

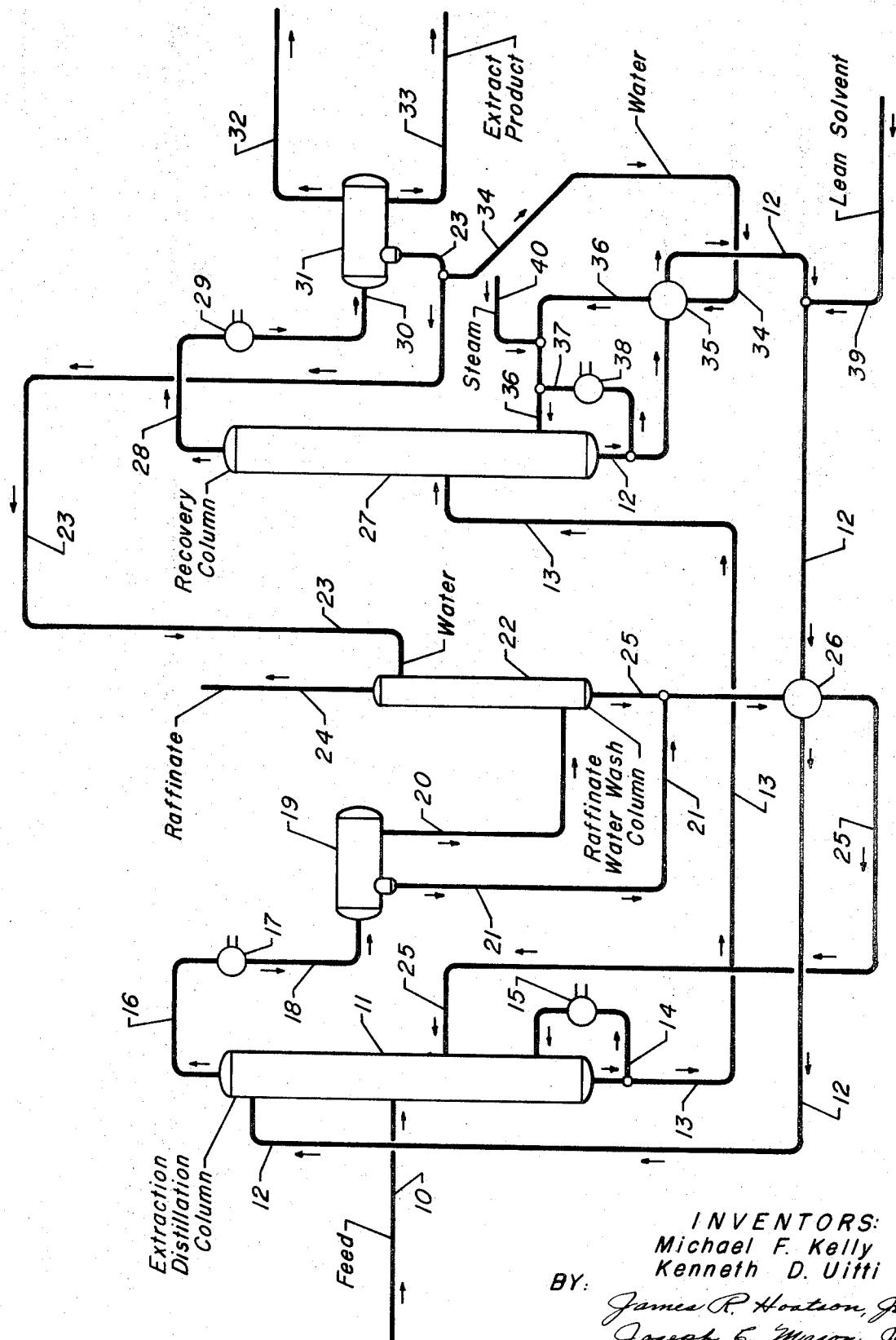
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M. F. KELLY ET AL

**3,551,327**

## **EXTRACTIVE DISTILLATION OF AROMATICS WITH A SULFOLANE SOLVENT**

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3,551,327

## EXTRACTIVE DISTILLATION OF AROMATICS WITH A SULFOLANE SOLVENT

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4 Claims

### ABSTRACT OF THE DISCLOSURE

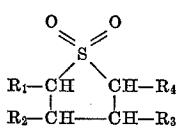
Process for the recovery of aromatic hydrocarbons utilizing the steps of extractive distillation, water washing of the raffinate phase, recovery and reuse of the wash water, and fractionation of the extract phase. Sulfolane is the preferred solvent and benzene is recovered as a preferred product stream.

