April 6, 1965 A. W. FRANCIS 3,177,263

CONCENTRATION OF SELECTED AROMATIC HYDROCARBONS
BY EXTRACTIVE EVAPORATION WITH AMMONIA

Filed Aug. 11, 1960 3 Sheets-Sheet 1

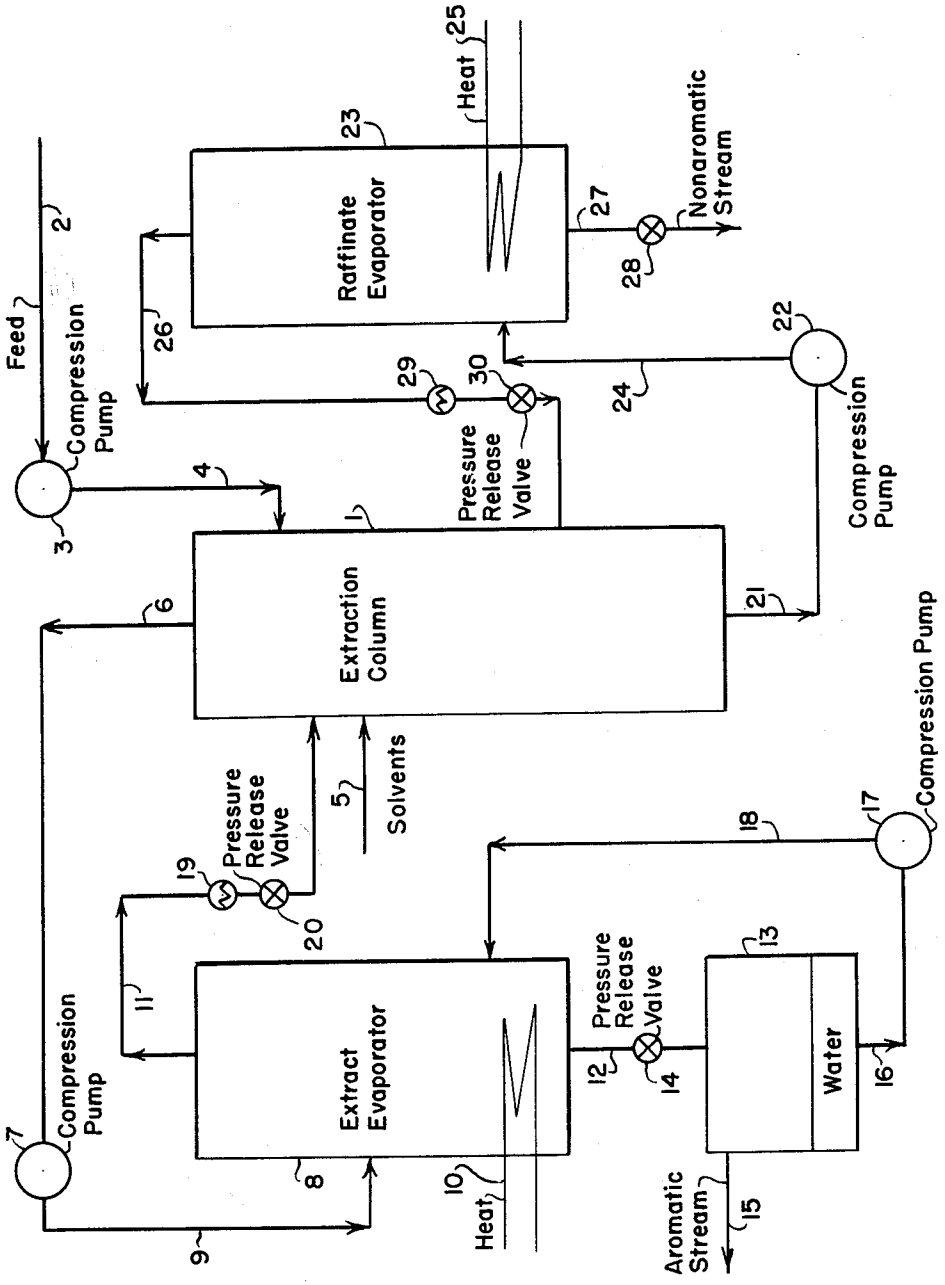


FIG. 1

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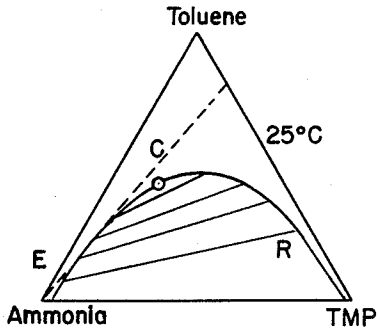


