

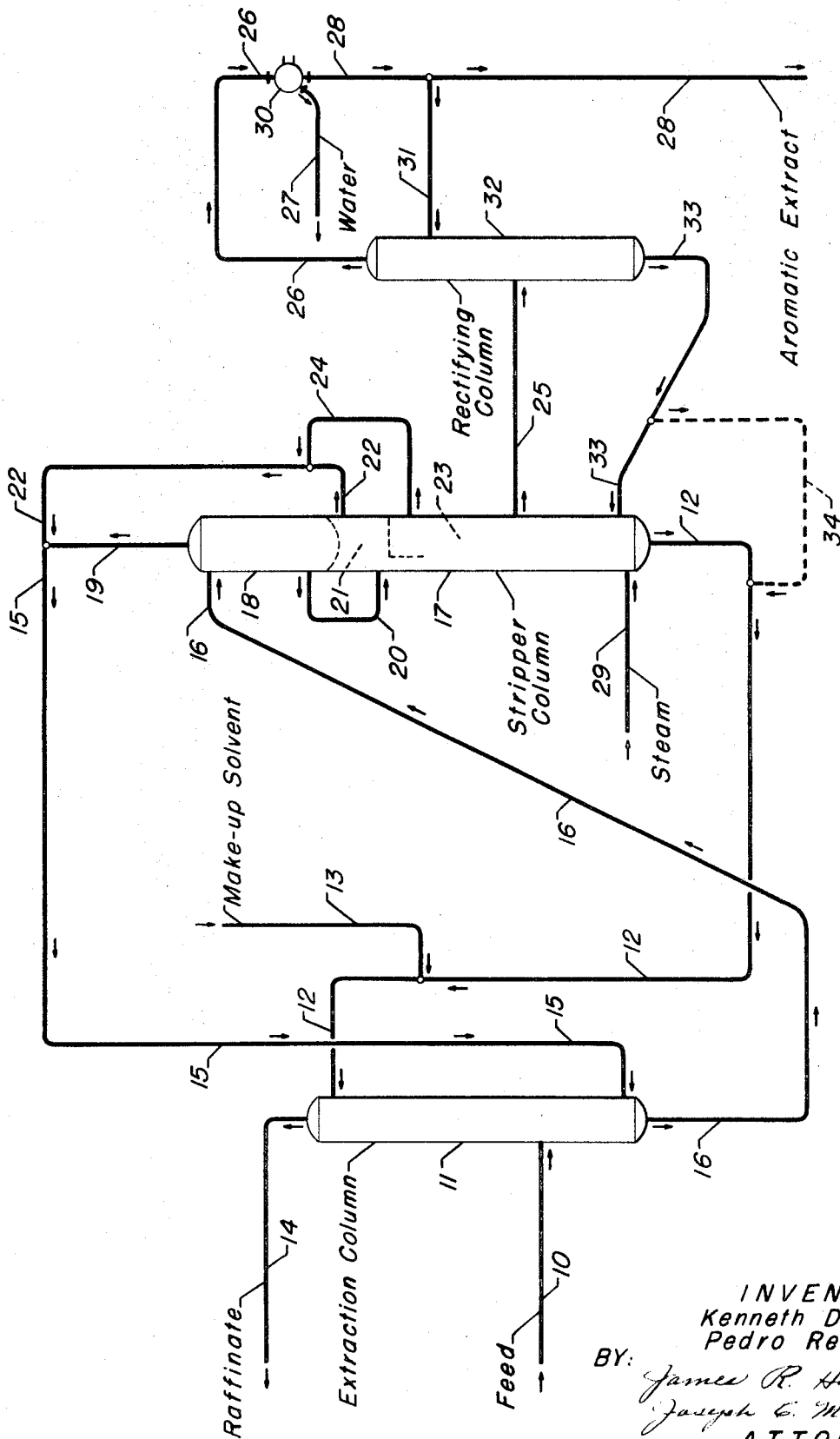
June 29, 1971

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3,590,092

METHOD FOR AROMATIC HYDROCARBON RECOVERY

Filed Sept. 11, 1968



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3,590,092

METHOD FOR AROMATIC HYDROCARBON
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Filed Sept. 11, 1968, Ser. No. 759,103

