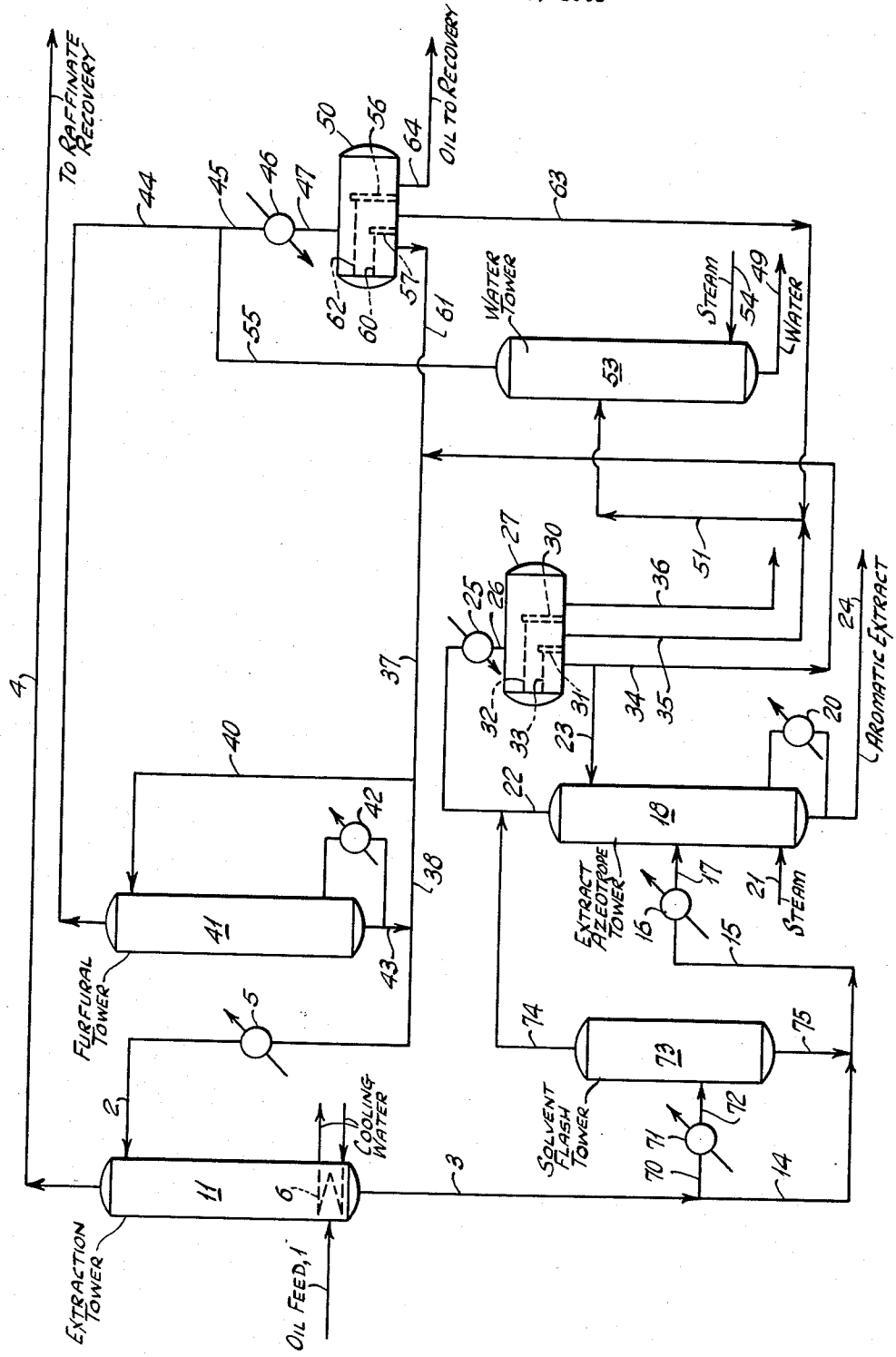
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FURFURAL SOLVENT SEPARATION OF AROMATICS FROM LIQUID MIXTURES

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FURFURAL SOLVENT SEPARATION OF AROMATICS FROM LIQUID MIXTURES

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This invention relates to the separation of liquid mixtures with a selective solvent. More particularly, it relates to the separation of aromatic hydrocarbons from mixtures with other hydrocarbons by solvent extraction with furfural followed by azeotropic distillation of the extract-solvent mixture. In one embodiment of this invention, naphthalene and alkyl naphthalenes are separated from gas oils by selective solvent extraction with furfural and the dissolved aromatics are concentrated and separated by a highly selective azeotropic distillation employing furfural as reflux.