FIG.2

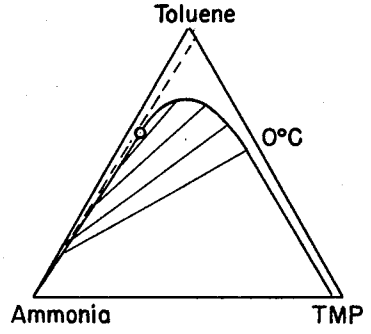


FIG.3

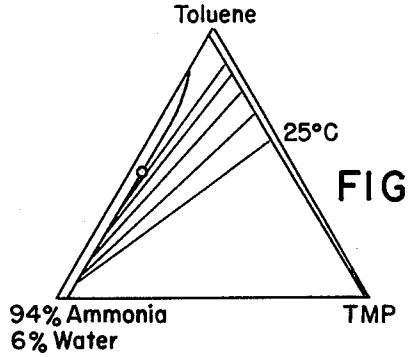


FIG.4

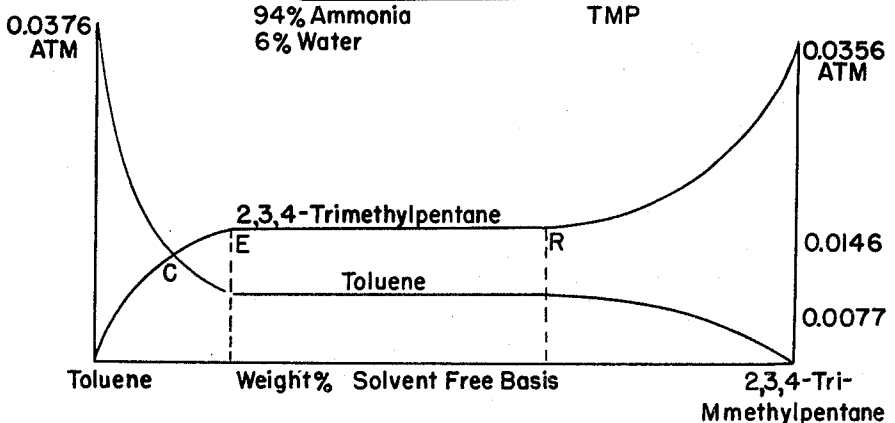


FIG.5

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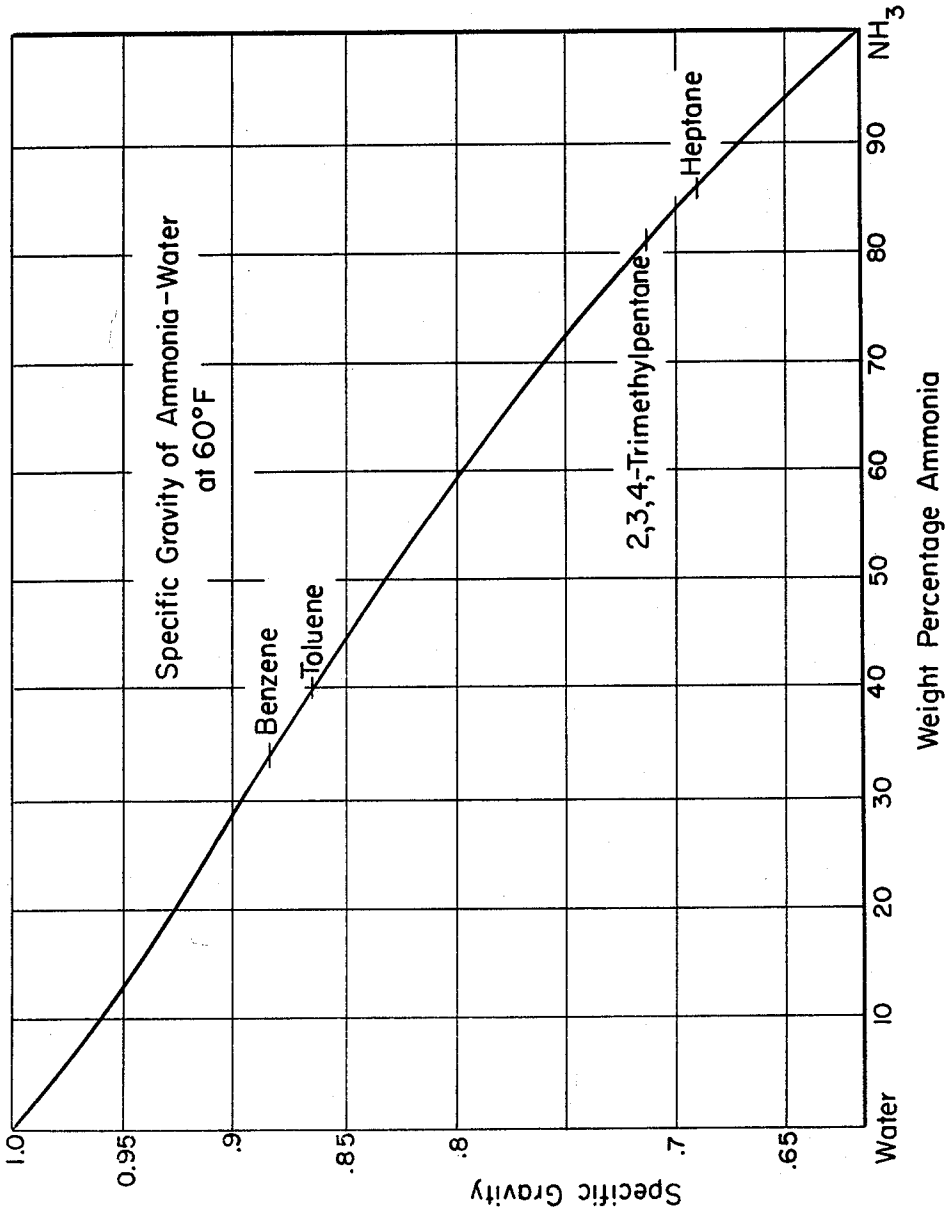


FIG.6

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CONCENTRATION OF SELECTED AROMATIC HYDROCARBONS BY EXTRACTIVE EVAPORATION WITH AMMONIA

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7 Claims. (Cl. 260—674)

This invention relates to the separation of aromatic hydrocarbons boiling at temperatures higher than 212° F. from a mixture of aromatic and nonaromatic hydrocarbons boiling at substantially the same boiling point. The invention is particularly directed to a process of solvent extraction to obtain susbtantially pure aromatic hydrocarbons boiling at temperatures higher than 212° F. from mixtures of aromatic and nonaromatic hydrocarbons using ammonia as the extraction solvent.

The need for obtaining quite pure streams of aromatic hydrocarbons has long been recognized in petroleum refining. These aromatic hydrocarbons are useful intermediates in the manufacture of petroleum chemicals as well as products in other branches of chemistry. The pure aromatic hydrocarbons are sold in quantity as solvents and make useful blending stocks in the manufacture of automotive fuel. Many of the most desired aromatic hydrocarbons are found in conjunction with nonaromatic hydrocarbons which boil at substantially the same boiling point. The separation of the aromatic hydrocarbon from the similarly boiling nonaromatic hydrocarbon is expensive. For example, it is desired to obtain toluene which boils at 110.6° C. from paraffinic or naphthenic hydrocarbons boiling at 100 to 120° C. with which the toluene is frequently found commingled. A typical paraffin is 2,3,4-trimethylpentane which boils at 113.5° C. There is a growing demand for toluene in purified form for which the impure toluene is not acceptable.

