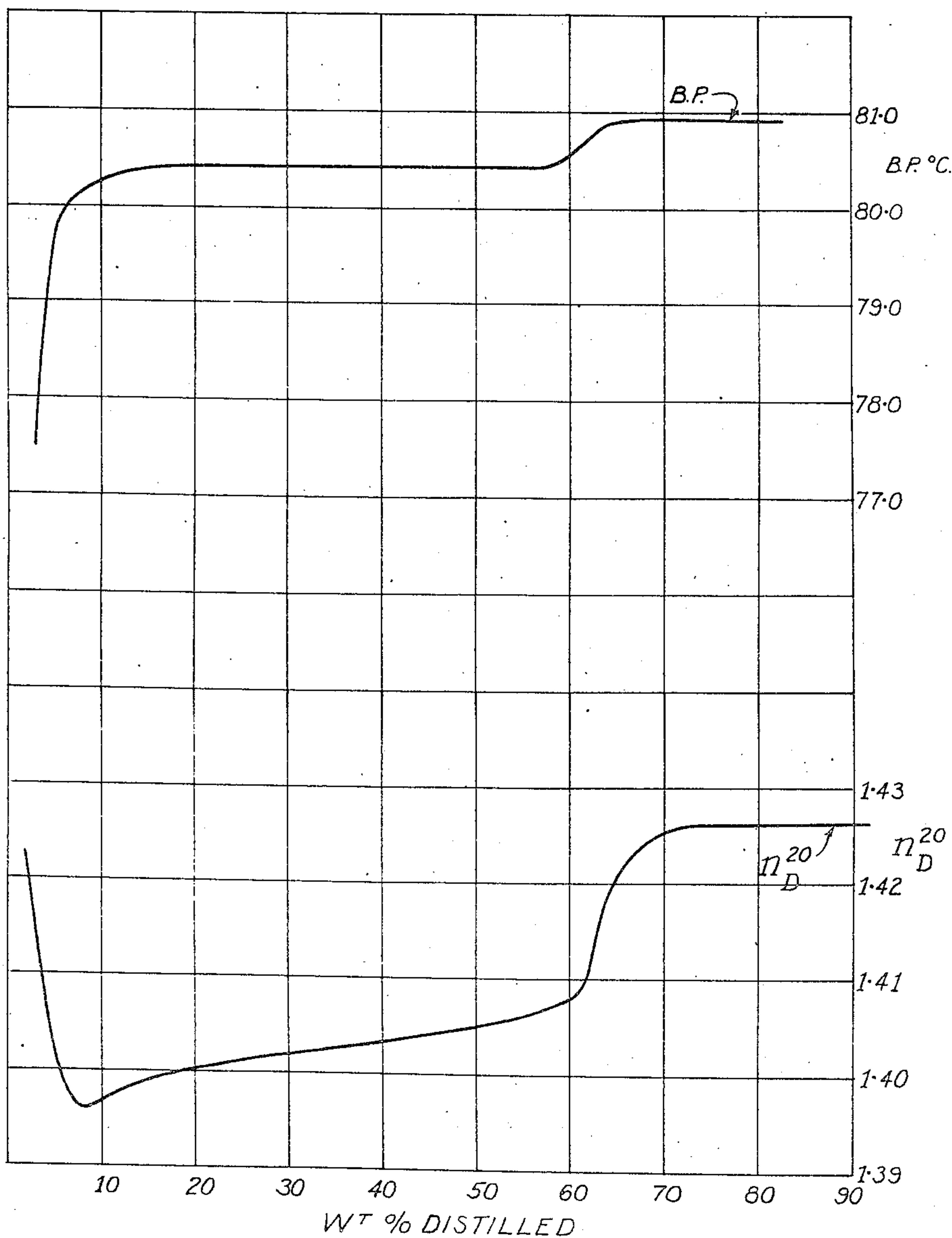
S. F. BIRCH ET AL

2,540,318

SEPARATION OF NARROW BOILING HYDROCARBON FRACTIONS

Filed Dec. 5, 1945

3 Sheets-Sheet 1



INVENTORS: **FIGURE 1.**
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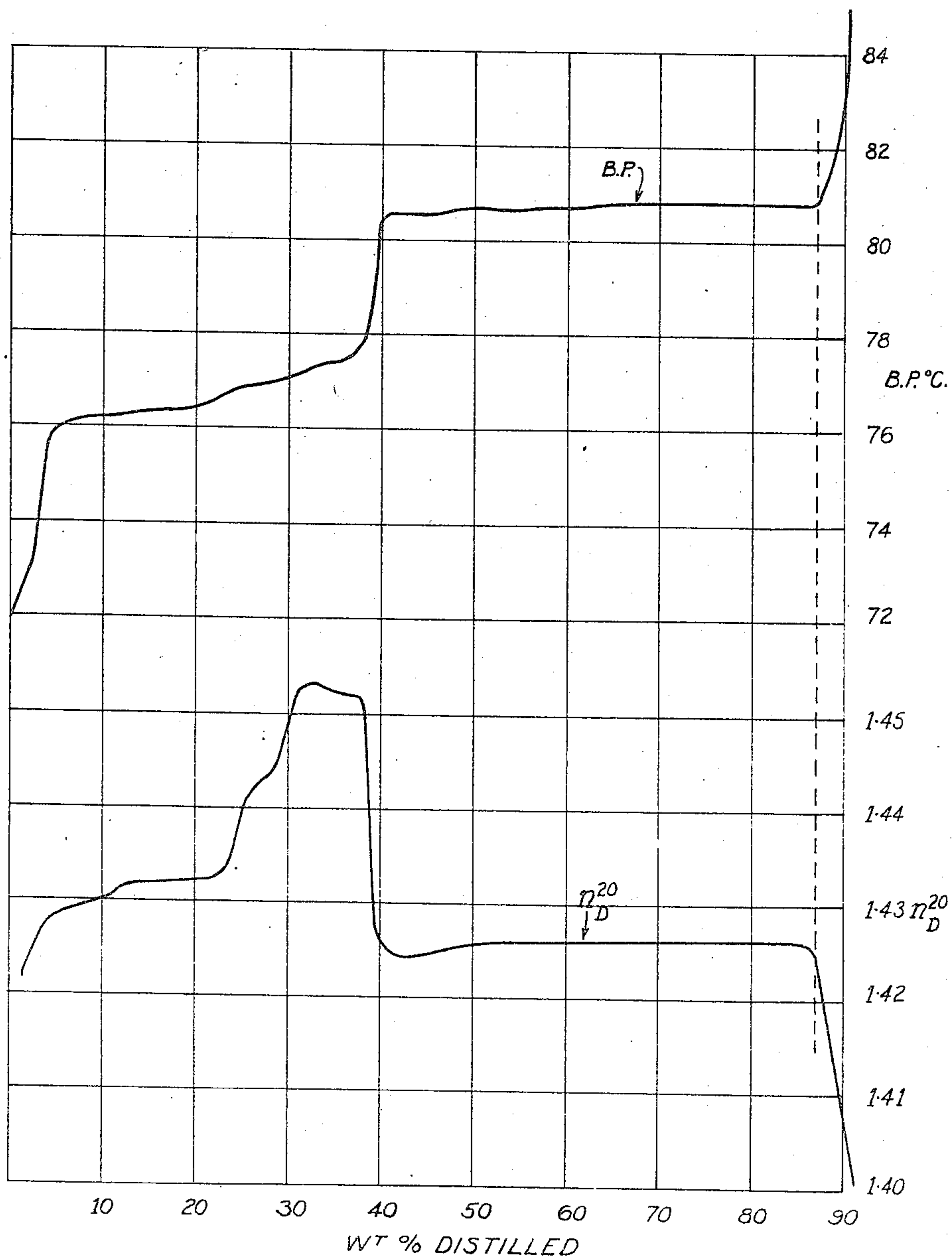
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SEPARATION OF NARROW BOILING HYDROCARBON FRACTIONS

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3 Sheets-Sheet 2



INVENTORS: FIGURE 2.
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3 Sheets-Sheet 3

