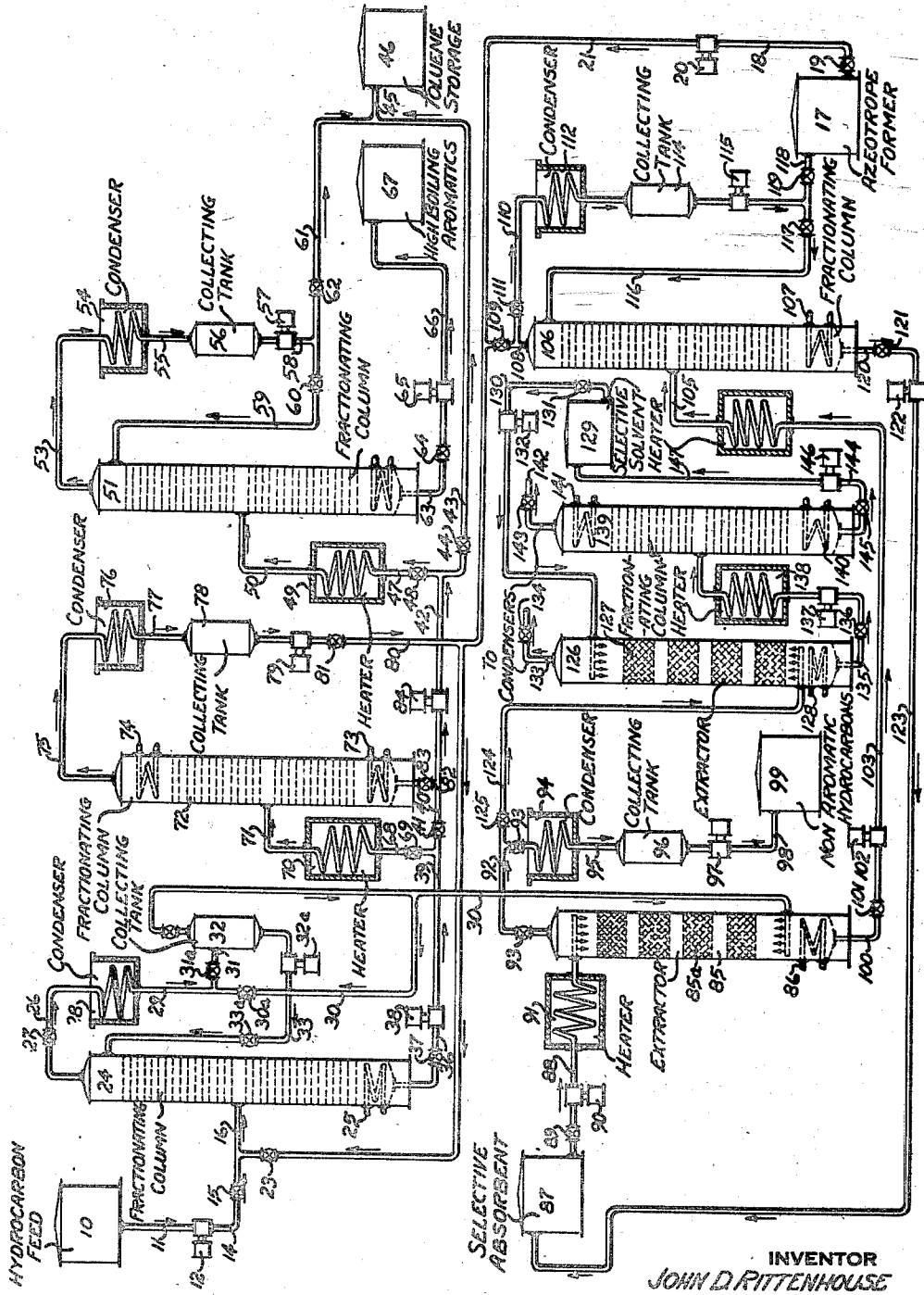
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RECOVERY OF AZEOTROPIC FORMER IN DISTILLATION OF HYDROCARBONS

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RECOVERY OF AZEOTROPIC FORMER IN DISTILLATION OF HYDROCARBONS

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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 the small differences in boiling points of the hydrocarbons contained in the petroleum fraction. The invention is particularly directed to an improved process for separating the hydrocarbons and the azeotrope former that are contained in the azeotropic distillate produced by the azeotropic distillation.