### BACKGROUND OF THE INVENTION

The present invention relates to the solvent extraction of aromatic hydrocarbons from a hydrocarbon charge stream. More specifically, the present invention relates to the recovery of solvent from the raffinate stream produced in a process which utilizes extractive distillation for the extraction of aromatic hydrocarbons from a hydrocarbon charge stream. More specifically, the present invention relates to an improved process for the recovery of solvent from the raffinate stream by means of an improved water wash technique.

It is well known in the art that the non-aromatic hydrocarbon raffinate which results from an aromatic hydrocarbon extraction process contains contaminating quantities of solvent and to some extent contaminating quantities of aromatic hydrocarbons. This solvent contaminant must be recovered not only because it may interfere with subsequent raffinate processing or ultimate raffinate use, but also because continual loss of solvent in the raffinate stream is prohibitively expensive. Additionally, the aromatic hydrocarbon contaminant, if any, must be recovered since these aromatic hydrocarbons represent valuable products and should be retained and recovered in as high purity and in as high concentration as economically feasible.

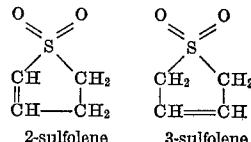
A typical solvent which is utilized in commercial aromatics extraction and which may be recovered in accordance with the practice of this invention is a solvent of the sulfolane - type. The solvent possesses a five membered ring containing one atom of sulfur and four atoms of carbon, with two oxygen atoms bonded to the sulfur atom of the ring. Generically, the sulfolane-type solvents may be indicated as having the following structural formula:



wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are independently selected from the group comprising a hydrogen atom, an alkyl group having from one to ten carbon atoms, an alkoxy radical having from one to eight carbon atoms, and an arylalkyl radical having from one to twelve carbon atoms. Other solvents which may be included within the process

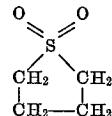
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are the sulfolenes such as 2-sulfolene or 3-sulfolene which have the following structures:



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10 Other typical solvents which have a high selectivity for separating aromatics from non-aromatic hydrocarbons and which may be processed within the scope of the present invention are 2-methylsulfolane, 2,4-dimethylsulfolane, methyl 2-sulfonyl ether, n-aryl-3-sulfonyl amine, 15 2-sulfonyl acetate, diethylene glycol, various polyethylene glycols, dipropylene glycol, various polypropylene glycols, dimethyl sulfoxide, N-methyl pyrrolidone, etc. The specifically preferred solvent chemical which is processed within the scope of the present invention is sulfolane, having the following structural formula:



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Because the typical solvents which are utilized in aromatics extraction are water soluble, it is the practice to extract the solvent from the raffinate stream by contact with an aqueous stream in a subsequent extraction means. 30 The extraction of the solvent from the raffinate with water may be undertaken in any suitable liquid-liquid contacting means as in a tower containing suitable packing, such as Berl Saddles or Raschig Rings, or in a tower containing suitable trays, or in a rotating disc contactor (RDC). The solvent may then be readily recovered from the aqueous solution by distillation.

It has been discovered in the commercial aromatics extraction units that the recovery of solvent sulfolane 40 from the raffinate by extraction with water does not correspond to the recovery which is to be anticipated based upon solubility data, and the assumption of reasonable efficiency of the extractor. The loss of sulfolane in the raffinate product has been found to be from five to eight 45 times as great as anticipated, and this loss is greatly above what is economically desirable.

As previously mentioned, one of the prior art techniques of recovering a solvent, such as sulfolane, from the raffinate has been to extract the solvent with water 50 in a water-wash column. However, operation in the traditional manner utilizes a large volume of water containing relatively small quantities of sulfolane solvent which is difficult to further separate into a concentrated solvent stream.

55 Accordingly, it would be desirable if the solvent could be recovered from the wash water in a facile and economical manner.

### SUMMARY OF THE INVENTION

60 Therefore, it is an object of this invention to provide a process for the extraction and recovery of aromatic hydrocarbons from a feed mixture containing aromatic and non-aromatic hydrocarbons with a sulfolane-type solvent.

65 It is another object of this invention to provide an improved process for the recovery of solvent from the raffinate stream utilizing water washing in a facile and economical manner.

70 It is a still further object of this invention to provide a process for the production of a raffinate product stream from an aromatic hydrocarbon extraction process which is substantially free of solvent contaminant.

Accordingly, the present invention provides a process for the extraction and recovery of aromatic hydrocarbons from a feed mixture containing aromatic and non-aromatic hydrocarbons with a sulfolane-type solvent which comprises the steps of: (a) introducing said feed mixture into an extractive distillation column at a locus intermediate the ends of said column under aromatic hydrocarbon absorbing conditions including the introduction of lean sulfolane-type solvent into the upper end of said column sufficient to countercurrently contact vapors of said feed mixture with said lean solvent thereby selectively absorbing aromatic components into said solvent; (b) withdrawing from the bottom of said column an extract phase comprising sulfolane-type solvent having aromatic hydrocarbons dissolved therein; (c) withdrawing from the top of said column a raffinate phase comprising non-aromatic hydrocarbons contaminated with solvent; (d) introducing said raffinate phase into a wash zone in contact with hereinafter specified water under conditions sufficient to absorb at least a portion of said solvent contaminant into the water; (e) withdrawing from said wash zone a non-aromatic hydrocarbon stream having reduced solvent contaminant content and a rich water stream containing solvent; (f) introducing said rich water stream into said distillation column of Step (a); (g) passing said extract phase into fractionation recovery means under fractionation conditions including the presence of stripping steam sufficient to produce a distillate vapor fraction comprising aromatic hydrocarbons and steam and a bottoms fraction comprising lean sulfolane-type solvent; (h) condensing said distillate vapor fraction thereby producing a product stream comprising aromatic hydrocarbons and a water stream; and, (i) passing at least a portion of said water stream of Step (h) into the wash zone of Step (d) as the specified wash water therein.

Another embodiment of this invention includes the process hereinabove wherein a portion of said water stream of Step (i) is introduced as steam into said fractionation recovery means of Step (g) and said bottoms fraction of Step (g) is introduced into the extractive distillation column of Step (a) as the specified lean solvent therein.

In essence, therefore, it can be seen that the present invention utilizes a water wash technique of the raffinate stream and the recovery of the solvent from the wash water by using the extractive distillation column for this purpose. In addition, the present invention embodies the unique concepts of water reuse in a facile and economical manner.

#### DETAILED DESCRIPTION OF THE INVENTION

As a broad general class, suitable feedstocks for the satisfactory practice of this invention include fluid mixtures having a sufficiently high concentration of aromatic hydrocarbons to economically justify recovery of these aromatic hydrocarbons as a separate product stream. The present invention is particularly applicable to hydrocarbon feed mixtures which contain at least 25% by weight aromatic hydrocarbons. A suitable carbon number range for the feedstock is from about 6 carbon atoms per molecule to about 20 carbon atoms per molecule and, preferably, from about 6 to 10 carbon atoms per molecule. One suitable source of feedstock is the debutanized reactor effluent from a conventional catalytic reforming process unit. Another suitable source of feedstock is the liquid by-product from a pyrolysis gasoline unit which has been hydrotreated to saturate olefins and diolefins thereby producing an aromatic hydrocarbon concentrate suitable for the solvent extraction technique described herein. Typically, the feedstock from a catalytic reforming process contains single ring aromatic hydrocarbons comprising a wide boiling mixture of benzene, toluene, and xylenes. These single ring aromatic hydrocarbons are also mixed with the corresponding paraffins and naphthenes which have been produced from such a catalytic reforming unit.

The preferred solvent which may be utilized in the pres-

ent invention is a solvent of the sulfolane type. As previously mentioned, this solvent is well known to those skilled in the art and typically possesses a five-membered ring containing one atom of sulfur and four atoms of carbon with two oxygen atoms bonded to the sulfur atom of the ring. Since this solvent is an article of commerce and is well known to those versed in the solvent extraction art, greater detail thereof need not be presented at this time.

10 The aromatic selectivity of the solvent can usually be enhanced by the addition of water to the solvent. Preferably, the solvents utilized in the practice of this invention contain small quantities of water in order to increase the selectivity of the overall solvent phase for aromatic hydrocarbons without reducing substantially the solubility of the solvent phase for aromatic hydrocarbons. The presence of water in the solvent composition further provides a relatively volatile material which is distilled from the solvent in the subsequent extractor-stripper following the 15 extraction zone, more fully discussed hereinafter, to vaporize the last traces of non-aromatic hydrocarbons from the solvent stream by steam distillation. Accordingly, the solvent composition of the present invention preferably contains from about 0.1% to about 20% by weight 20 water and, preferably, about 0.5% by weight depending upon the particular solvent utilized and the process conditions at which the extraction zone and the extractor-stripper are operated.

An essential feature of this invention is the utilization 25 of extractive distillation for the separation of aromatic hydrocarbons from non-aromatic hydrocarbons rather than a conventional liquid-liquid extraction technique which is well known to those skilled in the art. According to the concepts of this invention the feed mixture containing aromatic and non-aromatic hydrocarbons is introduced into the distillation column intermediate the ends thereof and typically at about the center of the column. Lean solvent is introduced above the hydrocarbon feed point, but generally below the top of the column. In some cases it is desirable to utilize a non-aromatic hydrocarbon reflux at the top of the column. The extractive distillation column thereby contains a stripping zone below the hydrocarbon feed point, an aromatics absorption zone between the feed point and the lean solvent inlet, including rectification which also takes place above the feed point inlet. The lean solvent contacts the hydrocarbon vapors and selectively dissolves the more soluble components comprising aromatic hydrocarbons. A resulting rich solvent having aromatic hydrocarbons dissolved 35 therein is removed from the bottom of the column. A raffinate vapor stream containing non-aromatic hydrocarbons and solvent is withdrawn from the top of the column and condensed. The condensed liquid is then preferably passed into a separation zone wherein the aqueous phase and the hydrocarbon phase separate from each other. In 40 one embodiment of this invention the aqueous phase is returned at least in part to the extractive distillation column at a locus preferably below the feed locus.

The non-aromatic hydrocarbon phase which has been 45 separated in the separation zone is introduced into a raffinate water wash column preferably at the bottom thereof and a hereinafter discussed aqueous stream is introduced into the top of the column. Suitable operating conditions are maintained in the water wash column so that the aqueous stream and the hydrocarbon phase are in intimate contact sufficient to absorb into the aqueous stream the contaminated quantities of solvent which have remained in the hydrocarbon phase. Accordingly, a rich water stream containing dissolved solvent is withdrawn 50 from the bottom of the water wash column and, as an essential part of this invention, introduced into the extractive distillation column wherein the solvent is separated from the water in a facile and economical manner.

The rich solvent stream which was removed from the 55 bottom of the extractive distillation column is introduced

into an aromatic recovery column which in commercial practice comprises a distillation column. Operating conditions are sufficient in the recovery column to produce an overhead vapor stream comprising aromatic hydrocarbons and water and to produce a bottoms stream which is lean solvent generally suitable for reuse in the process. Operation of the recovery column is also benefited by the use of stripping steam which is injected directly into the lower portion of the recovery column. Therefore, the overhead vapor stream is condensed and passed into separation means wherein the aqueous phase is separated from the aromatic hydrocarbon phase. The aromatic hydrocarbons are then removed from the process as a separate product stream. The aqueous phase is passed at least in part into the upper portion of the raffinate water wash column as the specified wash water therein. The remaining portion of the aqueous phase, if any, is passed into steam generation means usually by indirect heat exchange with the hot lean solvent from the bottom of the recovery column whereby steam is generated and introduced directly into the recovery column as stripping steam in the manner previously discussed.

Typically, the extractive distillation column is maintained under pressures from sub-atmospheric to atmospheric, e.g. up to about 100 p.s.i.g., although, generally, the top of the extractive distillation column is maintained at a pressure from 10 p.s.i.g. to about 20 p.s.i.g. The column is arranged to take only an overhead fraction and a bottoms fraction as separate product streams. Therefore, those skilled in the art from a knowledge of the prior art and from the teachings presented herein are well versed in the operation of the extractive distillation column of this type and, therefore, additional details thereof need not be presented here.

The aromatic recovery column, also commonly called the "solvent recovery column," is operated at relatively low pressures and sufficiently high temperatures to distill the aromatic hydrocarbons overhead as a distillate fraction thereby producing a bottoms fraction comprising lean solvent which is generally suitable for reuse in the extractive distillation zone. Again, precise choice of operating conditions for the aromatic recovery column depends on the feedstock characteristics, including aromatic hydrocarbon content and the composition of the solvent. Typically, when utilizing sulfolane as the solvent the top of the aromatic recovery column is operated at about 100 to 400 mm. Hg absolute. This sub-atmospheric pressure is employed in order to maintain a sufficiently low reboiler temperature to avoid thermal decomposition of the solvent. Preferably, the reboiler temperature should be maintained below about 360° F. when using sulfolane as the solvent.

