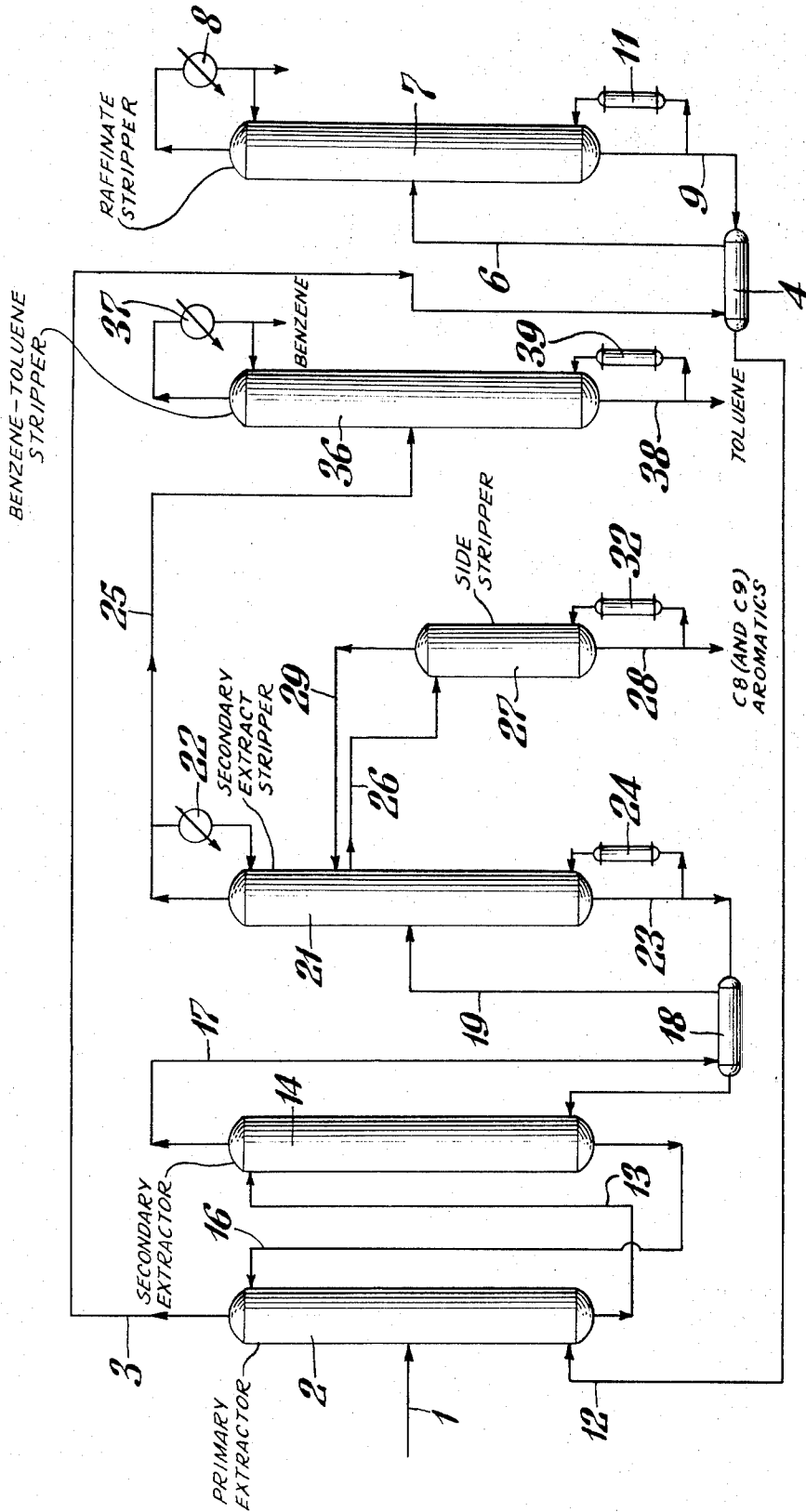


April 3, 1973

JUI CHUNG WANG

3,725,254

PROCESS FOR THE SEPARATION OF AROMATIC HYDROCARBONS
FROM A MIXED HYDROCARBON FEEDSTOCK
Filed July 13, 1971



1

3,725,254

PROCESS FOR THE SEPARATION OF AROMATIC HYDROCARBONS FROM A MIXED HYDROCARBON FEEDSTOCK

Jui Chung Wang, St. Albans, W. Va., assignor to Union Carbide Corporation, New York, N.Y.

