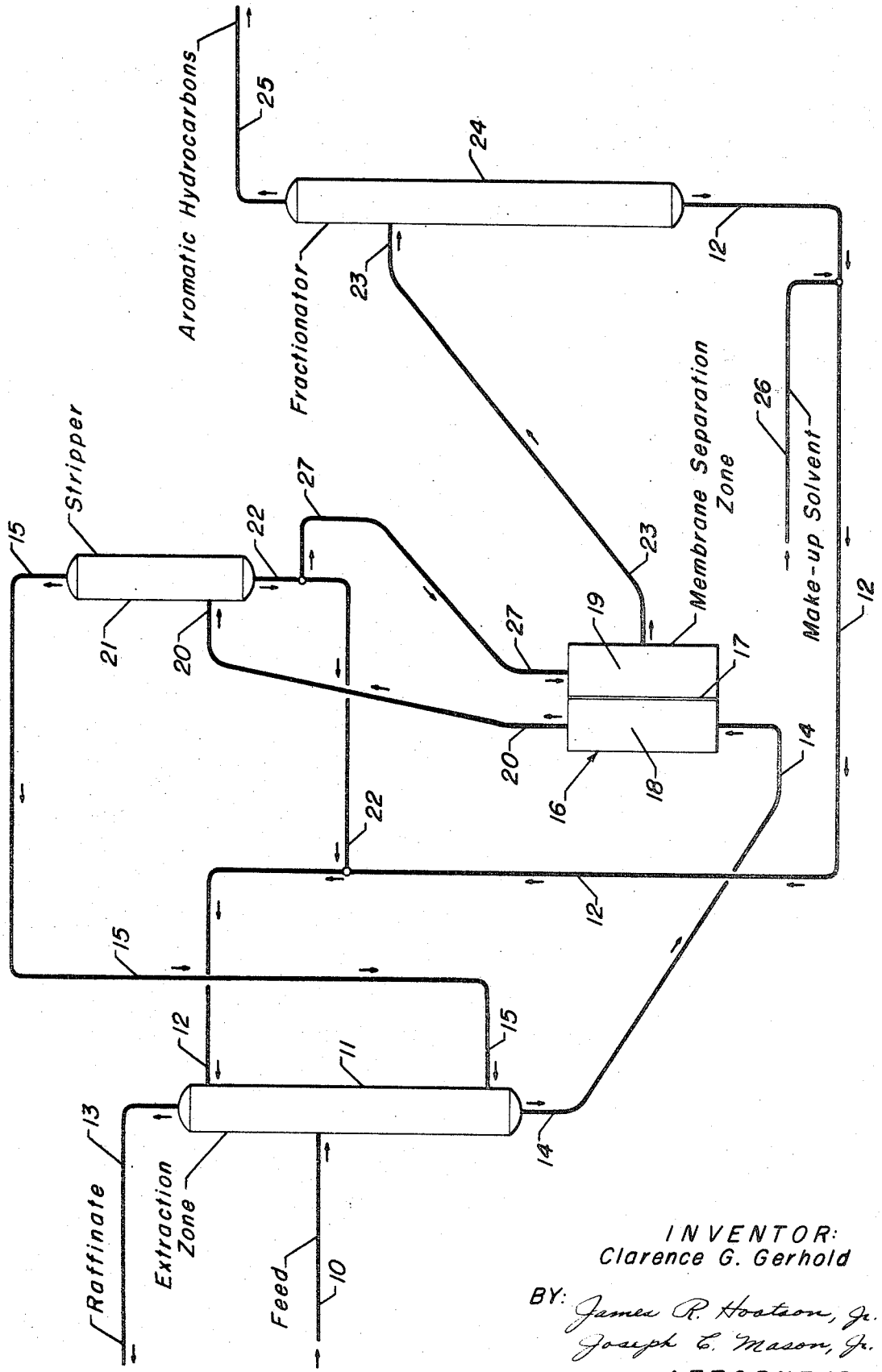
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METHOD FOR THE SOLVENT EXTRACTION OF AROMATIC HYDROCARBONS

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METHOD FOR THE SOLVENT EXTRACTION OF AROMATIC HYDROCARBONS

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ABSTRACT OF THE DISCLOSURE

Process for the recovery of aromatic hydrocarbons using the steps of solvent extraction, dialysis, and fractionation of the extract. Sulfolane is the preferred solvent, and benzene is recovered as a preferred product stream.