Gas oils from some aromatic crude sources and gas oils from thermal and catalytic cracking containing substantial quantities of useful aromatic hydrocarbons, for example, benzenoid, naphthalene, and naphthalenic hydrocarbons. This invention is particularly useful in the separation of naphthalene and naphthalene precursors, that is, naphthalenic hydrocarbons which may be converted to naphthalene, for example, by hydrodealkylation. These desirable aromatics are diluted with nonaromatic hydrocarbons of the same boiling range making their separation by simple distillation impossible. It is an object of this invention to separate aromatic hydrocarbons in concentrated form from mixtures with nonaromatic hydrocarbons. Other objects will be apparent from the following description and claims.

Solvent extraction is a well known process for the separation of aromatic hydrocarbons from mixtures with nonaromatic hydrocarbons of similar boiling range. Furfural has been found to be an excellent selective solvent in the separation of hydrocarbons of relatively high boiling point, for example, hydrocarbons useful in the manufacture of lubricating oils and catalytic cracking feed stocks. Furfural extraction has also been found useful in the manufacture of kerosine and low boiling gas oil products where a raffinate of low aromatic content is produced. However such lower boiling hydrocarbons, for example, those boiling within the range of 400 to 600° F. are considerably more soluble in furfural than lubricating oils or cracking feed stocks. At temperatures above about 100° F. both aromatic and nonaromatic hydrocarbons boiling in the range of 400 to 600° F. are relatively soluble and the selectivity for aromatic hydrocarbons is relatively decreased. Although substantially complete separation of aromatics from raffinate streams may be readily effected, nonaromatics are dissolved in the extract to an extent that it is not possible to separate extract fractions containing aromatics in a concentration above about 80 percent at conditions readily obtained with ordinary cooling water. For the separation of aromatics in a concentration above 80 percent, high solvent selectivity is necessary which in turn requires temperatures far below usual ambient atmospheric temperatures, for example, about 30° F. At these low temperatures the solvency of the furfural is substantially reduced so that high solvent ratios, for example, about 250 percent or higher are required to obtain acceptable yields.

In accordance with this invention, a liquid hydrocarbon mixture containing aromatic and nonaromatic hydrocarbons is contacted with liquid furfural effecting formation of a raffinate mix comprising a major portion of the nonaromatic hydrocarbons and an extract mix comprising a furfural phase containing dissolved hydrocarbons including a major portion of the aromatic hydrocarbons and the remaining nonaromatic hydrocarbons, and at least a part of said extract mix is distilled in a distillation zone in the presence of furfural reflux and added water vapor (steam) effecting separation of an azeotropic mixture comprising water, nonaromatic hydrocarbons and furfural from an aromatic rich bottoms fraction.

An advantage of the process of this invention is that aromatic concentrates containing more than 80 percent aromatics may be separated from gas oil boiling range hydrocarbons with furfural employing temperatures about usual ambient atmospheric temperatures and moderate solvent rates.

Another advantage of the process of this invention is that a single solvent is employed as both a selective solvent in an extraction step and as a component of the azeotropic mixture in an azeotropic distillation step.

The accompanying drawing diagrammatically illustrates one form of the process of this invention. Although the drawing illustrates one arrangement of apparatus in which the process of this invention may be practiced, it is not intended to limit the invention to the particular materials or apparatus described.