In summary, therefore, the present invention provides a method for the extraction and recovery of aromatic hydrocarbons which encompasses a novel water handling scheme operating in conjunction with a novel raffinate water wash technique so that not only may high quality aromatic hydrocarbons be produced, but also a non-aromatic hydrocarbon product stream which is sufficiently free of contaminant. It is to be noted that the water circuit is arranged so that contaminating quantities of non-aromatic hydrocarbons are not introduced into the aromatic hydrocarbon recovery column which if permitted would contaminate and lower the purity of the recovered aromatic hydrocarbons. It is also to be noted that the water circuit of the present invention permits maximum recovery of the solvent so that significant economy of operation in terms of minimum solvent loss may be realized.

The invention may be further understood with reference to the appended drawing which is a schematic representation of apparatus for practicing one embodiment of the invention.

## DESCRIPTION OF THE DRAWING

Referring now to the drawing, a hydrocarbon feedstock containing aromatic hydrocarbons and non-aromatic hydrocarbons, such as the desired product from a conventional catalytic reforming unit comprising benzene, toluene, and xylene mixed with corresponding naphthenes and paraffins, enters the system via line 10 and is introduced into extractive distillation column 11 at an intermediate locus between the ends thereof. Aqueous sulfolane as the lean solvent enters extractive distillation column 11 at an upper portion thereof via line 12 and a hereinafter specified aqueous stream containing additional solvent is introduced into extractive distillation column 11 via line 25. Extractive distillation column 11 contains suitable vapor-liquid contacting devices, such as valve trays, perforated plates, and the like. In addition to reboiler 15, column 11 is also equipped with conduit means 16 for removing an overhead vapor stream and a conduit 13 for removing a liquid rich solvent stream.

A distillate vapor stream comprising non-aromatic hydrocarbons and solvent is withdrawn from column 11 via line 16, condensed in condenser 17, and the condensed liquid passed by means of line 18 into separator-receiver 19. Suitable conditions are maintained in separator-receiver 19 including an adequate residence time to permit the separation of the aqueous phase from the hydrocarbon phase. The aqueous phase is withdrawn from the bottom of separator-receiver 19 via line 21 and processed, preferably, in a manner hereinafter discussed. The hydrocarbon phase comprising non-aromatic hydrocarbons and a residual amount of sulfolane solvent is withdrawn from separator-receiver 19 via line 20 and passed into water wash column 22 wherein the hydrocarbon solvent phase is intimately contacted with water from line 23. Raffinate wash column 22 can be a packed column, tray column, rotating disc contactor column, or any other suitable device for maintaining intimate contact between the raffinate hydrocarbon phase and wash water. As previously mentioned, the wash water is introduced into column 22 from line 23 and the substantially solvent-free raffinate product is passed overhead and out of the system via line 24. The water-sulfolane mixture is withdrawn from the bottom of wash column 22 via line 25 and a portion passed through reboiler means, not shown, for the supply of heat necessary to strip and drive the sulfolane into the aqueous phase. The net portion of rich water in line 25 is admixed preferably with the aqueous stream from line 21 and the admixture passed into heat exchanger 26 wherein the material in line 25 is cooled and the lean solvent from a source hereinafter described is heated sufficient for use in the extractive distillation column. The cooled aqueous stream comprising water and sulfolane in line 25 is now introduced into the lower portion of extractive distillation column 11 in the manner previously discussed.

The extract phase comprising sulfolane solvent having dissolved therein aromatic hydrocarbons is withdrawn via line 13. A portion of the withdrawn extract phase is recycled to column 11 via line 14 and reboiler 15. The net rich solvent in line 13 is passed into aromatic recovery column 27 at an intermediate location thereof. Operating conditions are maintained in the recovery column sufficient to separate the aromatic hydrocarbons from the solvent phase. The aromatic hydrocarbons are concentrated as a distillate fraction in admixture with steam and removed as a vapor from column 27 via line 28. The operation of recovery column 27 includes the use of steam stripping on the column in order to remove the final traces of aromatic hydrocarbons from the solvent. Therefore, the lower end of column 27 includes inlet locus for the introduction of steam from a source hereinafter disclosed. The bottoms product from column 27 contains the desired solvent plus water in sufficient amounts such that this bottoms material in line 12 comprises lean solvent 75 suitable for reuse in the extraction zone. A portion of the