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 in distilling the hydrocarbon fraction in the presence of an extraneous substance which has a preferential affinity for one of the components contained in the complex hydrocarbon fraction, thus causing a disturbance of the vapor pressure equilibrium that formally existed in the fraction in such a manner that the partial vapor pressure or fugacity of at least one component in the fraction is changed sufficiently to permit its separation by controlled fractional distillation. In such processes, the distillation effects the separation of the relatively more paraffinic hydrocarbons together with extraneous substance leaving as undistilled bottoms the relatively less paraffinic hydrocarbons which may or may not contain a portion of the extraneous substance. In the present description of my invention the aforesaid type of fractional distillation will be referred to as azeotropic distillation, the extraneous substance or substances which are added to the complex hydrocarbon fraction to effect the aforementioned change will be referred to as azeotropic formers and the overhead from the azeotropic distillation will be referred to as the azeotropic distillate.

One of the main difficulties in the azeotropic distillation process is in the separation or recovery of the azeotrope former from the hydrocarbons contained in the azeotropic distillate. One of the methods proposed for this purpose resides in washing the azeotropic distillate with water which is adapted to dissolve the azeotrope former from the azeotropic distillate and thus be separated from the hydrocarbons by settling

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and stratification. The solution of azeotrope former and water may be distilled to separate the azeotrope former from the water.

However, difficulty has been experienced to separate the azeotrope former substantially completely from the azeotropic distillate by washing with water since in many cases, the azeotrope former has a preferential solubility in the hydrocarbons as compared with the solubility in the water. The result is that the hydrocarbons must be washed with an excessively large amount of water in order to remove the last traces of the azeotrope former so that the hydrocarbons may be utilized and the azeotrope former recovered without sustaining a substantial loss of this more valuable material. To illustrate, it has been found that methyl ethyl ketone, particularly containing about 10% by volume of water, is a very efficient azeotrope former to effect the separation of non-aromatic hydrocarbons from a hydrocarbon fraction containing toluene. Yet the use of this azeotrope former offers the serious difficulty of recovering the methyl ethyl ketone from the azeotropic distillate. While the separation of the methyl ethyl ketone may be accomplished by washing with water, this has required about five or six volumes of water for each volume of azeotropic distillate. Even by washing the azeotropic distillate with this large amount of water, the hydrocarbon thus separated still contained about one percent of methyl ethyl ketone. Furthermore, in order to recover the methyl ethyl ketone from the very dilute wash solution, it is necessary to heat an excessively large volume of dilute methyl ethyl ketone-water solution.

It is thus an object of my invention to effect a substantially complete separation of the azeotrope former from the hydrocarbons contained in the azeotropic distillate and it is a particular object to effect the aforesaid separation in an efficient and economical manner without loss of azeotrope former.

It is a further object of my invention to effect the separation of the azeotrope former from the azeotropic distillate by the use of selective absorbents having a preferential absorbing power for the azeotrope former than for the hydrocarbons contained in the vaporized azeotropic distillate. A further object is to effect the sepa-

ration while the azeotropic distillate is in the vapor phase and the selective absorbent is in the liquid phase.

I have discovered that a substantially complete separation of the azeotrope formers from the vaporized azeotropic distillate may be accomplished by the use of absorbents having a preferential absorbing power for the azeotrope former than for the hydrocarbons. Thus, the separation according to my invention may be accomplished by simply intimately contacting the vaporized azeotropic distillate with a sufficient amount of selective absorbent at a suitable temperature to enable the selective absorbent to absorb or extract the vaporized azeotrope former from hydrocarbons and allowing the vaporized hydrocarbons to be withdrawn as an overhead vapor while the azeotrope former dissolved in the absorbent is removed as a liquid from the bottom of the extractor or absorber.

To illustrate the advantage of employing a selective absorbent for effecting the separation of the azeotrope former from the azeotropic distillate, a vaporized azeotropic distillate of hydrocarbons and methyl ethyl ketone of identical composition as that described above which was washed with water, was countercurrently contacted with about three volumes of the diethylene glycol to one of the azeotropic distillate measured as liquid. The extracted hydrocarbons thus recovered when condensed were substantially free from methyl ethyl ketone. Thus, it is possible by my invention to produce a hydrocarbon fraction which is free of azeotrope former by employing a considerably less amount of the selective absorber than when the azeotropic distillate is extracted with water.