Int. Cl. C07c 7/10; C10g 21/28

U.S. Cl. 260—674SE

5 Claims

ABSTRACT OF THE DISCLOSURE

Method for extracting and recovering aromatic hydrocarbons, such as benzene, toluene, and xylene, from a suitable feedstock using selective solvent, preferably, of the sulfolane type. The extracted aromatic hydrocarbons are recovered in high yield and high purity using a combination of extractive distillation, aromatic side-cut rectification, and fractionation. The method is uniquely applicable for recovering benzene-type hydrocarbons in extremely high purity from catalytic reformates.

BACKGROUND OF THE INVENTION

This invention relates to the extraction and recovery of aromatic hydrocarbons from feedstocks utilizing solvent extraction. It particularly relates to an improved method for the recovery of aromatic hydrocarbons from the extract phase from such solvent extraction operation wherein sulfolane has been used as the selective solvent.

It is known in the art that a conventional process for the recovery of high purity aromatic hydrocarbons, such as benzene, toluene, and xylene from various feedstocks, such as catalytic reformat, pyrolysis gasoline, etc., is liquid-liquid extraction utilizing a solvent like diethylene-glycol or sulfolane, each of which has high selectivity for the aromatic hydrocarbon components contained in the feedstock. Typically, in the practice of such prior art process, a hydrocarbon feed mixture is contacted in an extraction zone with an aqueous solvent composition which selectively dissolves the aromatic components from the hydrocarbon feedstock, thereby forming a raffinate phase comprising one or more non-aromatic hydrocarbons, and an extract phase comprising solvent having aromatic components dissolved therein. The extract phase is then usually distilled, yielding an overhead distillate containing a portion of the extracted aromatic component, a side-cut fraction comprising aromatic hydrocarbons, and a bottoms fraction comprising lean solvent generally suitable for reuse in the extraction zone. Frequently, to prevent loss of the solvent, the raffinate phase is washed with water in order to remove solvent from the raffinate phase.

Also, not infrequently, the extract phase is subjected to extractive distillation in order to remove a contaminating quantity of non-aromatic hydrocarbons from the extract phase. This extractive distillation operation is normally performed in order to make possible the recovery of nitration grade aromatic hydrocarbons, such as benzene and toluene. In many cases, it is known practice in the prior art to introduce added solvent into the extractive distillation column in order to enhance the separation therein of the non-aromatic hydrocarbon contaminants from the desired aromatic hydrocarbons. The source of the added solvent is either fresh solvent introduced from the outside or a returning portion of the lean solvent from the solvent regeneration facilities or from a solvent recovery column associated with the process.

Therefore, a typical prior art process for the recovery of aromatic hydrocarbons encompasses a solvent extraction step, an extractive distillation step, and a final dis-

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stillation step for the recovery of aromatic hydrocarbons from the solvent phase.

A particularly satisfactory prior art process is exemplified in U.S. Pat. No. 2,730,558 to C. G. Gerhold, hereinafter referred to as the Gerhold patent. The operation described in the Gerhold patent involves a solvent extraction column and a unique stripping column which comprises a flash zone, a vaporizing zone, and a stripping zone operating in such a manner as to substantially remove contaminating quantities of non-aromatic hydrocarbons from the extract phase in order to produce directly high purity aromatic hydrocarbons, such as benzene. This prior art process has, in general, been widely accepted in the industry with the result that there are over fifty of such plants operating throughout the world. However, in almost every instance, the solvent utilized in the Gerhold patent type of processing has been of the glycol type.