Many solvents have been proposed for extraction of aromatic hydrocarbons from mixtures of aromatic and nonaromatic hydrocarbons of similar boiling point. Liquid ammonia is a highly selective, cheap, non-corrosive solvent, operable at moderate pressures and easily separated from the products. However, like other proposed solvents, ammonia has two serious disadvantages. Ammonia is not only miscible in all proportions with most aromatic hydrocarbons, but it is also partly miscible with many nonaromatic hydrocarbons. Using pure liquid ammonia as a solvent, it is impossible to obtain more than about 90% toluene by extraction alone except at exceedingly low temperatures, which are uneconomical. A mixture of 80% toluene, 20% 2,3,4-trimethylpentane (or other paraffin) is miscible with liquid ammonia in all proportions at 25° C. or higher.

It has been proposed in U.S. Patent No. 2,396,299 to provide a higher purity of aromatic hydrocarbons when using liquid ammonia as a solvent by diluting the ammonia with water, ethylene glycol or one of many other liquids to diminish its solvent power. The proposed solution has the disadvantage of decreasing substantially the selectivity of the solvent, and of so increasing the number of plates or theoretical stages of extraction required. This results in decreased throughput and therefore greater expense.

The second major difficultly encountered in using liquid ammonia as an extraction solvent is caused by the fact that the density of ammonia changes unfavorably when diluted by ordinary dilution solvents. Pure liquid ammonia has a density lower than that of any hydrocarbon likely to be associated with the desired aromatic hydrocarbon. And yet when mixed with even small quantities of ordinary diluents, and with hydrocarbon mixtures possessing a reasonable content of aromatic hydrocarbons, the solvent density may become equal to or higher than that of the raffinate. It therefore becomes difficult to design a flow diagram free from the risk that the two liquid phases may become inverted. This is illustrated in FIGURE 6 attached hereto wherein the specific gravity at 60° F. is plotted against the weight percentage of ammonia in mixtures with water. Ethylene glycol-ammonia mixtures would give similar curves. Densities of n-heptane, benzene, 2,3,4-trimethylpentane, and toluene, typical components in the hydrocarbon system, have been located on the curve.

I have discovered that substantially pure aromatic hydrocarbons boiling at a temperature higher than 212° F. can be obtained from a mixture with similarly boiling nonaromatic hydrocarbons by first using substantially pure liquid ammonia as an extraction solvent in an extraction process and then conducting evaporation of the solvent from the extract without reflux under conditions which remove the ammonia and the small amount of nonaromatic hydrocarbons carried over with extract. Substantially all of the aromatic hydrocarbon in the mixture is left behind as a liquid. The solvent ammonia and the carried-over hydrocarbons are returned to the extraction zone after the gaseous ammonia has been converted to a liquid. The latter purification feature has been called extractive evaporation since the impurity, consisting of the nonaromatic hydrocarbons, is extracted from the extract by the evaporation of the solvent, leaving substantially pure aromatic hydrocarbons.

The object of this invention is to provide a process for separating aromatic hydrocarbons boiling at a temperature higher than 212° F. from nonaromatic hydrocarbons boiling at substantially the same boiling point.

A further object of this invention is to provide a simplified process for using the solvent power of ammonia to separate aromatic hydrocarbons boiling at a temperature higher than 212° F. from nonaromatic hydrocarbons boiling at substantially the same boiling point.

A further object of this invention is to provide a highly efficient continuous process for separating aromatic hydrocarbons boiling at a temperature higher than 212° F. from nonaromatic hydrocarbons boiling at substantially the same boiling point using ammonia under moderate temperature levels and mildly advanced pressure as the concentrating medium in a combination extraction and evaporation process.

These and other objects of the invention will be more fully disclosed in the following detailed discussion of the invention, which is to be read in conjunction with the attached figures.

FIGURE 1 shows diagrammatically a complete process for using liquid ammonia to concentrate aromatic hydrocarbons from a mixture of aromatic and nonaromatic hydrocarbons in accordance with the invention.

FIGURE 2 shows a ternary diagram for toluene and 2,3,4-trimethylpentane with ammonia as a solvent medium at a temperature of 25° C.

FIGURE 3 shows a ternary diagram for toluene and 2,3,4-trimethylpentane with ammonia as a solvent medium at a temperature of 0° C.

FIGURE 4 shows a ternary diagram for toluene and 2,3,4-trimethylpentane with a mixture of 94% ammonia and 6% water being used as the solvent medium at a temperature of 25° C.