BACKGROUND OF THE INVENTION

This invention relates to a separation process. It also relates to a solvent extraction process for the recovery of aromatic hydrocarbons from hydrocarbon mixtures utilizing a selective solvent.

The technique of aromatic hydrocarbon separation by solvent extraction is well known in the prior art. Generally, according to one well known procedure, a mixture of hydrocarbons comprising aromatic and non-aromatic hydrocarbons is introduced into an extraction column at an intermediate point thereof and contacted with a solvent which is selective for aromatic hydrocarbons. The separating conditions maintained in the extraction column are sufficient to produce a raffinate phase comprising substantially all of the non-aromatic hydrocarbons in the feedstock and an extract phase comprising the aromatic components of the feedstock dissolved in the selective solvent. Typically, the non-aromatic hydrocarbon raffinate phase is recovered and utilized in, for example, gasoline blending. The extract phase containing the aromatic hydrocarbons plus contaminating quantities of non-aromatic hydrocarbons is passed subsequently through various separation means for the recovery therefrom of the aromatic hydrocarbons in high concentration and high purity. Lean solvent, generally suitable for reuse in the extraction zone, is also recovered in the process of segregating and recovering the aromatic hydrocarbons.

One feature of the prior art processes is the freeing of the extract phase of substantially all of the non-aromatic hydrocarbons dissolved by or carried by the selective solvent. Usually, this is accomplished by introducing a non-aromatic hydrocarbon reflux stream comprising, for example, naphthenes and paraffins, into the extraction zone at a point intermediate between the hydrocarbon feed introduction point and extract phase withdrawal point. This reflux phase is desirably more volatile in the presence of the selective solvent than any of the aromatic components of the feedstock and, in effect, acts as a displacing agent for the higher boiling non-aromatic hydrocarbons out of the extract phase and into the raffinate stream within the extraction zone.

However, the forced migration of the non-aromatic hydrocarbon components from the extract phase to the raffinate phase is only partially successful since the prior art reflux streams also comprise non-aromatic hydrocarbons having such a high boiling point that these are not easily separable from the aromatic hydrocarbons in the subsequent typical extractive stripping operation. In effect, therefore, the purity of the ultimate aromatic hydrocarbon product stream is dependent to a large extent upon the ability of the extraction zone to separate both the relatively heavy and relatively light non-aromatic hydrocarbon components from the aromatic hydrocarbons. Another feature of the prior art schemes, having significant effect on commercial plants, is the operating costs for the various fractionation columns required subsequent to the extraction zone in order to recover aromatic hydrocarbons in high purity and high concentration.

Normally, the prior art schemes employ what is commonly called an extractive distillation operation which produces a separation between the contaminating non-aromatic hydrocarbons and the aromatic hydrocarbons. This extractive distillation column for commercial plants is enormous in size, expensive to operate, and not entirely successful in making the required separation between non-aromatic and aromatic hydrocarbons which would be most desirable. Therefore, it would be desirable if a scheme could be developed for the separation and recovery of aromatic hydrocarbons in a facile and economical manner while at the same time retaining and/or improving the quality of the various aromatic and non-aromatic product streams which are ultimately recovered in a commercial plant.

SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide a separation process.

It is another object of this invention to provide a solvent extraction process for the recovery of aromatic hydrocarbons from hydrocarbon mixtures.

It is still another object of this invention to provide an improved process for the separation and recovery of aromatic hydrocarbons in high purity via a solvent extraction technique in a facile and economical manner.

Therefore, the present invention provides a process for the extraction and recovery of aromatic hydrocarbons from a feed mixture comprising aromatic and non-aromatic hydrocarbons utilizing a selective solvent which comprises the steps of: (a) introducing said feed mixture into a solvent extraction zone maintained under aromatic hydrocarbon extraction conditions including the presence of said selective solvent sufficient to produce an extract phase comprising said solvent having aromatic hydrocarbons dissolved therein and a raffinate phase comprising non-aromatic hydrocarbons; (b) passing said extract phase into a first cell of a dialysis chamber containing at least two (2) cells separated by a membrane substantially permeable to said aromatic hydrocarbons and substantially impermeable to said solvent; (c) removing solvent from said first cell; and (d) recovering aromatic hydrocarbons from a permeate of a second cell of said dialysis chamber.

In effect, therefore, it can be seen that the essence of the present invention is based on a discovery that a membrane separation zone prior to the aromatic hydrocarbon distillation column permits significant economy of operation by removing the necessity for extractive distillation as known by the prior art.