More recently, however, the industry has been utilizing sulfolane as its preferred type for the reason that sulfolane has certain desirable advantages over the glycol solvents for the recovery of aromatic hydrocarbons from well known feedstocks. However, it has been commercially difficult to convert the many commercially operating units utilizing the Gerhold patent type of stripping column for operation with the sulfolane type of solvents.

Accordingly, the present invention provides improved means for operating the prior art processes, originally built for glycol type solvents, utilizing the sulfolane type of solvent.

SUMMARY OF THE INVENTION

Therefore, it is an object of this invention to provide a method for the recovery of aromatic hydrocarbons from the extract phase of a solvent extraction operation using sulfolane as the selective solvent.

It is another object of this invention to provide an improved method for the separation and recovery of aromatic hydrocarbons from a suitable feedstock in a facile and economical manner.

Thus, according to one embodiment of this invention, there is provided a method for recovering aromatic hydrocarbons from the extract phase from a solvent extraction zone which comprises the steps of: (a) introducing an extract phase containing solvent having aromatic hydrocarbons dissolved therein, said extract also contaminated with nonaromatic hydrocarbons into a flash zone under conditions sufficient to flash off and remove from said extract phase a portion of said contaminants; (b) passing the remainder of the extract phase from the flash zone into a separate vaporizing zone under conditions sufficient to remove additional contaminants as a vapor stream from said remainder; (c) introducing the extract phase residue having reduced contaminant content and comprising primarily solvent having aromatic hydrocarbons dissolved therein into a stripping zone; (d) withdrawing from said stripping zone an upper vapor fraction comprising the remainder of said contaminants, a side-cut vapor fraction comprising aromatic hydrocarbons, said side-cut vapor fraction also containing a minor quantity of solvent, and withdrawing from the bottom of said stripping zone a liquid fraction comprising lean solvent suitable for reuse in the solvent extraction zone; (e) passing at least a portion of said side-cut vapor fraction into a rectifying zone maintained under rectifying conditions, including the presence of hereinafter specified reflux stream; (f) withdrawing from the overhead of said rectifying zone a vaporous stream comprising light aromatic hydrocarbons and a bottoms fraction comprising heavy aromatic hydrocarbons and solvent contaminants; (g) condensing said overhead vapor stream and any remaining portion of said side-cut vapor fraction and passing part of the resulting condensate into said rectifying zone as reflux thereon; and, (h) recovering the remainder of said condensate.

Another more specific embodiment of this invention includes the method hereinabove wherein said bottoms fraction from the rectifying zone is returned to the stripping zone at a lower portion thereof.

It is noted from the hereinabove brief description of the present invention relative to the prior art that significant flexibility of operation is achieved by the expedient of introducing the side-cut vapor fraction containing the desired aromatic hydrocarbons from the extractive distillation column into a separate rectifying zone. Another feature of the present invention involves the return of the bottoms fraction from the rectifying zone to the extractive distillation or stripping zone. The details of these features will be more fully discussed hereinafter.

The hydrocarbon feedstock which may be separated by the improved method of the present invention comprises many different aromatic-nonaromatic mixtures. Typically, feedstocks applicable to the solvent extraction step include hydrocarbon distillate fractions (usually boiling within or near the gasoline boiling range) of natural gasoline or straight-run petroleum distillates and especially comprise reformed naphthas which are rich in aromatic compounds and which are particularly valuable as a source of mononuclear aromatic hydrocarbons, such as benzene, toluene, and xylene. In many cases, however, with the utilization of sulfolane as the selective solvent, it is difficult, if not impossible, to withdraw from the stripping column an aromatic concentrate of substantially high purity for desired commercial purposes. The side-cut vapor fraction referred to hereinabove frequently is contaminated not only with solvent which must be subsequently removed by other means, but is also contaminated with heavy aromatic hydrocarbons which prevent high purity mononuclear aromatic hydrocarbons from being recovered in high yield. These heavy aromatic hydrocarbons are those included in the broad class of C₁₀, C₁₁, and C₁₂ aromatic hydrocarbons.