FIGURE 5 is a plot of partial pressures of the hydrocarbon components in a mixture of toluene and 2,3,4-trimethylpentane against weight percentage on a solvent-free basis.

FIGURE 6 is a plot of specific gravity of mixtures of ammonia and water at 60° F. against the weight percentage of ammonia in mixtures with water.

Referring now to FIGURE 1, a method of operating the process will be described in detail. An elongated extraction column 1 is operated at a convenient temperature, such as 15° C., and a convenient pressure, such as 100 p.s.i.g. The pressure in the extractor is normally autogenous, that is, nearly equal to the vapor pressure of ammonia at the operating pressure. However, since the extractor is usually "liquid full," the pressure may be slightly higher, or even considerably higher if it will facilitate flow of products. A temperature of about 30° C. may be used in the extraction stage with corresponding pressure of 170 p.s.i.g. or more, but this produces lower concentrations of aromatic hydrocarbons, about 70% in the case of toluene. The larger amount of nonaromatic impurity to be removed by extractive evaporation means a greater relative recirculation of ammonia, involving cost for heat. On the other hand, it would economize on refrigerating costs. The optimum temperature is determined on economic grounds. The feed is a mixture of aromatic and nonaromatic hydrocarbons which, for purposes of illustration, may be a mixture of toluene and 2,3,4-trimethylpentane. The feed is passed through conduit 2, and put under extraction column pressure by means of the compression pump 3. The compressed feed is introduced into the extraction column 1 through the conduit 4 which terminates generally near the midpoint of the column. The feed comprises 16 parts by weight toluene and 37 parts by weight 2,3,4-trimethylpentane. Makeup ammonia is added to the extraction column 1 through the conduit 5 which terminates near the midpoint of the column 1. The extraction column is operated at 15° C. and 100 p.s.i.g. having any desired number of extraction plates, such as enough to provide maximum concentration of aromatics in the extract depending upon the particular feed charged. The extract is taken from the top of the column through the conduit 6 and in this illustrative example contains 300 parts by weight of ammonia, 16 parts toluene and 2 parts 2,3,4-trimethylpentane.

The extract is put under additional pressure in the compression pump 7 and introduced into the extract evaporator 8 through the conduit 9 which terminates near the midpoint of the extract evaporator 8. Heat is supplied to the extract evaporator 8 by means of the heating coil 10. The temperature in the extract evaporator is maintained at 60° C. and the pressure in the extract evaporator is maintained at 380 p.s.i.g. Under these conditions the liquid ammonia converts to a vapor and is withdrawn from the top of the evaporator 8 through the conduit 11. A suitable temperature range for the extract evaporator is found to be about 60° C. Substantially all the 2,3,4-trimethylpentane leaves with the ammonia and in addition a small amount of toluene leaves with the ammonia. The stream 11 comprises, therefore, 300 parts ammonia, 2 parts 2,3,4-trimethylpentane and 1 part toluene. The remaining 15 parts of pure toluene are removed from the bottom of the extract evaporator.

In the extract evaporation stage improvement in separation can be obtained by diluting the extract with a solvent such as water. The water flows with the toluene from the bottom of the evaporator through the conduit 12 into a separating chamber 13. The valve 14 in the conduit 12 is used to reduce the pressure to substantially atmospheric pressure and the water-toluene mixture forms two layers in the separating chamber 13. The toluene is withdrawn from the top layer through the conduit 15 as a substantially pure aromatic hydrocarbon. Water is withdrawn from the bottom of the separating chamber 13 through the conduit 16, and put under a pressure of 380 p.s.i.g. in the compression pump 17. The water under pressure is reintroduced into the extract evaporator through the conduit 18.

The ammonia with diluents 2,3,4-trimethylpentane and toluene in conduit 11 is cooled and liquefied in heat exchanger 19 and depressured to extraction zone pressure by means of the pressure release valve 20. The liquid ammonia is reintroduced into the extract column near the midpoint. Only sufficient makeup ammonia need be added through the conduit 5 to make up for losses in the system.

