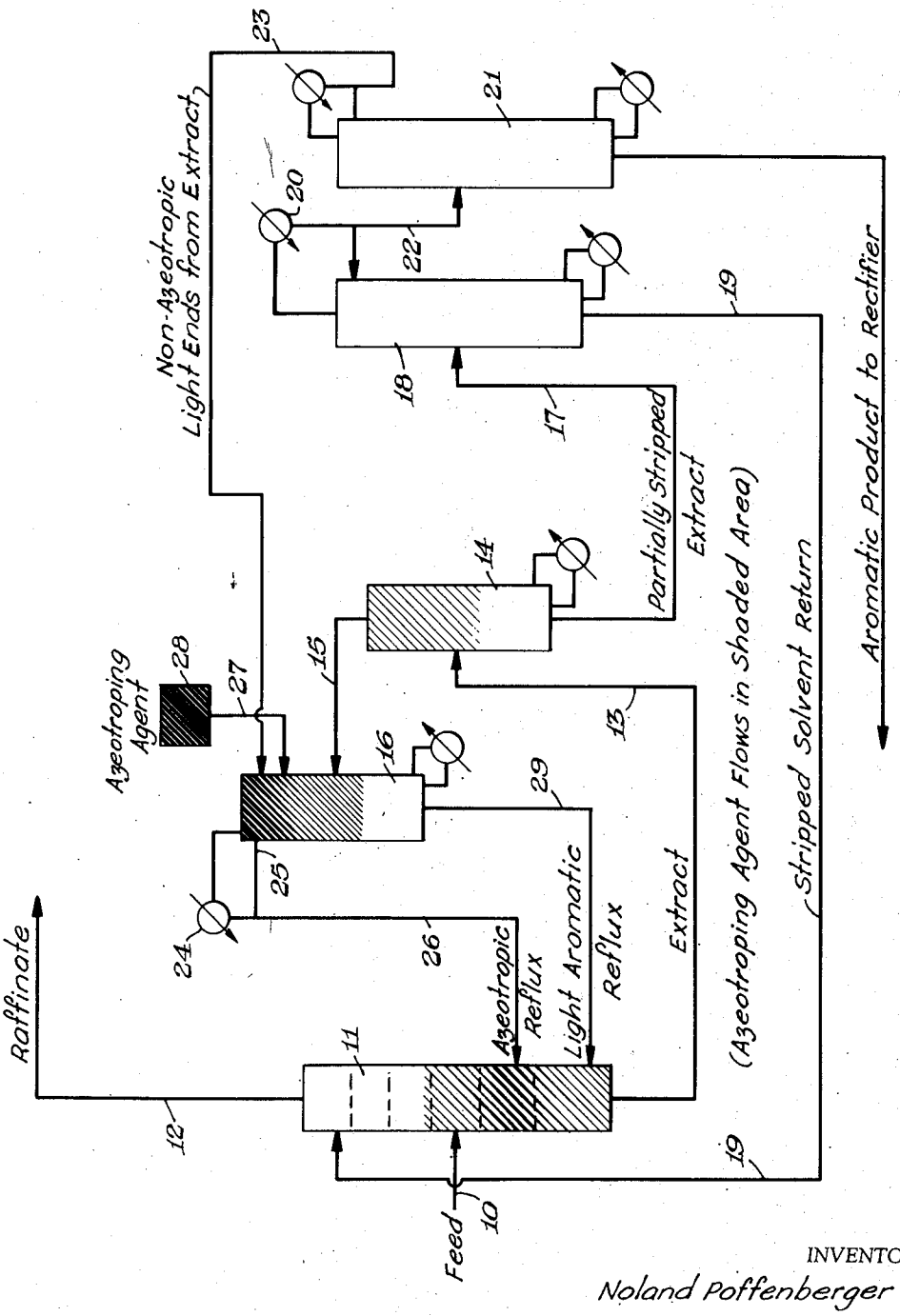
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PROCESS FOR EXTRACTION AND RECOVERY OF AROMATIC HYDROCARBONS FROM HYDROCARBON MIXTURES

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PROCESS FOR EXTRACTION AND RECOVERY OF AROMATIC HYDROCARBONS FROM HYDROCARBON MIXTURES

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This invention relates to an improved process for the selective solvent extraction and recovery of aromatic hydrocarbons from mixtures thereof with non-aromatic hydrocarbons. It relates in particular to a method whereby the separation and recovery of individual aromatic hydrocarbons of industrial grade or better is made possible without need for chemical treatment.