bottoms product is returned to column 27 via line 37 and reboiler 38. The remaining portion of the lean solvent in line 12 is introduced into steam generator 35 under conditions sufficient to generate steam therein from a water source hereinafter disclosed. The steam is withdrawn from generator 35 via line 36 and introduced into the lower end of column 27 as the stripping steam therein. Additional steam, as needed, from an extraneous source, may be introduced into the system via line 40. The cooled lean solvent is withdrawn from generator 35 via line 12, admixed with make-up lean solvent from line 39, passed through heat exchanger 36, previously discussed, and into the upper portion of extractive distillation column 11 in the manner previously discussed. By means not shown, a slip stream of approximately 5% to 10% by volume of 15 the total solvent inventory can be passed from line 12 to a solvent clean-up system not shown including a flash or vacuum column in order to remove decomposition products and/or contaminants from the solvent. After solvent clean-up, the solvent can be returned to the system, preferably, through line 39 previously mentioned.

The overhead vapor stream from column 27 in line 28 contains a concentrate of aromatic hydrocarbons and steam. This vapor stream can be admixed with make-up water, as needed, from a source not shown, condensed in condenser 29, and passed via line 30 into accumulator 31. Accumulator 31 is maintained under conditions sufficient to separate the steam condensate from the aromatic hydrocarbons thereby producing an aromatic hydrocarbon product stream which is withdrawn from the system via line 33 and a stream condensate fraction which is withdrawn from accumulator 31 via line 23. Normally gaseous material is withdrawn from the system via line 32, typically through the use of vacuum pumps which are utilized to maintain sub-atmospheric pressure on recovery column 27.

At least a portion of the steam condensate or water in line 23 is passed into the upper end of raffinate water wash column 22 as the specified wash water therein. The remaining water stream, if any, is passed via line 34 into steam generator 35 for the generation of steam therein which is utilized for stripping purposes in column 27, as previously discussed.

It was found by operating the present invention in the manner described that the raffinate in line 24 will contain less than about 10 parts per million of sulfolane solvent and will typically contain from about 1 to 5 parts per million of solvent. It was found that in a typical commercial version of this invention that as much as 25 to 400 pounds per day of sulfolane solvent could be saved over the processing techniques generally practiced by the prior art.

The invention claimed:

1. Process for the extraction and recovery of aromatic hydrocarbons from a feed mixture containing aromatic and non-aromatic hydrocarbons with a sulfolane-type solvent which comprises the steps of:

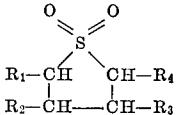
(a) introducing said feed mixture into an extractive distillation column at a locus intermediate the ends of said column under aromatic hydrocarbon absorbing conditions including the introduction of lean sulfolane-type solvent into the upper end of said column sufficient to countercurrently contact vapors of said

feed mixture with said lean solvent, thereby selectively absorbing aromatic components into said solvent;

- (b) withdrawing from the bottom of said column an extract phase comprising sulfolane-type solvent having aromatic hydrocarbons dissolved therein;
- (c) withdrawing from the top of said column a raffinate phase comprising non-aromatic hydrocarbons contaminated with solvent;
- (d) introducing said raffinate phase into a wash zone in contact with hereinafter specified water under conditions sufficient to absorb at least a portion of said solvent contaminant into the water;
- (e) withdrawing from said wash zone a non-aromatic hydrocarbon stream having reduced solvent contaminant content, and a rich water stream containing solvent;
- (f) introducing said rich water stream into said distillation column of Step (a);
- (g) passing said extract phase into fractionation recovery means under fractionation conditions including the presence of stripping stream sufficient to produce a distillate vapor fraction comprising aromatic hydrocarbons and steam, and a bottoms fraction comprising lean sulfolane-type solvent;
- (h) condensing said distillate vapor fraction thereby producing a product stream comprising aromatic hydrocarbons, and a water stream; and
- (i) passing at least a portion of said water stream of Step (h) into the wash zone of Step (d) as the specified wash water therein.

2. Process according to claim 1 wherein a portion of said water stream of Step (i) is introduced as steam into said fractionation recovery means of Step (g), and said bottoms fraction of Step (g) is introduced into the extractive distillation column of Step (a) as the specified lean solvent therein.

3. Process of claim 1 wherein said solvent comprises a sulfolane-type chemical of the general formula:



wherein  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  and  $\text{R}_4$  are independently selected from the group consisting of a hydrogen atom, an alkyl group having from one to ten carbon atoms, an arylalkyl radical having from one to twelve carbon atoms, and an alkoxy radical having from one to eight carbon atoms.

4. Process of claim 3 wherein said solvent comprises sulfolane.

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