A gas oil feed is passed through line 1 into extraction tower 11. In tower 11 the oil feed is contacted with liquid furfural in countercurrent flow. The furfural solvent may be "dry" that is substantially free of dissolved water or "wet" that is containing some dissolved water as is well known in the art of solvent extraction with furfural. Furfural is introduced into tower 11 through line 2 at a rate of about 120 to 300 volume percent of the oil feed. In extraction tower 11 aromatic components of the oil feed are preferentially dissolved in the furfural and aromatic rich extract mix is withdrawn from the bottom of tower 11 through line 3. Raffinate oil denuded of aromatics is removed from the top of tower 11 through line 4 and discharged to raffinate recovery facilities for removal of the small amount of dissolved furfural by conventional means. A temperature gradient of up to about 50° F. and preferably within the range of about 20 to 30° F. is maintained in tower 11. A desired temperature gradient may be maintained by heating the furfural passed to the top of the tower in exchanger 5 and cooling the bottom of the tower with water in coil 6. Desirably the temperature of the tower bottom is maintained as low as possible with cooling water, for example, about 80 to 100° F. When ambient atmospheric temperatures and dew points are too high to obtain cooling water of desired temperature from a conventional cooling tower or spray pond, the cooling water may be chilled by vacuum flashing, for example, water may be cooled to 60° F. by discharge to a vacuum zone maintained at a pressure of 0.256 pound per square inch absolute.

Extract mix is passed through lines 3, 14, and 15, preheater 16, and line 17 to extract-azeotrope tower 18. Tower 18 comprises a fractional distillation tower provided with a reboiler 20. Steam is introduced through line 21 to assist in distillation and provide the water required to satisfy the ternary azeotrope composition of hydrocarbon, furfural, and water. This azeotrope is removed as overhead vapor from tower 18 through line 22. The formation of a hydrocarbon-water-furfural azeotrope permits separation of all of the furfural and water and a part of the hydrocarbons as overhead products leaving the remaining hydrocarbon extract as bottoms. Additionally, the presence of furfural enhances the relative volatility of nonaromatic hydrocarbons as compared with the aromatic hydrocarbons so that the nonaromatic hydrocarbons appear in the azeotropic mixture taken overhead and the aromatics are concentrated in the bottoms. Aromatic concentrate is removed from the bottom of tower 18 through line 24.

Azeotrope vapors from tower 18 are discharged through line 22, cooled in condenser 25, and the resulting condensate is passed through line 26 to separator 27. Separator 27 is provided with weirs 30 and 31. Condensate in separator 27 separates into three phases separated by interfaces 32 and 33. The lower or heaviest phase is predominantly furfural and contains a small amount of dissolved oil and water. The furfural layer has an upper level at interface 33 and is confined by weir 31. Furfural layer is withdrawn through line 34 and a part is returned as reflux to tower 18 through line 23. The intermediate phase is predominantly water and contains a small amount of dissolved furfural and oil. The water layer has a lower level at interface 33 and an upper layer at interface 32. The water layer overflows weir 31 and is confined by weir 30. Water phase is withdrawn through line 35. The upper layer having a lower level at interface 32 is predominantly oil and contains a small amount of dissolved furfural and water. The oil phase overflows weir 30 and is withdrawn through line 36. Oil withdrawn through line 36 is similar to the raffinate discharged through line 4 and may be combined with it before or after separation of dissolved furfural.

Furfural phase withdrawn through line 34 may be passed through lines 37, and 38 to provide the solvent introduced into tower 11 through line 2. In this case the furfural will have a water content established by the equilibrium at the temperature and conditions of separator 27. If it is desired to control the water content of the furfural recycle stream at a lower value independently of the temperature of separator 27, the furfural may be dried by distillation in which a binary azeotrope comprising furfural and substantially all of the dissolved water is removed overhead from the remaining dry furfural. In this case, part or all of the wet furfural in line 37 is passed through line 40 to tower 41. Tower 41 is provided with a reboiler 42. Dry furfural is withdrawn through line 43 and returned to line 38. Vapor comprising furfural and water with a small amount of oil is withdrawn through lines 44 and 45, condensed in condenser 46, and the resulting condensate is passed through line 47 to separator 50.

Water phase containing dissolved furfural can also be freed of furfural by distillation since the azeotrope of water and furfural is lower boiling than either furfural or water. In this case an azeotrope containing all of the furfural and some of the water is removed overhead from the remaining furfural-free water which is withdrawn as bottoms. Water phase from separator 27 is withdrawn through lines 35, and 51, to water distillation tower 53. Steam is introduced into tower 53 through line 54. Water free of furfural is discharged from the bottom of tower 53 through line 49. Overhead vapor from tower 53, comprising water, furfural, and a small amount of oil, is discharged through line 55 and combined with the similar mixture in the line 44 from tower 41 for condensation and separation.

