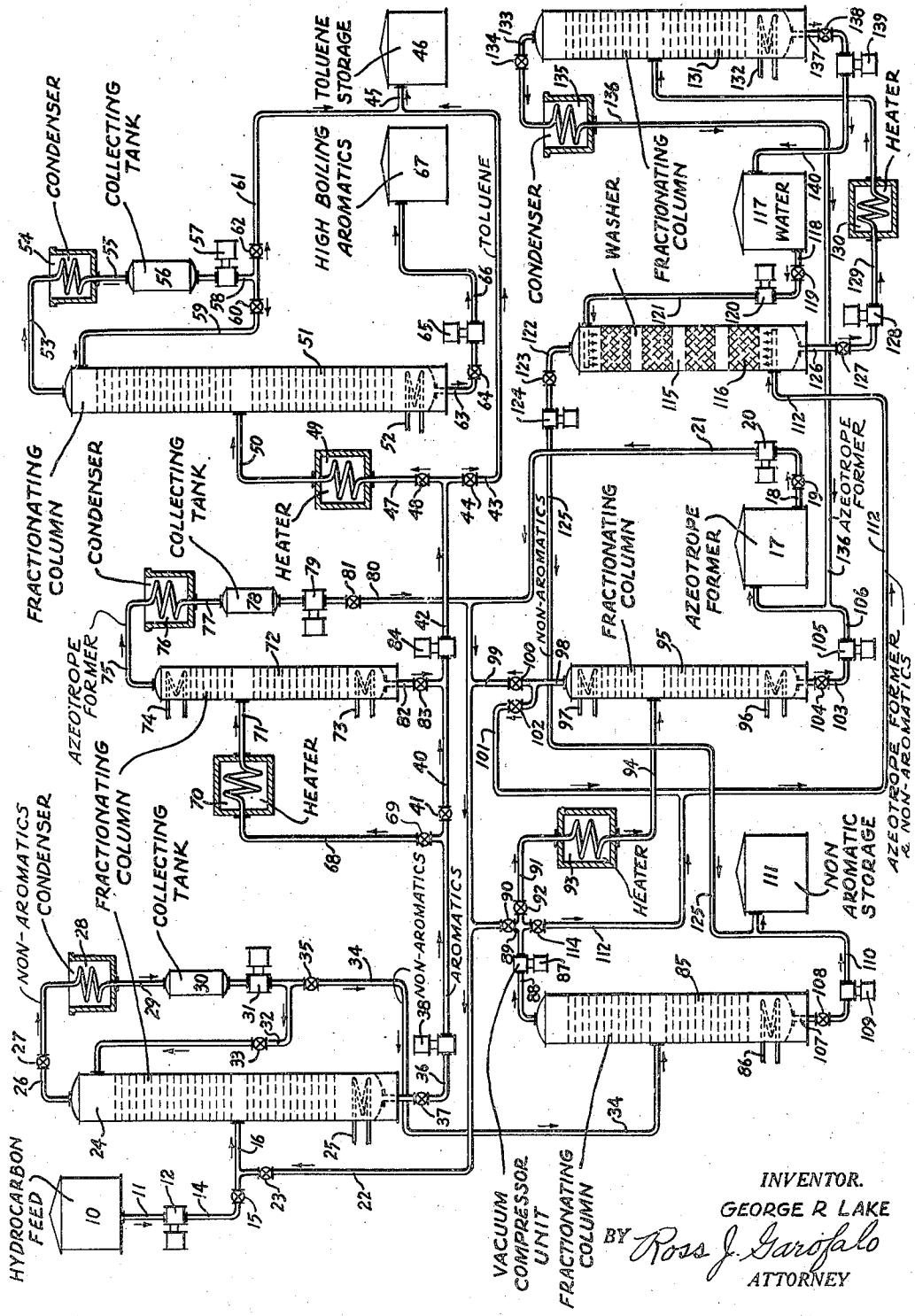
May 8, 1945. G. R. LAKE 2,375,478

DISTILLATION PROCESS

Filed Nov. 4, 1941



Patented May 8, 1945 2,375,478

UNITED STATES PATENT OFFICE

2,375,478

DISTILLATION PROCESS

George R. Lake, Long Beach, Calif., assignor to Union Oil Company of California, Los Angeles, Calif., a corporation of California

