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PROCESS FOR THE EXTRACTION AND RECOVERY OF AROMATIC HYDROCARBONS FROM HYDROCARBON MIXTURES

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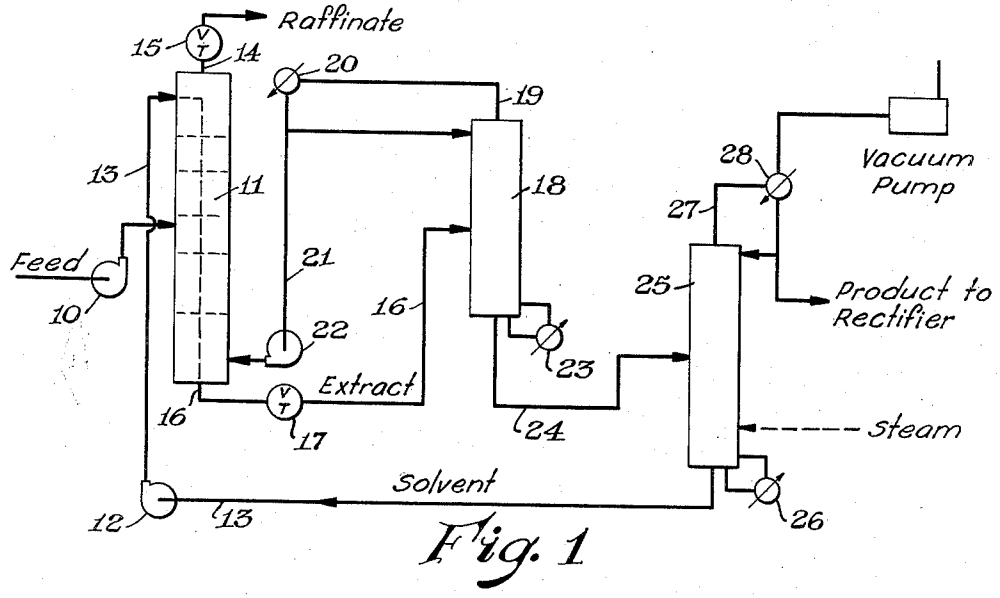

Fig. 1

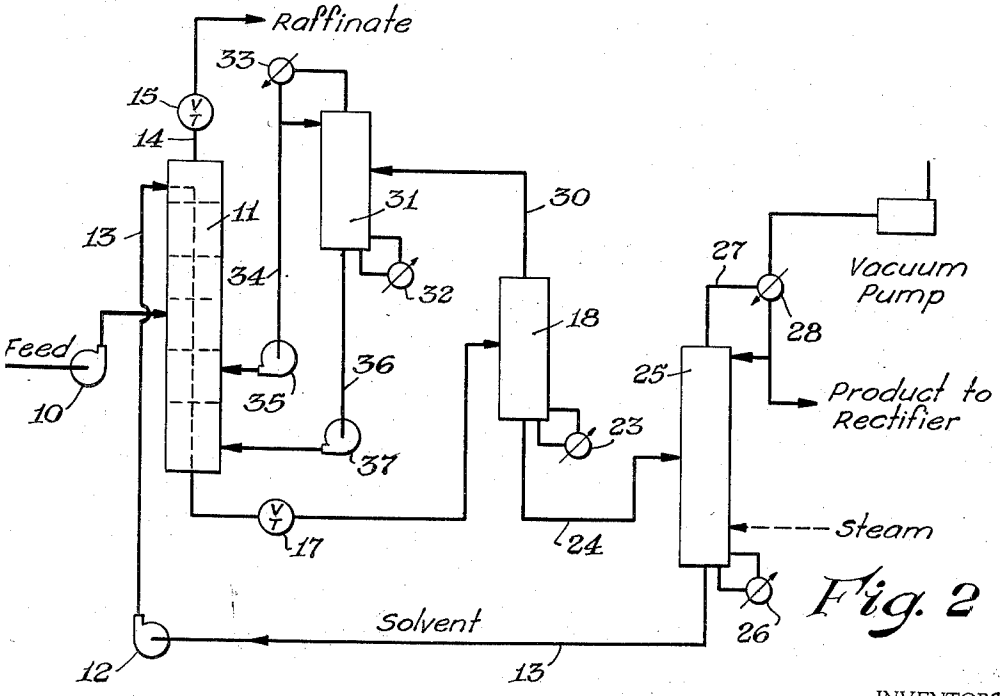

Fig. 2

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PROCESS FOR THE EXTRACTION AND RECOVERY OF AROMATIC HYDROCARBONS FROM HYDROCARBON MIXTURES