TABLE I

Extractive evaporation of aromatic-nonaromatic mixtures with liquid ammonia

Run	Diluent	Percent	Temp., °C.	Solvent Ratio, g./NH_3/g. Charge	Percent Aromatic	
					Charge	Product
Toluene (110.8°)—2,2,5-Trimethylhexane (124.1°)						
6	Water	3.5	60	7	89.2	92.3
7	do	6.7	60	7	89.2	92.5
p-Xylene (138.4°)—n-Octane (125.7°)						
10	Water	3.3	60	7	92.2	94.7
11	do	3.3	60	9	97.6	98.4
12	do	6.7	60	9	97.6	98.6
Toluene (110.63°)—2,3,4-Trimethylpentane (113.5°)						
1			60	6.2	88.8	91.3
2	Water	4.0	60	5.8	88.8	92.8
3	do	4.0	65	6.0	93.7	96.0
Toluene (110.63°)—3-Methylheptane (119.0°)						
4			60	5.9	89.0	91.3
5	Water	4.0	60	5.9	89.0	92.1
o-Xylene (144.41°)—n-Nonane (150.72°)						
8			66	8.2	89.0	90.2
9	Water	3.7	66	7.8	89.0	90.2

The raffinate is taken from the bottom of the extraction column 1 through the conduit 21 and in this illustrative example contains 3 parts ammonia and 35 parts trimethylpentane. The raffinate is put under additional pressure in the compression pump 22 and introduced into the raffinate evaporator 23 through the conduit 24 which terminates near the midpoint of the raffinate evaporator. Heat is supplied to the raffinate evaporator by means of the heating coil 25. The temperature in the raffinate evaporator is maintained at 40° C. and the pressure in the raffinate evaporator is maintained at 130 p.s.i.g. Under these conditions the ammonia converts to a gas and takes with it a small amount of 2,3,4-trimethylpentane through the conduit 26 at the top of the raffinate evaporator. This stream comprises 3 parts ammonia and 0.02 part 2,3,4-trimethylpentane. The remainder of the 2,3,4-trimethylpentane, 34.98 parts 2,3,4-trimethylpentane, is removed from the bottom of the raffinate evaporator through the conduit and depressured to substantially atmospheric pressure by means of the pressure release valve 28 located in the conduit 27. The recycle ammonia is cooled by the heat exchanger 29 located in conduit 26 and depressured by means of valve 30 to 120 p.s.i.g. Under these conditions the ammonia converts to a liquid and is returned to the extraction column 1.

Table I, shown hereinabove, presents 12 extractive evaporations of nonaromatics from aromatics boiling at a temperature higher than 212° F., the aromatics and nonaromatics having boiling points so close that separation by distillation is not practical. The "charge" in these runs is toluene or xylene mixed with a similarly boiling paraffin such as could be produced in a simple extraction with pure ammonia (88 to 89% toluene or xylene). The richer charges in runs 3 and 10 to 12 is such as could be produced by extractive evaporation. Thus, the purity of final product can be raised as high as desired merely by providing a sufficient relative amount of ammonia in the evaporation stage.

It is noted that in the evaporation stage pure ammonia is somewhat less efficient than ammonia diluted with water. It is, therefore, advantageous to dilute the extract in the evaporation stage with a limited amount of a suitable solvent such as water. This should not carry over into the extraction stage, however, since this would reduce the selectivity of the liquid ammonia. It would also introduce difficulties due to equal densities of the layers in extraction. The diluent for ammonia in the evaporator could be water, ethanolamine, ethylene glycol or any other substance miscible but not reacting with ammonia and not miscible with toluene. The low cost of water and its low miscibility with toluene make it the preferred diluent, although other diluents may give comparable enrichment in the evaporation.

The extraordinary success of this invention in providing substanially pure aromaic hydrocarbons boiling above 212° F. from closely boiling mixture of aromatic and nonaromatic hydrocarbons is due to a secondary selection during recovery of the aromatic hydrocarbon from the extract. It is called "extractive evaporation" and is distinct in principle from "extractive distillation." Under controlled conditions it is very effective in purifying aromatic hydrocarbons. Further purification of a given hydrocarbon after solvent extraction with liquid ammonia, for example, toluene in the toluene-2,3,4 - trimethylpentane-ammonia system, can be achieved by distillation of the extract layer. As the ammonia is distilled off, relatively more 2,3,4-trimethylpentane than toluene goes with the ammonia. This leaves a relatively purer toluene in the undistilled material. By recycling more ammonia greater purity of the aromatic hydrocarbon is obtained up to a substantially pure aromatic hydrocarbon product.