In each instance, for suitable feedstock of this invention, it is understood that such feedstock contains non-aromatic hydrocarbons as well as aromatic hydrocarbons; that is, the aromatic extract from the solvent extraction step comprises solvent having aromatic hydrocarbons dissolved therein but this extract is also contaminated with non-aromatic hydrocarbons including paraffins and naphthenes. Typically, the feedstock of the present invention as charged to the extraction step will contain from about 30% to about 60% by weight aromatic hydrocarbons; although, aromatic concentrations as high as 95% by weight may be used in some cases.

Solvent compositions which may be utilized in the practice of the present invention are those selected from the classes which have high selectivity for aromatic hydrocarbons. These aromatic selective solvents generally contain one or more organic compounds containing in their molecule at least one polar group, such as hydroxyl, amino, cyano, carboxyl or nitro radical. In order to be effective, the organic compounds of the solvent composition having the polar radical must have a boiling point substantially greater than the boiling point of water which preferably is included in the solvent composition for enhancing its selectivity, and in general, must also have a boiling point substantially greater than the end boiling point of the aromatic component to be extracted from the hydrocarbon feed mixture.

Organic compounds suitable for use as part of the solvent composition preferably are selected from the group of those organic-containing compounds which include the aliphatic and cyclic alcohols, cyclic monomeric sulfones, the glycols and glycol ethers, as well as the glycol esters and glycol ether esters. The mono- and poly-alkylene glycols in which the alkylene group contains from 2 to 3 carbon atoms, such as ethylene glycol, diethylene glycol, triethylene glycol, and tetraethylene glycol, propylene glycol, dipropylene glycol, and tripropylene glycol, as well as the methy, ethyl, propyl, and butyl ethers of the glycol hydroxyl groups and the acetic acid esters thereof, con-

stitute a satisfactory class of organic solvents useful in admixture with water as the solvent composition for use in the present invention. An illustrative glycol comprises triethylene glycol.

Additionally, excellent results may be obtained utilizing the cyclic monomeric sulfone, such as tetrahydrotrio-*phene-1,1-dioxide*. Still further, an organic compound particularly useful in the practice of this invention is a sulfolane which may be made by condensing a conjugated diolefin with sulfur dioxide and then subjecting the resulting product to hydrogenation, alkylation, hydration and/or other substitution or addition reactions. Typically, organic compounds belonging to the sulfolane class are 2-sulfolene, 2-methylsulfolane, 2,4-dimethylsulfolane, 2,4-dimethyl-4-sulfolane, methyl-3-sulfonyl ether, ethyl-3-sulfonyl sulfide, and others.

The apparatus embodied in the practice of the present invention may be any conventional or convenient type known to those skilled in the art. Also, the operating conditions suitable for the practice of this invention are generally conventional and well known to those skilled in the art, with exception of the precise temperatures and pressures for operating the extractive distillation column and side-cut rectifying column. Thus, from the teachings presented and from a general knowledge of the art, those skilled in the art will be able to choose all of the proper operating conditions to achieve the benefits ascribed to the practice of the present invention.

The amount of solvent utilized should be at least sufficient to dissolve the constituent to be extracted. It may be desirable to use a considerable excess over the theoretical amount of solvent composition necessary, especially when maximum purity and maximum recovery of the aromatic hydrocarbons are desired. Usually, in the extraction step, the solvent to feed ratios will range from about 1:1 to about 20:1 by volume, preferably, from about 5:1 to about 15:1 by volume. A summary of the conditions necessary for the practice of the sulfolane-type of operation may be found in *Petroleum Refiner*, volume 38, No. 9, September 1959, pages 185-192, the entire disclosure of which is incorporated herein by reference.

The solvent extraction step, as previously mentioned, is well known and may utilize apparatus of any type suitable for effecting counter-current contact between two liquid phases, at least partially, but not wholly miscible with each other and wherein the relatively more dense solvent may be brought into intimate contact with the relatively less dense hydrocarbon phase. Thus, the extraction zone which produces the solvent extract which is used as feedstock to the practice of the present invention may comprise a packed column or may contain a series of horizontal plates through which the liquid solvent flows in dispersed form and in counter-current flow relationship to the ascending hydrocarbon stream.