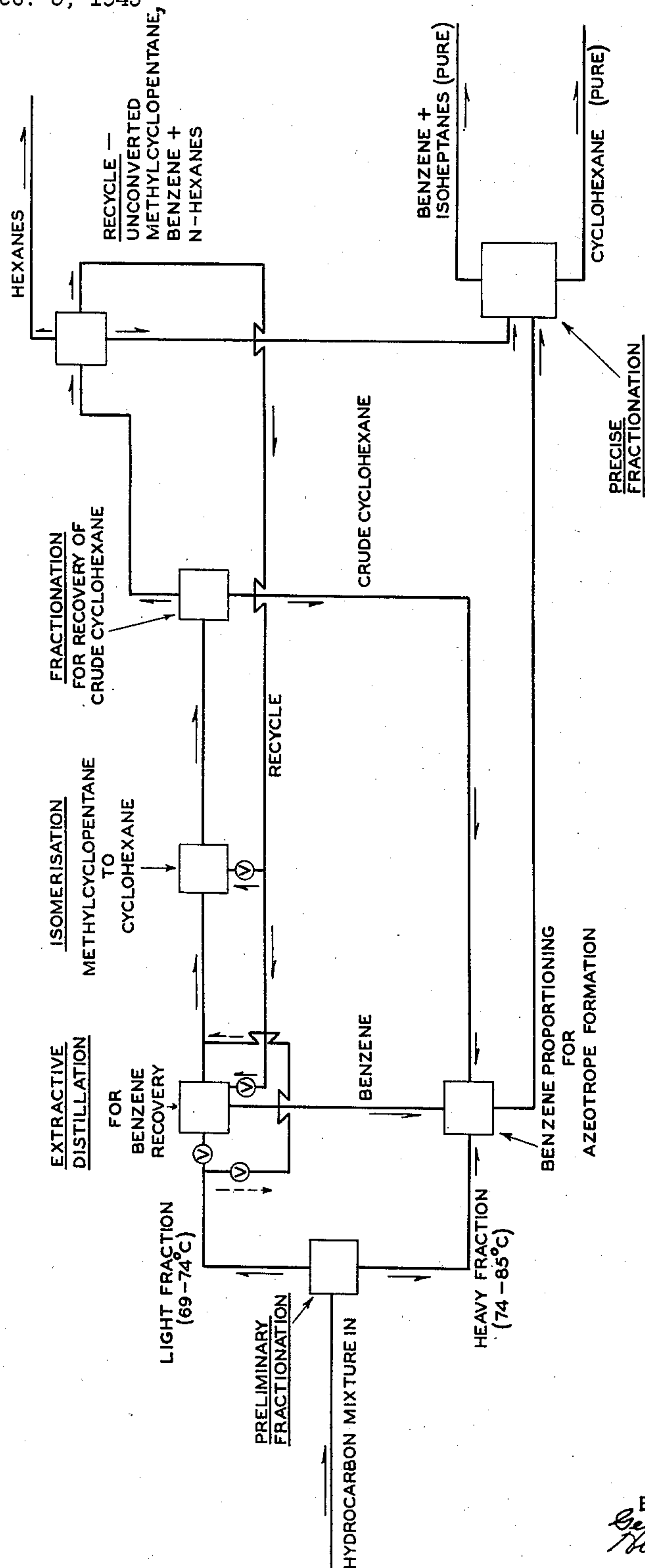


FIG. 3

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UNITED STATES PATENT OFFICE

2,540,318

SEPARATION OF NARROW BOILING
HYDROCARBON FRACTIONS

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Application December 5, 1945, Serial No. 632,966
In Great Britain December 5, 1944

2 Claims. (Cl. 260—666)

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The invention relates to the recovery of pure hydrocarbons from fractions containing them and more especially to the recovery of cyclohexane from petroleum naphtha.

The difficulty of separating pure hydrocarbons from petroleum fractions boiling over about 65° C. is well-known. The difficulty arises not only from the closeness of the boiling points of the constituents, but also from the deviations from Raoult's law which occur in this range, and particularly from the recurrence of constant boiling mixtures. The boiling points of some of the hydrocarbons in this range are shown in the following Table I.

