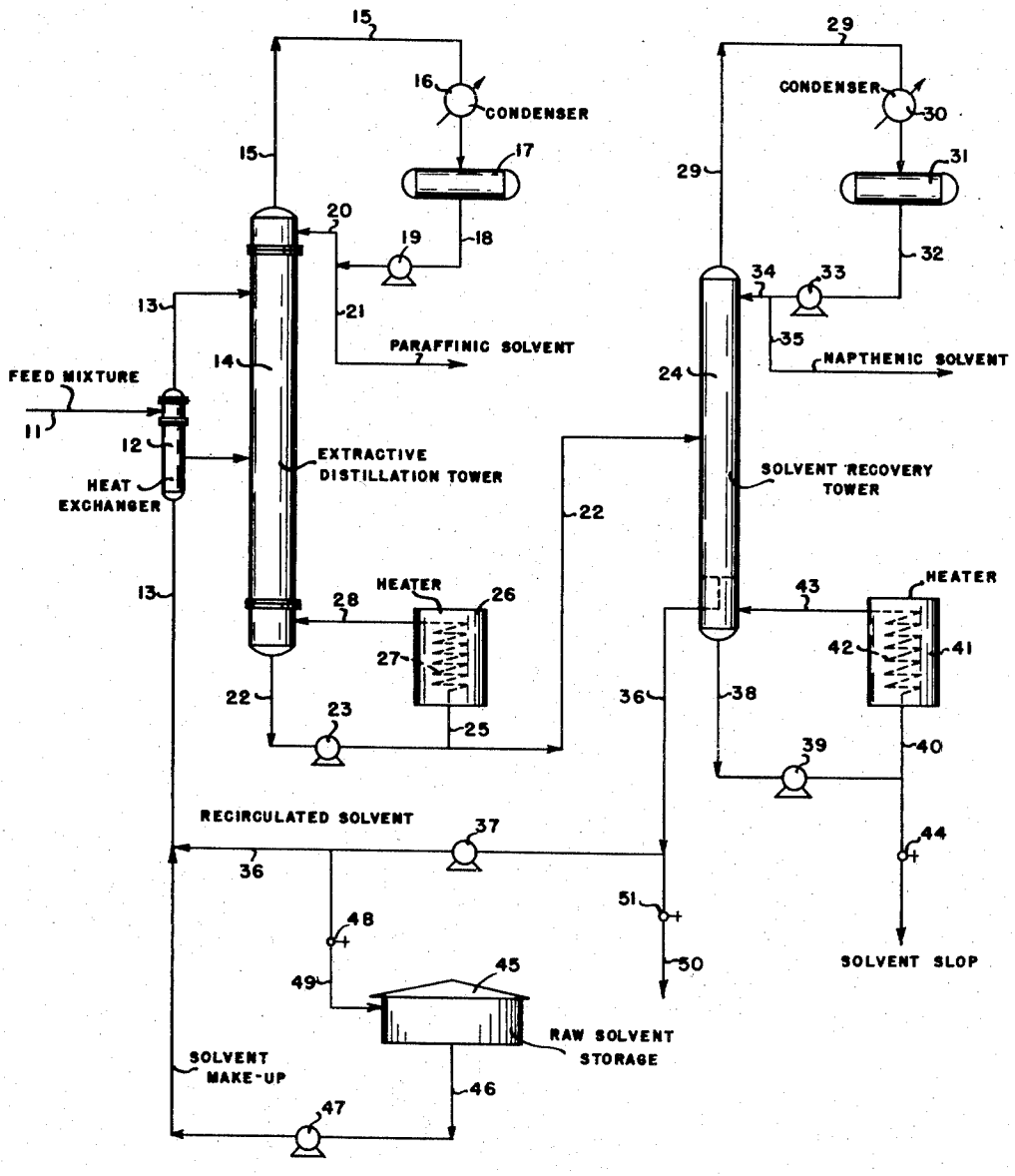
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EXTRACTIVE DISTILLATION PROCESS

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Morris R. Morrow, Jack W. Smalling, INVENTORS.

BY

Hamm B. McCulloch

AGENT.

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EXTRACTIVE DISTILLATION PROCESS

Morris R. Morrow and Jack W. Smalling, Baytown, Tex., assignors, by mesne assignments, to Standard Oil Development Company, Elizabeth, N. J., a corporation of Delaware

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The present invention is directed to a method of segregating pure hydrocarbons from hydrocarbon mixtures. More particularly, the invention has to do with extractive distillation of hydrocarbon mixtures to obtain a substantially pure hydrocarbon. In its more particular aspects, the invention is concerned with the extractive distillation of a hydrocarbon mixture in the presence of an aromatic hydrocarbon solvent.