Extractive evaporation is based on the recognized principle that in a system of two or more phases in equilibrium the partial pressure of any component is the same for each phase, regardless of its concentration in that phase.

Thus, in a two-liquid phase system of ammonia, toluene and 2,3,4-trimethylpentane at 25° C., as shown on the ternary diagram FIGURE 2, the lower hydrocarbon layer R, is 11% ammonia, 24% toluene (20.5 mol percent and 65% 2,3,4-trimethylpentane by weight (41.2 mol percent). It has by Raoult's law .412×.0356 (vapor pressure of 2,3,-4-trimethylpentane at 25° C.) or 0.0146 atmosphere pressure compared with only .205×.0376 or .0077 atmosphese pressure for toluene, in spite of the higher vapor pressure of pure toluene at 25° C., .0376 atmosphere pressure. The partial pressures are respectively the same from the ammonia-rich layer E, even though it contains only 3.0% 2,3,4-trimethylpentane by weight. Raoult's law is not applicable to this extract layer because it is far from an ideal mixture.

Evaporation of ammonia (partial pressure about 10 atmospheres) from this layer takes with it most of this 2,3,4-trimethylpentane in preference to the normally more volatile toluene. The operation, while it resembles azeotropic distillation and steam distillation, is in fact quite different; the distillate is not a true azeotrope because with reflux the ammonia would come off almost pure. In operation of the process care should be taken to avoid condensation and reflux in the upper portion of evaporator 8.

This explanation is made as though the extract evaporation were conducted at 25° C. This would provide an enrichment of the toluene in the residue. However, a higher temperature, 60° C. is recommended for the evaporation *after* separation of the phases at a lower temperature, so as to diminish the amount of ammonia required to carry over the nonaromatic hydrocarbon. At this higher temperature the corresponding pressures are as follows:

	Atmospheres
Ammonia	25
Toluene:	
Pure	0.185
Partial	0.038
2,3,4-trimethylpentane:	
Pure	0.174
Partial	0.072

again the partial pressure of the paraffin is nearly twice as great as that of the toluene from the extract as well as from the raffinate. At the suggested higher temperature, 60° C., the ammonia vapor pressure has increased only 2.5 fold while those of the hydrocarbons have increased five fold as compared with 25° C. Thus only half as much ammonia is required to carry over the hydrocarbon mixture.

Extractive evaporation is illustrated on FIGURE 5, showing the partial pressures of the hydrocarbon components plotted against weight percentage on a solvent-free basis. The pressures are constant over the range of the two-phase composition, and the pressures curve in the single phase regions to the pressure of the pure components. As ammonia is evaporated from the extract (dashed line EC in FIGURE 2) it will be noted that the composition is no longer on the binodal curve, and so no longer in equilibrium with R. The excess vapor pressure of 2,3,4-trimethylpentane over toluene decreases. At point C (FIGURES 2 and 5) they are equal. Enrichment is still obtained since the 2,3,4-trimethylpentane in the residue is substantially lower than in the feed. However, enrichment can be continued at a higher level by diluting the ammonia (in the evaporator, but not in the original extractor) so that in effect point E in FIGURE 5 is moved to the left toward pure toluene (solvent-free basis). The composition of the evaporating liquid remains closer to the binodal curves as shown in FIGURE 4. However, excessive dilution of the ammonia is ineffective because the new tie lines slope steeply up to the right indicating poor selectivity. The hydrocarbon layer is not much richer in 2,3,4-trimethylpentane than the ex-

tract. Dilution with water should be maintained within the range 0 to 10% by weight, the optimum being for water about 4% to 6%. Other factors which affect efficiency of extractive evaporation are temperature and the concentration of total hydrocarbons in the ammonia. The pressure under which the extractive evaporation occurs has also been found to be a factor in the efficiency of separation with improved results being obtained at the higher pressures. In general, the pressures in both evaporators will be autogenous, that is, substantially equal to the vapor pressure of liquid ammonia at the operating temperature. Higher temperatures permit higher concentrations since less ammonia is required to evaporate the 2,3,4-trimethylpentane. Improved results are obtained by increasing the proportion of ammonia thereby decreasing the concentration of total hydrocarbons in the ammonia. The disadvantage of the use of an excessive amount of ammonia is the problem of recycling, pressuring and depressuring, heating and cooling such a large volume of ammonia.