Table I

| Hydrocarbon | Boiling Point, °C./760 mm. |
|--------------------------------------|-------------------------------|
| n-Hexane..... | 68.75 |
| Methylcyclopentane..... | 71.85 |
| 2,2-Dimethylpentane..... | 78.90 |
| Benzene..... | 80.2 |
| 2,4-Dimethylpentane..... | 80.65 |
| Cyclohexane..... | 80.8 |
| 1,1-Dimethylcyclopentane..... | 88.05 |
| trans. 1,3-Dimethylcyclopentane..... | 90.5 |
| trans. 1,2-Dimethylcyclopentane..... | 91.90 |
| cis. 1,2-Dimethylcyclopentane..... | 100.8 |
| Toluene..... | 110.8 |

Some of the binary azeotropic mixtures known are shown in the following Table II.

Table II

| Constituents of azeotrope | | Mole. per cent of (1) in azeotrope | Boiling Point of azeotrope, °C. |
|---------------------------|--|------------------------------------|---------------------------------|
| 1 | 2 | | |
| Benzene..... | Methylcyclopentane ¹ | c. 10 | c. 71.5. |
| Do..... | 2,4-Dimethylpentane ² | 54.5 | 75.2 at 757 mm. |
| Do..... | Cyclohexane ² | 51.5 | 77.4 at 759 mm. |

¹ See Griswold and Ludwig Ind. Eng. Chem. 35, 117 (1943).
² See Richards and Hargreaves Ind. Eng. Chem. 36, 805 (1944).

Furthermore many mixtures such for example as toluene-methylcyclohexane mixtures, deviate markedly from the ideal, even though no definite azeotrope has been observed.

It is impossible to recover pure hydrocarbons such as cyclohexane from petroleum fractions by processes involving normal fractionation

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alone, as distinct from extractive distillation or the usual methods of azeotropic distillation.

We have found that by applying the indicated hydrocarbons it is possible having regard to their characteristics to recover substantially pure cyclohexane by precise fractionation from the mixtures referred to.

It is an object of the invention to obtain cyclohexane in as pure a state as may be desired from hydrocarbon mixtures containing it.

It is a further object to convert any methylcyclopentane which may be present into cyclohexane, and to recover the cyclohexane so formed; while it is a further object to recover any benzene which may be present in a pure state.

The separation of hydrocarbons by azeotropic distillation is discussed at some length in Research Paper RP. 1402 of the U. S. National Bureau of Standards, in which it is stated that "the organic compounds that form azeotropic mixtures with these hydrocarbons include those containing hydroxyl, carboxyl, cyanide, amino, nitro and other structural groups that tend to produce polarity in organic molecules" (Journal of Research of the National Bureau of Standards, vol. 27, p. 44). Furthermore, the desirable properties of an azeotrope-forming substance are stated in the reference to be as follows:

(a) Boiling point not more than 30° or 40° C. away from the boiling range of the hydrocarbons to be separated.

(b) Completely soluble in water and preferentially less soluble in the hydrocarbon at room temperature.

(c) Completely soluble in the hydrocarbon at the distillation temperature.

(d) Readily obtainable in a sufficiently pure state at reasonable cost.

(e) Non-reactive with hydrocarbons or with the material of the still. (Op. cit., p. 49.)

It is an advantage of the process of the invention over such more usual azeotropic distillation processes, that the addition of a non-hydrocarbon azeotrope forming component is not required, and thus there is no need to recover the added azeotrope component from the products. It is a further advantage of the process of the invention that the added azeotrope component will generally be present in substantial amounts in the fraction to be treated. It

is a further advantage that the added component does not require to be added in a pure state, so long as the impurities present do not interfere with the final distillation. It is a further advantage that the latent heat of vaporisation of the added azeotrope component is less than that of the more usual components, and therefore the heat requirements of the process of the invention are lower. It is a further advantage of the process that, whereas the usual processes of azeotropic distillation are only applied with great difficulty to the separation of pure naphthenes, the process of the invention is however useful in that application.

According to the invention a narrow boiling hydrocarbon fraction of known or determined composition is treated by the addition thereto of a hydrocarbon capable of forming a minimum constant boiling mixture with at least one of the constituents that it is desired to remove. A proportion of the said hydrocarbon may or may not be present in the fraction, and the mixture is then fractionated to remove the desired constituent or constituents and to recover the minimum constant boiling mixture in a substantially pure state.