In petroleum refining operations, it is often desirable to produce substantially pure paraffin hydrocarbons from hydrocarbon mixtures thereof. The pure paraffins obtained from petroleum refining operations have included iso-octane, normal heptane, and higher boiling paraffinic mixtures for use as reference fuels, solvents, specialties, and the like. It is also desirable to produce corresponding aromatic hydrocarbons or cycloparaffinic hydrocarbon compounds for use as solvents, specialties, motor and aviation gasoline components and as chemical raw materials. For example, cyclohexane is an important starting point in the production of adipic acid which is used in synthetic fiber production. The conventional practice in separating aromatic hydrocarbons from other hydrocarbons has been to extract the hydrocarbon mixtures containing the aromatics with selective solvents such as sulfur dioxide, phenol, aniline, furfural, nitrobenzene, and cresolic mixtures. Separation of cycloparaffins from acyclic paraffins has not been developed to any great extent because the separation between acyclic paraffinic components and cycloparaffinic components is very difficult and usually requires fractional distillation in very highly efficient distillation towers in combination with the so-called extractive distillation or vapor-liquid extraction where the boiling points between the cycloparaffins and the paraffins are not sufficiently great. Extractive distillation has been used, for example, in separating olefinic hydrocarbons from paraffins, such as the separation of butylenes from the butanes.

One great objection to extractive distillation has been the high initial cost of installing equipment and the cost of operating it. The solvents usually employed in extractive distillation are quite expensive and are not available in the refinery as a by-product and are often quite poisonous, requiring elaborate precautions to protect operating personnel. Thus, it will be seen from the foregoing discussion that there is a great need for an extractive distillation process employing a solvent which is readily available in most oil refining operations.

It is, therefore, the main object of the present invention to provide an extractive distillation process employing a hydrocarbon solvent.

Another object of the present invention is to provide a process for separation of one hydrocarbon component from another hydrocarbon component in a mixture thereof.

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Another object of the present invention is to separate by extractive distillation employing a hydrocarbon solvent mixtures of cycloparaffins and paraffins and other hydrocarbon mixtures into their component parts.

It has now been found that separation of various hydrocarbon mixtures, such as mixtures of cycloparaffins and paraffins, paraffins and aromatics, olefins and paraffins, paraffins and naphthenes, and naphthenes and aromatics, may be accomplished by an extractive distillation process employing as a solvent a mono-cyclic aromatic hydrocarbon fraction boiling in the range between 365° and 750° F.

The present invention may be described briefly as involving the heating of a narrow boiling hydrocarbon fraction in the gasoline boiling range such as, for example, a fraction boiling in the range between 145° and 160° F. containing normal hexane and methylcyclopentane, to a temperature of approximately the boiling point of the heaviest component of the mixture, following which the heated hydrocarbon fraction is contacted with a monocyclic aromatic hydrocarbon solvent boiling in the range between 365° and 750° F. under conditions that the mixture of paraffinic and cycloparaffinic constituents is substantially in the vapor phase and the aromatic solvent is in the liquid phase so that a separation is obtained between the methylcyclopentane and the normal hexane. The normal hexane in this particular instance will be obtained as the raffinate while the methylcyclopentane will be dissolved in the solvent and removed therewith to a solvent recovery tower where it may be separated by virtue of the difference in boiling points and recovered, with the solvent being recycled and reused in the process.

In conducting the extractive distillation in accordance with the present invention, it will be desirable to employ feed stocks, of the various mixtures mentioned before, having a boiling range no greater than about 50° F. to obtain the greatest benefit of the new extractive distillation process. While a 50° boiling range fraction may be employed in the practice of the present invention, it will usually be preferred to employ a feed having a boiling range no greater than 25° F. which will usually include only two component mixtures. Fractions having boiling ranges of 50° spread will include more than two components and the practice of the present invention may be used to obtain one component in a purified form from say two other components. Ordinarily, such fractions fed to the process of the present invention will contain two components and the feed stock should be so prepared that it will be composed of two types of hydrocarbons. For ex-

ample, a feed stock may include a paraffinic component and a cycloparaffinic component. The aromatic hydrocarbon solvent employed in the present invention will contain substantially mono-cyclic aromatic hydrocarbons to the exclusion of polycyclic hydrocarbons and may boil in the range from about 385° to 750° F. The solvent may be obtained from an aromatization process or the so-called hydroforming process which is well known in the industry. The fraction boiling between 365° and 750° F. containing substantially monocyclic aromatic hydrocarbons having 10 or more carbon atoms gives good results in the practice of the present invention.