Besides diethylene glycol mentioned above, selective absorbents which I have found suitable to effect the extraction of azeotrope formers from azeotropic distillates include phenolic compounds such as resorcinol, parachloro phenol, phenol, xylenol, pyrogallol, pyrocatechol, di- and tri-hydroxy toluene, tetrahydroresorcinol and pyrogallol, cresylic acid, polyhydric alcohols such as mono-, tri-, tetra and hexa-ethylene glycols and dipropylene glycol, amines such as mono-, di-, and tri-ethanolamine, 2-methyl propanol amine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, diethylene diamine, triethylene triamine, diphenylamine, xylidine, aniline, ortho phenylene diamine, alpha naphthol amine and phenyl hydrazine, fatty acids such as acetic, propionic and formic acids and glycolic acids, cyclic ketones such as cyclohexanone, alkyl ethers of polyglycols such as mono-ethylether of diethylene glycol, ethyl ether of ethylene glycol, heterocyclic compounds such as furfuryl alcohols, tetrahydro furfuryl alcohol, nitro-paraffins such as nitropropane, aromatic compounds such as poly nitrobenzenes, benzyl alcohol, benzonitrile and benzyl fluorides, ethers such as BB′ dihydroxy ethyl ether and para nitro diphenyl ether, aliphatic nitriles such as propionitrite, aliphatic fluorides such as hexo fluoro ethane.

Of the above selective absorbents, I have found such compounds as resorcinol, phenol, pyrogallol, pyrocatechol, BB′ dihydroxy ethylether, mono-, di-, tri-, tetra- and hexanonaethylene glycol, dipropylene glycol, propylene glycol, phenyl hydrazine, para chloro-phenol, para nitro diphenyl ether and acetic acid to be particularly suitable for separating such azeotrope formers as such ketones as acetone, methyl ethyl ketone, alcohols such as methyl ethyl and isopropyl alcohols, dioxane and morpholine from non-aromatic hydrocarbons having a boiling range of 200 to 240° F.

Azeotrope formers which may be separated according to my invention from azeotropic distillates produced by azeotropic distillation include all of the compounds disclosed above as selective absorbents for separating the azeotrope former from the azeotropic distillate. However, in effecting a separation of the azeotrope former from an azeotropic distillate, it is obvious that the same materials should not be employed as a selective absorbent as was employed to effect the azeotropic distillation. Whether a particular material will function as a selective absorbent to separate the azeotrope former from the azeotropic distillate depends upon the character of the azeotropic distillate such as the boiling point and solubility characteristics of the hydrocarbons and of the azeotrope former contained therein. For example, a compound may be efficient to perform the azeotropic distillation to separate hydrocarbons from a particular complex hydrocarbon fraction and may be inefficient to separate hydrocarbons from a complex hydrocarbon fraction of a different boiling point; yet this same compound may be useful as a selective absorbent to separate a different azeotrope former from the azeotropic distillate produced from such complex hydrocarbon fraction of different boiling point. To illustrate specifically, tetra ethylene glycol is a particularly efficient azeotrope former for separating relatively paraffinic hydrocarbons in the lubricating oil boiling range from the relatively nonparaffinic oil fractions and is of less efficiency for separating non-aromatic hydrocarbons from a toluene fraction. However, the tetra ethylene glycol is an efficient selective absorbent for removing an efficient azeotrope former such as methyl ethyl ketone from the azeotropic distillate obtained from the azeotropic distillation of a toluene fraction.

In selecting a selective absorbent for the separation of azeotrope former from a particular azeotropic distillate, it is preferable to choose one which has a materially higher boiling point than that of the azeotrope former so that the selective absorbent may be maintained in the liquid phase during the absorption and the subsequent separation of the azeotrope former and selective absorbent from each other may be readily accomplished by simple fractional distillation.

In general, when desiring to separate non-aromatic hydrocarbons from aromatic hydrocarbons, the azeotropic distillation is controlled to distill all non-aromatic hydrocarbons together with azeotrope former, leaving as bottoms the aromatic hydrocarbons which may or may not contain azeotrope former depending upon the quantity of azeotrope former employed. Depending upon the stock, the non-aromatic hydrocarbons contained in the azeotropic distillate may consist of a mixture of paraffin and naphthene hydrocarbons and it is another object of my invention to separate these non-aromatic hydrocarbons into component parts. In this connection, it is a particular object of my invention to separate the azetrope former from the vaporized azeotropic distillate by selective absorption as herein described and then subject the resulting hydrocarbon vapor to solvent extraction with a selective solvent which is adapted to extract the naphthene hydrocarbon vapors, leaving the paraffin hydrocarbons as an undissolved vapor.