According to one particular embodiment of the invention there is first isolated from a petroleum naphtha a fraction containing cyclohexane, 2,4-dimethylpentane, some benzene, (and any 2,2-dimethylpentane present) but only minor proportions of methylcyclopentane and other hydrocarbons. Then benzene content of this fraction is then adjusted so that the amount of benzene present is sufficient to form an azeotrope with the dimethylpentane, but insufficient to bring over in the overhead fraction any substantial amount of cyclohexane as a minimum constant boiling mixture, and the mixture is then passed to an efficient fractionation column in which the azeotropes are removed overhead and substantially pure cyclohexane is recovered as the bottoms product.

Figure 1 of the accompanying drawing shows the results obtained in distillation in a batch column of a mixture of 2,2-dimethylpentane, 2,4-dimethylpentane and cyclohexane practically free of benzene in a 100-plate column with a reflux ratio of 200:1. The charge stock was a cyclohexane concentrate from Iranian "isoheptane," the benzene being removed by extractive distillation. It was possible from this distillation to prepare pure cyclohexane.

Figure 1 shows that very marked deviations from Raoult's law occur with this mixture. It will be observed that the first fractions are a cyclohexane-paraffin mixture, and that the transition from such a mixture to pure cyclohexane was accompanied by a boiling point rise of only about 0.5° C. The example indicates the difficulty in preparing pure cyclohexane from mixtures containing less benzene than that required for the benzene-paraffin azeotrope formation. The curve of Figure 2 in comparison with that of Figure 1 shows the results under the same fractionating conditions in a batch column with a mixture of about the optimum benzene-paraffin ratio. The curves show clearly the greatly increased sharpness of cutting in the presence of added benzene.

We have found that at atmospheric pressure a minimum boiling azeotrope of 2,2-dimethylpentane and benzene is formed having the following properties:

| | |
|--------------------------------------|--------|
| Boiling point, °C----- | 76.0 |
| Benzene content, mole per cent----- | 52.5 |
| Refractive index (n_D^{20})----- | 1.4267 |

According to the invention when the fraction to be treated contains benzene in excess of that required for the removal of all the dimethylpentane already present, the composition of the mixture is adjusted by the addition thereto of dimethylpentane in quantity sufficient to form a minimum constant boiling mixture with the excess benzene.

Fig. 3 of the accompanying drawing is a flow sheet showing diagrammatically specific steps of the processes of this invention.

According to the invention also a hydrocarbon mixture of approximate boiling range 69–85° C. is fractionated to produce a lighter fraction boiling in the range 69–74° C. and a heavier fraction boiling in the range 74–85° C. The lighter fraction is passed either directly, or after passing through an intermediate extractive zone for recovery of benzene, to an isomerization zone in which methylcyclopentane is converted into cyclohexane, and thence to a fractionation zone in which crude cyclohexane is recovered as the bottoms product. The overhead product is fractionated in another zone to separate the unconverted methylcyclopentane and benzene still present from the hexanes, the fraction containing the methylcyclopentane and benzene being either recycled to the extractive zone or to the isomerization zone.

The crude cyclohexane is admixed with the heavier fraction and after the minimum constant boiling mixture has been adjusted in the determined proportions of its constituents, the mixture is passed to a zone of precise and efficient fractionation in which the cyclohexane is recovered in a substantially pure state. Thus in this particular embodiment of the invention there is recovered not only the cyclohexane originally present, but also that produced by the isomerisation of the methylcyclopentane.

The feedstock to this wider application of the process of the invention is conveniently an "isoheptane" or "cyclohexane" fraction as prepared in normal refinery processes. This fraction contains substantially the whole of the cyclohexane and methylcyclopentane contained in the petroleum. This fraction is fractionated and two fractions prepared. The lower boiling fraction contains the methylcyclopentane, the hexanes and some benzene, but only minor proportions of cyclohexane and the heptane paraffins. The higher boiling fraction contains the cyclohexane, 2,4-dimethylpentane, some benzene and any 2,2-dimethylpentane present, and only minor proportions of methylcyclopentane. These fractions are so prepared in the preliminary fractionation that hydrocarbons other than those indicated are substantially absent.

The lower boiling of these fractions is then passed to an isomerising zone, with or without previous treatment, i. e. extractive distillation, azeotropic distillation or solvent extraction, to remove the benzene present, wherein by the use of a catalyst complex prepared from aluminium chloride and hydrocarbons, a proportion of the methylcyclopentane present is converted into cyclohexane, and the normal hexane partially converted into methylpentanes. The cyclohexane so formed is recovered in the later stages of the process.