Filed July 13, 1971, Ser. No. 162,178

Int. Cl. C10g 21/02

U.S. Cl. 208—314

10 Claims

ABSTRACT OF THE DISCLOSURE

A continuous process for separating aromatic hydrocarbons from mixed hydrocarbon feedstock containing aliphatic and aromatic hydrocarbons, said aromatic hydrocarbons being comprised of benzene, toluene, and C₈ aromatics, comprising the following steps:

(a) Contacting the feedstock with a primary solvent and a secondary solvent in a primary extraction zone at a temperature in the range of about 50° C. to about 150° C. and a pressure in the range of about atmospheric pressure to about 200 p.s.i.a. wherein the primary solvent is a water-soluble organic solvent, which has a higher boiling point than and is non-azeotropic with the feedstock, and the secondary solvent is selected from the group consisting of paraffinic and naphthenic hydrocarbons and mixtures thereof, said hydrocarbons having higher boiling points than and being non-azeotropic with the feedstock, and wherein the primary solvent is maintained in sufficient amount to extract essentially all of the aromatic hydrocarbons from the feedstock and the secondary solvent is maintained in sufficient amount to act as a reflux for the feedstock;

(b) Withdrawing from the primary extraction zone primary extract comprising aromatic hydrocarbons and primary solvent and raffinate comprising aliphatic hydrocarbons and secondary solvent;

(c) Contacting said primary extract with the secondary solvent in a secondary extraction zone wherein the temperature and pressure are in the same range as in step (a) and the secondary solvent is maintained in sufficient amount to extract essentially all of the aromatic hydrocarbons from the primary extract;

(d) Withdrawing from the secondary extraction zone primary solvent and secondary extract comprising aromatic hydrocarbons and secondary solvent;

(e) Subjecting the raffinate to distillation in a raffinate distillation zone whereby the aliphatic hydrocarbons are separated from the secondary solvent;

(f) Withdrawing the secondary solvent from the raffinate distillation zone and recycling said secondary solvent to at least one of the extraction zones;

(g) Recycling the primary solvent withdrawn from the secondary extraction zone to the primary extraction zone;

(h) Subjecting the secondary extract to distillation in an aromatics distillation zone having a maximum temperature of 225° C., the temperature gradient being such throughout the zone that about 90 to 99 percent by weight of the benzene and toluene in the extract enters into the vapor phase at the top of the zone; the C₈ aromatics and about 1 to 10 percent by weight of the benzene and toluene in the extract concentrate in the liquid phase at a point between about the middle of the zone and the top of the zone; and the secondary solvent remains essentially in the liquid phase and enters the bottom of the zone;

(i) Withdrawing the vapor phase mixture of benzene and toluene from the aromatics distillation zone in step (h)

2

and subjecting same to distillation to separate the benzene from the toluene;

(j) Withdrawing the liquid phase C₈ aromatics, benzene, and toluene from the aromatics distillation zone in step (h) and subjecting same to distillation in a side-distillation zone, said side-distillation zone containing about 40 to 60 percent of the number of equilibrium stages contained in the aromatics distillation zone and having a maximum temperature of at least 75° C. less than the maximum temperature of the aromatics distillation zone, and separating the C₈ aromatics from the benzene and toluene;

(k) Recycling the benzene and toluene from step (j) to the aromatics distillation zone; and

(l) Withdrawing the secondary solvent from the aromatics distillation zone of step (h) and recycling such secondary solvent to at least one of the extraction zones.

FIELD OF THE INVENTION

This invention relates to an improvement in a process for the separation of aromatic hydrocarbons from a mixed hydrocarbon feedstock and, more particularly, to the recovery of aromatic hydrocarbons using minimal distillation requirements.

DESCRIPTION OF THE PRIOR ART

U.S. Pat. No. 3,492,365 issued on Jan. 27, 1970 to John R. Anderson and George S. Somekh, which is incorporated by reference herein, describes a process for the separation of aromatic hydrocarbons utilizing two extraction steps to provide an extract comprising the aromatic hydrocarbons from the original mixed feed dissolved in a so-called secondary solvent, the extraction medium in the second step. This solution or secondary extract is then subjected to distillation to separate the aromatic hydrocarbons from the solvent, the aromatics being subjected to further distillation to recover specific aromatics and the extraction solvents being recycled.

With the advent of the benzene-toluene-C₈ aromatics fraction (known and hereinafter referred to as BTX) as the principal raw material in the manufacture of petrochemicals, outstripping ethylene in this regard, and the increased demand for aromatics as a component in gasoline to increase its octane rating and thus reduce or eliminate the need for lead, which has been under fire as a pollutant, aromatics processes availed of in the past have come under close scrutiny with an eye toward improving process economics, which can be translated into, among other things, the use of less apparatus and decreased heat requirements.

Methods, other than that of U.S. Pat. No. 3,492,365 described above, have been used or suggested for aromatics separation; however, many require at least three conventional distillation columns containing a high number of equilibrium stages together with condensers and a high amount of reboiler heat duty to separate benzene, toluene, and the C₈ aromatics, not to mention the separation of solvents and reflux.

SUMMARY OF THE INVENTION

An object of this invention, therefore, is to provide a process for the separation of aromatic hydrocarbons from a mixed hydrocarbon feedstock whereby high purity and high recovery of aromatics are achieved while reducing the amount of apparatus and the external heating requirements.

3

Other objects and advantages will become apparent hereinafter.