Several processes are known for the selective extraction of aromatics from mixed hydrocarbon feeds such, for example, as the reformed naphthas. In general, such processes comprise countercurrent liquid-liquid contact between the mixed hydrocarbon feed and any of several selective solvents, with the extract phase, containing most of the aromatics, being withdrawn from one end of the system while a raffinate phase, containing little or no solvent and little or no aromatic hydrocarbon, is withdrawn from the other end of the extraction system. It is found that, the greater the carrying power of the selective solvent for aromatic hydrocarbons, the greater will be the amount of non-aromatics which leaves the extraction system with the extract phase. It is also noted that when the feed and the co-extracted non-aromatics contain considerable unsaturates it is difficult to separate such unsaturates from the aromatic hydrocarbons and, accordingly, the latter seldom meet the established standards for industrial or better grades of aromatics without a chemical treatment.

It is accordingly among the objects of the present invention to provide an improvement in processes for the selective solvent extraction of aromatic hydrocarbons from mixtures thereof with non-aromatics, some of which may be unsaturated, which will lead to the recovery of individual aromatics of industrial grades, or better, without necessity for a chemical after-treatment. A related object is to provide such an improved process in which the fractions of an aromatic-rich extract from such a mixed feed which normally cause difficulty in separation of the aromatics may be removed preferentially from the extract and return to the extraction system for displacement in large part to the non-aromatic raffinate. Another object is to provide such a method in which the troublesome light ends from the aromatic-rich extract are separated azeotropically from the balance of the extract and are returned to the extraction system. Other and related objects may appear hereinafter.

In accordance with the present invention, a mixed hydrocarbon feed, containing aromatic hydrocarbons and non-aromatic hydrocarbons, is supplied as a liquid phase to a countercurrent multistage extraction system near the middle, and a liquid which is a preferential solvent for aromatic hydrocarbons but which is substantially immiscible with non-aromatic hydrocarbons is supplied to the system near one end. A substantially aromatic-free and solvent-free raffinate is withdrawn from the same end and an aromatic-rich extract is withdrawn from the other end. The extract is prestripped to remove therefrom as vapors substantially all of the hydrocarbons which are more volatile than benzene, together with part of the benzene. The partially stripped extract is then fully stripped to recover the remaining hydrocarbons therefrom, the solvent is returned to the extraction system and the hydrocarbons are rectified. Any light ends from the rectification, boiling below benzene, are conveyed to a column to which the hydrocarbon vapors from the prestripping unit are also conveyed and in which the several hydrocarbons are admixed with an agent which forms azeotropes with at least part of the non-aromatic hydrocarbons. The resulting azeotropic fractions are taken overhead from said column and are condensed and returned to the extraction system at a point intermediate between the point at which the original mixed feed is introduced and the end from which the aromatic-rich extract is withdrawn, preferably at the point in the extractor where the hydrocarbons have the same analysis as those in the azeotrope. The aromatic-rich bottoms from the column in which the azeotrope is distilled are returned to the extraction system as reflux near the end from which the extract is withdrawn. The return of the non-aromatics has the effect of increasing the relative proportion of these materials in the feed, and, when equilibrium conditions are reached, substantially all of the non-aromatics in the feed are found in the raffinate. Any water returned with the azeotrope simply dissolves in the solvent with the usual effect of increasing its selectivity. The return of the light aromatics has the effect of increasing the carrying power of the solvent for aromatics and, when equilibrium conditions are reached, substantially all of the aromatics which enter the extractor with the feed are found in the stream of aromatics being sent to the rectifier. The azeotroping agent usually exerts little effect upon the solvent power of the extractant, but aids materially in separation of light ends from the extract.

The extraction system is operated under such pressure as may be needed to maintain the entire contents in the liquid condition at the temperature employed. Extraction is commonly effected at somewhat elevated temperatures, of the order of 50° to 150° C., and when the extract is removed at such temperature and released to a lower pressure in the prestripper, the light ends tend to flash away from the extract without supplying much, if any, additional heat thereto. Similarly, the low boiling azeotropes tend to flash from the azeotrope still with the addition of minimum quantities of heat, so that the process represents a significant heat economy. The heat supplied in the final stripper raises the solvent to the required temperature for use in the extraction system, and this same heat performs the work needed in the prestripper and the azeotrope still before it is lost to condensers.