The separation of pure cyclohexane from the higher boiling of the two fractions is carried out as follows:

The fraction processed should be of such a narrow boiling range that the number of hydrocarbons present is as small as possible. The chemical composition of the fraction is then determined, either spectroscopically or otherwise. It is not always necessary that the proportions of the individual hydrocarbons present be known, since in many cases sufficient information is obtained by a determination of the proportions of aromatic, naphthenic and paraffinic constituents. To this fraction of known composition is then added a hydrocarbon forming a minimum constant boiling mixture with one or more of the constituents of the fraction. It is necessary that the added component forms a constant boiling mixture with at least one of the constituents which it is necessary to remove to produce the required pure component. The added hydrocarbon may be, and generally is already present in some proportion in the fraction, and it is required that the amount of added component in the mixture finally submitted to fractionation for the recovery of the required pure component, be such that the undesired hydrocarbons and the added component can be distilled off as an overhead fraction, leaving the required pure component as residue. The amount of the azeotrope forming hydrocarbon added is thus the difference between the amount already present and that required for the removal of the undesired constituents in the aforesaid overhead fraction.

The final distillation is carried out in fractionating equipment of high efficiency, for the reason that in the case of cyclohexane recovery, the added component may form a minimum constant boiling mixture with cyclohexane as well as with the undesired component or components, and the column efficiency should be such that the minimum constant boiling mixture with the undesired component can be separated from the next boiling component, which in this case is the minimum boiling mixture of added component and cyclohexane. Reduction in the efficiency of fractionation of this stage is possible to some extent, at the expense however of loss of some of the cyclohexane in the overhead fractions. The use of several stages of fractionation in this operation is of advantage, either with or without adjustment of the proportion of added component between the various stages of the operation. Such multistage fractionation is within the scope of the invention.

It will be understood that the preparation of the fraction for the final distillation should be carried out so as to yield a product substantially free of higher boiling components.

The component added need not be pure. Thus in the preparation of cyclohexane by the process, the component added is generally benzene, and this can be added admixed with methylcyclopentane, a product which may be recovered from the isomerisation product of the earlier fractions, as will be more specifically indicated hereinafter.

The method of the invention may be carried out in the recovery of cyclohexane as hereinafter described.

A cyclohexane fraction is prepared boiling in the range approximately 65° to 85° C. By fractionation in a column equivalent to between 30 and 40 theoretical plates this is separated into two fractions. The lighter boiling fraction, distilling up to 74°-75° C. contains substantially the whole

of the hexanes (chiefly n-hexane) and methylcyclopentane, some benzene, and only minor proportions of other hydrocarbons. This fraction forms the feedstock to the isomerisation stage, and the proportion of benzene therein should not be excessive. In the isomerisation stage the methylcyclopentane is partly converted to cyclohexane, and the n-hexane to methylpentanes. We have found that under the most favourable conditions for the production of cyclohexane the proportion of doubly branched hexanes formed is small.

The product from the isomerisation stage passes to a fractionation zone, and is there separated into three parts. The first part being the lightest-boiling fraction contains the hexanes, and only minor proportions of methylcyclopentane and benzene, and this fraction may be passed to the normal refinery gasoline production plant. The second fraction contains methylcyclopentane, n-hexane, benzene, and a minor proportion of cyclohexane. This fraction may be recycled to the isomerisation zone, but by a process of extractive distillation, the benzene and the methylcyclopentane may be first separated from the hexane present. By this complete or partial separation, the benzene and paraffin content of the recycle feed to the isomerisation zone may be controlled, and a benzene concentrate containing methylcyclopentane also prepared. This concentrate may be used as additive azeotropic component instead of pure benzene in the final fractionation. The third fraction of the isomerization product is the cyclohexane, which may be purified in the final distillation stage for the production of the pure cyclohexane, or fractionated separately.

The second or residual fraction of the preliminary fractionation contains substantially the whole of the cyclohexane and 2,4-dimethylpentane present, and generally some benzene. To this fraction further benzene is then added, so that the amount present is sufficient to take overhead as the minimum constant boiling mixture all the dimethylpentane present. We have found, for example, that on distillation in a column equivalent to 100 theoretical plates, under efficient conditions of operation, a good yield of cyclohexane in a substantially pure state is thus obtained.