Application November 4, 1941, Serial No. 417,781

1 Claim. (Cl. 202—42)

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 change in the vapor pressure equilibrium that formerly existed in the fraction in such 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 the 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 azeotrope 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 azetropic distillate with water which is adapted to dissolve the azeotrope former from the azeotropic distillate and thus the azeotrope former may be separated from the hydrocarbons by settling and stratification. The solution of azeotrope former and water may be distilled to separate the azetrope 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 certain azeotrope formers such as methanol or 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 these azetrope formers offer the serious difficulty of recovering the azetrope former from the azeotropic distillate. While the separation of the azeotrope former 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 hydrocarbons thus separated still contained about one percent of azeotrope former. Furthermore, in order to recover the azeotrope former from the very dilute wash solution, it is necessary to heat an excessively large volume of dilute azeotrope former

While distillation to separate the azeotrope former from the hydrocarbons is perhaps the most economical manner and perhaps the most frequently employed method to separate a mixture of components of different boiling points, the distillation of the azeotropic distillate under substantially the same conditions employed in the primary azeotropic distillation of the original complex hydrocarbon charge merely results in distilling overhead a mixture of the hydrocarbons and azeotrope former in substantially the same proportions as they distilled from the original complex hydrocarbon charge. Hence, a separation of the azeotrope former from the azeotropic distillate cannot be made under such conditions.

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 a process involving a combination of distillation and washing and more specifically, it is an object to effect the separation by distilling the azeotropic distillate under such conditions as to separate a portion of one of the components contained in the azeotropic diistillate as a substantially pure product and then washing or extracting the remaining azeotropic distillate to separate the remaining portion of the component to leave the other component contained in the azeotropic distillate as a substantially pure product.

I have discovered that if the azeotropic distillate is subjected to fractional distillation at a pressure lower than the pressure employed for the azeotropic distillation, the component contained in the azeotropic distillate having the lowest boiling point at the reduced pressure, i. e. either the hydrocarbons or the azeotrope former, will be distilled as a fraction containing a portion of the higher boiling component, leaving as a distillation bottoms the remaining portion of the higher boiling component as a fraction substantially free from the lower boiling component. Thus, if the azeotropic distillate is composed of non-aromatic hydrocarbons having an average boiling point of, for example 220° F. and an azeotrope former having a boiling point of, for example 180° F., and if this azeotropic distillate was distilled from a mixture of aromatic and non-aromatic hydrocarbons at a distillation temperature of, for example 160° F. and atmospheric pressure, the separation of the azetotrope former from the non-aromatic hydrocarbons may be accomplished by distillation at a lower temperature than 160° F. which will necessitate a corresponding reduction in pressure below atmospheric in order to effect a distillation. Since in this case, the azeotrope former boils at a lower temperature than the non-aromatic hydrocarbons, this component will be separated as an overhead product and the non-aromatic hydrocarbons will remain as a distillation bottoms. However, a portion of the hydrocarbons may be taken overhead with the azeotrope former. The non-aromatic hydrocarbons will be substantially free from the azeotrope former so that these may be withdrawn from the system without resulting in loss of azeotrope former.

The extent of the temperature reduction and corresponding pressure reduction in order to effect the desired separation of azeotrope former from non-aromatic hydrocarbons will, of course, vary with the composition and characteristics of the particular azeotropic distillate and will further depend upon the economical and practical considerations with respect to the amount of non-aromatic hydrocarbons which may be tolerated with the recovered azeotrope former. In other words, if the subsequent treatment to be described of the overhead resulting from the aforesaid low pressure distillation may be satisfactorily and economically carried out to recover the azeotrope former therefrom in the presence of a relatively large amount of the non-aromatic hydrocarbons, the extent of temperature and pressure reduction in the aforesaid low pressure distillation to produce the mixture of azeotrope former containing such amount of non-aromatic hydrocarbons from the azeotropic distillate need not be as great as when it is necessary that the overhead contains a relatively small amount of the non-aromatic hydrocarbons in order to recover the azeotrope former therefrom. Since a portion of the hydrocarbons have been separated as a fraction free from azeotrope former, the washing of the remaining azeotropic distillate, i. e. the overhead from the low pressure distillation stage will result in a greater recovery of azeotrope former than is possible when the same amount of azeotrope former must be washed in the presence of a larger amount of hydrocarbons, assuming that the same percentage, i. e. 1% of azeotrope former must be lost to the hydrocarbons when washing with the same proportion of water. In general, I have found that reducing the temperature for the distillation approximately 50° F. below the temperature of the primary azeotropic distillation with a corresponding reduction in pressure will produce a satisfactory overhead azeotrope former which may be satisfactory and economically treated by the process hereinafter described.