According to the present invention, aromatic hydrocarbons are effectively separated from mixed hydrocarbon feedstocks containing aliphatic and aromatic hydrocarbons, said aromatic hydrocarbons being comprised of benzene, toluene, and C_8 aromatics by a continuous process comprising the following steps:

(a) Contacting the feedstock with a primary solvent and a secondary solvent in a primary extraction zone at a temperature in the range of about 50° C. to about 150° C. and a pressure in the range of about atmospheric pressure to about 200 p.s.i.a. wherein the primary solvent is a water-soluble organic solvent, which has a higher boiling point than and is non-azeotropic with the feedstock, and the secondary solvent is selected from the group consisting of paraffinic and naphthenic hydrocarbons and mixtures thereof, said hydrocarbons having higher boiling points than and being non-azeotropic with the feedstock, and wherein the primary solvent is maintained in sufficient amount to extract essentially all of the aromatic hydrocarbons from the feedstock and the secondary solvent is maintained in sufficient amount to act as a reflux for the feedstock;

(b) Withdrawing from the primary extraction zone primary extract comprising aromatic hydrocarbons and primary solvent and raffinate comprising aliphatic hydrocarbons and secondary solvent;

(c) Contacting said primary extract with the secondary solvent in a secondary extraction zone wherein the temperature and pressure are in the same range as in step (a) and the secondary solvent is maintained in sufficient amount to extract essentially all of the aromatic hydrocarbons from the primary extract;

(d) Withdrawing from the secondary extraction zone primary solvent and secondary extract comprising aromatic hydrocarbons and secondary solvent;

(e) Subjecting the raffinate to distillation in a raffinate distillation zone whereby the aliphatic hydrocarbons are separated from the secondary solvent;

(f) Withdrawing the secondary solvent from the raffinate distillation zone and recycling said secondary solvent to at least one of the extraction zones;

(g) Recycling the primary solvent withdrawn from the secondary extraction zone to the primary extraction zone;

(h) Subjecting the secondary extract to distillation in an aromatics distillation zone having a maximum temperature of 225° C., the temperature gradient being such throughout the zone that about 90 to 99 percent by weight of the benzene and toluene in the extract enters into the vapor phase at the top of the zone; the C_8 aromatics and about 1 to 10 percent by weight of the mixture of benzene and toluene in the extract concentrate in the liquid phase at a point between about the middle of the zone and the top of the zone; and the secondary solvent remains essentially in the liquid phase and enters the bottom of the zone;

(i) Withdrawing the vapor phase mixture of benzene and toluene from the aromatics distillation zone in step (h) and subjecting same to distillation to separate the benzene from the toluene;

(j) Withdrawing the liquid phase C_8 aromatics, benzene, and toluene from the aromatics distillation zone in step (h) and subjecting same to distillation in a side-distillation zone, said side-distillation zone containing about 40 to 60 percent of the number of equilibrium stages contained in the aromatics distillation zone and having a maximum temperature of at least 75° C. less than the maximum temperature of the aromatics distillation zone, and separating the C_8 aromatics from the benzene and toluene;

(k) Recycling the benzene and toluene from step (j) to the aromatics distillation zone; and

(l) Withdrawing the secondary solvent from the aro-

4

omatics distillation zone of step (h) and recycling such secondary solvent to at least one of the extraction zones.

BRIEF DESCRIPTION OF THE DRAWING

The sole figure is a schematic flow diagram of an illustrative embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

As noted above, there is an industrial need for BTX, which is available in high proportion, e.g., greater than 30 percent by weight, in a wide variety of hydrocarbon feedstocks such as reformed gasolines; coke oven light oils; cracked gasolines; and dripolenes, which, after hydrogenation, can contain as much as 70 to 98 percent BTX. These feedstocks also contain both aliphatic and cycloaliphatic hydrocarbons. Since the individual hydrocarbon compounds which make up these feedstocks are well known, they will not be discussed extensively; however, it can be pointed out that the major components of the feedstocks are hydrocarbons with boiling points ranging from 60° C. to 200° C. including straight-chain and branched-chain paraffins and naphthenes, such as n-heptane, isooctane, and methyl cyclohexane, and aromatics such as BTX.

The BTX fraction can include, benzene, toluene, the C_8 aromatics including ortho-xylene, meta-xylene, para-xylene, and ethyl benzene, and C_9 aromatics, which, if present at all, appear in the smallest proportion in relation to the other components.

In addition to feeds containing the BTX fraction, the process described herein can be applied to feeds containing, in the aromatics portion, per se mixtures of benzene and toluene or toluene and C_8 aromatics. This feature will be discussed further below.

The primary solvent is defined above as a water-soluble organic solvent, which has a higher boiling point than and is non-azeotropic with the feedstock. It is also polar. Examples of solvents which may be used in the process of this invention as primary solvents are dipropylene glycol, tripropylene glycol, dibutylene glycol, tributylene glycol, ethylene glycol, diethylene glycol, propylene glycol, butylene glycol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, sulfolane, N-methyl pyrrolidone, triethylene glycol, tetraethylene glycol, ethylene glycol diethyl ether, propylene glycol monoethyl ether, pentaethylene glycol, hexaethylene glycol, and mixtures thereof. The preferred group of solvents are polyalkylene glycols and the preferred solvent is tetraethylene glycol. It should be noted that the feedstock and primary solvent must be selected so that the definition of the primary solvent, set forth above, is satisfied, i.e., with respect to boiling point and azeotropic characteristics.