If it was found that the benzene was present in the residual fraction in amount in excess of that required for the removal of all the dimethylpentane as minimum constant boiling mixture, it was accordingly necessary to add dimethylpentane to the feedstock for the final distillation. The amount added in this case is determined in exactly the same manner as with the benzene. The 2,4-dimethylpentane is more generally present in excess than benzene, so that the addition of benzene is more usually necessary.

As indicating the influence of fractionation efficiency a hydrocarbon mixture was distilled under various conditions of fractionation efficiency. The composition of the charge stock distilled was, in wts. per cent. as follows:

| | |
|-------------------------------|------|
| n-Hexane | 0.1 |
| Methylcyclopentane | 5.2 |
| Cyclohexane | 58.9 |
| 2,2- and 2,4-dimethylpentanes | 13.7 |
| Benzene | 10.8 |
| Higher boiling material | 12.3 |

The results obtained from this series of distillations are summarised in the following table;

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Table III

| No. of the- oretical plates in column | Reflux Ratio | Cyclohexane recovered, weight per cent. of total in the charge | Purity of recov- ered cyclo- hexane |
|--|-----------------|--|---|
| 40 | 50:1 | 20.3 | 97.5 |
| 100 | 50:1 | 28.3 | 99.57 |
| 100 | 100:1 | 66.6 | 99.41 |
| 100 | 200:1 | 51.7 | 99.96 |
| | | 67.0 | 99.81 |
| | | 77.3 | 99.38 |

The increase in yield obtained by increasing the number of theoretical plates in the column and by increasing the reflux ratio under which the column is operated is evident.

As to the effect of benzene content on cyclohexane recovery the results given in the following Table IV were obtained by fractionating in a column having 100 theoretical plates operated at a reflux ratio of 200:1, a charge stock of varying benzene: 2.2- and 2.4-dimethylpentane ratio, but of substantially the same cyclohexane: dimethylpentane ratio.

The following Table IV indicates the effect of benzene content on cyclohexane recovery.

Table IV

| Benzene Content, Weight per cent | Dimethyl- pentane Content, Weight per cent | Weight per cent of total cyclohexane in charge re- covered pure | Purity of recovered cyclo- hexane |
|---|--|---|--|
| Nil | 15.3 | 62.4 | 99.62 |
| 5.4 | 14.5 | 58.8 | 99.84 |
| 10.8 | 13.7 | 67.3 | 99.72 |
| | | 51.7 | 99.96 |
| | | 67.0 | 99.81 |
| 15.1 | 13.0 | 77.3 | 99.38 |
| 21.7 | 12.0 | 82.5 | 99.63 |
| | | 85.7 | 99.54 |
| | | 77.1 | 99.93 |
| | | 80.0 | 99.80 |

From the results given in the foregoing tables the recovery of cyclohexane which may be expected from fractionation conditions of various efficiencies with various benzene-paraffin ratios in the feed, may be obtained. As in the above tables the cyclohexane recovered was of varying purity, the recoveries of cyclohexane of purity of 99.5 per cent., 99.0 per cent., and 97.0 per cent. have been calculated from the data of the above tables, and the results are summarised in the following table:

The following Table V indicates results obtained in the recovery of cyclohexane of varying purity.

Table V

| No. of plates in Column | Reflux Ratio | Per cent benzene in feed | Per cent paraffin in feed | Per cent of cyclohexane in feed recovered of purity— | | |
|----------------------------------|-----------------|--------------------------------|---------------------------------|---|------|-------|
| | | | | 97% | 99% | 99.5% |
| 40 | 50:1 | 10.8 | 13.7 | 23.4 | | |
| 100 | 50:1 | 10.8 | 13.7 | 36.7 | 30.9 | 28.5 |
| 100 | 100:1 | 10.8 | 13.7 | 76.5 | 68.1 | 64.5 |
| 100 | 200:1 | 10.8 | 13.7 | 89.8 | 80.7 | 74.7 |
| 100 | 200:1 | Nil | 15.3 | 75.0 | 65.7 | 63.5 |
| 100 | 200:1 | 5.4 | 14.5 | 79.6 | 71.0 | 68.3 |
| 100 | 200:1 | 10.8 | 13.7 | 89.8 | 80.7 | 74.7 |
| 100 | 200:1 | 15.1 | 13.0 | 97 | 90.6 | 85.8 |
| 100 | 200:1 | 21.7 | 12.0 | 88.1 | 83.4 | 82.1 |