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 source of feedstock is the debutanized reactor effluent from a conventional catalytic reforming process unit. Another source of satisfactory 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 unit contains single ring aromatic hydrocarbons comprising a wide boiling mixture of benzene, toluene, and xylene. These single ring aromatic hydrocarbons are admixed with the corresponding paraffins and naphthenes which have been produced by such a catalytic reforming unit.

The preferred solvent which may be utilized in the present invention is a solvent of the sulfolane-type. 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 (4) atoms of carbon with two (2) 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.

Other solvents which may be included and may satisfactorily be used in the practice of this invention are the sulfolenes, such as 2-sulfolene and 3-sulfolene. Still further, other typical solvents which have a high selectivity for separating non-aromatic hydrocarbons and which may be processed within the scope of the present invention are 2 - methyl - sulfolane, 2,4 - dimethylsulfolane, methyl-2-sulfonylether, n - aryl - 3 - sulfonylamine, 2-sulfonylacetate, diethyleneglycol, various polyethyleneglycols, dipropyleneglycol, various polypropyleneglycols, dimethylsulfoxide, N-methylpyrrolidone, various mixtures of the above, and the like. As previously mentioned, the specifically preferred solvent for use in the practice of the present invention is sulfolane.

The aromatic selectivity of the solvent can usually be further 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 enhance the selectivity of the overall solvent phase for aromatic hydrocarbons over non-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 therein which is distilled from the solvent in the prior art schemes in the extractive distillation operation. However, practice of the present invention effectively eliminates the need for extractive distillation and in place thereof utilizes a membrane separation zone, more fully discussed hereinafter. The solvent composition of the present invention, therefore, preferably contains from about 0.5% to about 20% by weight water and typically from about 10% by weight depending upon the particular solvent utilized and the process conditions at which the extraction zone is operated.

The extraction zone of the present invention is operated at elevated temperature and sufficiently elevated pressure to maintain the feedstock, the solvent, and the reflux stream, if any, in liquid phase. Typically, suitable temperatures, when using sulfolane as the solvent, are within the range from about 80° F. to about 400° F., and preferably from about 175° F. to 300° F. Similarly, suitable pressures are generally from within the range from atmospheric pressure to about 400 p.s.i.g. and, preferably, from 50 to 150 p.s.i.g.

Following the extraction step, the extract phase, according to the present invention, is passed into a membrane separation zone or dialysis chamber in order to separate solvent and non-aromatic hydrocarbons from the aromatic hydrocarbons.

Generally, a suitable dialysis chamber contains at least two enclosed cells, but may contain from 2 to 100 cells or more separated by membranes having a film thickness ranging from 0.05 to 10 mils. It is essential in the practice of this invention that the membrane chosen be substantially permeable to aromatic hydrocarbons and substantially impermeable to the contaminating quantities of non-aromatic hydrocarbons and substantially impermeable to

the selective solvent which was used in the previous extraction zone.

In practice, the extract phase is introduced into a first chamber wherein it contacts one side of a permeation membrane. The aromatic hydrocarbons permeate at a more rapid rate through the membrane than do the other components of the system. One of the critical requirements in the selection of a suitable membrane is that it be substantially impermeable to the contaminating quantities of the nonaromatic hydrocarbons, as previously mentioned. It is also preferable that the membrane be substantially impermeable to the solvent, but it is recognized that it may be desirable to permit some solvent to permeate through the membrane together with the aromatic hydrocarbons.

Examples of permeation membranes are films of cellulose esters, cellulose ethers, blends of cellulose esters and cellulose ethers, and other cellulose derivatives, herein collectively referred to as "cellulose derivatives." These cellulose derivatives may be modified by reacting the free hydroxyl groups contained therein with an organic reagent, such as aldehydes, aldehyde-alcohol mixtures, organic diisocyanates, organic monoisocyanates, organic phosphorous halides, or by a sequence of modifications, such as modification with an aldehyde followed by modification with an organic diisocyanate. Films of copolymers of vinyl chloride and vinylidene chloride may be used. Other suitable membranes include 2-chlorobutadiene, polyethylene, polypropylene, polytetrafluoroethylene, copolymers of butadiene and styrene, copolymers of isoprene and isobutylene, cross-linked copolymers of ethylene and propylene, vulcanized natural rubber, and the like. Laminated permeation memmbranes made from the above listed materials can also be employed. A laminated membrane, for example, may consist of a thin layer or film of a selective membrane material mounted upon a thicker film of a membrane material having a high permeation rate. (As used herein, the term "permeation" is intended to include "dialysis" since according to this invention, the two functions are not distinct.) Best results can be obtained by using a permeation membrane which has the highest selectivity for permeating aromatics to the total exclusion of non-aromatic hydrocarbons, but it is important to note that the particular membrane used is not a critical factor so long as it performs the function of permeating aromatic hydrocarbons in preference to other hydrocarbons. The permeation membrane employed should be as thin as possible and yet provide the required strength to withstand differential pressure across the membrane which may be from 1 to 500 p.s.i.