The selective solvent extraction to separate the

paraffin from the naphthene hydrocarbons is preferably carried out by passing the hydrocarbon vapor countercurrent to the selective solvent while maintaining a temperature in the extraction column sufficiently elevated to prevent the paraffin hydrocarbons from condensing, yet sufficiently low to prevent the selective solvent from vaporizing. Preferably, a selective solvent is chosen which has a substantially higher boiling point than the hydrocarbons so that vaporization of the selective solvent is effectively prevented. Selective solvents for this purpose include substantially all of the aforementioned selective absorbents but when a selective solvent is chosen which is the same compound used for the selective absorption, a lower temperature and preferably a higher pressure should be maintained than is employed in the selective absorption process for separating the azeotrope former. In other words, during the selective absorption step to remove the azeotrope former, the temperature of absorption should be sufficiently elevated to prevent the hydrocarbons contained in the azeotropic distillate from condensing or from being extracted by the selective absorbent, yet sufficiently low to effect the extraction of the azeotrope former. If the temperature is maintained lower than such conditions, the selective absorbent will also extract hydrocarbons, such as the relatively more naphthenic hydrocarbons as well as the azeotrope former. During the selective solvent extraction step to separate the naphthene hydrocarbons from the paraffin hydrocarbons employing the same compound, the temperature must be maintained at a lower level, otherwise if maintained at a higher or equal level to that of the absorption step, the hydrocarbons will remain in the vapor state and hence will not be extracted by the selective solvent. However, by choosing a different compound for the selective extraction than was employed for the selective absorption, it is possible, depending upon the characteristics of the compound such as its solvent power, to effect the extraction at the same, lower or higher temperature than employed during the selective absorption step. In some cases, the extraction of the naphthenic hydrocarbons may be accomplished by employing a higher pressure even though the same temperature is employed as that employed for the selective absorption step. Selective solvents which I have found particularly suitable include phenol, benzyl alcohol, nitrobenzene, aniline, phenyl ethanolamine, triethylene tetramine, para phenetidine, triacetin, acetonylacetone, monoethyl ether of diethylene glycol, tetrahydro furfuryl alcohol, furfural, diglycol diacetate, methyl ether of diethylene glycol, isopropanolamines, dipropylene glycol, benzyl and phenyl ether of ethylene glycol, nitrophenol, ethyl phenylethanolamine, ortho nitrochlorobenzene, propionitrile and epichlorohydrin.

Other objects, features and advantages of my invention will be apparent to those skilled in the art from the following description of the invention which represents a diagrammatic arrangement of apparatus for carrying out my invention. In the following example, the invention will be described as applied to the separation of toluene from a hydrocarbon fraction employing methyl ethyl ketone containing about 10% by volume of water as the azeotrope former for the recovery of the toluene and diethylene glycol as the selective solvent for the extraction of the azeotrope former from the azeotropic distillate containing the non-aromatic hydrocarbons.

However, it will be observed that this example is not to be taken as limiting my invention since the process is applicable to separate other components from complex substances employing other azeotrope formers under conditions adapted to effect the desired separation.

In the drawing, the hydrocarbon feed to be resolved into its component parts, such as for example, a hydrocarbon extract fraction obtained by solvent extracting gasoline with liquid sulfur dioxide, said fraction having a boiling range of about 200 to 240° F. and consisting of substantially 45% by volume of toluene, 20% by volume of paraffin hydrocarbons and 35% by volume of naphthene hydrocarbons, is taken from tank 10 via line 11 and is pumped by pump 12 through line 14 controlled by valve 15 into line 16. Azeotrope former, such as methyl ethyl ketone, containing about 10% water, is taken from tank 17 via line 18 controlled by valve 19 and is pumped by pump 20 through lines 21 and 22 and valve 23 into line 16 where it is mixed with the hydrocarbon feed from tank 10. The mixture of hydrocarbon feed and azeotrope former in the ratio of approximately two parts of the azeotrope former and one part of hydrocarbon feed in the example herein given, is passed into fractionating column 24 where the mixture is subjected to fractionation, heat being supplied by closed steam coil 25. If desired, the azeotrope former may be introduced directly into the fractionating column at any other point as near the top of the column in which case it will act in part as reflux for the fractionation. In the fractionating column, the distillation is controlled so as to distill overhead an azeotrope consisting of the paraffin, olefin and naphthene hydrocarbons together with substantially all of the methyl ethyl ketone and water. In the example herein given, this is accomplished at an overhead temperature of approximately 160–170° F. and at atmospheric pressure. If desired, the azeotropic distillation may be carried out either at atmospheric or superatmospheric pressure or under a vacuum. The above overhead mixture is removed from the fractionating column via line 26, controlled by valve 27 and may be heated or cooled in 28 and passed via line 29 into line 30 controlled by valve 30*a* to the methyl ethyl ketone-water recovery system, as will be described hereinafter. In some cases, the azeotropic distillate obtained in line 26 will separate out when properly cooled, a portion of the azeotropic distillate as a condensate having substantially the same composition as the uncondensed vapor, which may be recycled to the fractionating column to serve as reflux. This may be accomplished by passing the partially cooled azeotropic distillate via line 31 controlled by valve 31*a* into a separator 32 from which the condensate may be recycled by line 33 controlled by valve 33*a* and pump 32*a* to the fractionating column 24. The uncondensed vapors are removed via line 34 controlled by valve 35 and passed into line 30.