The foregoing results demonstrate clearly that the optimum recovery of cyclohexane is obtained at a particular benzene concentration, this con-

centration being close to that giving the composition of the benzene-dimethylpentane minimum boiling azeotrope referred to; and they determine the optimum benzene concentration for the particular example referred to. For feedstocks of composition differing from that of the example by appreciable amounts, the optimum benzene content may readily be computed from these results, bearing in mind that the ratio between benzene and 2.2- plus 2.4-dimethylpentane is the important factor, the ratio of cyclohexane to either of these components being of relatively minor importance. In this connection, an important condition is that the cyclohexane content should not be too low; for whatever the amount of cyclohexane present, for a feed of given benzene and dimethylpentane content, with a fixed fractionating efficiency the loss of cyclohexane in the intermediate fractions will be the same in amount. Thus for a low cyclohexane proportion in the feed, the per cent. of cyclohexane which it is possible to separate pure will be lower than for a feed of high cyclohexane content.

We claim:
1. A process for the treatment of a hydrocarbon mixture boiling approximately in the range 69-85° C. consisting essentially of cyclohexane, benzene, 2,2-dimethylpentane, methylcyclopentane and minor proportions of other hydrocarbons, which comprises fractionally distilling the said mixture to produce a methyl-cyclopentane-containing fraction boiling approximately in the range 69-74° C. and an isoheptane and cyclohexane-containing fraction boiling approximately in the range 74-85° C., the methyl-cyclopentane-containing fraction being passed to an isomerisation zone, in which methylcyclopentane is converted into cyclohexane, the fraction thereupon being passed to a fractionation zone in which the crude cyclohexane is recovered as bottoms product, the overhead product being fractionated in another zone to separate the unconverted methylcyclopentane and benzene still present from the hexanes, the crude cyclohexane recovered being admixed with the isoheptane and cyclohexane-containing fraction, and thereafter adjusting the proportion of benzene in the mixture so obtained to provide sufficient benzene to form a minimum constant boiling mixture with all of the isoheptane present but insufficient benzene to bring over in an overhead fraction any substantial quantity of cyclohexane and thereafter subjecting the adjusted mixture to frictional distillation with precision whereby the isoheptanes and benzene are removed, in an overhead fraction, as minimum constant boiling mixtures and whereby substantially pure cyclohexane is recovered as a bottoms product.

2. A process for the treatment of a hydrocarbon mixture boiling approximately in the range 69-85° C. consisting essentially of cyclohexane, benzene, 2,2-dimethylpentane, methylcyclopentane and minor proportions of other hydrocarbons, which comprises fractionally distilling the said mixture to produce a methyl-cyclopentane-containing fraction boiling approximately in the range 69-74° C., and an isoheptane and cyclohexane-containing fraction boiling approximately in the range 74-85° C. the methyl-cyclopentane-containing fraction being first passed through an extractive distillation zone for the recovery of some of the benzene present, and thence to an isomerisation zone, in which methylcyclopentane is converted into cyclohexane, the

isomerised fraction thereupon being passed to a fractionation zone in which the crude cyclohexane is recovered as bottoms product, the overhead product being fractionated in another zone to separate the unconverted methylcyclopentane and benzene still present from the hexanes, the crude cyclohexane recovered being admixed with said isoheptane and cyclohexane-containing fraction, and thereafter adjusting the proportion of benzene in the mixture so obtained to provide sufficient benzene to form a minimum constant boiling mixture with all of the isoheptane present but insufficient benzene to bring over in an overhead fraction any substantial quantity of cyclohexane and thereafter subjecting the adjusted mixture to fractional distillation with precision whereby the isoheptanes and benzene are removed, in an overhead fraction, as minimum constant boiling mixtures and whereby substantially pure cyclohexane is recovered as a bottoms product.

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JOHN HABESHAW.
CLARENCE BARNES COLLIS.

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