The secondary solvent is defined above as a solvent selected from the group consisting of paraffinic and naphthenic hydrocarbons and mixtures thereof, said hydrocarbons having higher boiling points than and being non-azeotropic with the feedstock. As for the primary solvent, both the feedstock and secondary solvent must be selected so that the definition of the secondary solvent is satisfied. Examples of secondary solvents which may be used alone or together are n-decane, n-dodecane, 2-methyl decane, 2,2-dimethyl decane, n-hexyl cyclohexane, 2-methyl hexyl cyclohexane, tridecane, n-tetradecane, n-pentadecane, n-hexadecane, n-heptadecane, n-octadecane and n-nonadecane. Generally, a mixture in the form of a fraction wherein the components boil within a particular range is used.

The apparatus used in the process both for extraction and distillation is conventional, e.g., an extraction column of the multistage reciprocating type containing a plurality of perforated plates centrally mounted on a vertical

shaft driven by a motor in an oscillatory manner can be used as well as columns containing pumps with settling zones, sieve trays with upcomers, or even a hollow tube while the distillation can be conducted in a packed or bubble plate fractionating column. Countercurrent flows are utilized in both extraction and distillation columns.

Referring to the drawing:

The feedstock is introduced through line 1 at about the middle tray of primary extractor 2; primary solvent, essentially free of water (trace amounts may be present), is introduced at the top tray of primary extractor 2; and secondary solvent is introduced below the bottom tray of primary extractor 2. The function of the secondary solvent in the primary extractor is to act as a reflux, i.e., to purify the aromatics present in the feedstock.

As stated above, the primary solvent is introduced into and maintained in the primary extractor in sufficient amount to extract essentially all of the aromatic hydrocarbons from the feedstock and the secondary solvent is introduced into and maintained therein in sufficient amount to act as a reflux for the feedstock. Generally, to accomplish the extraction the ratio of primary solvent to feedstock in the primary extractor is in the range of about 6 to about 16 parts by weight of primary solvent to one part by weight of feedstock. This broad range can be expanded upon where non-preferred solvents are used. A broad range of about 8 to about 14 parts by weight of primary solvent to one part by weight of feedstock and a preferred range of about 9 parts to about 11 parts of primary solvent per part of feedstock can be used successfully for the solvent of preference and other like solvents. In final analysis, however, the ratio is selected by the technician based on experience with the particular feedstock and depends in part upon whether high recovery or high purity is being emphasized. The same is true of the secondary solvent, the suggested ratio of primary solvent to secondary solvent in the primary extractor being in the range of about 0.5 part to about 20 parts by weight of primary solvent to one part by weight of secondary solvent and, preferably, about 5 parts to about 15 parts by weight of primary solvent per part of secondary solvent.

The temperature in the primary extractor is in the range of about 50° C. to about 150° C. and is preferably in the range of about 80° C. to about 110° C., especially for the solvent of preference.

The pressure in the primary extractor is in the range of about atmospheric pressure to about 200 pounds per square inch absolute (p.s.i.a.). As is well known in the art, however, one selected pressure is not maintained throughout the extraction zone, but, rather, a high pressure within the stated range is present at the bottom of the zone and a low pressure again within the stated range is present at the top of the zone with an intermediate pressure in the middle of the zone. The pressures in the zone depend on the design of the equipment and the temperature, both of which are adjusted to maintain the pressure within the stated range, which is important if the preferred mode of taking a liquid overhead in the extraction zones is to be achieved.

The raffinate is such a liquid taken overhead. It includes the feed aliphatics, essentially all of the reflux secondary solvent, some entrained primary solvent, and may contain C₉ aromatics in very small proportion. The raffinate leaves the primary extractor via overhead line 3 and passes to heat exchanger 4 where it is heated to about its boiling point and may be partially vaporized if desired thus reducing the heating requirements in the raffinate stripper. In this heated state, the raffinate then passes into raffinate stripper 7 via line 6 where the bulk of the aliphatics along with some C₉ aromatics, if any, are removed as a vapor overhead and pass through condenser 8. A portion of the condensate is returned to the top tray of raffinate stripper 7 as a reflux which aids in purifying the raffinate by knocking down the high boilers.

The secondary solvent (including entrained primary solvent and which may include other high boiling aliphatics from the feed) is removed as bottoms and passes through line 9 where part is diverted through reboiler 11 and returns to raffinate stripper 7 below the bottom tray as a vapor to provide most of the heating requirement. The balance of the secondary solvent proceeds via line 9 to heat exchanger 4 where it is cooled to the extraction temperature.

The secondary solvent continues via line 12 to a point below the bottom tray of the primary extractor.

The primary extract, which includes the feed aromatics, the bulk of the primary solvent, a small amount of secondary solvent entrained in the primary solvent, and possibly some high boiling aliphatics, passes as bottoms from primary extractor 2 through line 13 to the top of secondary extractor 14.

Initially, secondary solvent is fed into secondary extractor 14 at the bottom from a reservoir to provide secondary solvent in sufficient amount to extract essentially all of the aromatic hydrocarbons from the primary extract. Generally, the ratio of secondary solvent to primary solvent is in the range of about 0.1 part to about 5 parts by weight of secondary solvent per part by weight of primary solvent and, preferably, about 0.3 part to about 0.7 part by weight of secondary solvent for each part by weight of primary solvent. These ratios are especially relevant for the solvent of preference or like solvents; however, although such ratios may be used for other solvents, it is suggested that the technician select ratios based on experience with particular feedstocks as mentioned for the other ratios above. The same reservoir is used to provide make-up secondary solvent to maintain the described ratio in the secondary extractor. After the cycle has started up, however, the bulk of the secondary solvent is that which is recycled from the distillation zones.