Preferably, the extract phase is introduced into the first chamber in liquid phase and the permeated aromatic hydrocarbons removed continuously from the opposite side of the membrane or from a second cell also in the liquid state. However, it is within the concepts of this invention for the operating conditions to be chosen in order for the permeate to be removed in the vapor state. Additionally, the membrane separation zone may be operated with the introduction of a carrier fluid, either liquid or vapor as the case may be, into said second cell in order to aid in the continual withdrawal of the permeate from the second cell. According to one embodiment of this invention, the carrier liquid may be water, or, preferably, may be a portion of the aqueous lean solvent. It has been found that operation of the membrane separation zone with a carrier liquid is advantageous since permeation is a non-equilibrium process. Therefore, it is essential that the aromatic hydrocarbons be removed as rapidly as possible from the opposite side of the membrane so that the greatest differential aromatic concentration gradient may be maintained across the membrane.

The permeated aromatic hydrocarbon, including in some cases solvent, is preferably introduced into a fractionation column for the separation of the aromatic hydro-

carbons from the solvent which also passed through the membrane and/or to recover specific aromatic hydrocarbons as separate product streams. Needless to say, if the membrane is selective enough to reject both solvent and non-aromatic hydrocarbons, then the permeate comprises aromatic hydrocarbons which may be sent directly to storage without additional processing. Generally, however, sufficient quantities of solvent will pass through the membrane so that the subsequent distillation step may be necessary. The aromatic distillation column is operated at low pressures, but at sufficiently high temperatures in order to distill the aromatic hydrocrabons overhead as a distillate fraction thereby producing a bottoms fraction comprising lean solvent which is generally suitable for reuse in the solvent extraction zone. Again, the choice of operating conditions depends upon the feedstock characteristics and the composition of the solvent. Preferably, the top of the aromatic distillation column is maintained at from 100 to 400 mm. Hg absolute. These subatmospheric pressures must be employed in order to maintain a sufficiently low reboiler temperature to avoid thermal decomposition of the solvent, particularly when the solvent is of the sulfolane-type. Preferably, the reboiler temperature should be maintained below about 360° F. when using saturated sufolane as the solvent.

Returning now to the membrane separation zone: the non-permeated material comprising, for example, solvent and non-aromatic hydrocarbons, and in some cases residual aromatic hydrocarbons, is withdrawn from the first cell of the membrane separation zone and passed into solvent recovery facilities. Although not a requirement of the board embodiment of this invention, it is desirable to recover the solvent for reuse in the solvent extraction zone since these aromatic selective solvents are far too expensive to be lost. Therefore, in one embodiment of this invention, the non-permeated material is passed into a stripping column operating under conditions sufficient to strip the non-aromatic hydrocarbons and aromatic hydrocarbons, if any, out of the solvent. Normally, this stripping operation will be performed in a distillation tower utilizing steam as the stripping medium. The non-aromatic hydrocarbon (and aromatic hydrocarbons, if any) components are removed overhead as a distillate product and, preferably, utilized at least in part as the reflux stream on the solvent extraction zone, as previously mentioned. The bottoms from the stripping column comprise solvent generally suitable for reuse in the solvent extraction zone and, preferably, is returned as such to the extraction zone. A specific embodiment of this invention also utilizes a portion of the bottoms from the stripping zone as the carrier fluid in the membrane separation zone, as previously mentioned.

The operating conditions for the stripping column to separate non-aromatic hydrocarbons from solvent will depend upon the characteristics of the feed material; that is, the type of non-aromatic hydrocarbons present and the type of solvent which was utilized in the extraction zone. Typically, the stripper will be maintained under pressures from atmospheric to about 100 p.s.i.g., although, generally, the top of the stripper column is maintained at from 10 to 20 p.s.i.g. Those skilled in the art from knowledge of the prior art and the teachings presented herein have sufficient information for the operation of a stripper column of this type that additional details thereof need not be presented here.