The invention may be more fully understood with reference to the appended drawing.

DESCRIPTION OF THE DRAWING

Referring now to the accompanying drawing, a suitable feedstock, such as a catalytic reformat containing, for example, commercial quantities of benzene and toluene is introduced into the process via line 10. Lean solvent from a source hereinafter specified is introduced into the upper part of extraction column 11 via line 12. When using sulfolane as the solvent, extractor 11 is maintained at an elevated temperature and pressure, say, 250° F. and 75 p.s.i.g., sufficient to maintain the solvent and feedstock in liquid phase. Since the solvent has selectivity for the aromatics in the feed, the aromatic hydrocarbons are preferentially dissolved into the solvent phase. The rejected non-aromatic hydrocarbons are withdrawn from extractor 11 via line 14. By means not shown, the raffinate phase is subsequently water washed to remove small

quantities of dissolved solvent and is thereafter used generally as a blending stock in motor gasoline.

The operating conditions chosen for extractor 11 are sufficient to provide substantial dissolving of the aromatic hydrocarbons into the selective solvent. For purposes of this illustration, the selective solvent is sulfolane. In commercial practice, the efficiency of aromatic hydrocarbon removal is influenced to a considerable extent by the amount of non-aromatic hydrocarbons which are also left behind in the solvent phase. Therefore, a light, primarily non-aromatic hydrocarbon stream commonly called a "back-wash stream" is introduced into the lower portion of extractor 11 via line 15 from a source hereinafter specified wherein it countercurrently contacts the extract phase being withdrawn from extractor 11 via line 16. This back-washing step apparently results in the displacement from the extract phase of heavier non-aromatic contaminants which have been carried into the extract phase. Basically, the object of the backwashing is to displace the heavy feed non-aromatic hydrocarbons from the lighter non-aromatic hydrocarbons which are more easily separated from the aromatic hydrocarbons in the subsequent processing steps. This is conveniently done by introducing a light, primarily non-aromatic hydrocarbon fraction into the lower portion of extractor 11 as previously mentioned.

The extract phase comprising solvent having aromatic hydrocarbons dissolved therein, but also still being contaminated with non-aromatic hydrocarbons is withdrawn from extractor 11 and passed via line 16 into the upper portion of stripper column 17 into flash zone 18.

Stripping column 17 is essentially a distillation zone containing at least two vaporizing sections which function to flash off and vaporize a portion of the non-aromatic hydrocarbon contaminants contained in the extract phase in line 16. A preferred form of the stripping column comprises a vertical column containing three distinct sections; that is, an uppermost primary flashing section 18, a lower or intermediate flashing or vaporizing section 21, and a lowermost stripping section 23 vapor sealed from the upper sections of the column and wherein true stripping of the rich solvent is obtained.

The operating conditions in stripping column 17 may be varied widely, but generally the conditions are one of essentially atmospheric pressure; although, in some cases, flash zones 18, 21, and upper portion of 23 may be maintained under vacuum conditions. Therefore, in a broad sense, stripper column 17 utilizing, say, sulfolane as the solvent operates under a pressure from 90 mm. Hg to absolute to 15 p.s.i.g. and a temperature from 200° F. to 500° F.

Returning now to the operation of stripper column 17, the rich solvent phase, as previously mentioned, is introduced into flash zone 18 at essentially atmospheric pressure, e.g., 2 p.s.i.g. and a temperature desirably at 250° F. Under these conditions, a portion of the non-aromatic hydrocarbons is flashed off and removed via line 19. The remainder of the extract phase is now passed via connecting line 20 into vaporizing section 21 wherein another portion of the non-aromatic hydrocarbons is vaporized and removed from the column as a vapor stream via line 22. Finally, the residue of the extract stream now comprising sulfolane solvent having the desired aromatic hydrocarbons dissolved therein, but still containing non-aromatic hydrocarbons is passed into the lowermost stripping section 23 wherein a true stripping operation takes place.