The combined condensates from towers 41 and 53 are passed to separator 50. Separator 50 is similar in design and function to separator 27. Furfural phase having an upper level at interface 60 and confined by weir 57 is withdrawn through line 61 and combined with the furfural phase in line 34 for eventual recycle to extraction tower 11. Water phase between interfaces 60 and 62 overflows weir 57 but is confined by weir 56. Water phase is withdrawn through line 63 and combined with the water from line 35 for furfural separation in water distillation tower 53. Oil layer separating above interface 62 overflows weir 56 and is withdrawn through line 64. This oil may be combined with oil in line 36 or 4 for furfural separation and recovery, not shown.

A part of the furfural in the extract-mix may be separated prior to the azeotropic distillation and thereby substantially reduce the amount of azeotrope which must be separated as an overhead product. Since less azeotrope is formed, substantially less steam is required to satisfy the azeotrope composition with savings in utilities costs. Preseparation of a part of the furfural also provides a means of controlling the amount of azeotrope formed and in turn of controling the amount of nonaromatic oil separated in the azeotropic distillation. This preseparation of furfural is effected by passing at least a part of the extract-mix in line 3 through line 70, heat exchanger 71 and line 72 into solvent flash tower 73. In tower 73, a part of the furfural in the extract-mix is vaporized and withdrawn through line 74. These vapors are combined with the vapors in line 22 for condensation and phase separation. Extract-mix partially denuded of furfural is withdrawn through line 75 and passed through line 15 to extract tower 18. Solvent flash tower 73 may be operated independently of the pressure of extract azeotrope tower 18 by providing separate vapor recovery facilities, not shown. In the latter case, solvent flash tower 73 may be operated at a lower pressure or advantageously under a vacuum to effect increased separation of solvent.

High extraction yields, for example, in excess of about 90 percent of the aromatics contained in the gas-oil feed are obtained in the extraction step of this process. High extraction yields are favored by high solvent ratios and relatively high extraction temperatures. At high extraction yield levels, because of the lower solvent selectivity at conditions favoring high yields, a substantial amount of nonaromatic hydrocarbons is also extracted so that the concentration of aromatics in the extracted hydrocarbon is at least 70 percent and preferably within the range of about 80 to 85 percent. Since most of the aromatics are included in the extract, the raffinate contains very little aromatic hydrocarbon and is therefore particularly valuable in the manufacture of heating oils, diesel fuel oils, catalytic cracking feed stocks and other products where aromatics are undesirable.

In the azeotropic distillation step, the concentration of aromatics in the extract is increased to about 90 percent or higher by selectively removing nonaromatic hydrocarbons. The azeotropic distillation is effected at a top tower temperature of about 290 to 300° F. and with a bottom tower temperature of about 400 to 450° F. Some extract vaporization in the azeotropic distillation tower reboiler is desirable to provide the heat required in vaporizing the azeotrope separated as an overhead product. Steam is added at the bottom of the azeotropic distillation tower at a rate of about 0.1 pound per pound of extract mix to satisfy the composition required to form the azeotrope and to assist in the distillation and the stripping of furfural from the extract bottoms product. Furfural rich phase, separated from the condensed azeotrope distilled overhead, is returned to the azeotropic distillation tower as reflux to provide rectification of the hydrocarbons rising in the tower effecting stripping of the aromatic constituents therefrom.

Example

In accordance with the process of this invention, a gas oil produced by catalytic cracking is treated for recovery of aromatics. The catalytic cracked gas oil charge stock has the following tests:

Gravity, ° API	30.0
Distillation, ASTM, IBP, ° F.	400
Distillation, ASTM, EP, ° F.	550
Hydrocarbon analysis, percent by vol.:	
Aromatics	55.0
Paraffins	34.0
Naphthenes	11.0

The gas oil charge is contacted at a rate of 2500 barrels per day (b.p.d) with furfural in a countercurrent contactor at a solvent dosage of 175 volume percent. A temperature gradient of 40° F. is maintained in the contactor with the top temperature (raffinate) of 120°

F. and bottom temperature (extract) of 80° F. Raffinate mix is stripped to separate dissolved furfural and produce a raffinate product in a yield of 47.3 volume percent of the charge oil.