The separation of the lower boiling constituent, i. e. azeotrope former, from the higher boiling constituent, i. e. non-aromatic hydrocarbons present in the overhead mixture resulting from the low pressure distillation of the azeotropic distillate, is accomplished by washing the mixture with water in the usual manner in order to dissolve the water soluble azeotrope former from the hydrocarbons. Water soluble azeotrope former which may be separated from hydrocarbons in this manner includes methyl ethyl ketone.

In some cases, particularly when an azeotrope former is used which is water insoluble and hence cannot be separated by water washing, the separation of the remaining azeotrope former may be accomplished by extraction with a solvent which is adapted to selectively dissolve the azeotrope former and substantially none of the hydrocarbons at the temperature of extraction. The extraction of the azeotrope former by means of the selective solvent may also be employed in the case of the water soluble azeotrope formers.

Selective solvents adapted to separate the azeotrope former from the non-aromatic hydrocarbons include particularly suitable selective solvents namely the polyhydric alcohols, the ethanolamines, diethylene triamine and nitromethane.

As a modification of my invention as described above, I may subject the overhead from the low pressure distillation of the azeotropic distillate to fractional distillation in a second distillation stage at a higher pressure than maintained in the low pressure stage which will result in distilling all of the non-aromatic hydrocarbons together with a portion of the azeotrope former, leaving substantially pure azeotrope former as a distillation bottoms which may be returned to the azeotropic distillation process. The small amount of overhead resulting from this second fractional distillation consisting of a mixture of the azeotrope former and non-aromatic hydrocarbons may then be washed or extracted as above described to separate the azeotrope former from the hydrocarbons. Thus, by operating the azeotrope former recovery system in the two distillation stages as in the above manner, a hydrocarbon fraction is produced which is relatively free from azeotrope former in the first distillation stage and an azeotrope former fraction is produced which is relatively free from hydrocarbons in the second distillation stage. Also, in the second distillation stage, a relatively small amount of a mixture of both hydrocarbons and azeotrope former is produced which is washed or extracted as described above.

As stated above, the second distillation is car-

ried out at a higher pressure and higher temperature than the first stage distillation. These temperature and pressure conditions may be lower than the temperature-pressure conditions of the primary azeotropic distillation but higher than the first stage distillation or they may be the same or higher than the primary azetropic distillation.

While I have described the distillation of the azeotropic distillate as being carried out at a low pressure and temperature, I may also effect separation of the azeotrope former from the hydrocarbons by carrying out the distillation at a higher pressure and temperature than the primary azeotropic distillation. In this case, however, the distillation at high pressure will result in distilling an overhead product consisting of substantially all of the hydrocarbons together with a portion of the azeotrope former, leaving the remaining portion of the azeotrope former free from hydrocarbons as a distillation bottoms. The overhead mixture may then be washed or extracted, as described above, to separate the remaining azeotrope former contained in the overhead from the hydrocarbons. This procedure will result in the employing of a smaller amount of water or solvent than when treating the entire azeotropic distillate or by using the same quantity of water or solvent will result in greater reduction in loss of azeotrope former to the hydrocarbons.

By carrying out the distillation part of the azeotrope former recovery system in two stages as above described, it is only necessary to wash or extract a relatively small amount of the mixture of azeotrope former and non-aromatic hydrocarbons. This is advantageous in that it will require the use of considerably less water or solvent and will result in considerably less loss of azeotrope former to the hydrocarbons than in the case where the entire azeotropic distillate is washed with water.

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 drawing, the hydrocarbon feed to be resolved into its component parts 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 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 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 fractionation column, the distillation is controlled so as to distill overhead an azeotrope consisting of the relatively non-aromatic hydrocarbons together with substantially all of the azeotrope former. 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, condensed in condenser 28 and passed via line 29 into collecting tank 30. The condensate consisting of the azeotrope former and non-aromatic hydrocarbons is withdrawn from the bottom of the collecting tank 30 by pump 31 and part thereof may be passed via line 32 controlled by valve 33 to fractionating column 24 to serve as reflux for the fractionation. The remaining portion of the condensate is passed via line 34 and valve 35 to the azeotrope former recovery system as will be described hereinafter.