The temperature and pressure in the secondary extractor is kept within the same range as that described for the primary extractor.

The primary solvent essentially free of aromatics, with the small amount of dissolved and entrained secondary solvent becomes the bottoms of the secondary extractor and returns to the top of the primary extractor via line 16. The primary solvent thus avoids high distillation temperatures which lead to its degradation.

The feed aromatics extracted from the primary extract together with the bulk of the secondary solvent (including about one and a half percent dissolved and entrained primary solvent) make up the secondary extract, which passes as a liquid overhead via line 17. A portion of the secondary extract may be diverted from line 17 in accordance with the improvement described in the application of G. R. Atwood, Ser. No. 146,952, filed on May 26, 1971, for an Improvement in a Process for the Separation of Aromatic Hydrocarbons from a Mixed Hydrocarbon Feedstock, and returned to primary extractor 2 to provide the reflux requirement, i.e., the amount of secondary extract returned to the primary extractor is sufficient to provide the secondary solvent required to act as a reflux for the feedstock as discussed above. The balance of the secondary extract continues via line 17 to heat exchanger 18 where it is heated to its boiling point and may be partially vaporized and then passes into about the middle of aromatics stripper 21 through line 19.

The temperature at the top of aromatics stripper 21 is sufficient to vaporize benzene and toluene while the temperature at the bottom of the stripper is not permitted to exceed 225° C. in order to avoid degradation of primary solvent entrained in the secondary solvent. Since the highest temperatures are at the bottom of the stripper this means that the temperature in the distillation zone is not permitted to exceed 225° C. The temperature of reboiler 24 is maintained at 225° C. in order to maintain the high temperature required in stripper 21.

Raffinate stripper 7 and reboiler 11 follow the same temperature requirement as the aromatics stripper and its attendant reboiler. It will be seen later that the other reboilers used in the process require much lower temperatures thus saving a great deal of reboiler heat duty. Also temperatures at the bottom of the other columns used in this process are a good deal lower than strippers 21 and 7.

Atmospheric pressure is generally used in all of the distillation columns, but other pressures, both super-atmospheric and subatmospheric, can be used.

As stated heretofore, the secondary extract passes as a liquid through line 19 into about the middle of aromatics stripper 21. From this point, the secondary solvent proceeds downward in the stripper to line 23.

Aromatics stripper 21 performs three functions in the instant process. The top third of the column separates the benzene-toluene from the C_8 and higher aromatics; the middle third essentially removes the last traces of secondary solvent from the C_8 and higher aromatics; and the bottom third separates essentially the last traces of C_8 and higher aromatics from the secondary solvent.

Stripper 21 performs its functions by virtue of a temperature gradient in the column ranging from the stated maximum temperature to the temperature necessary for the vaporization of benzene and toluene. Through this temperature gradient, a high concentration of liquid C_8 aromatics also builds up in the upper half of the column as discussed below and the secondary solvent passes as bottoms.

The benzene-toluene product is carried overhead as a vapor to avoid revaporization and passes through line 25. A portion of the vapor is diverted through condenser 22 and is returned as a condensate to the top tray of aromatics stripper 21 to provide reflux.

The ratio of the amount of product returned as reflux to the amount of product recovered from the distillation column is known as the reflux ratio of the distillation column. It is advantageous to have a low reflux ratio since less heat is then needed to vaporize the product in the column. The reflux ratio in stripper 21, generally is in the range of 1.5 to 2.5 in the instant process, but varies according to the amount of aromatics in the feed, e.g., the lower the aromatics content of the feed the higher the ratio.

A liquid draw-off, high in C_8 aromatics (and possibly containing C_9 aromatics), but essentially free of secondary solvent, is generally removed at a location about halfway between the feed point (entry of line 19) and the top stage of stripper 21 and passes through line 26 to side-stripper 27. The side-stripper can also be referred to as a side-distillation zone.

The liquid draw-off also contains a small portion of benzene and toluene. Generally, about 90 to 99 percent by weight of the benzene-toluene in the secondary extract goes into the vapor phase and is carried overhead and about 1 to 10 percent by weight of the benzene-toluene in the secondary extract becomes a part of the liquid draw-off. The location of the draw-off is determined by the point at which the C_8 (and C_9) aromatics are present as a liquid in highest concentration with respect to the rest of the column. This point is usually approximated by the technician based on an analysis of the components of the secondary extract in the column and their location with respect to the column.

The liquid C_8 (and C_9) aromatics pass down the column 26 to the top stage of side-stripper 27 which contains about 40 to 60 percent of the number of equilibrium stages contained in the aromatics distillation zone and does not need condenser apparatus.

The liquid C_8 (and C_9) aromatics pass down the column and are taken off as bottoms through line 28 where a portion is diverted into reboiler 32 and returns to a point below the bottom tray of side-stripper 27 to provide most of the side-stripper's heating requirements and assist in

purification of the C_8 (and C_9) aromatics in the side-stripper. The bottoms can be further distilled to separate the C_8 (and C_9) aromatics, if desired.