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8 Claims. (Cl. 260—674)

This invention relates to an improved process for the extraction and recovery of benzene and other aromatic hydrocarbons from liquid hydrocarbon mixtures containing them. It relates in particular to a method for improving the carrying capacity of solvents used in extraction of aromatics from hydrocarbon mixtures, and is adapted to be used in the recovery of benzene, toluene, xylenes, ethyl benzene and higher aromatics from such feeds as are obtained by reforming natural gasoline. However, the invention is not limited to operations on such reformed gasolines.

It is known that aromatic hydrocarbon fractions of liquid mixtures containing one or a mixture of such other types of hydrocarbons as saturated and unsaturated aliphatic hydrocarbons and cycloaliphatic hydrocarbons can be extracted from the mixtures using selective solvents flowing countercurrent to the mixed feed. The solvents are substantially immiscible with the predominantly non-aromatic raffinate. The mere removal of aromatics in the extract is no great problem. The various solvents which have been suggested differ both in their carrying power for aromatics and in their selectivity, and the raffinate which is obtained may be substantially free from aromatics or it may contain considerable amounts of aromatics, depending on the extractive solvent used and the techniques employed. Thus, the extract may contain substantially all or only a part of the aromatic portion of the feed, depending on the solvent and the conditions used. The principal problem arises from the strong tendency of most solvents for aromatic hydrocarbons to dissolve, as well, much of the non-aromatic material in the feed. This, in turn, leads to an acute problem in the purification of the extract, as the C_6 to C_{10} non-aromatics boil in the same range as the C_6 to C_{10} aromatics, and the two types of compounds cannot be separated by usual distillation techniques if much olefinic material is present. As a consequence, the recovered aromatic fractions are not sufficiently pure to meet accepted standards for "industrial" and "nitration" grades of aromatics. Their diolefinic impurities tend to polymerize, forming gummy resins, and the mono-olefins prevent the aromatics from meeting the established standards such, for example, as those relating to bromine index or to "acid wash color."

These and related problems are discussed, and one method for recovery of pure aromatic fractions of mixed hydrocarbon feeds is disclosed in the copending application of the present inventors and another, entitled "Aromatic Hydrocarbons by Solvent Extraction," Serial No. 255,688, filed November 9, 1951, now Patent No. 2,770,664, as a continuation-in-part of application Serial No. 198,578, filed December 1, 1950 (now abandoned). That method comprises introducing the mixed feed into a countercurrent multistage extraction system near the middle, introducing diethylene glycol into one end of the system into contact with the hydrocarbons, withdrawing substantially aromatic-free raffinate from the system at the same end and aromatic-rich extract from the other end, stripping the extract to separate its aromatic content,

returning part of the aromatics as reflux to the said other end, and withdrawing the remainder of the aromatic hydrocarbon as product. The diethylene glycol preferably contains 0.5 to 10 percent by weight of water. The method just described is more effective than those of the prior art, especially in the recovery of single aromatics from narrow feed cuts, but, in common with other known methods, requires much heat input to the stripping still or stills which is lost in condensation of the aromatic distillates. Further, most of the known processes are limited in their extraction efficiencies by the carrying power of the solvent employed for the mixture of aromatics present in the feed. They are also limited by the presence, in the predominantly aromatic portion of the extract, of significant amounts of non-aromatic fractions boiling between benzene and toluene and between toluene and ethylbenzene or the xylenes.

To be acceptable, the process employed for extraction of aromatic hydrocarbons from mixed feeds should take advantage of all factors tending to increase either or both the selectivity and the carrying capacity of the extractant employed, and it should yield industrial or better grades of the individual aromatic hydrocarbons. If possible, these conditions should be accompanied by a practical measure of heat economy.

It is among the objects of the present invention to provide a method for the economical and substantially complete recovery, from hydrocarbon mixtures having a wide boiling range and containing two or more of the aromatic hydrocarbons: benzene, toluene, the xylenes, ethyl benzene, cymene, cumene, mesitylene, and the like, of one or several of the aromatic hydrocarbons, in a state of purity satisfactory for use in chemical processes and preferably without need for an acid wash to remove olefins. A related object is to provide such a method whereby the carrying capacity of the extractant for aromatic hydrocarbons is increased, without material decrease in its selectivity, through selection and control of the type and amount of hydrocarbon returned to the extractor as reflux and control of the condition of the extractant fed to the extractor. Another object is to provide such a method wherein the hydrocarbon employed as reflux may be recovered from the extract without supplying additional heat thereto. Yet another object is to provide a method whereby the paraffin portion of the feed is diverted to the raffinate and the amount thereof appearing in the extract is minimized. Further objects include the provision of a method, as aforesaid, wherein a small amount of extractant is required, relative to the requirements of other processes, and in which there may be used smaller stripping column and heat exchanger capacity per unit of product than required in other processes. Other objects may become apparent hereinafter.

The method of the present invention may be used to extract aromatic hydrocarbon constituents from liquid hydrocarbon mixtures having a wide or a narrow boiling range. The mixed hydrocarbon feed is of petroleum origin and contains considerable non-aromatic material. It is immaterial to the process whether such feed is one obtained by cracking so-called aromatic or naphthenic petroleum stocks, or is the product of a catalytic reforming operation, so long as it contains mixed aromatic hydrocarbons of the benzene series.

The selective solvent used as the extractant is preferably diethylene glycol, alone or diluted with up to 10 percent by weight of water, as this solvent most readily extracts all of the aromatics from the mixed feed and easily yields individual aromatics of high purity in the process. Other solvents which may be used, with somewhat less advantageous results, include ethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, and mixtures of these with one another or with diethylene

glycol. In most cases, the addition of small amounts of water increases the selectivity of the solvent or solvent mixture employed and prevents loss of solvent to the raffinate.

In carrying out the method of the present invention, a liquid mixture of aromatic and non-aromatic hydrocarbons is fed to a counterflow multistage extraction system near the middle, under enough pressure to keep the contents of the system liquid at the prevailing temperature, while the selective solvent is supplied to the system near one end, coming into extractive two-phase liquid contact with the feed. (In a preferred embodiment, the hydrocarbons and the solvent are heated to a temperature above the atmospheric pressure boiling point of the most volatile aromatic hydrocarbon present and preferably not much above that of the next higher boiling aromatic. Thus, when benzene and toluene are both present, the extraction system is operated conveniently at a temperature above 80° C. and preferably not much above 110° C., though temperatures up to 120° or 125° C. may be used.) A raffinate which is substantially free from aromatic hydrocarbons is withdrawn from the end of the system at or near which the solvent is admitted. The extract, which is rich in aromatic hydrocarbons, is withdrawn from the other end of the system and is fed to a prestripper, preferably insulated, operated at a pressure no higher, and preferably lower, than that maintained in the extractor. Little or no heat, other than that in the extract, needs be supplied to the prestripper, and the vapors of the lowest boiling aromatic present and any co-extracted non-aromatics boiling at or below the same temperature are released continuously to a condenser from which the condensate may be pumped to the extractor as reflux, entering near the end from which the extract was removed. Alternatively, and advantageously, the vapors from the prestripper may be led to a small rectifying column from which the light non-aromatics pass overhead and, after condensation, are pumped into the extractor at a point nearer the center than that at which the more highly aromatic reflux is returned near the end of the system. The remaining and generally larger portion of the extract leaves the bottom of the prestripper and goes to a main stripper column from which aromatics pass as overhead to a rectifying system for final separation of the aromatics. The main stripper may be operated at atmospheric pressure or under vacuum. Most conveniently it is run at atmospheric pressure as a partial steam still, small amounts of steam being injected near the bottom of the column to form a steam "blanket" which protects the hot solvent from degradation. Part of the steam serves to drive off aqueous azeotropes of the aromatics at temperatures below the normal boiling points of those hydrocarbons. The selective solvent is withdrawn from the bottom of the heated stripper and is returned to the extractor, usually at a temperature sufficient to heat the fluids therein to the desired extraction temperature.

The prestripped light portion of the extract which is returned as reflux to the extractor materially increases the selectivity of the extractant under those conditions which give constant carrying capacity to the solvent, and increases the carrying capacity of the solvent under those conditions which give constant selectivity. Thus, any returned non-aromatics have the effect of altering the initial ratio of such materials in the feed stock, and tend to decrease the proportion of such non-aromatics going to the extract and to increase the proportion of such materials going to the raffinate. At the same time, the light aromatic fraction returned to the extractor increases the capacity of the solvent phase for aromatic hydrocarbons. The net result is the substantially complete extraction of aromatics, the extract containing only a minimum of light non-aromatics. Although the carrying capacity of glycolic extractants for mixtures of several aromatic hydrocarbons (e. g., benzene, toluene and xylenes) is not as great as that for a single aromatic hydrocarbon, the extractive power of such solvents on mixed feeds of wide boiling range becomes nearly as great as that on feeds of narrow boiling range when most of the lightest aromatic hydrocarbon present is returned as reflux.

The relative solubilities of various aromatic hydrocarbons in diethylene glycol are shown in the following table, in percent by weight.

	Anhydrous Glycol, 25° C.	Glycol and 2 percent water	
		25° C.	150° C.
Benzene	31.3	25	52.6
Toluene	17.2	13.3	21.8
Xylenes	8.7	7	14

A similar preference is shown by other glycols for the lighter aromatic hydrocarbons. The use of the lightest aromatic present as reflux to the extractor results in an increased carrying power for all the aromatics, while the return of mixed aromatics as reflux cannot do so. To illustrate, assume that the mixed feed employed is such as to deliver to the extractor in unit time 10 parts by weight of benzene, 20 parts of toluene and 20 parts of xylene, and that, in the same unit of time there is to be recovered 50 parts by weight of the mixed aromatics, using a reflux ratio of 4 parts of recycled aromatic for each part by weight of recovered aromatic. Assuming first the use of a mixed reflux containing all the aromatic hydrocarbon constituents of the feed, in the proportions in which they exist in the feed, the desired results are obtained under the following conditions:

	Total Aromatics from Extractor		Reflux		Product to Rectifier	
	Weight per-cent	Weight per unit time	Weight per-cent	Weight per unit time	Weight per-cent	Weight per unit time
Benzene	20	50	20	40	20	10
Toluene	40	100	40	80	40	20
Xylene	40	100	40	80	40	20
Total	100	250	100	200	100	50

Hence, enough solvent must be recirculated to provide carrying capacity for 5 times as much toluene and xylene as is being introduced to the extractor, to effect total aromatics extraction. When, on the other hand, only the benzene is returned as reflux, the following conditions will give the desired complete recovery of aromatics:

	Total Aromatics from Extractor		Reflux		Product to Rectifier	
	Weight per-cent	Weight per unit time	Weight per-cent	Weight per unit time	Weight per-cent	Weight per unit time
Benzene	84	210	100	200	20	10
Toluene	8	20	-------	-------	40	20
Xylenes	8	20	-------	-------	40	20
Total	100	250	100	200	100	50

In this case, only the amount of solvent needs be recirculated to provide carrying capacity for the amounts of toluene and xylenes being fed to the extractor. The effect of the benzene reflux is to give the solvent a carrying power for the mixed aromatics approaching that of the same solvent for benzene alone.

The practice of the invention may be understood and

will be described with reference to the annexed drawings in which

Fig. 1 is a flow diagram of the process of the invention; and

Fig. 2 is a flow diagram of a modification of the process.

Referring first to Fig. 1, mixed liquid hydrocarbon feed containing both non-aromatic and aromatic hydrocarbons is introduced through pump 10 under pressure to a counter-current multistage extractor 11 at a point near the middle of the extractor. A selective solvent for aromatic hydrocarbons, which is essentially immiscible with the aliphatic hydrocarbon constituents of the feed, and is at a temperature above 40° C., and preferably from 80° to 125° C., is introduced through pump 12 and line 13 under pressure to the extractor 11 near one end thereof. A raffinate, substantially freed from aromatic constituents, is withdrawn from that same end of extractor 11 through line 14 and throttle valve 15. The aromatic-rich extract is withdrawn from the other end of the extractor 11 through line 16 and throttle valve 17 or equivalent means for maintaining a pressure differential between the extractor and the outlet of line 16. The said extract flows from line 16 to a prestripper 18 which is at a lower pressure than that in the extractor. The light ends of the aromatic content of the extract, usually benzene, together with most of the light aliphatic portion of the extract, escape from the prestripper 18 through line 19 to condenser 20, where they are condensed and returned through line 21 and pump 22 to extractor 11 near the end thereof from which the extract is withdrawn. Though usually not necessary, heat may be added to prestripper 18 by reboiler 23. The bottoms from prestripper 18, consisting of all of the solvent from the extract phase, all of the higher aromatics, and the same amount of benzene as is in the original feed, flows through line 24 to a main stripper column 25. Heat is supplied to column 25 by reboiler 26, and distillation of the aromatics from the extract may be facilitated and the water content of the solvent may be adjusted by injection of steam to column 25, near its bottom. The aromatics pass overhead from column 25 as vapor through line 27 to condenser 28, under vacuum if desired. The condensed aromatics may thereafter be freed from water and rectified to separate and recover commercially pure fractions. The stripped solvent is withdrawn as bottoms from column 25 through line 13 and pump 12 for return to the extractor 11. The temperature of the so-returned solvent is usually high enough to heat the contents of the extractor to the desired extraction temperature which is above the boiling point of the lightest aromatic in the feed at the pressure prevailing in the prestripper 18.

In the method diagrammed in Fig. 2, the light ends of the extract, including the lightest aromatic from the feed, are flashed from prestripper 18 through line 30 to a column 31 equipped with a reboiler 32 and condenser 33. Sufficient reflux is maintained to column 31 to separate the non-aromatic light ends from the predominantly aromatic (benzene) portion of the material treated in column 31. The non-aromatic condensate from condenser 33 is returned through line 34 and pump 35 to the extractor 11, entering most advantageously at a point between the central point of entry for the raw mixed feed and the end from which the aromatic-rich extract is removed. The highly aromatic bottoms, usually 90 percent or more benzene, from column 31 are returned through line 36 and pump 37 to the extractor at a point nearer the end from which the extract is withdrawn than the point at which line 34 returns the predominantly non-aromatic reflux. The process represented by Fig. 2 is otherwise the same as that described with respect to Fig. 1.

The extractor 11 is illustrated as though it were a vertically disposed column, but it should be understood that it may be any countercurrent multistage extractor system capable, at each stage, of operation under pressure sufficient to maintain all components of both the hydrocarbon phase and the extract phase in the liquid state at the operating temperature. Thus, the extraction system may comprise a series of closed vessels, provided with mixing and settling means, from which the raffinite phase flows in one direction and the extract phase in the other.

In the operations contemplated in the prior application identified above, the extract phase is taken to a stripper from which the total aromatic content is taken overhead, and most of the resulting mixed aromatic distillate is returned as reflux to the extractor. Hence, the reflux, in that prior method, has essentially the same mixture of aromatics in about the same proportions as the mixture contained in the initial feed. To effect complete stripping in one unit, in that manner, considerably more heat is required than in the present method. The respective amounts of steam required for stripping benzene, toluene and the xylenes from the extract are progressively larger, and the volume of extract to be stripped is large in the prior process because of the limited carrying capacity of the solvent when the mixed aromatics are returned as reflux. When treating feeds of wide boiling range to free them of the mixture of aromatics therein, most of the non-aromatics found in the extract boil near benzene. Hence, the prestripping of the extract to remove most of the benzene provides a mixture going to the final stripper, in the present process, having much less non-aromatics than does the extract fed to the single stripper in the prior process.

The following contrasting examples were carried out using the same mixed hydrocarbon feed, the same solvent, the same temperature and pressure conditions in the extraction zone, and a constant 10-to-1 solvent-to-feed ratio to extract 98 percent of the aromatics from the feed. The feed stock in each case was a gasoline having a boiling range from 150° to 300° F. which had been reformed by contact with a platinum catalyst in the so-called "Platforming" procedure described in Industrial and Engineering Chemistry, vol. 42, page 582 (1950). This feed contained 5.5 percent by weight of benzene, 24.5 percent of toluene, and 26.8 percent of xylenes and higher aromatics. The solvent used was diethylene glycol containing 2 percent of water, and the temperature in the extractor was kept at 50° to 60° C. When a single stripper was used and a portion of the mixed aromatics was returned to the extractor as reflux, the carrying capacity of the solvent for the aromatics present was 10 percent, and the amount of reflux was necessarily limited to the weight of the feed or about 1.75 times the weight of total aromatics being recovered to prevent loss of aromatics to the raffinate. Under these conditions, the purity of the aromatic product was only about 90 percent, the balance being a mixture of paraffinic and olefinic impurities. By way of contrast, when the extract was prestripped as in the method outlined in Fig. 1, and the benzene and light non-aromatic overheads from the prestripper were returned as reflux, the carrying capacity of the solvent for aromatics was found to be 20 percent and 3.5 pounds of reflux could be used per pound of recovered product without loss of aromatics to the raffinate. The aromatic product fed from the final stripper 25 to rectifiers consisted of 97.5 percent aromatic and only 2.5 percent of easily separable non-aromatics. When using the procedure illustrated in Fig. 2, under otherwise the same conditions, the purity of the recovered aromatics was increased further to about 98 percent. In the foregoing examples, the solvent in each case was carrying its capacity of aromatics as it left the extractor, and any increase in reflux ratio or decrease in solvent-to-feed ratio resulted in loss of aromatics to the raffinate, while any decrease in the reflux ratio or increase in the solvent-to-feed ratio resulted in isolation of a more impure product.

It has been shown that the nature of the reflux stream materially influences the carrying capacity of the solvent and that return of light ends as reflux increases the selectivity of the solvent. Accordingly, at a given solvent-to-

feed ratio, the present method yields a purer aromatic product than prior methods, and conversely, an aromatic product of any given quality can be obtained in this method when using a lower solvent-to-feed ratio than is required to make such a product in prior processes.

The present process minimizes the problems arising from the presence of olefins in the extract. It has been shown that most of those olefins are separated from the product in the prestripper 18 and are returned as reflux to the extractor. It has been noted before that olefins tend to concentrate in fractions boiling below benzene, between benzene and toluene, and between toluene and the higher aromatics, such as the xylenes. This permits nearly complete separation of the small amounts of olefins reaching the rectifying stage of the present process as heads and middle cuts. Any small traces remaining may be removed if desired by clay treatment, by chlorination, or by sulfuric acid treatment, but it is found that rectification alone provides individual aromatics with low bromine index values (Analytical Chemistry 19, 869 (1947)) within the tolerance limits for industrial grades of those aromatics. The process yields a benzene fraction consistently which freezes at 5.2° to 5.5° C. and is suitable for practically all industrial and chemical purposes without further treatment. The toluene and xylene products are of "industrial" grades or better, as defined in the ASTM standards.

The process of the invention may employ any of the glycols or mixtures thereof suggested above. The glycolic solvent employed must be one which is substantially immiscible with non-aromatic hydrocarbons, to prevent substantial loss of solvent in the substantially aromatic-free raffinate. Some glycols are miscible with non-aromatic hydrocarbons when anhydrous, but become substantially immiscible therewith when small amounts of water are dissolved in the glycol. In the appended claims, then, the term "glycolic selective solvent" is intended to means any glycol or mixture of glycols, together with such water as may be needed to avoid substantial miscibility with the predominantly non-aromatic raffinate at the temperature prevailing in the extractor. If the glycol used tends to follow the raffinate, it is convenient to introduce a small amount of water countercurrent to the raffinate to extract the glycol therefrom. The water employed may, for convenience, be that which is separated from the aromatics in the stripping and rectifying stages.

We claim:

1. A process for the separation of a plurality of aromatic hydrocarbons of the benzene series from a mixture thereof with non-aromatic hydrocarbons which comprises introducing the mixture into a counterflow multistage extraction system near the middle; introducing a glycolic selective solvent, which is substantially immiscible with non-aromatic hydrocarbons, into one end of the system into extractive contact with the hydrocarbon phase therein; maintaining the extraction system under pressure sufficient to keep the flowing contents liquid, and maintaining the flowing contents of the extraction system at a temperature above 40° C.; withdrawing substantially aromatic-free and glycol-free raffinate from the same end of the system as that at which solvent is introduced; withdrawing the aromatic-rich glycolic extract from the other end of the system; prestripping said extract under evaporative conditions to liberate the majority of only the most volatile aromatic therefrom together with non-aromatics of equivalent volatility; condensing the so-liberated vapors and using the so-condensed material as the sole hydrocarbon reflux to the extraction system; returning said reflux to the extraction system near its said other end; conducting the remainder of the extract to a heated zone; stripping the remaining aromatic hydrocarbons from the solvent in said zone; subjecting the said remaining aromatic hydrocarbons to rectification; withdrawing them as product from the system; and returning the substantially hydrocarbon-free solvent to the extraction system.

2. The process as claimed in claim 1, wherein the feed contains benzene and significant amounts of higher aromatics of the benzene series, and the hydrocarbons released from the extract for return to the extractor are chiefly benzene and lighter non-aromatics.

3. The process as claimed in claim 1, wherein the feed contains benzene and significant amounts of higher aromatics of the benzene series, and the temperature in the extraction zone is kept above 80° C. and below 125° C.

4. The process as claimed in claim 1, wherein the selective solvent employed is predominantly diethylene glycol.

5. The process as claimed in claim 4, wherein the diethylene glycol contains from 0.5 to 10 percent by weight of water.

6. The process claimed in claim 1, wherein the temperature in the extraction system is maintained mainly by the hot solvent returned to that system from the heated stripping zone.

7. The process claimed in claim 1, wherein the extraction system is operated under superatmospheric pressure and at a temperature above the atmospheric pressure boiling point of the most volatile aromatic present, and the reflux stream is obtained by flashing the vapors of said aromatic from the extract at a lower pressure in the prestripping zone.

8. A process for the separation of a plurality of aromatic hydrocarbons of the benzene series from a mixture thereof with non-aromatic hydrocarbons which comprises introducing the mixture into a counterflow multistage extraction system near the middle; introducing a glycolic selective solvent, which is substantially immiscible with non-aromatic hydrocarbons, into one end of the system into extractive contact with the hydrocarbon phase therein; maintaining the extraction system under pressure sufficient to keep the flowing contents liquid, and maintaining the flowing contents of the extraction system at a temperature above 40° C.; withdrawing substantially aromatic-free and glycol-free raffinate from the same end of the system as that at which solvent is introduced; withdrawing the aromatic-rich glycolic extract from the other end of the system; prestripping said extract under evaporative conditions to liberate the majority of only the most volatile aromatic therefrom together with non-aromatics of equivalent volatility; fractionating the prestripped vapors to form an overhead portion rich in non-aromatics and a bottom portion consisting chiefly of the most volatile aromatic hydrocarbon from the original feed; returning the aromatic bottoms as reflux to the extraction system near the end from which the extract is removed; condensing the overhead portion and returning it as reflux to the extraction system at a point between the last said end and the middle; conducting the remainder of the extract to a heated zone; stripping the remaining aromatic hydrocarbons from the solvent in said zone; rectifying the aromatic hydrocarbons and returning the substantially hydrocarbon-free solvent to the extraction system.

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