The monocyclic aromatic hydrocarbons having 10 carbon atoms are particularly desirable solvents in the practice of the present invention. Such monocyclic aromatic hydrocarbons will include the tetramethylbenzenes such as 1,2,4,5-tetramethylbenzene, 1,2,3,5-tetramethylbenzene, and 1,2,3,4-tetramethylbenzene, 1,2-dimethyl-3-ethylbenzene, 1,2-dimethyl-4-ethylbenzene, and the like. Especially beneficial solvents for use in the present invention are the tetramethylbenzenes including durene, isodurene, prehnitene, and mixtures thereof.

As mentioned before, the temperatures employed in the practice of the present invention will depend upon the boiling point of the feed stock. As a general rule, it may be stated that the feed stock should be heated to the boiling point of the highest boiling component therein and contacted with the monocyclic aromatic solvent at a temperature in the range between the boiling point of the heaviest component in the feed stock and about 50° higher. Stating this another way, the extractive distillation may be performed in a suitable distillation tower with a temperature gradient being maintained across the tower. The temperature at the top of the tower will be about the boiling point of the highest boiling component in the feed mixture while the temperature at the bottom of the tower will be at least about 50° greater.

The ratios of solvent to feed stock may range from about 1 to 1 to about 20 to 1. Ordinarily, it will be desirable to use about five volumes of solvent to one volume of feed stock. The actual amount selected will depend, of course, on the composition of the feed mixture being subjected to the extractive distillation and the product purity desired.

The invention will now be further illustrated by reference to the drawing in which the single figure presents a flow diagram of one method of practicing it.

Referring now to the drawing, numeral 11 designates a charge line through which a feed mixture, for example a mixture of methylcyclopentane and normal hexane boiling in the range between 145° and 160° F., is introduced into the system from a source not shown. The feed mixture discharges by line 11 into a heat exchange device 12 where it is passed in heat exchange with the solvent flowing through line 13 as will be described further. The heat exchange causes the feed stock to be heated to a temperature of about 160° F. and it is discharged at this temperature into an extractive distillation tower 14 which is provided with suitable internal baffling equipment such as bell cap trays or other packing material to insure intimate contact between vapors and liquids. The feed stock is introduced at about a midpoint in tower 14 so that the tower is thereby divided into what may be called an extraction stage and a stripping stage, the portion of the tower above the feed inlet being the extraction stage and that below the feed inlet being the stripping stage. The portion of tower above the solvent inlet may also be designated as a product purifying or rectifying stage. The feed, in a vaporous form, flows upwardly in tower 14 and countercurrently contacts aromatic solvent boiling in the range between 365° and 750° F. comprising substantially only monocyclic aromatic hydrocarbons, which is introduced by line 13. As the solvent and hydrocarbon feed contact each other a separation is effected between paraffinic constituents thereof and the cycloparaffinic or naphthenic constituents, the latter being dissolved in the solvent whereas the paraffinic constituents are separated as a raffinate. The raffinate comprising substantially the paraffinic hydrocarbon, normal hexane, discharges from extractive distillation tower 14 by line 15, is cooled and condensed in condenser 16, and is discharged into reflux accumulator drum 17. The accumulated hexane in drum 17 is withdrawn by line 18 and pump 19 and divided into two streams, one stream being injected back into the top of tower 14 by line 20 to provide reflux and the other portion withdrawn by line 21 as product for use as may be desired. For example, the normal hexane may be employed as a paraffinic solvent.

The solvent, including naphthenic hydrocarbons extracted from the feed mixture, is withdrawn from extractive distillation tower 14 by line 22 and pump 23 and also is divided into two streams, one of which is routed by line 22 to solvent recovery tower 24 and the other by line 25 to heater or reboiler 26 where that portion of the divided stream is heated in coil 27 to maintain the proper temperature gradient across tower 14 and returned to the base of tower 14 by line 28. The portion of the extract discharged by line 22 into solvent recovery tower 24 is subjected to distillation to recover overhead by line 29 a fraction consisting substantially of the naphthenic components of the feed mixture. This fraction is cooled and condensed in condenser 30 and accumulated in reflux accumulator 31 from whence it is discharged by line 32 and pump 33 for division into two streams, one of which returns to solvent recovery tower 24 by line 34 to provide reflux therein and the other is discharged by line 35 as naphthenic solvent product. Should the naphthenic product contain substantial quantities of low boiling aromatics, a second extractive-distillation step may be used to obtain pure naphthenes and pure aromatic products.

The aromatic solvent is withdrawn from near the base of tower 24 by line 36 and is pumped by pump 37 to line 13 where it is returned as has been described to extractive distillation tower 14. Heat is provided for recovery of the naphthenic components in tower 24 by withdrawing from the bottom thereof by line 38 heavy fractions which are pumped by pump 39 and line 40 into a reboiler or heater 41 where heat is provided on passage through coil 42 to cause distillation in tower 24. The heated heavy fractions are returned to the base of tower 24 by line 43. To prevent buildup of heavy fractions in the system, it may be necessary from time to time to discharge a solvent slop fraction from the system and this may be accomplished conveniently by opening valve 44 in line 40.