The temperature of reboiler 32 and also the maximum temperature of stripper 27 is at least 75° C. less than the temperature of reboiler 24. Consequently, there is a great saving in reboiler heat duty in the substitution of a side-stripper for a distillation column similar to stripper 21. Further, the condensers associated with strippers such as 21 and 36 are not needed here since reflux is provided by the liquid draw-off itself entering side-stripper 27 through line 26. The side-stripper strips essentially the last trace of benzene and toluene from the C_8 (and C_9) aromatics and, in so doing, generates some of the vapor needed to provide heat in stripper 21. This, of course, is a saving of reboiler heat duty in stripper 21. This generated vapor which is made up of benzene and toluene passes overhead from side-stripper 27 through line 29 and into stripper 21 at a point just above the liquid draw-off.

The secondary solvent, which still includes some dissolved and entrained primary solvent, passes as bottoms from stripper 21 via line 23 where a portion of it is directed into reboiler 24 and returns as a vapor to a point below the bottom tray of stripper 21 to provide most of its heating requirement while the balance of the secondary solvent passes through heat exchanger 18 where it is cooled to the extraction temperature and continues through line 38 until it reenters the bottom of secondary extractor 14. As stated above, make-up secondary solvent is introduced at this point, if needed, to maintain the proper ratio.

The undiverted benzene-toluene vapor passes through line 25 to the middle of benzene-toluene fractionator 36 where the benzene is carried overhead through condenser 37. A portion of the condensate is returned to the top stage of fractionator 36 as a reflux and the balance of the liquid benzene is collected as high purity product. The toluene passes as bottoms through line 38 where a portion of it is diverted into reboiler 39 and returns to a point below the bottom tray of fractionator 36 to provide most of the fractionator's heating requirement and assist in the purification of the benzene. As for the side-stripper, the reboiler (maximum) temperature is at least 75° C. less than the reboiler (maximum) temperature of stripper 21, a considerable saving of reboiler heat duty.

A variation of the described process is a case where either benzene, toluene, or the C_8 aromatics are not present in the initial feed. In this case, stripper 21 is operated to take the low boiler as a vapor overhead and the liquid draw-off to side-stripper 27 is mainly the high boiler. Stripper 36 is not needed in this variation; however, the basic process remains essentially the same.

The following examples illustrate the invention:

Example 1

The process is carried out in a continuous manner using the system illustrated in the drawing and as heretofore described.

Tetraethylene glycol is employed as the primary solvent and an aliphatic fraction boiling in the range of 204° C. to 257° C. and containing in part dodecane is employed as the secondary solvent.

The feedstock has the following composition:

Component:	Percent by volume at 25° C.
Benzene	20.0
Toluene	25.0
C_8 aromatics	30.0
C_9 aromatics	5.0
Aliphatics	20.0

100.0

The drums containing primary solvent and secondary solvent are maintained at about 110° C. so that the solvents will enter the extraction columns at about 100° C. The primary extract is a twenty-eight stage mixer-settler thermostated at 100° C. The primary solvent, feedstock, and secondary solvent are fed into the primary extractor at the first stage, tenth stage, and below the twenty-eighth stage, respectively.

The primary extract then passes to the first stage at the top of the secondary extractor where it enters at a temperature of about 100° C. This secondary extractor is identical to the primary extractor in all respects except that it has only eighteen stages. The secondary solvent also enters the secondary extractor at about 100° C. at a point below the eighteenth stage.

The primary raffinate passes to the raffinate stripper, which is made of glass and has a section packed with stainless steel packing.

The aromatics-laden secondary solvent is withdrawn from the first stage of the secondary extractor and passes to the aromatics stripper, which is made of glass and has a section packed with extruded stainless steel packing.

Atmospheric pressure is maintained in each of the columns and a maximum operating temperature of 110° C. is maintained in the extractors.

The ratio of primary solvent to feedstock in the primary extractor is maintained at 10:1 (by weight); the ratio of primary solvent to secondary solvent in the primary extractor is maintained at 10:1 (by weight); and the ratio of secondary solvent to primary solvent in the secondary extractor is maintained at 0.48:1 (by weight).

The reboiler temperature is 225° C. in the aromatics and raffinate strippers and is 146° C. and 130° C. in the side-stripper and benzene-toluene fractionator, respectively. These temperatures represent the bottoms and maximum temperatures in the respective strippers.

The number of equilibrium stages and the reflux ratios are as follows:

	Number of equilibrium stages	Reflux ratio
Aromatics stripper.....	20	2.0
Raffinate stripper.....	15	1.0
Side-stripper.....	11	2.3
Benzene-toluene fractionator.....	30	3.0

The side-stripper is of smaller diameter than the other columns.

The liquid stream from the aromatics stripper to the side-stripper is taken off at a point halfway between the point at which the feed enters the aromatics stripper and the top stage of the aromatics stripper. This point is selected on the basis of an analysis of the point of maximum liquid concentration in the aromatic stripper.

The benzene-toluene vapor passes overhead from the aromatics stripper to the benzene-toluene stripper.

Analysis of products is by vapor liquid chromatography except for benzene which is analyzed by freezing point determination using the method of ASTM No. D-1016-55.