The bottoms in the fractionating column 24 consisting of the relatively more aromatic hydrocarbons 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 the desired aromatic hydrocarbon, for example, 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 toluene 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 fractioned 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 hydro-

carbons 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 via line 34 and valve 35 into fractionating column 85 provided with heater 86. As stated above, the distillation in column 85 is carried out at a lower temperature and a corresponding lower pressure than the azeotropic distillation in column 24. This may be controlled by means of a vacuum pump or compressor 87 provided in the vapor line 88 and the regulation of valves in the inlet and outlet lines to the fractionating column. Thus, if the azeotropic distillation is carried out at atmospheric pressure, the pressure maintained in column 85 may be at sub-atmospheric. If the pressure of the azeotropic distillation is superatmospheric, either a lower super-atmospheric pressure or a vacuum may be maintained in the column 85 and if the azeotropic distillation is carried out under vacuum, a higher vacuum must be maintained in column 85. In the fractionating column 85, the azeotrope former is distilled and removed via line 88 and compressor or vacuum pump 87. This fraction contains a relatively small amount of the relatively non-aromatic hydrocarbons. In such cases where the overhead contains an unobjectionable amount of hydrocarbons, it may be passed via line 89 controlled by valve 90 into line 22 and thus recycled to the azeotropic distillation. However, the relatively non-aromatic hydrocarbons may be removed from the overhead product by closing valve 90 and passing the overhead fraction via line 91 controlled by valve 92 through heater 93 and line 94 into fractionating column 95 provided with heater 96 and reflux control 97 where the distillation is carried at a higher pressure than in column 85 which may be either the same, higher or lower than the pressure of the azeotropic distillation in column 24. The pressure in column 95 is controlled by the compressor or vacuum pump 87 and the regulation of valves in the inlet and outlet lines to the fractionating column. The overhead from fractionating column 95 consisting of a mixture of azeotropic former and relatively non-aromatic hydrocarbons is withdrawn via line 98 and if desired may be recycled to the fractionating column 24 via line 99 and valve 100 and lines 22 and 16. Preferably, this overhead is passed via line 101 and valve 102 and treated as hereinafter described.

The bulk of the azeotrope former is withdrawn as bottoms from the fractionating column 95 via line 103 controlled by valve 104 and is pumped by pump 105 through line 106 into azeotrope former storage tank 17. The relatively non-aromatic hydrocarbons are withdrawn as bottoms from the fractionating column 85 via line 107 controlled by valve 108 and are pumped by pump 109 through line 110 into storage tank 111.

The overhead from column 95 passed into line 101 and consisting of a mixture of the azeotrope former and the relatively non-aromatic hydrocarbons is passed via line 112 into the bottom of washer 115 provided with packing material, such as broken tile 116, for effecting intimate countercurrent contact with water which is introduced into the washer from tank 117 via line 118 controlled by valve 119 and pumped by pump 120 through line 121 into top of the washer. The contact of the distillate of azeotrope former and hydrocarbons introduced into the washer with the water causes the distillate to separate into two phases, i. e., an upper phase consisting of the non-aromatic hydrocarbons and a lower phase consisting of azeotrope former and water. The upper phase is withdrawn via line 122 and valve 123 and is pumped by pump 124 through lines 125 and 110 into storage tank 111. The washing operation is preferably carried out at an elevated temperature of approximately 300° F. under superatmospheric pressure in those cases where the azeotrope former is difficultly soluble in water. While I have described the use of water to extract the azeotrope former from the azeotropic distillate in washer 115, it will be observed that the separation of the azeotrope former may be accomplished by extraction with a solvent which is selective for the azeotrope former, such as for example, tetra ethylene glycol.

The lower phase is withdrawn via line 126 controlled by valve 127 and is pumped by pump 128 through line 129 and heater 130 into fractionating column 131 provided with heater 132 where the azeotrope former is removed as an overhead vapor via line 133 controlled by valve 134, condensed in condenser 135 and returned via lines 136 and 106 to storage tank 17. The undistilled water or solvent substantially free from azeotrope former is removed via line 137 controlled by valve 138 and is pumped by pump 139 through line 140 to storage tank 117. It will be understood that when the water or solvent has a lower boiling point than the azeotrope former, the distillation in column 131 will distill the water or solvent as an overhead fraction leaving the azeotrope former as a bottoms fraction in which case the overhead is condensed and passed to storage tank 117 and the bottoms will be passed to storage tank 117.

Instead of passing the overhead from column 85 consisting of the mixture of azeotrope former and hydrocarbons to the higher pressure column 95 in order to separate a mixture of the azeotrope former and hydrocarbons from a bottoms fraction of substantially pure azeotrope former, the overhead from column 85 may be passed via lines 88 and 112 directly to the washer 115 where it may be treated as above described either in the vapor phase or preferably in the liquid phase by first condensing the overhead mixture.

As stated above, the fractional distillation in column 85 may be carried out under a higher pressure and temperature than the temperature and pressure maintained in column 24 for the azeotropic distillation. In such case, the overhead product from column 85 will consist of substantially all of the hydrocarbons together with a portion of the azeotrope former while the bottoms in the column will consist of the remainder of the azeotrope former substantially free from hydrocarbons. This overhead from column 85

may be condensed and passed directly to the washer 115 or it may be passed to column 95 where it may be distilled at a lower pressure and temperature than in column 85 to produce an overhead mixture of azeotrope former and hydrocarbons, leaving the remaining hydrocarbons as a distillation bottoms in the column. The overhead mixture from column 95 may then be passed to the washer 115 as above described. The bottoms from column 85 consisting of substantially pure azeotrope former may then be recycled to the column 24 or passed to storage. The bottoms from column 95 consisting of substantially pure hydrocarbons may be passed to storage.

Preferably, when the column 85 is operated under a lower pressure and temperature than the azeotropic distillation in column 24, the overhead consisting of all of the azeotrope former with a portion of the hydrocarbons is passed to the higher pressure distillation column 95 in order to remove as much of the azeotrope former as is possible as a fraction free from hydrocarbons, thereby reducing the amount of azeotrope former to be recovered by washing and thus reducing the amount of water or solvent required to effect the separation of the azeotrope former from the hydrocarbons. When the column 85 is operated at a higher pressure than column 24, a substantial portion of the azeotrope former will have been removed as a bottoms fraction in column 85 and hence the overhead therefrom may be passed directly to the washer 115. However, it is within the scope of my invention to refractionate this overhead at a reduced pressure in column 95 and to wash or extract the overhead from this column.

The following is a specific example of my invention as applied to specific hydrocarbon fractions employing a specific azeotrope former.

In one experiment, approximately 100 liters of a carefully fractionated hydrocarbon fraction having a boiling range of about 200 to 240° F. consisting of approximately 20% by volume of toluene and the remainder, paraffin and naphthene hydrocarbons, was fractionally distilled in the presence of about 160 liters of a mixture of 144 liters of methyl ethyl ketone and 16 liters of water at an overhead temperature of 170° F. and at atmospheric pressure. The distilled overhead was condensed at a temperature of 70° F. and allowed to settle in a settling chamber which caused the condensate to stratify into two layers which were separated from each other. The upper layer consisted of 80 liters of non-aromatic hydrocarbons and 142 liters of methyl ethyl ketone containing a trace of water while the lower layer consisted of about 16 liters of water and 2 liters of methyl ethyl ketone. The distillation bottoms consisted of about 20 liters of toluene of about 100% purity.

The upper layer consisting of the 142 liters of methyl ethyl ketone and 80 liters of hydrocarbons was then distilled at a temperature of about 250° F. under a pressure of about three atmospheres which resulted in producing an overhead consisting of about 80 liters of hydrocarbons and 80 liters of methyl ethyl ketone. The bottoms from this distillation consisted of about 62 liters of methyl ethyl ketone substantially free from hydrocarbons which was passed to storage.

The overhead from this last named distillation under pressure and consisting of about 80 liters each of hydrocarbons and methyl ethyl ketone was then countercurrently contacted with about 500 liters of water at a temperature of about 300° F. under a pressure of about two atmospheres which resulted in producing as separate fractions about 580 liters of a dilute methyl ethyl ketone and about 80 liters of hydrocarbons which were substantially free from methyl ethyl ketone. The dilute methyl ethyl ketone was mixed with the 16 liters of water and 2 liters of methyl ethyl ketone previously separated and this mixture was then distilled at a temperature of about 164° F. which resulted in distilling overhead an azeotrope of methyl ethyl ketone and water consisting of about 82 liters of methyl ethyl ketone and 9 liters of water which was employed for the azeotropic distillation of further amounts of the mixture of aromatic and non-aromatic 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 claim.

I claim:

A process for the treatment of a complex normally liquid hydrocarbon fraction having a boiling range of from about 200 to 240° F. to separate it into component parts of dissimilar characteristics which comprises distilling said complex hydrocarbon fraction in the presence of a sufficient amount of methyl ethyl ketone as an azeotrope former to produce an azeotropic distillate consisting of at least one of the hydrocarbons contained in said complex hydrocarbon fraction together with said azeotrope former, thereby leaving at least one of the remaining hydrocarbons contained in said complex hydrocarbon fraction in the residue, distilling said azeotropic distillate at a different temperature and pressure than the temperature and pressure of distillation of said complex hydrocarbon fraction to produce a fraction relatively free from one of the components contained in said azeotropic distillate and a fraction containing a mixture of hydrocarbons and azeotrope former, extracting said last named mixture with an agent adapted to dissolve one of said components and substantially none of the other components contained in said mixture and separating a solution of said agent and dissolved component from the undissolved component.

GEORGE R. LAKE.