This invention relates to a process of azeotropic distillation to prepare pure hydrocarbons from complex petroleum fractions which are difficult to separate by ordinary fractional distillation due to small differences in boiling points existing in the hydrocarbons contained in the fraction and is a continuation-in-part of our copending application, Serial No. 550,581, now abandoned.

The process of separating one hydrocarbon component from another hydrocarbon component of substantially the same boiling point, contained in a complex hydrocarbon fraction, by azeotropic distillation is well known. This process consists of distilling the hydrocarbon fraction in the presence of an extraneous substance which has a preferential affinity for one of the hydrocarbon components contained in the fraction, thus causing a disturbance of the vapor pressure equilibrium that formerly existed in the fraction in such a manner that the partial vapor pressure or fugacity of at least one component of the fraction is changed sufficiently to permit its separation by controlled fractional distillation. Here-tofore in such an azeotropic process there has been effected the separation of the relatively more paraffinic hydrocarbons with the extraneous substance leaving as undistilled bottoms relatively more aromatic hydrocarbons which may or may not contain a portion of the extraneous substance. In the present description of our invention the aforesaid type of distillation will hereinafter be referred to as azeotropic distillation, and the overhead product consisting of the extraneous substance together with the component or components most affected by said extraneous substance will hereinafter be referred to as the azeotropic distillate, and the residue remaining as bottoms from the azeotropic distillation will hereinafter be referred to as azeotropic bottoms. For example, in separating an aromatic hydrocarbon from a hydrocarbon fraction containing as well olefinic, paraffinic and naphthenic hydrocarbons, it has been the practice to add to such a fraction an extraneous substance such as for example acetone or methyl ethyl ketone which has the effect of increasing the vapor pressure of the relatively more paraffinic hydrocarbons. Thus by distilling a hydrocarbon fraction containing benzene in the presence of acetone it is possible to take overhead as the azeotropic distillate an aze trope of acetone and the non-aromatic hydrocarbons present in said hydrocarbon fraction, leaving substantially all of the benzene as azeotropic bottoms. It is frequently necessary to acid treat and redistill the azeotropic bottoms in order to obtain essentially pure benzene. The preparation of pure toluene has been accomplished in a similar manner using azeotrope formers of different properties, as for example methyl ethyl ketone.

Another disadvantage inherent in such a process is the necessity of redistilling the azeotropic bottoms to obtain aromatics in essentially pure form; thus, for the recovery or removal of an aromatic hydrocarbon contained in a petroleum fraction in the amount of about 5%, it has been necessary in the conventional method of azeotropic distillation to distill overhead 95% of the hydrocarbon fraction together with a sufficient amount of an azeotrope former to effect the necessary boiling point depression of this 95% non-aromatics contained in the fraction.

It is an object of our invention to prepare pure hydrocarbons in a new and novel manner from petroleum fractions which are impossible of separation by means of ordinary fractional distillation. It is a further object of our invention to effect this separation by a method in which distillation and extraction loads are greatly reduced.

A more specific object of our invention is to employ an azeotrope former having the reverse effect of those here-tofore employed thus decreasing the boiling point of the relatively aromatic hydrocarbons permitting their recovery in the azeotrope distillate rather than in the azeotrope bottoms and to leave the relatively non-aromatic hydrocarbons as a distillation residue.

Further objects and advantages of our invention will be apparent to those skilled in the art from the description thereof that proceeds.

We have discovered that it is possible by employing the new and novel type azeotrope formers hereinafter disclosed, to reverse the order of azeotropic formation as obtained in the conventional azeotropic distillation of complex hydrocarbon fractions. In the application of azeotropy to petroleum fractions a great number of azeotrope formers have been employed which exert a change in the vapor pressure relationship existing in said hydrocarbon fraction in such a manner that the lower boiling azeotropes are formed with the paraffin hydrocarbons followed by the naphthenic, olefinic, diolefinic and finally aromatic hydrocar-
bons. In this manner the distillation of a complex petroleum fraction in the presence of such an azo trope former consists in taking overhead initially an azotropic mixture comprising predominately paraffin hydrocarbons with the specific azo trope former employed, continued distillation in the presence of said azo trope former gives an azotropic overhead comprising predominately naphthenic hydrocarbon together with the azo trope former, and subsequently in the same manner azotropic mixtures of olefinic and diolefinic hydrocarbons with said azo trope former may be taken overhead leaving the complex hydrocarbon as azotropic bottoms. For purposes of this disclosure the hydrocarbon types as contained in any particular fraction will be designated as relatively non-aromatic or relatively aromatic depending upon their position in the above series. Thus in the discussion of conventional azeotrope above the ease of azo trope formation with the azo trope formers employed progresses from the relatively non-aromatic to the relatively aromatic hydrocarbons.