The recoveries, in percent by weight, for benzene, toluene, and the C₈ aromatics are 99.9, 99.9, and 96+, respectively, and the purity for the same feed components is 99.8+.

Example 2

Example 1 is repeated except that the system is revised to substitute a column with condenser similar to the aromatics stripper for the side-stripper. The aromatics stripper is then used as the benzene stripper, the new column is used as the toluene stripper, and the benzene-toluene fractionator becomes the C₈ aromatics stripper. The reboiler

temperature in each is 225° C. This temperature represents the bottoms and maximum temperature in the stripper.

The number of equilibrium stages and the reflux ratios for the strippers are as follows:

	Number of equilibrium stages	Reflux ratio
Benzene stripper.....	45	12
Toluene stripper.....	40	10
C ₈ + aromatics stripper.....	20	3.5
Raffinate stripper.....	15	1.0

The recovery and purity are the same as in Example 1.

It is apparent from the foregoing that more apparatus and heat are necessary to accomplish the same result in this example as in Example 1.

What is claimed is:

1. A continuous process for separating aromatic hydrocarbons from mixed hydrocarbon feedstock containing aliphatic and aromatic hydrocarbons, said aromatic hydrocarbons being comprised of benzene, toluene, and C₈ aromatics, comprising the following steps:

- contacting the feedstock with a primary solvent and a secondary solvent in a primary extraction zone at a temperature in the range of about 50° C. to about 150° C. and a pressure in the range of about atmospheric pressure to about 200 p.s.i.a. wherein the primary solvent is a water-soluble organic solvent, which has a higher boiling point than and is non-azeotropic with the feedstock, and the secondary solvent is selected from the group consisting of paraffinic and naphthenic hydrocarbons and mixtures thereof, said hydrocarbons having higher boiling points than and being non-azeotropic with the feedstock, and wherein the primary solvent is maintained in sufficient amount to extract essentially all of the aromatic hydrocarbons from the feedstock and the secondary solvent is maintained in sufficient amount to act as a reflux for the feedstock;
- withdrawing from the primary extraction zone primary extract comprising aromatic hydrocarbons and primary solvent and raffinate comprising aliphatic hydrocarbons and secondary solvent;
- contacting said primary extract with the secondary solvent in a secondary extraction zone wherein the temperature and pressure are in the same range as in step (a) and the secondary solvent is maintained in sufficient amount to extract essentially all of the aromatic hydrocarbons from the primary extract;
- withdrawing from the secondary extraction zone primary solvent and secondary extract comprising aromatic hydrocarbons and secondary solvent;
- subjecting the raffinate to distillation in a raffinate distillation zone whereby the aliphatic hydrocarbons are separated from the secondary solvent;
- withdrawing the secondary solvent from the raffinate distillation zone and recycling said secondary solvent to at least one of the extraction zones;
- recycling the primary solvent withdrawn from the secondary extraction zone to the primary extraction zone;
- subjecting the secondary extract to distillation in an aromatics distillation zone having a maximum temperature of 225° C., the temperature gradient being such throughout the zone that about 90 to 99 percent by weight of the benzene and toluene in the extract enters into the vapor phase at the top of the zone; the C₈ aromatics and about 1 to 10 percent by weight of the benzene and toluene in the extract concentrate in the liquid phase at a point between about the middle of the zone and the top of the zone;

and the secondary solvent remains essentially in the liquid phase and enters the bottom of the zone;

- (i) withdrawing the vapor phase mixture of benzene and toluene from the aromatics distillation zone in step (h) and subjecting same to distillation to separate the benzene from the toluene;
- (j) withdrawing the liquid phase C_8 aromatics, benzene, and toluene from the aromatic distillation zone in step (h) and subjecting same to distillation in a side-distillation zone, said side-distillation zone containing about 40 to 60 percent of the number of equilibrium stages contained in the aromatics distillation zone and having a maximum temperature of at least 75°C . less than the maximum temperature of the aromatics distillation zone, and separating the C_8 aromatics from the benzene and toluene;
- (k) recycling the benzene and toluene from step (j) to the aromatics distillation zone; and
- (l) withdrawing the secondary solvent from the aromatics distillation zone of step (h) and recycling such secondary solvent to at least one of the extraction zones.

2. The process of claim 1 wherein the temperature in the extraction zones is in the range of about 80°C . to about 110°C .

3. The process of claim 1 wherein the ratio of primary solvent to feedstock in the primary extraction zone is maintained in the range of about 6 parts to about 16 parts by weight of primary solvent to one part by weight of feedstock; the ratio of primary solvent to secondary solvent in the primary extraction zone is maintained in the range of about 0.5 part to about 20 parts by weight of primary solvent to one part by weight of secondary solvent; and the ratio of secondary solvent to primary solvent in the secondary extraction zone is maintained in the range of about 0.1 to about 5 parts by weight of secondary solvent to one part by weight of primary solvent.

4. The process of claim 2 wherein the ratio of primary solvent to feedstock in the primary extraction zone is maintained in the range of about 9 to about 11 parts by weight of primary solvent to one part by weight of feedstock; the ratio of primary solvent to secondary solvent in the primary extraction zone is maintained in the range of about 5 parts to about 15 parts by weight of primary solvent to one part by weight of secondary solvent; and the ratio of secondary solvent to primary solvent in the secondary extraction zone is maintained in the range of about 0.3 to about 0.7 part by weight of secondary solvent to one part by weight of primary solvent.