The solvent employed may be any of the selective solvents for aromatics. Such solvents include the polyglycols, phenols, glycol monoethers, glycol monoesters, various alcohols, alkanolamines, amines and amides. Of these, the polyglycols are preferred. This group includes diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol and mixtures of these with one another and often with some water.

The commonly occurring non-aromatics in an aromatized hydrocarbon feed, which may follow the aromatics into the extract, include such saturates as the pentanes, cyclohexane, methylcyclohexane, n-hexane, 3-methylpentane, and 2-methylpentane, and such typical unsaturates as pentenes, hexenes, methylcyclopentene and cyclohexene, as well as some hexadienes and cyclohexadiene. Occasionally some compounds of similar molecular size are found having acetylenic unsaturation (triple bonds).

The azeotroping agents which may be employed are any of a large group of compounds, non-reactive under prevailing conditions with the selective solvent employed, which are known to form low-boiling binary azeotropes with the lighter hydrocarbons present in the mixed feed.

Especially desirable are those agents which form azeotropes with the non-aromatic hydrocarbons present but which do not do so with benzene. Numerous useful compounds are listed in a "Table of Azeotropes and Nonazeotropes," by L. H. Horsley, Analytical Chemistry, vol. 19, pages 508–609 (1947) and vol. 21, pages 831–873 (1949). The useful compounds include, but are not limited to, acetone, acetonitrile, allyl alcohol, 2-butanone, butyl alcohol, isobutyl alcohol, sec-butyl alcohol, tert-butyl alcohol, butyraldehyde, isobutyraldehyde, ethanol, ethyl acetate, ethyl formate, ethyl nitrate, methanol, methyl formate, methyl propionate, nitroethane, nitromethane, 1-propanol, 2-propanol, propylene oxide, propyl formate and pyridine. The preferred azeotroping agent for use in the present process is acetone, which does not form an azeotrope with benzene, but does so with most of the non-aromatic hydrocarbons having 5 to 7 carbon atoms. In some cases, there is no objection to the azeotroping agent forming an azeotrope with benzene as well as with the non-aromatics. Methanol, ethanol, 1-propanol and 2-propanol are among the most satisfactory agents in such a case.

The new process will be described with reference to the annexed drawing, the single figure of which is a flow diagram of the process.

A mixed aromatic and non-aromatic hydrocarbon feed is introduced through line **10** into a countercurrent multistage extraction system **11** near the middle. A liquid selective solvent for aromatic hydrocarbons is introduced into extractor **11** near one end, and a raffinate, substantially free from aromatics and from the selective solvent, is withdrawn from the same end through line **12**. An extract, containing aromatic hydrocarbons dissolved in the solvent is withdrawn from the other end of extractor **11** through line **13** and is conveyed to a prestripping still **14** from which the hydrocarbons which are more volatile then benzene, and at least part of the benzene, are distilled through overhead line **15** and conveyed to an azeotrope still **16**. The partially stripped extract is withdrawn as bottoms from still **14** through line **17** to a final stripper **18**, in which enough heat is supplied to free the solvent of its hydrocarbon content. The stripped solvent is withdrawn as bottoms from the heated final stripper **18** through line **19** and is returned to extractor **11**. The hydrocarbon vapors passing overhead from stripper **18** are condensed by condenser **20** and the condensate flows to a fractionating column **21** through line **22**. Any non-aromatic light ends of the hydrocarbons fed to column **21** are taken overhead, condensed, and passed through line **23** to the azeotrope still **16**. The aromatic hydrocarbons are taken as bottoms from column **21** and are sent to a rectifying system for recovery of individual aromatics. The light ends from prestripper **14** and those from column **21** are mixed in the azeotrope still **16** with an agent which forms azeotropes of low boiling point at least, and preferably only, with the light non-aromatic hydrocarbons present. The azeotropes pass overhead through condenser **24**, from which part of the condensate is returned through line **25** as reflux to still **14** and the balance is returned through line **26** to the extraction system **11**, entering at a point intermediate between the point of entry of the mixed feed and the point of withdrawal of the aromatic-rich extract. The azeotroping agent is admitted as required to still **16** through line **27** from a supply vessel **28** to maintain the desired analysis at the head of still **16**. The bottoms from still **16**, consisting chiefly of benzene, the light hydrocarbons which do not azeotrope with the agent employed and are less voltatile than the azeotropes, and possibly small amounts of the azeotroping agent, are returned through line **29** to extractor **11**, entering near the end from which the aromatic-rich extract is withdrawn.

The azeotroping agent flows through that part of the system which is shaded in the annexed drawing. The amount of azeotroping agent employed is normally very small. Thus, since the carrying power of the solvent for aromatics is most commonly from 10 to 20 per cent, there will ordinarily be considerably less than 1 per cent of non-aromatics in the extract entering the prestripper **14**. In most cases, the amount of azeotroping agent needed to form an azeotrope with the hydrocarbons does not exceed the weight and is often as little as 10 to 15 per cent of the weight of the hydrocarbons. Hence, in practical operations, the amount of azeotroping agent needed ranges from about 0.1 to 1 per cent of the weight of solvent being circulated to the extractor, though the use of somewhat larger proportions is not harmful to the process and the use of smaller amounts will still be advantageous in reducing the amount of non-aromatics moving with the aromatics toward the rectifying system. Approaching the problem from another direction, the usual solvent extraction system forms an extract in which the hydrocarbons consist of at least 98 per cent aromatics and 2 per cent or less of non-aromatics. If 4 parts by weight of the extracted hydrocarbons are returned to the extractor as reflux for each part by weight of purified aromatic product, the impurities in the initial extract represent 0.1 part by weight for each part of purified product being recovered at the end of the train. The amount of azeotroping agent required is then from 0.01 to 0.1 pound for each pound of recovered aromatic hydrocarbon.

The azeotroping agents useful in the process have in common the property of dissolving in the aromatic-rich extract phase leaving the extractor to a sufficient extent so that the large flow of solvent relative to the amount of azeotroping agent effectively removes that agent from the extractor and prevents it from being lost to the raffinate phase. The prestripper **14** and final stripper **18** assure the absence of azeotroping agent from the lean solvent returned through line **19** to the extractor **11**.

To illustrate the difficulty of separating a pure aromatic hydrocarbon from its mixture with unsaturated non-aromatics by simple rectification, the following example is given:

A reformed naphtha having a boiling range from 140° to 320° F. was subjected to careful fractionation. The original mixture had a bromine index of 2660 (Analytical Chemistry, vol. 19, page 869 (1947)). Bromine index is the volume, in milliliters, of 0.01 normal bromate-bromide reagent which will react with the unsaturates in a 100 milliliter sample of the hydrocarbon being tested. Careful rectification showed the following even distribution of unsaturates in all fractions boiling below 230° F. (110° C.).

Fraction	Weight	Boiling Range, ° C. at 760 mm.	Weight percent Aromatics	Bromine index
1	18	29. 5–50. 5	0	Not measured.
2	23	50. 5–61. 5	0	Do.
3	66	61. 5–70. 0	0	1950.
4	53	70. 0–81. 0	39. 0	2720.
5	21	81. 0–81. 0	74. 5	1820.
6	9	81. 0–91. 0	18. 0	2260.
7	38	91. 0–94. 0	0. 7	1780.
8	50	94. 0–110. 0	26. 5	2970.
Total	278			

Some improvement is obtained when the raw feed is subjected to countercurrent extraction with a selective solvent, the extract is stripped substantially free of its hydrocarbon content, and the hydrocarbons are then subjected to rectification, as may be seen from the following results obtained when the same feed as in the foregoing example was extracted with diethylene glycol and the recovered hydrocarbon portion of the extract was

rectified. Results on the portions boiling up to 110° C. are given below:

Fraction	Weight	Boiling Range, ° C. at 760 mm.	Weight percent Aromatics	Bromine index
1	8	74. 5–77. 5	48	1240.
2	8	77. 5–79. 5	90	500.
3	8	79. 5–79. 5	98	260.
4	43	79. 5–80. 0	99	112.
5	87	80. 0–80. 0	99	112.
6	15	80. 0–80. 5	96	170.
7	21	80. 5–110. 0	80	Not measured.
Total	190			

It is noted that the distribution of unsaturation has been altered by the extraction process but that significant amounts of unsaturates are still found in the products boiling at the proper temperature for benzene.

The same feed was extracted at 70° C. in the same manner with 10 volumes of diethylene glycol per volume of feed, and with 4 pounds of benzene from the aromatic stream being returned as reflux to the extractor for each pound of aromatics being recovered from the rectifier, and 0.1 pound of acetone was supplied to the azeotrope still for each pound of aromatics being recovered. The light ends were almost completely removed by the acetone and only very small amounts of light hydrocarbons were found in the aromatic stream entering fractionating tower **21**. The azeotropes of acetone and light hydrocarbons were returned to the extractor, as illustrated in the drawing, and the aromatic bottoms from still **16**, returned as reflux to the extractor, consisted essentially of benzene. The portion of the final aromatic stream which boiled up to 110° C. had the following analysis:

Fraction	Weight percent	Boiling Range, ° C. at 760 mm.	Weight percent aromatics	Bromine Index	Freezing Point, ° C.
1	7	74. 5–79. 0	70	1000	
2	26	79. 0–79. 0	99	200	4. 6
3	25	79. 0–79. 5	100		5. 3
4	26	79. 5–80. 5	100	50	5. 4
5	9	80. 5–80. 5	100		5. 5
6	7	80. 5–110. 0	90	100	
Total	100				

The benzene recovered from the finishing stills had a freezing point of 5.3° to 5.5° C., a boiling range of less than 2° C., and in all respects met the specifications for industrial grade benzene (A. S. T. M.—specification: D836–47) without further chemical treatment. The higher aromatics present were also obtained in a degree of purity meeting their respective standards for industrial grades.

Similarly advantageous results are obtained when using methanol, ethanol, 1-propanol, 2-propanol, or a butyl alcohol, or propylene oxide, ethyl formate, nitromethane, or one of the other previously named azeotroping agents in place of the acetone of the foregoing example. Since most of these form azeotropes with benzene as well as with the light non-aromatics from the extract, there is less sharp separation of aromatics from non-aromatics in the azeotrope still, but the return of the azeotropes to the extractor near the end thereof from which the aromatic-rich extract is removed results in the same favorable shift in the equilibrium conditions, displacing more non-aromatics to the raffinate and yielding a purer aromatic stream to the rectifiers.

I claim:

1. In a process in which a mixture of aromatic and non-aromatic hydrocarbons is subjected to countercurrent multistage extraction in the liquid phase with a selective solvent for aromatic hydrocarbons and an extract rich in aromatic hydrocarbons is withdrawn from one end of the extraction system, the extract is stripped of its hydrocarbon content and the stripped solvent is returned to the other end of the extraction system, the improvement which consists in: effecting at least part of the said stripping operation in the presence of a small but effective amount of an agent which is non-reactive with the solvent and is capable of forming low-boiling azeotropes with at least part of the non-aromatic hydrocarbon portion of the extract but does not form an azeotrope with benzene, separating the azeotropes and benzene from the extract and from one another, and returning the azeotropes and at least part of the extracted benzene separately to the extraction system nearer the end thereof from which the extract is withdrawn than the end to which the solvent is introduced, the azeotropes being returned thereto at a point nearer the middle of the system than at which the benzene is returned.

2. The process claimed in claim 1, wherein the azeotroping agent employed is acetone.

3. In a process in which a mixture of aromatic and non-aromatic hydrocarbons is subjected to countercurrent multistage extraction in the liquid phase with a selective solvent for aromatic hydrocarbons and an extract rich in aromatic hydrocarbons is withdrawn from one end of the extraction system, the extract is stripped of its hydrocarbon content and the stripped solvent is returned to the other end of the extraction system, the improvement which consists in: supplying to the extraction system, in amount from 0.1 to 1 per cent of the weight of solvent, an agent which is non-reactive with the solvent and which forms low-boiling azeotropes at least with part of the light non-aromatic portion of the extract; boiling from said extract in a prestripping operation the hydrocarbons therein which are more volatile than benzene together with part of the benzene, and together with said azeotrope-forming agent; separating the low-boiling azeotropes by distillation from higher boiling portions of said hydrocarbons; returning said higher boiling portions to the extraction system near the end from which the extract is withdrawn while returning the azeotropes to the extraction system at a point between said end and the middle; and recovering aromatic hydrocarbons from that portion of the extract remaining after the prestripping operation.

4. The process claimed in claim 3, wherein the azeotroping agent employed is one which forms azeotropes with at least part of the non-aromatic hydrocarbon portion of the extract but does not form an azeotrope with benzene.

5. The process claimed in claim 4, wherein the azeotroping agent is acetone.

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