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, 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 extractor **11**. Aqueous sulfolane as the lean solvent enters the extractor at an upper portion thereof via line **12** and non-aromatic hydrocarbon reflux from a source hereinafter described enters extractor **11** at the lower end thereof via line **15**. A raffinate stream is withdrawn from extractor **11** via line **13** as a product stream. An extract phase comprising sulfolane solvent having aromatic hydrocarbons dissolved therein and which is contaminated with minor amounts of non-aromatic hydrocarbons, such as the corresponding naphthenes and paraffins, is withdrawn from extractor **11** via line **14**.

According to the practice of this invention, the extract phase in line **14** is passed into membrane separation zone **16** which contains a first cell **18**, a second cell **19**, separated by a cellulose derivative membrane **17**. The membrane, for example, may be a modified cellulose acetate-butyrate membrane of 0.5 mil thickness. The membrane separation zone **16** is of sufficient size so that a residence time may be maintained sufficient to permit the permeation of the aromatic hydrocarbons from cell **18** through membrane **17** into second cell **19**. A small amount of solvent also passes through membrane **17** thereby creating a permeate comprising a concentrate of aromatic hydrocarbons in second cell **19**.

The non-permeated portion comprising solvent and non-aromatic hydrocarbons is withdrawn from separation zone **16** via line **20** and introduced into steam stripping column **21** at an upper portion thereof. Suitable operating conditions are maintained in stripper **21** to produce an overhead fraction comprising non-aromatic hydrocarbons which is withdrawn via line **15** and, preferably, returned as reflux to extraction zone **11**, as previously described. A bottoms material is withdrawn from stripper **21** via line **22** and since this material comprises lean sulfolane solvent suitable for use in the extraction zone, it is passed at least in part via lines **22** and **12** into extraction zone **11**.

As previously described, the material in cell **19** of separation zone **16** comprises a concentrate of aromatic hydrocarbons. Since permeation is a non-equilibrium process, it is essential that this concentrate of aromatic hydrocarbons. Since permeation is a non-equilibrium process, it is essential that this concentrate of aromatic hydrocarbons be withdrawn as rapidly as possible from cell **19**. In order to permit the continuous operation of membrane separation zone **16**, a portion of the lean solvent in line **22** is passed via line **27** into cell **19** in an amount sufficient to, preferably, decrease the aromatic concentration in cell **19** to a point below the aromatic concentration in cell **18**. The permeate is withdrawn from separation zone **16** via line **23** and passed into aromatic fractionation column **24**.

Column **24** is maintained under conditions sufficient to separate the aromatic hydrocarbons from the solvent phase. The aromatic hydrocarbons are concentrated as a distillate fraction and removed from column **24** via line **25**. The operation of column **24** includes the use of steam stripping on the column in order to remove the final traces of aromatic hydrocarbon from the solvent. Therefore, the lower end of column **24** contains the desired solvent plus water in sufficient amounts such that the material withdrawn from column **24** via line **12** comprises lean solvent suitable for reuse in the extraction zone. Makeup solvent, as needed, may be introduced into the system via line **26**.

PREFERRED EMBODIMENT

Therefore, from the description presented thus far, it can be seen that the present invention in its preferred embodiment provides a method for the extraction and recovery of aromatic hydrocarbons from a feed mixture comprising aromatic and non-aromatic hydrocarbons utilizing a selective solvent which comprises the steps of: (a) introducing said feed mixture into a solvent extraction

zone maintained under aromatic hydrocarbon extraction conditions including the presence of said selective solvent sufficient to produce an extract phase comprising said solvent having aromatic hydrocarbons dissolved therein and contaminated with non-aromatic hydrocarbons, and a raffinate phase comprising non-aromatic hydrocarbons; (b) passing said extract phase into a first cell of a dialysis chamber containing at least two cells separated by a membrane substantially permeable to said aromatic hydrocarbons and substantially impermeable to said solvent and non-aromatic hydrocarbons; (c) removing from said first cell a first mixture comprising solvent and non-aromatic hydrocarbons; (d) removing from a second cell of said chamber a second mixture comprising aromatic hydrocarbons and solvent; (e) introducing said first mixture into a first separation zone maintained under conditions sufficient to produce a first fraction enriched in non-aromatic hydrocarbons and a second fraction comprising solvent; (f) introducing said second mixture into a second separation zone maintained under conditions sufficient to produce a product fraction comprising aromatic hydrocarbons, and a solvent fraction comprising lean solvent suitable for reuse in said extraction zone; and (g) passing at least a portion of said solvent fraction of Step (f) and at least a portion of said second fraction of Step (e) into said extraction zone as the specified selective solvent.