Extraction with liquid ammonia is most selective when it is used anhydrous or pure. That is, the tie lines have a minimum adverse slope under such conditions, as shown on FIGURES 2 and 3, as compared with FIGURE 4. It is essential, in this process, that the extraction be conducted with substantially pure ammonia to provide the maximum selectivity during extraction, and it is preferred that during the extractive evaporation of the extract a suitable diluent be added to the extract up to the amount providing improved efficiency in the extractive evaporation.

The invention has been amply illustrated in the detailed discussion of the invention. These examples are given only to illustrate the invention and are not intended as limitations. The only limitations intended are found in the attached claims.

I claim:

1. A process for separating a mixture of (1) aromatic hydrocarbons having a boiling point higher than 212° F. and (2) nonaromatic hydrocarbons boiling at substantially the same temperature which comprises contacting said mixture of aromatic and nonaromatic hydrocarbons with liquid ammonia containing substantially no diluent in an extraction zone at an extraction temperature and at least autogenous pressure, withdrawing from said extraction zone an extract comprising the aromatic hydrocarbons, amomnia and a small portion of the nonaromatic hydrocarbons, substantially increasing the pressure of the extract and introducing the extract into an extract evaporation zone at the elevated pressure, adding sufficient heat to the extract evaporation zone to raise the temperature of said extract to a temperature higher than that of said extraction zone and to convert the ammonia to a gas, withdrawing gaseous ammonia, and along with the ammonia substantially all of the nonaromatic hydrocarbons and a portion of the aromatic hydrocarbons from said extract evaporation zone with substantially no condensation and substantially no reflux, withdrawing separately substantially pure aromatic hydrocarbons from said extract evaporation zone, reducing the pressure of the gaseous ammonia and hydrocarbons withdrawn from said extract evaporation zone to the pressure of the extraction zone, returning the ammonia and hydrocarbons contained therein in liquid form to the extraction zone, withdrawing from said extraction zone a raffinate comprising nonaromatic hydrocarbons and liquid ammonia, substantially increasing the pressure of the raffinate and introducing the raffinate into a raffinate evaporation zone at the elevated pressure, adding sufficient heat to the raffinate oration zone to the temperature of the extraction zone, drawing ammonia from said raffinate evaporation zone, cooling the ammonia withdrawn from said raffinate evaporation zone to the temperature of the extraction zone, reducing the pressure of the ammonia to the pressure of the extraction zone, returning the ammonia in liquid form to the extraction zone, and separately withdrawing nonaromatic hydrocarbons from said raffinate evaporation zone.

2. Claim 1 further characterized in that a diluent is introduced into said extract evaporation zone, the diluent is removed with the substantially pure aromatic hydrocarbon, separated from said substantially pure aromatic hydrocarbons and returned to said extract evaporation zone.

3. Claim 2 further characterized in that the diluent is water.

4. Claim 1 further characterized in that the extraction temperature is from 0° C. to +30° C., and the pressure is at least autogenous.

5. Claim 1 further characterized in that the aromatic hydrocarbon is toluene.

6. Claim 1 further characterized in that the aromatic hydrocarbon is xylene.

7. Claim 3 further characterized in that the diluent is added to the separated extract in an amount to provide a concentration up to 10 percent in the extract evaporation zone.

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ALPHONSO D. SULLIVAN, *Primary Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,177,263 April 6, 196!

Alfred W. Francis

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, lines 8 and 9, for "atmosphese" read -- atmosphei --; column 8, line 17, beginning with "oration zone" strike out all to and including "evaporation zone," in line 18, same columr and insert instead -- evaporation zone to convert the ammonia tc a gas, withdrawing ammonia from said raffinate evaporation zone, --.

Signed and sealed this 24th day of August 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents