COMBINATION OF EXTRACTIVE DISTILLATION AND LIQUID EXTRACTION PROCESS FOR SEPARATION OF A HYDROCARBON FEED MIXTURE

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An extractive distillation zone is used in combination with a liquid phase extraction zone to provide relatively highly aromatic heavy and light extracts and a relatively aromatic-free raffinate stream. The process allows a feed mixture which contains raffinate materials in at least two fractions of aromatics to contact an extractive distillation zone in which solvent passed thereinto dissolves the heavy aromatics from the feed stock. The overhead vapors from the extractive distillation zone are condensed and passed into a liquid phase extraction zone where the light aromatic fraction of the feed stock is extracted and substantially separated from the non-aromatic raffinate components. The raffinate, light extract and heavy extract materials are separately recovered. The process is applicable to most hydrocarbon separations and in particular can be used in the petrochemical industry to separate close boiling aromatic and non-aromatic materials.

16 Claims, 1 Drawing Figure
COMBINATION OF EXTRACTIVE DISTILLATION AND LIQUID EXTRACTION PROCESS FOR SEPARATION OF A HYDROCARBON FEED MIXTURE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The field of art to which this invention pertains is a combination extractive distillation-liquid phase extraction process. More particularly, this process is applicable to the extraction art and in particular to the hydrocarbon separation processes or petrochemical separation processes.

2. Description of the Prior Art

The prior art related to solvent extraction processes and combinations thereof has attempted to solve the problems associated with the separation of non-aromatics from an aromatic containing feed stock which is to be separated into at least two aromatic rich fractions. The old processes have typically utilized such flow schemes as pre-fractionation of the feed stock to remove heavy aromatics from the feed stock followed by passage of the remaining non-aromatics and light aromatics into a liquid phase extraction zone where the final separation of non-aromatics from the light aromatics can be accomplished thereby rendering a heavy aromatic stream, a light aromatic stream and a non-aromatic raffinate stream. Some of the other prior art processes have utilized pre-fractionation processes to separate a feed stock into two boiling range materials with the overhead and bottoms fractions from the fractionator going to separate aromatic separation systems. In this manner the feed stream is separated into two non-aromatic raffinate fractions and two aromatic fractions.

The process of our invention allows a feed stock which contains a broad range of aromatic boiling components and non-aromatic components to be separated into a heavy aromatic stream, a light aromatic stream and a raffinate stream through the use of combination of an extractive distillation column and a liquid phase extraction zone and offers certain advantages when compared to the use of dual liquid phase extraction zones.

A dual liquid phase extraction combination requires a pre-fractionator in addition to the two liquid phase extractors. The process of our invention can essentially eliminate the need for a pre-fractionator and the use of a separate liquid phase extractor and provide a single zone (the extractive distillation zone) in which the combination of liquid phase extraction and pre-fractionation of the heaviest components of the feed stock can be combined in a single operation.

SUMMARY OF THE INVENTION

Our invention is a combination process utilizing an extractive distillation zone which allows a feed stock to be separated into a heavy aromatic containing extract stream and an overhead vapor stream. The overhead vapor stream is condensed and then passed into a liquid phase extractor for separation of the remaining non-aromatic components from the remaining lighter aromatic components. The non-aromatic raffinate material from the liquid phase extractor can be recovered as can be the aromatics present in the light aromatic containing extract stream. This process combination allows recovery of an aromatic free raffinate stream and non-aromatic free light and heavy extract streams.

A broad embodiment of our invention resides in a process for the recovery of two aromatic fractions and non-aromatics from a hydrocarbon feed mixture containing aromatic and non-aromatic hydrocarbons, which process comprises: (a) passing said feed into an extractive distillation zone maintained under extractive distillation conditions including the presence of liquid solvent capable of selectively dissolving a first aromatic fraction of said two fractions to provide a first rich solvent stream containing said first aromatic fraction and a first overhead vapor stream comprising non-aromatic and second aromatic fraction material; (b) recovering said first aromatic fraction from said first rich solvent and passing solvent remaining after said recovery back to said extractive distillation zone of step (a); (c) condensing at least a portion of said first overhead vapor stream to form a condensed feed; (d) passing condensed feed into a liquid phase extraction zone maintained at extraction conditions including the presence of a liquid solvent capable of selectively dissolving the second aromatic fraction material in said condensed feed and a hereinafter defined reflux to provide a second rich solvent stream containing the second aromatic fraction and non-aromatics and a raffinate phase comprising non-aromatic hydrocarbons; (e) passing said second rich solvent stream into a stripping zone maintained under stripping conditions to remove non-aromatics from said second rich solvent to provide a second overhead vapor comprising non-aromatics and a third rich solvent comprising said second aromatic fraction and solvent; (f) condensing second overhead vapor and returning at least a portion thereof to said liquid-liquid extraction zone of step (d) as the above mentioned reflux; (g) recovering said second aromatic fraction from said third rich solvent and passing solvent remaining after said recovery back to said liquid phase extraction zone.

BRIEF DESCRIPTION OF THE DRAWING

The attached drawing illustrates a preferred embodiment of the process flow of our invention.

A feed stream which contains non-aromatic hydrocarbons together with at least two different boiling range aromatic hydrocarbons passes via line 14 into extractive distillation zone 1. Extractive distillation zone 1 is operated at extractive distillation conditions including the downward passage of liquid solvent through line 18 into an upper portion of the extractive distillation zone 1. Heat is supplied to this column by reboiler heat input means 20 by which vapor is caused to countercurrently contact downfalling liquid. The liquid solvent flowing downward selectively dissolves the heaviest aromatic components of the feed stock and the conditions in the bottom of the extractive distillation zone are regulated so that essentially only aromatic materials are dissolved in the solvent. The aromatic rich solvent, referred to as the first rich solvent stream, passes out of the extractive distillation column via line 19 to be passed into a recovery column 6. Recovery column 6 is typically a simple fractionator which contains reboiler means 21 which allows heat to be passed into the recovery column to cause vaporization of the heavy aromatics selectively dissolved in the solvent passing through line 19. Regenerated lean solvent passes out of the bottom of recovery column via line 18. A portion
or all of the solvent recovered by line 18 may be passed into the extractive distillation zone 1. It is contemplated that additional portions of solvent from outside sources might pass into the extractive distillation column through this line. Quantities of solvent may be removed via line 18 for regeneration or other treating and recycled back into the extractive distillation zone 1.

On the upper portion of recovery column 6 there is a condenser 13 which receives the heavy aromatic vapors through line 22, condenses them, and passes vapors and liquid into the overhead receiver 7 which allows liquid material to be removed from the process via line 23. A portion of the liquid material from the overhead receiver 7 may be refluxed via line 24 to the recovery column to maintain top temperatures at a controlled level.

A first overhead vapor stream which comprises essentially all of the non-aromatics and most of the lighter aromatics present in the feed stock which originally passed via line 14 into extractive distillation column 1 is withdrawn from zone 1 via line 15. The vaporous materials passing through line 15 pass into a condenser 9 forming vapor and liquid materials which pass via line 15 into overhead receiver 8. Overhead receiver 8 collects liquids and acts as a surge tank. Part of this liquid can pass as reflux via line 17 for maintaining top temperature control in the extractive distillation zone 1. The remaining condensed first overhead vapor stream passes via line 16 into the liquid phase extractor 2. A portion of the material passing through line 16 may be recovered itself as a product, or other enriched aromatic materials may be interjected as secondary feed stocks into line 16 to be passed into the liquid phase extraction zone 2.

Liquid phase extraction zone 2 is typically a vessel which can allow a liquid-liquid contacting of liquid solvents and liquid feed stocks. Typically the liquid phase extraction zone 2 contains a rotating disc contactor or bubble-deck trays or any other internal devices which are known in the art to promote intimate contacting of the downfalling solvent with upflowing liquid feed stocks. Liquid feed stock passes via line 16 preferably into a lower section of the liquid phase extraction zone 2.

The liquid phase conditions which are maintained in liquid phase extraction zone 2 allow an essentially aromatic and solvent-free raffinate stream, that is a stream comprising mainly non-aromatics, to pass out of the liquid phase extraction zone 2 via line 26. Passing into the uppermost portion of the liquid phase extraction zone 2 via line 25 is a lean solvent. The solvent flows downwardly contacting liquid feed which passes into the extractor 2 via line 16. Also shown passing into the extractor 2 is line 28 which carries a reflux stream which will be defined below. The purpose of the reflux stream is to provide a light non-aromatic component in the lowermost portion of the extraction zone which can cause the heavier molecular weight non-aromatics which boil near the boiling point of the aromatics in the solvent in this portion of the extractor to be removed from the solvent. The lighter molecular weight reflux stream is generally more soluble than the heavier paraffinic and cycloparaffinic materials.

A second rich solvent stream passes out of the liquid phase extraction zone 2 via line 27. This second rich solvent stream contains light aromatics and some non-aromatic materials.