The lowermost section of stripper column 17 is typically maintained at a pressure of from 1 to 10 p.s.i.g., typically about 3 p.s.i.g., and a temperature of from 200° F. to 500° F., typically, about 220° F. at the draw-off point for the remainder of the non-aromatic hydrocarbons via line 24, and typically a pressure of 5 p.s.i.g. and a temperature of 425° F. at the bottom of stripper

column 17. Steam as necessary is introduced into the lowermost portion of stripper zone 23 via line 24.

Operating under these conditions, the remainder of the non-aromatic hydrocarbons, as previously mentioned, is removed via line 24 and combined with the non-aromatic hydrocarbons removed via lines 22 and 19 and then passed via line 15 after condensing by means not shown and introduced into the lower portion of extraction column 11 in the manner previously discussed.

A side-cut vapor fraction is withdrawn via line 25 and passed into rectifying column 32 which is maintained under rectification conditions. Typically, the conditions maintained in rectifying column 32 include a temperature from 200° F. to 250° F. and a pressure from 1 to 10 p.s.i.g. An overhead stream comprising the desired aromatic hydrocarbons, benzene and toluene, is withdrawn via line 26, condensed in condenser-separator 30, and passed out of the system via line 28. Any water condensed and removed in separator 30 is also removed from the system via line 27. A bottoms fraction comprising primarily sulfolane solvent and heavy aromatic hydrocarbons of the C₁₀, C₁₁, and C₁₂ type (if any) is withdrawn via line 33 and in a preferred embodiment of this invention passed into the lower portion of stripper column 17. Alternatively, a portion of the material in line 33 or all of the material in line 33, if desired, may be passed via line 34 into line 12 as lean solvent suitable for reuse in the extraction zone. Therefore, it can be seen that the lean solvent which in the preferred embodiment of this invention is returned to extractor column 11 via line 12 comprises solvent obtained from the bottom of stripper column 17 and from the bottom of rectifying column 32. A portion of the high purity aromatic hydrocarbon stream in line 28 is diverted via line 31 and passed into the upper section of rectifying column 32 as reflux thereon.

Returning now to stripper column 17, a bottoms fraction comprising lean sulfolane solvent suitable for reuse in the extraction zone is withdrawn via line 12 and in a preferred embodiment of this invention is returned to the upper section of extraction zone 11 as lean solvent in the manner previously discussed. Make-up solvent as needed may be introduced into the system via line 13.

PREFERRED EMBODIMENT

From the teachings presented hereinabove, the preferred embodiment of this invention includes a method for recovering monocyclic aromatic hydrocarbons from a feedstock containing aromatic and non-aromatic hydrocarbons which comprises: (a) introducing said feedstock into a solvent extraction zone maintained under conditions including the presence of lean sulfolane solvent sufficient to separate said feedstock into a raffinate phase containing non-aromatic hydrocarbons and an extract phase comprising sulfolane having aromatic hydrocarbons dissolved therein and containing contaminating quantities of non-aromatic hydrocarbons; (b) passing said extract phase into a flash zone maintained under essentially atmospheric pressure conditions sufficient to flash off and remove from said extract phase a portion of said contaminants; (c) introducing the remainder of the extract phase from the flash zone into a separate vaporizing zone maintained under essentially atmospheric pressure sufficient to remove additional quantities of said contaminants from said remainder; (d) introducing sulfolane having aromatic hydrocarbons dissolved therein and having reduced contaminant content into a stripping zone maintained under a pressure from 1 to 10 p.s.i.g. at a temperature from 200° F. to 500° F. sufficient to produce (i) an upper vapor fraction comprising the remainder of said contaminants, (ii) a side-cut vapor fraction comprising aromatic hydrocarbons, but containing a minor quantity of sulfolane, (iii) a bottoms fraction comprising sulfolane suitable for reuse in said extraction zone of step (a); and, (e) passing said side-cut vapor fraction into a rectifying column maintained under con-

ditions sufficient to remove an overhead fraction consisting of aromatic hydrocarbons and a bottoms fraction comprising sulfolane.

A distinctly preferred embodiment of this invention includes the preferred method hereinabove wherein a portion of said upper vapor fraction of step (a) is condensed and passed into said rectifying column as reflux thereon and the bottoms stream of step (e) is introduced into said stripping zone.

The invention claimed:

1. Method for recovering aromatic hydrocarbons from the extract phase of a solvent extraction zone which comprises the steps of:

- (a) introducing an extract phase containing solvent having aromatic hydrocarbons dissolved therein, said extract also contaminated with nonaromatic hydrocarbons, into a flash zone under conditions sufficient to flash off and remove from said extract phase a portion of said contaminants;
- (b) passing the remainder of the extract phase from the flash zone into a separate vaporizing zone under conditions sufficient to remove additional contaminants as a vapor stream from said remainder;
- (c) introducing the extract phase residue having reduced contaminant content and comprising primarily solvent having aromatic hydrocarbons dissolved therein into a stripping zone;
- (d) withdrawing from said stripping zone an upper vapor fraction comprising the remainder of said contaminants, a side-cut vapor fraction comprising aromatic hydrocarbons, said side-cut vapor fraction also containing a minor quantity of solvent, and withdrawing lean solvent from the bottom of said stripping zone;
- (e) passing at least a portion of said side-cut vapor fraction into a rectifying zone and therein separating the same into a light aromatic overhead vapor and a solvent-containing bottoms fraction; and
- (f) supplying to the solvent extraction zone said lean solvent from step (d) and the solvent content of said bottoms fraction from step (e).

2. Method according to claim 1 wherein said bottoms fraction of step (e) is returned to said stripping zone.

3. Method according to claim 1 wherein said solvent comprises sulfolane.

4. Method for recovering monocyclic aromatic hydrocarbons from a feedstock containing aromatic and non-aromatic hydrocarbons which comprises:

- (a) introducing said feedstock into a solvent extraction zone maintained under conditions including the presence of lean sulfolane solvent sufficient to separate said feedstock into a raffinate phase contain-

ing non-aromatic hydrocarbons, and an extract phase comprising sulfolane having aromatic hydrocarbons dissolved therein and containing contaminating quantities of non-aromatic hydrocarbons;

- (b) passing said extract phase into a flash zone maintained under essentially atmospheric pressure conditions sufficient to flash off and remove from said extract phase a portion of said contaminants;
 - (c) introducing the remainder of the extract phase from the flash zone into a separate vaporizing zone maintained under essentially atmospheric pressure sufficient to remove additional quantities of said contaminants from said remainder;
 - (d) introducing sulfolane having aromatic hydrocarbons dissolved therein and having reduced contaminant content into a stripping zone maintained under a pressure from 1 to 10 p.s.i.g., and a temperature from 200° F. to 500° F. sufficient to produce
 - (i) an upper vapor fraction comprising the remainder of said contaminants,
 - (ii) a side-cut vapor fraction comprising aromatic hydrocarbons, but containing a minor quantity of sulfolane, and,
 - (iii) a bottoms fraction comprising sulfolane suitable for reuse in said extraction zone of step (a);
 - (e) passing said side-cut vapor fraction into a rectifying column maintained under conditions sufficient to remove an overhead fraction consisting of aromatic hydrocarbons and a bottoms stream comprising sulfolane;
 - (f) introducing the last-named bottoms stream into the lower portion of said stripping zone; and
 - (g) supplying lean sulfolane solvent from the lower portion of the stripping zone to said solvent extraction zone.
5. Method according to claim 4 wherein a portion of said upper vapor fraction of step (d) is condensed and passed into said rectifying column as reflux thereon.

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U.S. Cl. X.R.

208—321, 325