A still further preferred embodiment of this invention includes the method hereinabove wherein additionally a carrier liquid is introduced into said second cell.

The invention claimed is:

1. Method for the extraction and recovery of aromatic hydrocarbons from a feed mixture comprising aromatic and non-aromatic hydrocarbons utilizing a selective solvent of the sulfolane type which comprises the steps of:

(a) introducing said feed mixture into a solvent extraction zone maintained under aromatic hydrocarbon extraction conditions including the presence of said selective solvent sufficient to produce an extract phase comprising said solvent having aromatic hydrocarbons dissolved therein and a raffinate phase comprising non-aromatic hydrocarbons;

(b) passing said extract phase into a first cell of a dialysis chamber containing at least two cells separated by a membrane substantially permeable to said aromatic hydrocarbons and substantially impermeable to said solvent;

(c) removing solvent from said first cells; and,

(d) recovering aromatic hydrocarbons from the permeate of a second cell of said dialysis chamber; and

(e) returning at least a portion of said solvent recovered from step (c) into said extraction zone

2. Method according to claim 1 wherein said membrane is selected from the group consisting of cellulose derivatives, polyethylene, polypropylene, polytetrafluoroethylene, polymers of 2-chlorobutadiene, copolymers of butadiene and styrene, copolymers of isoprene and isobutylene, cross-linked copolymers of ethylene and propylene, and vulcanized natural rubber.

3. Method according to claim **2** wherein said membrane comprises a cellulose derivative.

4. Method according to claim **1** wherein additionally a carrier liquid is introduced into said second cell.

5. Method according to claim **4** wherein said carrier liquid is selected from the group consisting of water and aqueous solvent.

6. Method for the extraction and recovery of aromatic hydrocarbons from a feed mixture comprising aromatic and non-aromatic hydrocarbons utilizing a selective solvent which comprises the steps of:

(a) introducing said feed mixture into a solvent extraction zone maintained under aromatic hydrocarbon extraction conditions including the presence of said selective solvent sufficient to produce an extract phase comprising said solvent having aromatic hydrocarbons dissolved therein and contaminated with non-aromatic hydrocarbons, and a raffinate phase comprising non-aromatic hydrocarbons;

(b) passing said extract phase into a first cell of a dialysis chamber containing at least two cells separated by a membrane substantially permeable to said aromatic hydrocarbons and substantially impermeable to said solvent and non-aromatic hydrocarbons;

(c) removing from said first cell a first mixture comprising solvent and non-aromatic hydrocarbons;

(d) removing from a second cell of said chamber a second mixture comprising aromatic hydrocarbons and solvent;

(e) introducing said first mixture into a first separation zone maintained under conditions sufficient to produce a first fraction enriched in non-aromatic hydrocarbons and a second fraction comprising solvent;

(f) introducing said second mixture into a second separation zone maintained under conditions sufficient to produce a product fraction comprising aromatic hydrocarbons, and a solvent fraction comprising lean solvent suitable for reuse in said extraction zone; and,

(g) passing at least a portion of said solvent fraction of Step (f) and at least a portion of said second fraction of Step (e) into said extraction zone as the specified selective solvent.

7. Method according to claim **6** wherein said solvent is of the sulfolane-type.

8. Method according to claim **6** wherein said first fraction of Step (e) is introduced into said extraction zone as reflux therein.

9. Method according to claim **7** wherein said membrane is selected from the group consisting of cellulose derivatives, polyethylene, polypropylene, polytetrafluoroethylene, polymers of 2-chlorobutadiene, copolymers of butadiene and styrene, copolymers of isoprene and isobutylene, cross-linked copolymers of ethylene and propylene, and vulcanized natural rubber.

10. Method according to claim **9** wherein said membrane comprises a cellulose derivative.

11. Method according to claim **8** wherein additionally a carrier liquid is introduced into said second cell.

12. Method according to claim **11** wherein said carrier liquid comprises a portion of said second fraction of Step (e).

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