The stripping zone 3 functions to remove the non-aromatic materials from the second rich solvent stream to provide a third rich solvent stream containing essentially no non-aromatic materials. The stripping zone is typically a simple fractionation zone which contains a reboiler heat input means 34 which can be regulated at a temperature which can cause the relatively highly volatile non-aromatics to be stripped from the downfalling second rich solvent stream. The non-aromatic materials stripped from the second rich solvent which passes into the stripper 3 via line 27, pass out of the stripper via line 29 and into a condensing zone such as a heat exchanger cooler 11 to be condensed into liquids. These liquids pass via line 29 into overhead receiver 10 wherein a portion of all of the liquid passed into the receiver can be used as a reflux stream which passes via line 28 into liquid phase extraction zone 2. A portion of the non-aromatic reflux passing through line 28 may be recovered and additional portions, when needed, may pass into the upper sections of the stripping zone 3 to be used as a reflux stream to control the top temperature in that particular zone. The stream passing via line 29 out of the stripping zone 3 is typically referred to as a second overhead vapor stream and contains non-aromatics and some light aromatics.

A third rich solvent comprising the solvent and the remaining essentially non-aromatic-free aromatics passes out of the bottom portion of stripping zone 3 via line 30 and into a recovery zone 4 wherein the light extract aromatics can be flashed or distilled overhead while the relatively aromatic-free solvent can pass as a lean solvent stream via line 25 back into the upper portion of the liquid phase extraction zone 2. A portion of a solvent returned via line 25 may be passed into regeneration operations not shown for the removal of polymers or by-products, and additional quantities of fresh solvent can be added via this line into this portion of the process. The light extract material which comprises essentially a light aromatics fraction of the original feed stream passing through line 14 is recovered as a vapor via line 31 and preferably is cooled via cooler 12 and passed into overhead receiver 5. Line 32 can carry the light aromatic extract materials out of the overhead receiver 5 to be collected as product. Optionally, a portion of the liquid materials recovered in the overhead receiver may be passed via line 33 back into the recovery column 4 as reflux to maintain top temperature control in that column. Heat input means 35 can be used to control the column bottoms temperature.

Not shown on the accompanying drawing are the various control means utilized to effectively maintain levels, pressures and temperatures in the various zones along with those means utilized to induce flow between the various zones and to maintain overall stable operations. It is contemplated that those knowledgeable in the art would be able to design specific process control loops which can be utilized to effectively control temperatures, pressures and flow rates between and among the various zones and pieces of equipment described above.

**DETAILED DESCRIPTION OF THE INVENTION**

The cost of aromatics extraction from a paraffin and naphthene containing feed is tied to the range of car-
carbon numbers in the charge to the aromatics recovery unit by the utility requirements of operating this unit. A more economical operation occurs with a smaller aromatic carbon number range. As an example, when feeding a mixture containing benzene, toluene and xylenes, a more economical operation of the aromatic extraction step would be achieved if the feed was split into a first fraction containing only benzene and toluene and a second fraction containing only toluene and xylenes and these aromatics were then extracted. The range of carbon numbers would in this way be reduced from 3 to 2. However, the utilities cost of this initial splitting of the feed has been found to offset the resulting savings in the aromatic extraction, and the capital cost of the process is increased by the requirement of having two extraction units instead of one.

Our invention eliminates the need for a prefractionator in a process which utilizes the lower utility cost of extracting aromatics from separate fractions having a lower carbon number range than the feed stream. A hydrocarbon feed stock containing non-aromatic hydrocarbons and aromatic hydrocarbons including benzene and C₆ aromatics suitable for separation according to the process of this invention includes fluid mixtures having sufficiently high concentrations of aromatic hydrocarbons to economically justify the recovery of the aromatic hydrocarbons contained therein as a separate product stream. While the present invention is applicable to hydrocarbon feed mixtures which contain at least about 25 percent by weight aromatic hydrocarbons, a particularly preferred feed mixture contains at least 75 percent by weight aromatics. A suitable carbon number range for the hydrocarbon feed mixture is from about six carbon atoms per molecule to about 20 carbon atoms per molecule, and more preferably from about six to about 10 carbon atoms per molecule. A suitable hydrocarbon feed source is the debutanized reactor effluent from a conventional catalytic reforming unit. Another suitable feed stock source 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 techniques hereinafter described. Typically, the feedstock derived from a catalytic reforming process or from pyrolysis gasoline unit will contain single ring aromatic hydrocarbons comprising a wide boiling mixture of benzene, toluene and xylenes. These single ring aromatic hydrocarbons are also mixed with paraffins and naphthenes in the corresponding boiling range. A particularly preferred feed stock is a naphtha fraction, particularly a hydrotreated liquid by-product from a pyrolysis gasoline unit or a debutanized effluent from a catalytic reforming unit containing at least about 75 percent aromatic hydrocarbons by weight. Particularly preferred is a C₆-C₉ naphtha fraction.