The bottoms in the fractionating column 24 consisting of the aromatic fraction of toluene are withdrawn via line 36 controlled by valve 37 and are pumped by pump 38 through line 39. If the hydrocarbon feed to the azeotropic distillation has been carefully fractionated to produce a fraction free from aromatic hydrocarbons other than toluene and if the azeotropic distillation has been carried out under such conditions as to remove all of the non-aromatic hydrocarbons and azeotrope

former, the bottoms from the fractionating column may be passed directly via lines 36, 39, 40 controlled by valve 41, 42, 43 controlled by valve 44 and 45 into storage tank 46. However, in the event the charging stock has not been carefully fractionated to remove aromatic hydrocarbons heavier than toluene, such as xylene, etc., the bottoms in the fractionating column 24 will contain all or substantial amounts of such aromatic hydrocarbons. In the event it is desired to recover the aromatic hydrocarbon mixture per se, it is passed directly to tank 46 as described above. However, if it is desired to separate the toluene from the remaining aromatic hydrocarbons, the bottoms are passed via lines 36, 39, 40, 42 into line 47 controlled by valve 48 from which it passes through heater 49 and line 50 into fractionating column 51 where the mixture is fractionated to remove the toluene as an overhead product aided by heat from the heater 52. The vaporized touene is removed from the top of the fractionating column 51 via line 53, condensed in condenser 54 and passed via line 55 into collecting tank 56. The condensate may be withdrawn from the collecting tank by pump 57 and passed into line 58. If desired, part of the condensate may be cycled via line 59 controlled by valve 60 to the fractionating column 51 to serve as reflux for the fractionation. The remaining portion is passed via line 61 controlled by valve 62 through line 45 into storage tank 46. The bottoms from the fractionating column, consisting of xylene or a mixture of xylene and higher boiling aromatic hydrocarbons, is withdrawn via line 63 controlled by valve 64 and pumped by pump 65 and line 66 into storage tank 67.

In the event the bottoms fraction from the fractionating column 24 contains a portion of the azeotrope former, this may be removed by passing the bottom fraction via lines 36, 39 and 68 controlled by valve 69 through heater 70 and line 71 into fractionating column 72 provided with a heater 73 and reflux cooling coil 74 where the azeotrope former may be fractionated and removed via line 75, condensed in condenser 76 and passed via line 77 into collecting tank 78 from which it may be returned to the fractionating column 24 by pump 79 and line 80 controlled by valve 81 and lines 22 and 16. The bottoms from the fractionating column 72 may be passed via line 82 controlled by valve 83 into line 42 from which it may be passed by pump 84 either directly to the storage tank 46 or to fractionating column 51 in accordance with the above disclosure.

The toluene or the mixture of toluene and higher boiling aromatic hydrocarbons obtained in tank 46 and the higher boiling aromatic hydrocarbons obtained in tank 67 may be treated with clay which may be accomplished at a temperature of about 230° F. employing 1 to 5 pounds of clay per barrel of the hydrocarbon fraction. If desired, the clay treatment may precede the fractionation in fractionating column 51 in which case the fractionation in 51 may serve either to rerun the clay treated stock and/or to fractionate the high boiling aromatic hydrocarbons from the toluene. In place of clay treatment, the aromatic fraction may be cooled and then treated with 1 to 10 pounds of sulfuric acid per barrel of the hydrocarbons followed by neutralization with clay or caustic alkali. The acid treatment serves to remove small traces of undesirable unsaturated hydrocarbons which may be detrimental in color stability and nitration of the toluene.

In order to recover the azeotrope former from the azeotropic distillate, the distillate is passed in the vapor state into the bottom of the extractor or absorber 85 provided with packing material such as broken tile 85a and with heater 86 where the vapors are countercurrently contacted with selective absorbent withdrawn from tank 87 via line 88 controlled by valve 89 and pump 90 which passes the absorbent through heater 91 into the top of the extractor 85. In the extractor, the selective absorbent extracts the methyl ethyl ketone and water from the azeotropic distillate permitting the hydrocarbons to be separated as a vapor substantially free from either the selective absorbent or azeotrope former. The extraction is preferably carried at a temperature sufficiently elevated so that the hydrocarbon phase remains in the vapor state and the extract phase of azeotrope former and selective absorbent is in the liquid phase. In order to obtain this condition, the selective absorbent for the azeotrope former should have a boiling point above that of the temperature of extraction. Thus, when employing diethylene glycol as the selective absorbent in the example herein given, the temperature of extraction is preferably carried out at 350° F., employing approximately three volumes of the diethylene glycol to one volume of the azeotropic distillate measured as a liquid. In some cases, it may be desirable to effect the extraction with the selective absorbent at a lower temperature than under the conditions prescribed above, i. e., sufficiently low to extract the relatively less paraffinic hydrocarbons such as the naphthene hydrocarbons as well as the azeotrope former, leaving the paraffinic hydrocarbons as vapors which may then be separated from the solution of relatively less paraffinic hydrocarbons, azeotrope former and selective absorbent. The relatively less paraffinic hydrocarbons may then be separated from the solution by cooling and stratifying the mixture which effects a rejection of hydrocarbons from the solution.

The extracted vapor consisting of non-aromatic hydrocarbons free from methyl ethyl ketone and water and selective absorbent is withdrawn via line 92 controlled by valve 93, and passed via valve 93' to condenser 94 from which the condensate passes via line 95 into collecting tank 96. The condensate is pumped by pump 97 and line 98 into storage tank 99.

The liquid extract phase consisting of methyl ethyl ketone, water and selective absorbent is withdrawn from the bottom of the extractor 85 via line 100 controlled by valve 101 and is pumped by pump 102 through line 103, heater 104 and line 105 into fractionating column 106 provided with heater 107 where the azeotrope former, i. e., methyl ethyl ketone containing about 10% by volume of water is stripped from the selective absorbent and passes via line 108 controlled by valve 109 through lines 22 and 16 into the fractionating column 24 in order to effect the azeotropic distillation of the hydrocarbon feed. The azeotrope former may be passed via line 110 controlled by valve 111, condensed in condenser 112 and condensate collected in collecting tank 114 from which it is withdrawn by pump 115, and a portion recycled via line 116 controlled by valve 117 to fractionating column 106 to serve as reflux for the fractionation. The remaining condensate may be passed via line 118 controlled by valve 119 into storage tank 117.

The bottoms in fractionating column 106 consisting of the selective absorbent are withdrawn

via line 120 controlled by valve 121 and are pumped by pump 122 through line 123 into storage tank 87.

As indicated above, the vapors from the extractor 85 may be extracted in the vapor phase with a selective solvent in order to separate these vapors into paraffin hydrocarbons and naphthene hydrocarbons or into a fraction which is relatively paraffinic and a fraction which is relatively non-paraffinic. This is accomplished by passing the hydrocarbon vapors from the extractor 85 through lines 92 and 124 controlled by valve 125 into the bottom of the extractor 126 provided with packing material such as broken tile 127 and heater 128 where the vapors are countercurrently contacted with selective solvent withdrawn from tank 129 via line 130 controlled by valve 131 and pump 132 from which the solvent passes into the top of the extractor 126. In the extractor, the selective solvent extracts the naphthene hydrocarbons from the vapor permitting the paraffin hydrocarbons to be separated as a vapor substantially free from either the selective solvent or naphthene hydrocarbons. The extraction is preferably carried out at a temperature sufficiently elevated so that the paraffin hydrocarbons remain in the vapor phase and the selective solvent and naphthene hydrocarbons are in the liquid phase. In order to obtain this condition, the selective solvent for the naphthene hydrocarbons should have a boiling point above that of the temperature of the extraction. Thus, when employing benzyl alcohol as the selective solvent in the example herein given, the temperature of extraction is preferably carried out at about 250° F. employing approximately three volumes of the selective solvent to one volume of the hydrocarbons measured as a liquid.

The extracted vapor consisting of the paraffin hydrocarbons is withdrawn via line 133 controlled by valve 134 and is passed to a condenser where the vapors are condensed. The liquid extract phase consisting of the selective solvent and naphthene hydrocarbons is withdrawn from the bottom of the extractor 126 via line 135 controlled by valve 136 and is pumped by pump 137 through heater 138 into fractionating column 139 provided with heater 140 and reflux cooling coil 141 where the naphthene hydrocarbons are distilled from the selective solvent and pass via line 142 controlled by valve 143 to a condenser where the hydrocarbons are condensed. The bottoms in the fractionating column 139 consisting of the selective solvent are withdrawn via line 144 controlled by valve 145 and are pumped by pump 146 through line 147 into storage tank 129.

In the foregoing example, a bottoms toluene fraction of essentially 100% purity was produced in fractionating column 24 representing all of the toluene in the original feed charged to the azeotropic distillation. When the vaporized azeotropic distillate consisting of the nonaromatic hydrocarbons, methyl ethyl ketone and water from the fractionating column 24 was selectively absorbed in extractor 85 to remove the methyl ethyl ketone and water and the hydrocarbon vapors therefrom were extracted in the vapor phase with the benzyl alcohol in the extractor 126, a paraffinic hydrocarbon overhead distillate was produced representing about 20% of the feed stock which contained about 80% paraffins and 20% naphthenes, the paraffinic distillate having a gravity of 64° A. P. I. The bottom fraction in the extractor when separated from the selective solvent in fractionating column 139 had a gravity of 54° A. P. I. and was recovered in a yield of about 35%, containing about 80% naphthene hydrocarbons and about 20% paraffin hydrocarbons.