In the operation by our process to reverse the above order and thereby to take overhead initially in an azotropic distillation of a complex hydrocarbon fraction an azotropic mixture of the relatively more aromatic hydrocarbons contained in the fraction together with the azo trope former of the type we have discovered. We have found this unusual procedure to be possible by employing an azo trope former consisting of a naphthenic hydrocarbon preferably boiling below but not more than 9° C. below the relatively more aromatic component contained in said complex hydrocarbon fraction. Thus in the azotropic distillation of a complex petroleum fraction employing an azo trope former of the type described above we are able to obtain as our initial azo trope distillate a minimum boiling mixture of the aromatic component of said fraction together with said azo trope former and in successive stages azotropic mixtures of diolefinic, olefinic and naphthenic hydrocarbons with the azo trope former employed.

In the operation of our process we may employ for example a petroleum fraction of relatively narrow boiling range containing a fraction of 1% to about 10% by volume or more of an aromatic hydrocarbon as well as paraffinic, naphthenic, and olefinic hydrocarbons from which it is desired to remove said aromatic hydrocarbon. This fraction is subjected to controlled distillation in the presence of an added naphthenic material boiling below but not more than 9° C. below the specific aromatic hydrocarbon, and more fully in the last paragraph. The effect of such a distillation is to give an overhead product consisting of substantially all of the aromatic hydrocarbons contained in the fraction as an azotropic mixture with the above naphthenic compound leaving as azotropic bottoms substantially all of the relatively non-aromatics contained in the above fraction which may or may not contain small percentages of the azo trope former employed. By suitable modification of the above described process we are also able to separate such secondary fractions by means of side cuts in the above distillation or by secondary distillation of the primary azotropic bottoms in the presence of an additional amount of our azo trope former. The recovery of the aromatic, olefinic or naphthenic components of such processes may be accomplished in our process by any desirable means such as a secondary azotropic distillation with one of many conventional azo trope formers whereby the naphthenic azo trope former employed in the primary azotropic distillation may be separated as a secondary azotropic distillate, leaving substantially all the aromatic in relatively pure form as secondary azo trope bottoms.

Thus in the recovery of benzene contained in the amount of about 5% in a petroleum fraction boiling in the range of 170° to 200° F. by means of our process, a suitable quantity of methyl cyclopentane is added to the hydrocarbon fraction and the mixture subjected to a distillation whereby an azo trope of methylcyclo- pentane and substantially all of the benzene is obtained as an overhead product which may or may not contain small amounts of lower boiling non-aromatic hydrocarbons. In this connection we have found that the presence of hexane in the fraction is not objectionable inasmuch as an azo trope is formed between benzene and hexane boiling at about 68.3° C. and therefore, is recovered with the methylcyclopentane.

The benzene may be recovered from this azo trope distillate by subjecting the mixture to controlled fractional distillation in the presence of a secondary azo trope former such as acetone whereby the methylcyclopentane and any lower boiling non-aromatic material is recovered as an azotropic mixture with the acetone, leaving as azotropic bottoms essentially pure benzene.

It is within the spirit and scope of our invention to employ any desired method in separating the azotropic mixture of aromatic, olefinic, or naphthenic hydrocarbons with our particular azo trope formers such as for example solvent extraction, extractive distillation, azotropic distillation and the like.

We have also found this process to be applicable to the separation of sulfur type compounds such as thiophene, methyliothiophene, dimethyl-thiophene, and the like which are oftimes contained as undesirable contaminants in petroleum fractions. It is also within the scope of our invention to employ this process for the purification of raw mixtures of thiophene and other compounds occurring as intermediate products in the preparation of thiophene and its homologs.

We do not wish to limit ourselves by the above description of our invention inasmuch as we may employ it on any desired base without using a suitable naphthenic type azo trope former. Thus, we may separate toluene from a petroleum fraction in which it is contained by azo tropically distilling said fraction in the presence of an azo trope former of the type hereinbefore disclosed such as for example ethylcyclopentane. In like manner we may separate by means of our invention xylenes, cumenes or other high boiling aromatics contained in petroleum stocks.