Solvents capable of selectively dissolving and extracting aromatic hydrocarbons from a mixture of aromatic and non-aromatic hydrocarbons are well known to those trained in the art. A preferred solvent is a solvent of the sulfolane type. A sulfolane type solvent possesses a 5 member ring containing one atom of sulfur and 4 atoms of carbon with 2 oxygen atoms bonded to the sulfur atom of the ring. Generically, the sulfolane type solvents have a structural formula as noted by formula 1:

\[
\begin{align*}
\text{O} & \quad \text{S} \\
\text{R}_1 & \quad \text{R}_2 \\
\text{H} & \quad \text{O} \\
\text{R}_3 & \quad \text{R}_4 \\
\text{H} & \quad \text{S}
\end{align*}
\]

wherein \( R_1, R_2, R_3 \) and \( R_4 \) are independently selected from the group comprising a hydrogen atom and alkyl group having from one to 10 carbon atoms, an alkoxy radical having from one to eight carbon atoms, and an arylalkyl radical having from one to 12 carbon atoms.

Other solvents analogous to the sulfolane type solvents which may be included within this process are sulfolenes such as 2-sulfolene or 3-sulfolene which have the structure as illustrated in formulas 2 and 3:

\[
\begin{align*}
\text{O} & \quad \text{S} \\
\text{R}_1 & \quad \text{R}_2 \\
\text{H} & \quad \text{O} \\
\text{R}_3 & \quad \text{R}_4 \\
\text{H} & \quad \text{S}
\end{align*}
\]

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-arylsulfonyl amine, 2-sulfonyl acetate, diethylene glycol, various polyethylene glycols, dipropylene glycol, various polypropylene glycols, dimethyl sulfoxide, N-methyl pyrrolidone, etc.

A specifically preferred solvent chemical to be utilized in the present invention is the chemical sulfolane wherein according to formula 1, \( R_1, R_2, R_3 \) and \( R_4 \) each comprise a hydrogen atom. The structural formula of sulfolane is set out in formula 4:

\[
\begin{align*}
\text{O} & \quad \text{S} \\
\text{R}_1 & \quad \text{R}_2 \\
\text{H} & \quad \text{O} \\
\text{R}_3 & \quad \text{R}_4 \\
\text{H} & \quad \text{S}
\end{align*}
\]

Since these aromatic selective solvents are well known to those trained in the art and, in particular, since sulfolane type solvents are articles of commerce widely utilized in the solvent extraction art, greater detail thereon need not be presented herein.

The aromatic selectivity of aromatic selective solvents such as sulfolane can usually be enhanced by the addition of water to the solvent. Preferably the solvent utilized in the practice of this invention contains small quantities of water to increase the selectivity of the overall solvent phase for the aromatic hydrocarbons without reducing in a substantial manner, the solubility of the solvent in the aromatics. Further, the presence of water in the solvent composition provides a relatively volatile material which can be distilled from the solvent to vaporize the last traces of non-aromatic hydrocarbons from the solvent stream by steam distillation. Accordingly, a preferred solvent composition to be utilized in the process of the present invention con-
tains about 0.1 percent to about 20 percent by weight water and more particularly from about 0.5 to about 1 percent by weight, depending upon the particular solvent utilized and the process conditions at which the solvent extraction zone and extractive distillation zone are operated.

The first aromatic or heavy extract stream is typically the heaviest aromatic components of the feed stock passed into the extractive distillation zone. In particular the first aromatic fraction contains very little, if any, non-aromatic components and in most instances will contain less than about a few percent or even down to a few tenths of a weight percent or even less of non-aromatic components. Specifically, the first aromatic stream has an average boiling point which is much higher than the average boiling point of the second or light aromatic stream.

The second aromatic or light extract stream is typically the lightest boiling aromatic components found in the feed stock passed into our process. Specifically, the second aromatic stream has a lower boiling point and lower average molecular weight as compared to the first aromatic stream. This stream in our process shall contain essentially no non-aromatic components. However, in some instances the operating conditions may be unsteady and a few weight percent of non-aromatic or reflux type material may be present in this stream.

Both first and second aromatic streams can contain water which may be present in the system to effect selectivity of the solvent for aromatics. Neither of these aromatic streams should contain solvent if the recovery systems for which they are recovered are operated properly.

The raffinate stream typically contains essentially all of the non-aromatic components passed into our process via the feed stream to the extractive distillation zone. The raffinate stream generally contains small quantities of solvent which can be recovered from the raffinate by water washing. The raffinate may also contain as many as a few percent of aromatic components due to the inability of the liquid phase extraction zone to totally recover and separate aromatic components from the non-aromatic components. Typically, the raffinate stream will contain less than about 1 or 2 wt. percent of aromatic components when it is recovered from a well operated process. The raffinate stream is generally recovered from the upper portion of the liquid phase extraction zone.