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

I claim:

1. A process for the treatment of a complex hydrocarbon fraction to separate chemically similar hydrocarbon components therefrom from other hydrocarbon components contained therein which ordinarily distill from the hydrocarbon fraction in the same temperature range as said chemically similar hydrocarbon components distill therefrom which comprises distilling said complex hydrocarbon fraction in the presence of a sufficient amount of an azeotrope former to produce a vaporized mixture consisting of at least one of the components contained in said complex hydrocarbon fraction together with said azeotrope former, thereby leaving at least one of the components contained in said complex hydrocarbon fraction in the residue, extracting said vaporized mixture in the vapor state in an extraction zone with a liquid selective absorbent adapted to absorb the azeotrope former in preference to the hydrocarbon vapors and separating a solution of said liquid absorbent and azeotrope former from said hydrocarbon vapors said azeotrope former being an organic compound which is not readily separable from said vaporized mixture of azeotrope formers and hydrocarbons by extraction with water and said liquid absorbent being a substantially non-aqueous polar organic compound different from the azeotrope former, said absorbent being readily separable from the extracted mixture of liquid absorbent and dissolved azeotrope former.

2. A process for the treatment of a complex hydrocarbon fraction to separate chemically similar hydrocarbon components therefrom from other hydrocarbon components contained therein which ordinarily distill from the hydrocarbon fraction in the same temperature range as said chemically similar hydrocarbon components distill therefrom which comprises distilling said complex hydrocarbon fraction in the presence of a sufficient amount of an azeotrope former to produce a vaporized mixture consisting of at least one of the components contained in said complex hydrocarbon fraction together with said azeotrope former, thereby leaving at least one of the components contained in said complex hydrocarbon fraction in the residue, extracting said vaporized mixture in the vapor state in an extraction zone with a liquid absorbent adapted to dissolve the azeotrope former in preference to the hydrocarbon vapors, said liquid absorbent being introduced into said extraction zone in a direction countercurrent to said vaporized mixture and separating a solution of said solvent and azeotrope former from said hydrocarbon vapors said azeotrope former being an organic compound which is not readily separable from said vaporized mixture of azeotrope formers and hydrocarbons by extraction with water and said liquid absorbent being a substantially non-aqueous polar organic compound different from the azeotrope former, said absorbent being readily separable from the extracted mixture of liquid absorbent and dissolved azeotrope former.

3. A process for the treatment of a complex hydrocarbon fraction to separate chemically similar hydrocarbon components therefrom from other hydrocarbon components contained therein which ordinarily distill from the hydrocarbon fraction in the same temperature range as said chemically similar hydrocarbon components distill therefrom which comprises distilling said complex hydrocarbon fraction in the presence of a sufficient amount of an azeotrope former to produce a vaporized mixture consisting of at least one of the components contained in said complex hydrocarbon fraction together with said azeotrope former, thereby leaving at least one of the components contained in said complex hydrocarbon fraction in the residue, extracting said vaporized mixture in the vapor state in an extraction zone with a liquid selective absorbent adapted to absorb the azeotrope former in preference to the hydrocarbon components and separating a solution of said liquid absorbent and azeotrope former from said hydrocarbon vapors said azeotrope former being an organic compound which is not readily separable from said vaporized mixture of azeotrope formers and hydrocarbons by extraction with water and said liquid absorbent being a substantially non-aqueous polar organic compound different from the azeotrope former, said absorbent being readily separable from the extracted mixture of liquid absorbent and dissolved azeotrope former, said liquid absorbent having a boiling point substantially higher than the boiling point of said azeotrope former and distilling said solution of liquid absorbent and azeotrope former to separate said liquid absorbent from said azeotrope former.

4. A process as in claim 1 in which said azeotrope former comprises methyl ethyl ketone and said selective absorbent comprises diethylene glycol.