Besides methyl and ethylcyclopentane mentioned other alkylated cyclopentanes may be used for effecting separations wherein the relatively aromatic hydrocarbons are distilled overhead as azo trope formers with the alkylated cyclopentanes. These are selected according to the relative boiling points of the stock or naphthenic homologs to be used in the process depending on the stock to be treated. These include the cyclopropanes, cyclobutanes, cyclohexanes, cycloheptanes and the like. As described herein in the preferred azo trope formers are those naphthenes which boil but not more than
5° C. Below the aromatic hydrocarbon which is to be azeotroped. The novelty and the advantages of our invention become immediately apparent to those skilled in the art from the foregoing description thereof. Our invention is unique in two separate and distinct manners. We have employed for the separation of one hydrocarbon from another-hydrocarbon a third hydrocarbon; the azeotrope formed consisting of a third hydrocarbon rather than a different type organic compound as heretofore employed, and we have also reversed the normal procedure of azeotopic distillation by forming a lower boiling azeotrope with the relatively aromatic rather than the relatively non-aromatic hydrocarbons.

By means of our process we are able to recover small amounts of aromatic hydrocarbons from petroleum fractions, and at the same time greatly reduce the distillation and extraction loads normally incurred in their recovery by ordinary methods. This may be clearly shown by comparison of our method of benzene recovery using methylocyclopentane as the primary azeotropic former and acetone as the secondary azeotropic former with the conventional azeotropic method of benzene recovery in which acetone is employed as the azeotropic former, and is extracted from the azeotropic mixture by water extraction. Comparative data on these processes are given in Table 1 below, and are based on a feed stock consisting of 100 parts of a mixture of 95 parts of cyclohexane and 5 parts of benzene.

**Table 1**

**Direct azeotroping with acetone—Case I**

<table>
<thead>
<tr>
<th>Type</th>
<th>Distillate Parts</th>
<th>Total</th>
<th>Total distillate, 382 parts.</th>
<th>Total to extract, 317 parts.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distillation, Azeotropic.</td>
<td>Acetone</td>
<td>222</td>
<td>222</td>
<td>222</td>
</tr>
<tr>
<td>Distillation, Azeotropic.</td>
<td>Cyclohexane</td>
<td>95</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>Extraction, water</td>
<td>Acetone</td>
<td>222</td>
<td>Extract 317 parts with water</td>
<td>222</td>
</tr>
<tr>
<td>Total distillate, 382 parts.</td>
<td>Total</td>
<td>317</td>
<td>Total to extract, 317 parts.</td>
<td>Total to extract, 317 parts.</td>
</tr>
</tbody>
</table>

**Azeotroping with methylocyclopentane—Case II**

<table>
<thead>
<tr>
<th>Type</th>
<th>Distillate Parts</th>
<th>Total</th>
<th>Total distillate, 539 parts.</th>
<th>Total to extract, 317 parts.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distillation, Azeotropic.</td>
<td>Acetone</td>
<td>45</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>Distillation, Azeotropic.</td>
<td>Methylcyclopentane</td>
<td>55</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>Distillation, Azeotropic.</td>
<td>Benzene</td>
<td>55</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>Extraction, water</td>
<td>Acetone</td>
<td>45</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>Total distillate, 539 parts.</td>
<td>Total</td>
<td>55</td>
<td>Total to extract, 100 parts.</td>
<td>Total to extract, 100 parts.</td>
</tr>
</tbody>
</table>

Inspection of these data shows that case I would require the distillation of 539 barrels of overhead and the extraction of 317 barrels of distillate to remove the 5 barrels of benzene, while case II would require the distillation of only 205 barrels of overhead and the extraction of only 100 barrels of distillate to remove the same quantity of benzene. The use of methylocyclopentane therefore decreases the distillation load by approximately 334 barrels or 62%, and the extraction load by approximately 217 barrels or 68%. Furthermore, this advantage is incurred in any application of our process for the extraction of relatively small amounts of hydrocarbon components.