To compensate for heavy fractions which may be withdrawn from the system, it may be neces-

sary from time to time to add additional solvent to the system. This additional solvent may be introduced from raw solvent storage tank **45** by way of line **46** and pump **47** which connects into line **13**. Under some conditions, it may be desirable to discharge some of the recirculated solvent into the solvent storage tank **45** and this may be accomplished conveniently by opening valve **48** in branch line **49**.

It will be noted from the foregoing description taken with the drawing that besides causing a separation between the paraffinic components of the feed mixture and the naphthenic components of the feed mixture, it is also possible to purify the aromatic solvent itself by virtue of withdrawing a slop stream of solvent since this slop stream will include only the highest boiling components. The recirculated solvent will become more and more purified as it circulates in the system. It may be desirable, therefore, in some instances to withdraw a portion of the recirculated solvent by line **50** controlled by valve **51** for use as may be desired.

It will be seen from the foregoing description that a simple and effective extractive distillation process has been provided to obtain separation between hydrocarbon components of a mixture having narrow boiling ranges.

In order to illustrate the invention further, references may be made to the following tabulation in which the relative volatility of a mixture of a paraffin and a typical naphthene, as represented by normal heptane and methylcyclohexane, in the presence of conventional solvents is compared with their relative volatility in the presence of a solvent having a boiling point between 365° and 750° F. and containing substantially only monocyclic aromatic hydrocarbons, in accordance with the present invention.

Solvent	Weight T, Hydrocarbon in Solution	Relative Volatility in Presence of Solvent (Normal Heptane/Methylcyclohexane)
Aniline	10	1.52
Do	20	1.38
Phenol	15	1.25
Monocyclic Aromatic Hydrocarbons boiling between 365°-750° F	20	1.25

The relative volatilities shown in the foregoing table are calculated in accordance with the following equation, based on Raoult's law:

$$\gamma_{1 \text{ to } 2}=\frac{Y_1X_2}{X_1Y_2}$$

where $\gamma_{1 \text{ to } 2}$ is the selectivity of adsorption, Y_1 is the mole fraction of paraffins in the vapor, X_1 is the mole fraction of paraffins in the liquid, Y_2 is the mole fraction of naphthene in the vapor, and X_2 is the mole fraction of naphthenes in the liquid, computed on a solvent-free basis. Thus, for a given solvent the higher the value for gamma, the higher the selectivity. It will be seen that the gamma for the solvent employed in the practice of the present invention compares very favorably with the gamma of conventional polar solvents employed in the prior art.

It will be apparent that conducting an extractive distillation with a hydrocarbon solvent is much more advantageous than conducting an extractive distillation with a polar solvent since storage problems are not complicated by highly dissimilar materials and the danger from poisons is substantially less when conducting extractive distillations employing a monocyclic aromatic hydrocarbon solvent boiling in the range between 365° and 750° F. than when employing a solvent such as aniline, phenol or furfural. Another great advantage of the solvent employed in the present invention is its relatively low cost since it may be available in most refining operations as a by-product stream.

The invention has been described by an example in which the aromatic hydrocarbon solvent boiling in the range between 365° and 750° F. has been employed in one tower to remove one component from two or more components. It will be apparent to the skilled workman that two or more towers may be used to separate a plurality of components from each other. Thus, a mixture of paraffins, naphthenes, and aromatics may be extractively distilled in accordance with the present invention to separate paraffins from naphthenes and aromatics which are dissolved in the solvent. In the solvent recovery tower the naphthenes and aromatics lower boiling than the aromatic hydrocarbon solvent would be separated by distillation from the latter and the mixture of the two may then be extractively distilled in a second tower to separate the naphthenes from the aromatics. Similarly, a mixture of paraffins and naphthenes may be separated from aromatics in one tower and the mixture then subjected again to extractive distillation to separate paraffins from naphthenes. Numerous modifications of the invention will suggest themselves to the skilled workman.

The nature and objects of the present invention having been fully described and illustrated, what we wish to claim as new and useful and to secure by Letters Patent is:

An extractive distillation method for separating naphthenes from paraffins which comprises countercurrently contacting a vaporized liquid mixture of a naphthene and a paraffin boiling in the gasoline range and having a boiling range no greater than 50° F. in a distillation zone with tetramethylbenzene at a temperature above the boiling range of the mixture to form a raffinate phase including the paraffin and an extract phase comprising the naphthene and tetramethylbenzene, and separating said phases.

MORRIS R. MORROW.
JACK W. SMALLING.

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