5. A process for the treatment of a hydrocarbon fraction containing toluene and non-aromatic hydrocarbons to separate toluene from the non-aromatic hydrocarbons contained therein which ordinarily distill from said hydrocarbon fraction in the same temperature range as toluene distills therefrom which comprises distilling said hydrocarbon fraction in the presence of a sufficient amount of methyl ethyl ketone as azeotrope former to vaporize the non-aromatic hydrocarbons together with the methyl ethyl ketone thereby leaving toluene in the residue substantially completely separated from the hydrocarbons other than toluene, extracting said vaporized mixture in the vapor state in an extraction zone with a liquid absorbent adapted to absorb the azeotrope former in preference to the hydrocarbon vapors and separating a solution of said liquid absorbent and azeotrope former from said hydrocarbon vapors said azeotrope former being an organic compound which is not readily separable from said vaporized mixture of azeotrope formers and hydrocarbons by extraction with water and said liquid absorbent being a substantially non-aqueous polar organic compound different from the azeotrope former, said absorbent being readily separable from the extracted mixture of liquid absorbent and dissolved azeotrope former.

6. A process for the treatment of a hydrocarbon fraction containing toluene and non-aromatic hydrocarbons to separate toluene from the non-aromatic hydrocarbons contained therein which ordinarily distill from said hydrocarbon fraction in the same temperature range as toluene distills therefrom which comprises distilling said hydrocarbon fraction in the presence of a sufficient amount of methyl ethyl ketone to vaporize the non-aromatic hydrocarbons together with the methyl ethyl ketone thereby leaving toluene in the residue substantially completely separated from the hydrocarbons other than toluene, extracting said vaporized mixture in the vapor state in an extraction zone with diethylene glycol to absorb said methyl ethyl ketone and separating a solution of said diethylene glycol and methyl ethyl ketone from said non-aromatic hydrocarbon vapors.

7. A process for the treatment of a complex hydrocarbon fraction containing three different types of hydrocarbons to separate chemically similar hydrocarbon components therefrom from other hydrocarbon components contained therein which ordinarily distill from the hydrocarbon fraction in the same temperature range as said chemically similar hydrocarbon components distill therefrom which comprises distilling said complex hydrocarbon fraction in the presence of a sufficient amount of an azeotrope former to produce a vaporized mixture containing two of said components contained in said complex hydrocarbon fraction together with said azeotrope former, thereby leaving one of said components contained in said complex hydrocarbon fraction in the residue, extracting said vaporized mixture in the vapor state in an extraction zone with a liquid absorbent adapted to absorb the azeotrope former in preference to the hydrocarbon vapors, separating a solution of said liquid absorbent and azeotrope former from said hydrocarbon vapors, passing said hydrocarbon vapors in contact with a selective solvent adapted to extract one of the hydrocarbon components while leaving the other hydrocarbon component in the vapor state and separating a solution of the extracted hydrocarbon component and selective solvent from the other unextracted hydrocarbon component said azeotrope former being an organic compound which is not readily separable from said vaporized mixture of azeotrope formers and hydrocarbons by extraction with water and said liquid absorbent being a substantially non-aqueous polar organic compound different from the azeotrope former, said absorbent being readily separable from the extracted mixture of liquid absorbent and dissolved azeotrope former.

8. A process for the treatment of a complex hydrocarbon fraction containing paraffin, naphthene and aromatic hydrocarbons to separate chemically similar hydrocarbon components therefrom from other hydrocarbon components contained therein which ordinarily distill from the hydrocarbon fraction in the same temperature range as said chemically similar hydrocarbon components distill therefrom which comprises distilling said complex hydrocarbon fraction in the presence of a sufficient amount of an azeotrope former to produce a vaporized mixture containing paraffin and naphthene hydrocarbons together with said azeotrope former, thereby leaving aromatic hydrocarbons in the residue, extracting said vaporized mixture in the vapor state in an extraction zone with a liquid absorbent adapted to absorb the azeotrope former in preference to the hydrocarbon components, separating a solution of said liquid absorbent and azeotrope former from said hydrocarbon vapors, passing said hydrocarbon vapors in contact with a selective solvent adapted to extract the naphthene hydrocarbons while leaving the paraffin

hydrocarbons in the vapor state, separating a solution of the extracted naphthene hydrocarbons and selective solvent from the unextracted paraffin hydrocarbons and separating the naphthene hydrocarbons from the selective solvent said azeotrope former being an organic compound which is not readily separable from said vaporized mixture of azeotrope formers and hydrocarbons by extraction with water and said liquid absorbent being a substantially non-aqueous polar organic compound different from the azeotrope former, said absorbent being readily separable from the extracted mixture of liquid absorbent and dissolved azeotrope former.

9. A process as in claim 7 in which said selective solvent comprises benzyl alcohol.

10. A process as in claim 1 in which said selective solvent comprises a polyhydric alcohol.

11. A process as in claim 1, in which said azeotrope former comprises a ketone selected from the group consisting of acetone and methyl ethyl ketone and said selective absorbent com-

prises an absorbent selected from the group consisting of glycols and alkyl ethers of glycols.

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