**Example I**

In this experiment a petroleum fraction boiling in the range of about 70° C. to about 90° C. and having approximately the following composition was employed:

- Benzene: 10%  
- Cyclohexane: 70%  
- Dimethylpentane (3,8 and 2,3): 15%  
- Other non-aromatic hydrocarbons: 5%

Upon examination of these data it is evident that such a fraction is impossible to separate into its individual components by ordinary fractional distillation and also the presence of small amounts of benzene prohibits the separation of ordinarily separable components such as cyclohexane and the higher boiling dimethylpentanes by the formation of closely boiling azeotropes with each. Thus, we may have in a given fraction two reasons for the removal of aromatic hydrocarbon contained therein. We may desire to remove the aromatic hydrocarbon and recover it as such for the value of said aromatic or we may desire to remove the aromatic hydrocarbon in order to facilitate the preparation of pure non-aromatic hydrocarbons.

**Table 2**

<table>
<thead>
<tr>
<th>Component</th>
<th>Boiling Point</th>
<th>Boiling point of acetone with Benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>80.3</td>
<td>80 to 85</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>80.7</td>
<td>77.5</td>
</tr>
<tr>
<td>2,3 or 3,3-dimethylpentane</td>
<td>95 to 85</td>
<td>80 to 85</td>
</tr>
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Ten volumes of the above stock together with 10 volumes of methylocyclopentane were charged to a fractionating column of approximately 30 theoretical plates. This mixture was subjected to a controlled fractional distillation whereby an azeotrope of methylocyclopentane and benzene was taken overhead at a temperature of approximately 75° C. The benzene, methylocyclopentane and 55% methylocyclopentane and 10% benzene boils at approximately 75° C. Also going overhead with this mixture were approximately 0.3 volume of low boiling non-aromatics contained in the original fraction. This primary azeotropic distillate consisting of approximately 10 volumes of methylocyclopentane, 1 volume of benzene and 0.3 volume of low boiling non-aromatics other than methylocyclopentane was subjected to a secondary azeotropic distillation in the presence of 13 volumes of acetone. The overhead product from this secondary azeotropic distillation was obtained at 51.4° C. and consisted of an azeotropic mixture of 10 volumes of methylocyclopentane and 12 volumes of acetone together with 0.3 volume of the low boiling non-aromatics leaving as azeotropic bottom one volume of essentially pure benzene. The methylocyclopentane-acetone azeotrope from this secondary azeotropic distillation was broken by means of water washing, the acetone being recovered.
from the water by simple distillation. Employing a feed stock such as the one herein described containing small amounts of lower boiling aromatics, it may be necessary for the recovery of the methylcyclohexane and azetrope former to subject the extract of the above water washing to a simple distillation to separate said low boiling non-aromatics from the methylcyclohexane.

The azetrope bottoms from the primary azetotropic distillation consisted of 7 volumes of cyclohexane and 2 volumes of dimethylnapthene and higher boiling non-aromatics. Due to the absence of benzene azetropes in these bottoms it was possible to obtain by means of simple fractional distillation cyclohexane of 95% to 97% purity. Any 2,2,3-trimethylbutane boiling point 80.8° C., 2,4-dimethylnapthene boiling point 80.8° C., or 2,2,4-trimethylnapthene boiling point 78.9 contained in the original fraction would remain as impurities in the cyclohexane, but apparently these compounds are present in petroleum distillates in very small traces and do not prevent the production of cyclohexane by the above process of more than 95% purity.

The example described above is not meant to limit our invention as it is within the spirit and the scope of this invention to perform a separation of any of the hydrocarbon components hereinafter listed from fractions in which they are contained, and it is also within the scope of this invention to separate sulfur compounds in the same manner from petroleum fractions in which they are contained.

The foregoing description of our invention is not to be taken as limiting our invention but only illustrative thereof, since many variations may be made by those skilled in the art without departing from the spirit and scope of the following claims.

We claim:

1. A process for the treatment of a complex hydrocarbon fraction comprising aromatic components and non-aromatic components having from 6 to 9 carbon atoms to separate one component from the other components contained therein which ordinarily distill from said hydrocarbon fraction in the same temperature range as said component distills therefrom, which comprises azetrotopically distilling said complex hydrocarbon fraction in the presence of a sufficient amount of an added azetrole former consisting of a naphthene boiling below, but not more than about 9° C. below, said aromatic components to vaporize the aromatic components contained in said fraction together with said added azetrole former as a minimum boiling azetrotic mixture thereby leaving the non-aromatic components as distillation bottoms.