5. The process of claim 4 wherein the primary solvent is tetraethylene glycol.

6. A continuous process for separating aromatic hydrocarbons from mixed hydrocarbon feedstock containing aliphatic and aromatic hydrocarbons, said aromatic hydrocarbons being comprised of two members of the group consisting of benzene, toluene, and C_8 aromatics, comprising the following steps:

- (a) contacting the feedstock with a primary solvent and a secondary solvent in a primary extraction zone at a temperature in the range of about 50°C . to about 150°C . and a pressure in the range of about atmospheric pressure to about 200 p.s.i.a. wherein the primary solvent is a water-soluble organic solvent, which has a higher boiling point than and is non-azeotropic with the feedstock, and the secondary solvent is selected from the group consisting of paraffinic and naphthenic hydrocarbons and mixtures thereof, said hydrocarbons having higher boiling points than and being non-azeotropic with the feedstock, and wherein the primary solvent is maintained in sufficient amount to extract essentially all of the aromatic hydrocarbons from the feedstock and the secondary solvent is maintained in sufficient amount to act as a reflux for the feedstock;

- (b) withdrawing from the primary extraction zone primary extract comprising aromatic hydrocarbons and primary solvent and raffinate comprising aliphatic hydrocarbons and secondary solvent;

- (c) contacting said primary extract with the secondary solvent in a secondary extraction zone wherein the temperature and pressure are in the same range as in step (a) and the secondary solvent is maintained in sufficient amount to extract essentially all of the aromatic hydrocarbons from the primary extract;

- (d) withdrawing from the secondary extraction zone primary solvent and secondary extract comprising aromatic hydrocarbons and secondary solvent;

- (e) subjecting the raffinate to distillation in a raffinate distillation zone whereby the aliphatic hydrocarbons are separated from the secondary solvent;

- (f) withdrawing the secondary solvent from the raffinate distillation zone and recycling said secondary solvent to at least one of the extraction zones;

- (g) recycling the primary solvent withdrawn from the secondary extraction zone to the primary extraction zone;

- (h) subjecting the secondary extract to distillation in an aromatics distillation zone having a maximum temperature of 225°C ., the temperature gradient being such throughout the zone that about 90 to 99 percent by weight of the lowest boiling member in the extract enters into the vapor phase at the top of the zone; the highest boiling member and about 1 to 10 percent by weight of the lowest boiling member in the extract concentrate in the liquid phase at a point between about the middle of the zone and the top of the zone; and the secondary solvent remains essentially in the liquid phase and enters the bottom of the zone;

- (i) withdrawing the vapor phase lowest boiling member from the aromatics distillation zone in step (h);

- (j) withdrawing the liquid phase mixture of highest boiling member and lowest boiling member from the aromatics distillation zone in step (h) and subjecting same to distillation in a side-distillation zone, said side-distillation zone containing about 40 to 60 percent of the number of equilibrium stages contained in the aromatics distillation zone and having a maximum temperature of at least 75°C . less than the maximum temperature of the aromatics distillation zone, and separating the highest boiling member from the lowest boiling member;

- (k) recycling the lowest boiling member from step (j) to the aromatics distillation zone; and

- (l) withdrawing the secondary solvent from the aromatics distillation zone of step (h) and recycling such secondary solvent to at least one of the extraction zones.

7. The process of claim 6 wherein the temperature in the extraction zones is in the range of about 80°C . to about 110°C .

8. The process of claim 6 wherein the ratio of primary solvent to feedstock in the primary extraction zone is maintained in the range of about 6 parts to about 16 parts by weight of primary solvent to one part by weight of feedstock; the ratio of primary solvent to secondary solvent in the primary extraction zone is maintained in the range of about 0.5 part to about 20 parts by weight of primary solvent to one part by weight of secondary solvent; and the ratio of secondary solvent to primary solvent in the secondary extraction zone is maintained in the range of about 0.1 to about 5 parts by weight of secondary solvent to one part by weight of primary solvent.

9. The process of claim 7 wherein the ratio of primary solvent to feedstock in the primary extraction zone is maintained in the range of about 9 to about 11 parts by

13

weight of primary solvent to one part by weight of feedstock; the ratio of primary solvent to secondary solvent in the primary extraction zone is maintained in the range of about 5 parts to about 15 parts by weight of primary solvent to one part by weight of secondary solvent; and the ratio of secondary solvent to primary solvent in the secondary extraction zone is maintained in the range of about 0.3 to about 0.7 part by weight of secondary solvent to one part by weight of primary solvent.

10. The process of claim 9 wherein the primary solvent is tetraethylene glycol.

14**References Cited****UNITED STATES PATENTS**

3,492,365	1/1970	Anderson et al. --	260—674 SE
3,402,124	9/1968	Jones -----	203—84
3,494,861	2/1970	Munro -----	203—98
3,554,873	1/1971	Luther et al. -----	203—98
2,309,653	2/1943	Leum et al. -----	203—99

HERBERT LEVINE, Primary Examiner

U.S. Cl. X.R.

208—323; 260—674 SE; 203—39, 84