Extract mix is flashed effecting vaporization and separation of 70 percent of the furfural producing a flashed extract mix containing 37 percent furfural. Flashed extract mix at a rate of 2673 b.p.d. is passed to a distillation column. Exhaust steam at a rate of 95,080 pounds per day is introduced into the tower bottom and the top of the tower is refluxed with furfural to maintain a top tower temperature of 300° F. An azeotrope is distilled overhead containing furfural, the steam introduced into the tower bottom and 367 b.p.d. of hydrocarbon. Aromatic concentrate is withdrawn from the bottom of the tower at a rate of 1317 b.p.d. The composition of the aromatic concentrate is 94 percent aromatics, 5 percent paraffins and 1 percent naphthenes. The aromatic concentrate contains 90.0 percent of the aromatics contained in the catalytic cracked gas oil feed.

We claim:

1. A method for the separation of an aromatic rich fraction from a liquid hydrocarbon mixture which comprises contacting said mixture with a solvent comprising liquid furfural effecting formation of a raffinate mix comprising a hydrocarbon phase containing dissolved furfural and an extract mix comprising a furfural phase containing dissolved hydrocarbons consisting of 70 to 85 percent aromatic hydrocarbons, distilling at least a part of said extract mix in a distillation zone in the presence of a reflux as hereinafter provided and added steam at a rate of about 0.1 pound of steam per pound of extract mix passed to said distillation zone into an overhead vapor comprising water, hydrocarbon and furfural and a bottoms liquid consisting of said aromatic rich fraction containing at least 90 percent aromatic hydrocarbons, condensing said overhead vapor forming a hydrocarbon rich phase, a water rich phase and a furfural rich phase, separating said hydrocarbon rich phase, said water rich phase and said furfural rich phase, and passing at least a portion of said furfural rich phase as said reflux to said distillation zone.

2. The process of claim 1 wherein said liquid hydrocarbon mixture is a gas oil produced by catalytic cracking.

3. The process of claim 1 wherein said extract mix is flashed under conditions effecting vaporization and separation of a part of the furfural contained therein and the resulting extract mix partially denuded of furfural is passed to said distillation zone.

4. A method for the separation of an aromatic fraction containing at least 90 percent by volume of aromatic hydrocarbons from a catalytic cracked gas oil

which comprises contacting said gas oil with a liquid solvent comprising furfural at a solvent ratio within the range of about 120 to 300 volumes of solvent to 100 volumes of said gas oil in a solvent extraction zone, withdrawing extract mix comprising furfural and dissolved hydrocarbons consisting of 70 to 85 percent aromatic hydrocarbons from said extraction zone at a temperature within the range of about 80 to 100° F. while maintaining a temperature gradient through said extraction zone less than about 50° F., passing at least a part of said extract mix to a distillation zone in contact with a reflux as hereinafter provided and added steam at a rate of about 0.1 pound of steam per pound of extract mix passed to said distillation zone, distillatively separating an overhead vapor comprising an azeotrope of water, furfural and hydrocarbon from a bottoms product comprising aromatic hydrocarbons of at least 90 percent by volume purity, condensing said overhead vapor forming an oil-rich phase, a water-rich phase and a furfural-rich phase, and passing at least a portion of said furfural rich phase as said reflux to said distillation zone.

5. A method for the separation of an aromatic rich fraction from a liquid hydrocarbon mixture which comprises contacting said mixture with a solvent comprising liquid furfural effecting formation of a raffinate mix comprising a hydrocarbon phase containing dissolved furfural and an extract mix comprising a furfural phase containing dissolved hydrocarbons consisting of 70 to 85 percent aromatic hydrocarbons, heating said extract mix, vaporizing a part of the furfural in said extract mix, separating furfural vapor from remaining liquid extract mix, passing said remaining liquid extract mix to a distillation zone, distillatively separating said remaining liquid extract mix in said distillation zone in the presence of a reflux as hereinafter provided and added steam at a rate of about 0.1 pound of steam per pound of extract mix passed to said distillation zone into an overhead vapor comprising water, hydrocarbon and furfural and a bottoms liquid consisting of said aromatic rich fraction containing at least 90 percent aromatic hydrocarbons, condensing said overhead vapor forming a hydrocarbon rich phase, a water rich phase and a furfural rich phase, separating said hydrocarbon rich phase, said water rich phase and said furfural rich phase, and passing at least a portion of said furfural rich phase as said reflux to said distillation zone.

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