2. A process for the treatment of a complex hydrocarbon fraction containing an aromatic hydrocarbon having from 6 to 9 carbon atoms to separate one component from the other components contained therein which ordinarily distill from said hydrocarbon fraction in the same temperature range as said component distills therefrom, which comprises azetrotopically distilling said complex hydrocarbon fraction in the presence of a sufficient amount of an added azetrole former consisting of a naphthene boiling below, but not more than about 9° C. below, said aromatic components to vaporize the aromatic hydrocarbon together with said added azetrole former as a minimum boiling azetroptic mixture thereby leaving non-aromatic hydrocarbons as distillation bottoms.

3. A process for the treatment of a complex hydrocarbon fraction containing benzene as well as olefinic, naphthenic, and paraffinic hydrocarbons to separate the benzene from the aromatic components contained therein which ordinarily distill from said hydrocarbon fraction in the same temperature range as the benzene prohibiting its separation by simple fractional distillation, which comprises azetrotopically distilling said complex hydrocarbon fraction in the presence of a sufficient amount of added methylcyclohexane to vaporize said benzene together with said added methylcyclohexane as a minimum boiling azetroptic mixture thereby leaving non-aromatic hydrocarbons as distillation bottoms.

4. A process for the treatment of a complex hydrocarbon fraction containing toluene as well as olefinic, naphthenic and paraffinic hydrocarbons to separate the toluene from the other components contained therein which ordinarily distill from said hydrocarbon fraction in the same temperature range as the toluene prohibiting the separation of said toluene by means of simple fractional distillation, which comprises azetrotopically distilling said complex hydrocarbon fraction in the presence of a sufficient amount of added ethylcyclohexane to vaporize said toluene together with said added ethylcyclohexane as a minimum boiling azetroptic mixture thereby leaving the non-aromatic hydrocarbons as distillation bottoms.

5. A process for the treatment of a complex hydrocarbon fraction containing an aromatic hydrocarbon having from 6 to 9 carbon atoms to separate one component from the other components contained therein which are ordinarily separable by simple fractional distillation but may not be separated in the presence of said aromatic component due to the formation of closely boiling azetrotes with said aromatic components, which comprises removing said aromatic component from the fraction by azetrotopically distilling said complex hydrocarbon fraction in the presence of a sufficient amount of an added azetrole former consisting of a naphthene hydrocarbon boiling below, but not more than about 9° C. below said aromatic hydrocarbon to vaporize said aromatic hydrocarbon together with said added azetrole former as a minimum boiling azetroptic mixture thereby leaving non-aromatic hydrocarbons as distillation bottoms and distilling said bottoms in the absence of the aromatic hydrocarbon to yield pure components.

6. A process for the treatment of substantially pure cyclohexane from a complex hydrocarbon fraction containing benzene as well as cyclohexane which fraction is impossible of separation in the presence of said benzene due to the formation of closely boiling azetrotic mixtures of benzene and cyclohexane and benzene and other non-aromatic hydrocarbons present in said fraction, which comprises azetrotopically distilling said complex hydrocarbon fraction in the presence of a sufficient amount of added methylcyclohexane to vaporize said benzene together with said added methylcyclohexane and cyclohexane.
9  A process for the treatment of a complex hydrocarbon fraction containing benzene as well as naphthenic and paraffinic hydrocarbons to separate the benzene from the other hydrocarbon components contained therein which ordinarily distill from said hydrocarbon fraction in the same temperature range as the benzene prohibiting its separation by simple distillation, which comprises azeotropically distilling said complex hydrocarbon fraction in the presence of a sufficient amount of added methylcyclopentane to vaporize said benzene together with said added methylcyclopentane as a minimum boiling azeotropic mixture thereby leaving the non-aromatic hydrocarbons as distillation bottoms.

8. The process as set forth in claim 1 in which the napththene is an alkyl cyclopentane.

9. The process as set forth in claim 1 in which the complex hydrocarbon fraction contains xylene as well as olefinic, naphthenic and paraffinic hydrocarbons.

10. The process as set forth in claim 3 in which the complex hydrocarbon fraction contains cyclohexane, benzene, 2,3 and 2,3 dimethyl pentane.

11. The process as set forth in claim 5 in which the complex hydrocarbon fraction is of narrow boiling range and includes a naphthenic hydrocarbon boiling in the range of an aromatic compound contained in said fraction which aromatic compound prevents separation of said naphthenic hydrocarbon by the formation of azeotropes within the fraction of said aromatic hydrocarbon with the naphthenic and paraffinic hydrocarbons, which azeotropes have small boiling point differences.

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