The reflux stream is typically a stream comprising aromatic and non-aromatic components which are present in the feed stock passed into our process. Specifically the reflux stream can contain in addition to non-aromatic components some of the light weight aromatic components which typically are found in the second aromatic or light extract stream recovered from the process. The reflux stream components when compared to the raffinate’s non-aromatic components, are generally of lower average molecular weight, and have a lower average boiling point. The reason that the reflux stream contains lighter weight non-aromatic components as compared to the raffinate stream is that the lower molecular weight non-aromatics are more easily dissolved in most polar solvents and therefore end up in the solvent stream removed from the liquid phase extraction zone. Since the heavier weight non-aromatic components may have boiling points close to the aromatics removed from the liquid phase solvent extraction zone, they may not be easily separable. The lighter non-aromatic materials which are easily separated from the aromatics in solvent removed from the extraction zone can be used as reflux stream in the bottom portion of the liquid phase extraction zone to push the heavier non-aromatic paraffin and naphthene components out of the solvent phase and into the raffinate phase to be eventually recovered as raffinate material.

When the feed stock used in our process contains aromatics such as benzene, toluene and the full range of xylene isomers along with non-aromatic paraffins and naphthenes having carbon numbers of anywhere from about five to about nine carbon atoms per molecule, the first aromatic or heavy extract stream would contain essentially all of the xylene isomers, a portion of the toluene and a lesser portion of the benzene. The second aromatic or light extract stream would contain essentially all of the benzene together with some of the toluene and a lesser amount of xylene. The split in toluene between the first and second aromatic streams will be generally dictated by the type of operation taking place in the extractive distillation zone. The raffinate recovered from such a process having the above described feed stock composition would contain essentially all of the non-aromatic paraffins and naphthenes together with a small portion of the aromatic components due to the inability, in some instances, of the extractor to totally separate aromatics from non-aromatics in the liquid phase extraction step. The reflux stream passed back into the liquid phase extraction zone will contain appreciable quantities of aromatics along with lighter paraffins and naphthenes. Particularly the reflux stream could contain such aromatics as benzene, toluene and in some rare instances even some xylene but this is not likely.

The first overhead vapor stream removed from the extractive distillation column via line 15 will contain essentially all of the non-aromatic components of the feed stock which are recovered eventually as raffinate material. The first overhead vapor stream will also contain essentially all of the light aromatics which are recovered eventually from the liquid phase extraction zone. In instances in which the feed stock comprises benzene, toluene and xylene aromatics along with C₆-C₈ paraffins and naphthenes, the first overhead vapor would contain essentially all of the benzene of the feed stock together with a portion of the toluene and all of the paraffins and naphthenes.

The second overhead vapor stream comprises what is referred to in the art as a liquid phase extraction zone reflux stream. Typically, the second overhead vapor stream can be removed from the stripping zone which would receive the second rich solvent from the liquid phase extraction zone. The second overhead vapor stream comprises portions of light aromatic hydrocarbons which will eventually end up as the light aromatic or extract product plus the more volatile naphthenes and paraffins present in the feed stock which is passed into the liquid phase extraction zone. Typically in an instance in which benzene, toluene, xylene aromatics and C₆-C₈ paraffins and naphthenes are present in the feed stock used in our process, the second overhead vapor stream will contain some benzene and toluene together with more volatile paraffins and naphthenes of the raffinate stream. A typical composition of the second overhead vapor stream or the reflux stream will be
about 44 mole percent aromatics and about 56 mole percent paraffins and naphthenes. The aromatics present in the reflux are generally the lightest aromatics present in the feed stock passing into our process; the same holding true for the paraffins and naphthenes present in this stream. The second overhead vapor stream may in some cases contain water vapor which has been stripped from the solvent in the stripping zone. In these instances the solvent is used with water to enhance its selectivity.

An alternative flow that is not shown in the drawing utilizes the same cooling, condensing and collection system for the overhead vapor streams of both the extractive distillation zone and the stripping zone on the liquid-phase extraction zone. Line 29 leaving the extractive stripper would connect with line 15 between the extractive distillation column and cooling means 9. This results in the reflux to the liquid-phase extraction zone entering with the feed.

The first rich solvent stream is the solvent stream withdrawn from the extractive distillation zone and generally essentially pure aromatic hydrocarbons are dissolved in it. Specifically, the aromatic hydrocarbons are the heavier aromatics present in the feed stock passed into this zone. The second rich solvent stream comprises the solvent stream withdrawn from the liquid phase extraction zone and typically contains the lighter aromatic components of the feed stock together with a measureable portion of light and in some cases heavier paraffinic and naphthene materials originating present in the feed stock. The third rich solvent stream withdrawn from the stripping zone is quite similar in composition to the second rich solvent stream except that substantially all of the paraffins and naphthenes present in the second rich solvent stream are removed from that stream with the third rich solvent stream comprising essentially the lighter aromatic streams of the feed stock. This stream may contain small portions of paraffins and naphthenes, but in most instances will be produced as an essentially 100 percent aromatic stream or a solvent-free basis.

Extractive distillation conditions and techniques are generally well known to those trained in the art and vary depending upon the particular feed stock and aromatic selective solvent utilized in the process. Typically in our invention when referring to extractive distillation conditions or an extractive distillation zone, we refer to a zone of operations in which a feed stock containing two fractions of aromatic hydrocarbons together with non-aromatic hydrocarbons are contacted at such conditions, including the presence of liquid solvent selective for the heavier aromatic hydrocarbons, as to cause essentially all of the non-aromatic portions of the feed stock together with a sizeable portion of the aromatic fractions and typically the light aromatic portions of the feed stock to be vaporized, while the liquid solvent selectively dissolves the heavier aromatic components passed into this zone. As can be seen, the extractive distillation conditions or extractive distillation zone allows both a simple fractionation and a liquid phase extraction to take place in a single vessel or zone and in many instances can eliminate the need for separate pre-fractionating facilities to be used in conjunction with a liquid phase extraction zone. Typically, the bottoms fraction will contain less than a few thousand parts per million and preferably less than about 900 ppm. by weight of non-aromatic components. Typical operating conditions in an extractive distillation zone when utilizing a sulfolane solvent include a pressure of anywhere from a few millimeters of mercury up to about 50 psig. or higher, an overhead temperature varying anywhere from 135°F. up to 300°F. or higher and a bottom temperature of about from 170°F. up to about 355°F. or higher. Sulfolane solvent to feed ratios can vary anywhere from about 1:1 to about 2:1, depending, as do the pressure and temperature, on feed composition. Preferred solvent to feed ratios when processing a C10-C18 naphtha cut are from about 2:1 to about 6:1. The important factor to consider in defining extractive distillation conditions is that the feed passing into the extractive distillation column is to be substantially vaporized with the heavier aromatic portion essentially solubilized in the solvent utilized.

The condensed first overhead vapor stream eventually is passed into a liquid phase solvent extraction zone maintained under aromatic hydrocarbon extraction conditions including the presence of a solvent. In a preferred embodiment the solvent is of the same type utilized in the extractive distillation zone which is, preferably, a sulfolane solvent. Provided in the liquid phase extraction zone is an extract phase comprising a solvent having aromatic hydrocarbons and a minor amount of non-aromatic hydrocarbons dissolved therein and a raffinate phase comprising non-aromatic hydrocarbons. Typically, the raffinate material is water washed to remove any of the solvent which may be entrained therein. Preferably, the extraction conditions utilized are regulated to maintain the solvent and hydrocarbons passed into the liquid phase extraction zone in the liquid phase to embody a liquid phase solvent extraction. As in the case of extractive distillation operations, the conditions, apparatus and mode of operation associated with the solvent extraction zone are well known to those trained in the art. For example, see Petroleum Refiner, No. 8 Vol. 38, September, 1959, pages 185–192, the teachings of which are specifically incorporated by reference into this specification.

Also embodied within the solvent extraction zone is the concept of displacing non-aromatic hydrocarbons from the extract phase at the lower end of the solvent extraction zone by utilizing the known technique of a non-aromatic reflux stream at that point. It is preferred that this reflux stream comprise relatively light non-aromatic hydrocarbons and some aromatic hydrocarbons. The exact reflux introduced into the lower section of the solvent extraction zone varies depending upon the degree of non-aromatic hydrocarbon rejection desired in the extraction zone. Preferably, the reflux is at least about 10 percent by volume of the extract phase so as to insure effective displacement of the heavy non-aromatic hydrocarbons from the extract phase into the raffinate phase. According to the process of the present invention, at least a portion, if not all, of the reflux required in a solvent extraction zone is provided by the non-aromatic overhead stream derived from the stripping zone, preferably after condensation and water removal.

The solvent extraction zone is operated under conventional conditions including elevated temperatures and a sufficiently elevated pressure to maintain the solvent, reflux streams and hydrocarbon charge in the liquid phase. When utilizing sulfolane, suitable temperatures are about 80°F. to about 400°F., preferably about 175°F. to about 300°F. and suitable pressures are about
atmospheric to about 400 psig, preferably about 50 to 150 psig. Solvent quantities should be sufficient to dissolve substantially all of the aromatic hydrocarbons present in the solvent extraction zone feed. Preferred are solvent to feed ratios, by volume, of about 2.1 to about 10:1 when utilizing a C₆-C₈ range naphtha cut as feed.

The extract from the liquid phase solvent extraction zone contains aromatic hydrocarbons, solvent and a lesser amount of non-aromatic hydrocarbons, i.e., less than 30-50 mole % on a hydrocarbon basis. It is passed into a stripping zone to remove therefrom essentially all of the non-aromatic hydrocarbons. The stripping zone is maintained under stripping conditions well known to those trained in the art, including moderate pressures and sufficiently high reboiler temperatures in order to vaporize all of the non-aromatic hydrocarbons and, as a result, a portion of the solvent and aromatic hydrocarbons from the bottoms portion of the stripping zone. This is necessary to produce a bottoms fraction stream relatively free of non-aromatic hydrocarbons and containing aromatic hydrocarbons and solvent. The non-aromatics are removed overhead, in admixture with some solvent and aromatics, in many cases, and are passed, usually after condensation and water removal to the hereinbefore described solvent extraction zone to provide at least a portion of specified reflux stream.

While the particular stripping zone utilized is not critical to the practice of the present invention, the process of the present invention is particularly suited to the utilization of the stripping zone contained in the prior art glycol type extraction. (U.S. Pat. No. 2,730,558). However, an extractive type stripper as utilized in conventional, grass roots, sulfolane units is equally suited to the process of the present invention. Such a stripping zone will be maintained under a pressure of atmospheric to about 100 psig, although a top pressure of about 5 psig to about 25 psig is preferred. The reboiler temperature is a function of feed composition and is preferably maintained at a level sufficient to produce a bottoms fraction containing less than 2000 ppm. weight non-aromatics on a hydrocarbon basis. Maximum stripping is accomplished by introducing the extract feed into the upper portion of the stripping zone in a manner well known to those trained in the art.

When utilizing a stripping zone as exemplified in U.S. Pat. No. 2,730,558, the liquid phase solvent extraction zone extract is first passed into a flash zone wherein a portion of the non-aromatics is flashed off. The remaining extract is then passed into a vaporizing section wherein another portion of the non-aromatics are vaporized. Finally, the residue of the extract stream, now comprising sulfolane solvent and aromatics but still containing a minor amount of non-aromatics, is passed to a lowermost stripping section wherein a true stripping operation of the remaining non-aromatics takes place. The bottom of the stripping zone is typically maintained at a temperature of about 200°F. to 300°F. preferably a temperature of about 300°F. to about 425°F. The non-aromatic hydrocarbons recovered from the various sections of the stripping zone are condensed and usually after intermediate water removal, passed as reflux to the solvent extraction zone. If desired, additional sulfolane solvent beyond that contained in the original extract may be added to the upper portion of the stripping section to enhance aromatic recovery therein and for improving non-aromatic rejection by improving the selectivity.

Recovering the light and heavy aromatic extract can be accomplished through the use of recovery zones. Preferably, a recovering zone is a fractionating zone and may typically utilize steam as an input stripping medium to aid in the separation of the aromatic hydrocarbons from the solvent. Typically the recovery zones are maintained under fractionation conditions generally well known to the art such as low pressures and sufficiently high temperatures to distill the respective aromatic hydrocarbons overhead and to provide a relatively hydrocarbon-free extract product stream. The recovery fractionating zone is preferably maintained anywhere from about 100 to about 400 millimeters pressure absolute since subatmospheric pressures must generally be employed to maintain a sufficiently low reboiling temperature to avoid thermal decomposition of the sulfolane solvent.

The individual recovery or fractionating zones in which relatively pure solvent can be recovered can provide lean solvent to be used in the respective liquid phase extraction zone and the extractive distillation zone. In many cases, and are preferred to operate the respective recovery columns independently so that the solvent utilized in the liquid phase extraction zone is maintained within a process loop including the liquid phase extractor, the stripping zone and recovery column for those two zones. Likewise, the recovery column utilized for extractive distillation zone will allow the solvent utilized in the extractive distillation zone to be recovered in relatively pure state from that recovery column. It is contemplated that during normal processing conditions that some of the solvent from either the recovery column connected to the stripping zone or the recovery column connected to the extractive distillation zone may be diverted to the other control loop depending upon the particular operations or factors which would require such diversion. If in a preferred instance sulfolane is used in both the extractive distillation zone and in the liquid phase extraction zone there is no real reason why a lean solvent cannot be removed from either the recovery columns and passed into either the extractive distillation column or the liquid phase extraction zone except for upset which would be caused by varying bottoms temperatures from these individual recovery systems.

Each of the recovery zones may also contain full instrumentation and reflux loops to allow the overhead temperature to be maintained at a given and controlled temperature to maintain stable operations in the zone. Likewise, both the reboiler heat input means to the individual recovery systems may be set up upon control loops which would monitor the bottoms temperature or any other temperature in the columns to maintain it at a steady state to maintain stable operations throughout the system.

We claim as our invention:

1. A process for the recovery of two aromatic fractions and non-aromatics from a hydrocarbon feed mixture containing aromatic and non-aromatic hydrocarbons, which process comprises:
   a. passing said feed into an extractive distillation zone maintained under extractive distillation conditions including the presence of liquid solvent capable of selectively dissolving a first aromatic fraction of said two fractions to provide a first rich solvent
stream containing said first aromatic fraction and a first overhead vapor stream comprising non-aromatic and second aromatic fraction material; b. recovering said first aromatic fraction from said first rich solvent and passing solvent remaining after said recovery back to said extractive distillation zone of step (a); c. condensing at least a portion of said first overhead vapor stream to form a condensed feed; d. passing condensed feed into a liquid phase extraction zone maintained at extraction conditions including the presence of a liquid solvent capable of selectively dissolving the second aromatic fraction material in said condensed feed and a hereinafter defined reflux to provide a second rich solvent stream containing the second aromatic fraction and non-aromatics and a raffinate phase comprising non-aromatic hydrocarbons; e. passing said second rich solvent stream into a stripping zone maintained under stripping conditions to remove non-aromatics from said second rich solvent to provide a second overhead vapor stream comprising non-aromatics and a third rich solvent stream comprising said second aromatic fraction and solvent; f. condensing second overhead vapor and returning at least a portion thereof to said liquid-liquid extraction zone of step (d) as the above mentioned reflux; g. recovering said second aromatic fraction from said third rich solvent and passing solvent remaining after said recovery back to said liquid phase extraction zone.

2. Claim 1 in that said hydrocarbon feed contains aromatics selected from the group consisting of benzene, toluene, xylenes and C₆ aromatics and non-aromatics selected from the group consisting of paraffins and cyclo-paraffins having from about five to about nine carbon atoms per molecule.

3. Claim 2 in that said second aromatic fraction comprises benzene and toluene.

4. Claim 1 in that said hydrocarbon feed contains aromatics selected from the group consisting of benzene, toluene and xylenes and non-aromatics selected from the group consisting of paraffins and cyclo-paraffins having from about five to about nine carbon atoms per molecule.

5. Claim 4 in that said first aromatic fraction comprises toluene and xylenes.

6. Claim 4 in that said second aromatic fraction comprises benzene and toluene.

7. Claim 4 in that said raffinate stream comprises paraffins and cyclo-paraffins having from about five to about nine carbon atoms per molecule.

8. Claim 4 in that said reflux comprises paraffins and cyclo-paraffins having an average boiling point which is lower than the average boiling point of the raffinate stream.

9. Claim 1 in that at least one of said solvents comprises a sulfolane type chemical of the general formula: \[ \text{O} \quad \text{O} \]

wherein R₁, R₂, R₃, and R₄ are independently selected from the group consisting of hydrogen, alkyl groups having from one to about 10 carbon atoms, and an alkoxy radical having from one to about eight carbon atoms.

10. Claim 9 in that at least one of said solvents comprises sulfolane.

11. Claim 9 in that at least one of said solvents comprises a sulfolane selected from the group consisting of 2-sulfolene and 3-sulfolene.

12. A process for the recovery of a heavy aromatic extract comprising toluene and xylene, a light aromatic extract comprising benzene and toluene and a non-aromatic raffinate comprising paraffins and cyclo-paraffins having from about five to about nine carbon atoms per molecule from a hydrocarbon feed stock, which process comprises:

a. passing said feed into an extractive distillation zone maintained under extractive distillation conditions including the presence of a sulfolane solvent to provide a first rich solvent substantially free of non-aromatics and containing toluene and xylene and a first overhead vapor stream comprising benzene, toluene and raffinate components; b. recovering toluene and xylene from said first rich solvent as said heavy extract and passing solvent remaining after said recovery back to said extractive distillation zone of step (a); c. cooling said first overhead vapor stream to form a condensed feed; d. passing condensed feed into a liquid phase extraction zone maintained at extraction conditions including the presence of a sulfolane solvent and a hereinafter defined reflux stream to provide a second rich solvent stream containing benzene and toluene and non-aromatics, and a raffinate phase substantially free of aromatics; e. passing said second rich solvent stream into a stripping zone maintained under stripping conditions to remove non-aromatics from said second rich solvent as a second overhead vapor stream containing said non-aromatics from said second rich solvent and from a third rich solvent substantially free of non-aromatics containing benzene and toluene; f. cooling second overhead vapor and returning at least a portion thereof to said liquid phase extraction zone of step (d) as said reflux stream; g. recovering benzene and toluene from said third rich solvent as said light extract and passing solvent remaining after said recovery back to said liquid phase extraction zone of step (d).

13. Claim 12 in that said solvent utilized in said extractive distillation and liquid-phase extraction zone is the same.


15. Claim 12 in that the average boiling point of said reflux is lower than the average boiling point of said raffinate.

16. Claim 12 in that said first overhead vapor stream from the extractive distillation zone and said second overhead vapor stream from said stripping zone are cooled and collected in a common overhead system and said reflux of step (f) is thereby commingled with the feed to the liquid-phase extraction zone.