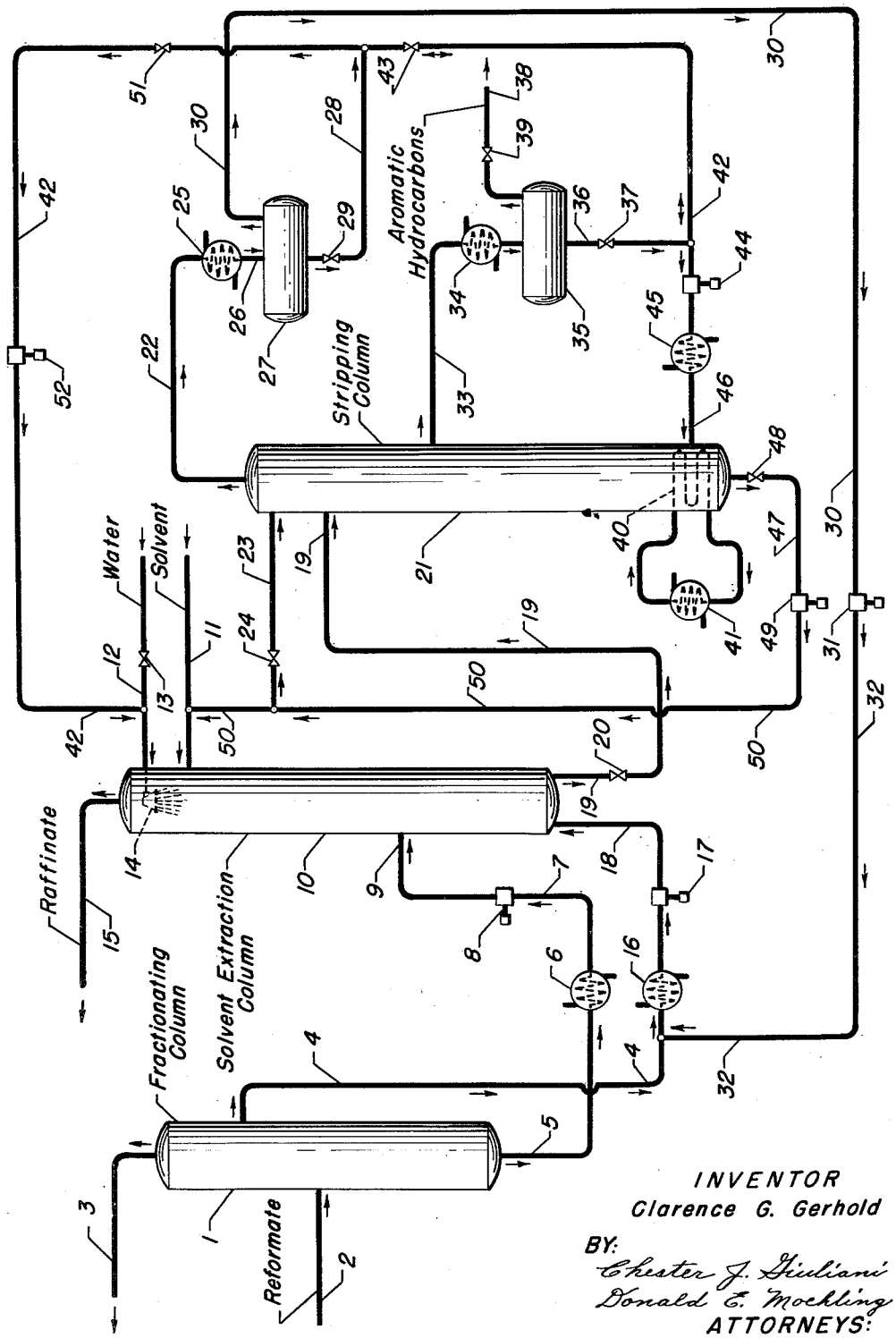
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SELECTIVE SOLVENT EXTRACTION PROCESS FOR THE SEPARATION OF MIXTURES OF AROMATIC AND NON-AROMATIC HYDROCARBONS

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SELECTIVE SOLVENT EXTRACTION PROCESS FOR THE SEPARATION OF MIXTURES OF AROMATIC AND NON-AROMATIC HYDROCARBONS

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This application is a continuation-in-part of my copending application Serial No. 304,558, filed August 15, 1952, now abandoned, which in turn is a continuation-in-part of application Serial No. 238,508, filed July 25, 1951, now abandoned.

This invention relates to a process for the separation of hydrocarbon mixtures with the aid of a selective solvent for the purpose of separating and recovering the aromatic hydrocarbon components of the mixture. In one of its more specific applications the process of the present invention serves to segregate a particular specie of aromatic hydrocarbon, such as benzene and/or toluene, from other classes of hydrocarbons that are normally contained in petroleum distillates, and utilizes a solvent which may be indefinitely recycled in the system, yields the desired hydrocarbon product in a state of high purity and separates the same substantially in its entirety from the feed stock charged to the process.

The present invention is concerned with an improvement in the type of separation process wherein a mixture of various classes of hydrocarbons is introduced into an extraction zone at an intermediate point thereof and is countercurrently contacted therein with a solvent selective for the aromatic hydrocarbons contained in the mixture, a raffinate phase comprising substantially all of the non-aromatic hydrocarbons in the feed stock is removed from the end portion of the extraction zone at which the solvent is introduced, an extract phase comprising the aromatic components of the feed stock dissolved in the selective solvent is removed from the other end portion of the extraction zone and the aromatic solute is subsequently recovered by stripping the extract phase.

In accordance with the present invention the extract phase is substantially freed, prior to its removal from the extraction zone, of substantially all of the non-aromatic components dissolved by the solvent from the feed stock by introducing a light paraffinic hydrocarbon which is more volatile in the presence of the solvent than either the aromatic or raffinate components of the feed stock into the extraction zone at a point closer to the point of removal of the extract phase than the point of introduction of the feed stock and displacing into the raffinate stream the residue of non-aromatic component dissolved in the solvent from the feed stock by the more volatile light paraffin, thereafter separating the more volatile non-aromatic component contained in the resultant extract phase by stripping the extract after its removal from the extraction zone.

The recovery of a substantially pure aromatic hydrocarbon product from a mixed hydrocarbon feed stock containing non-aromatic hydrocarbons of approximately the same boiling point as the extract by stripping the extract phase is feasible only because the presence of the solvent in the distillation zone has less effect on the boiling point of the raffinate compounds dissolved in the solvent than it does on the boiling point of the extract compounds also dissolved in the solvent. In general, the solvent tends to retain in solution the more soluble aromatic component, even at temperatures of the solvent considerably above the boiling point of the extract. This retentivity of the solvent for the preferentially soluble aromatic compound is shown by the fact that when the extract

phase is subsequently stripped, the raffinate-type compound dissolved in the solvent vaporizes therefrom more readily (i.e., at a lower temperature) than the aromatic component comprising the extract dissolved therein. In the present solvent extraction-recovery process, wherein the extract phase is contacted before it enters the stripping zone with a displacing agent comprising a light paraffinic hydrocarbon more volatile than the feed stock raffinate, the latter component is displaced therefrom and replaced with the more volatile light paraffin. The removal of all of the raffinate-type compound from the extract phase is thus accomplished with less extract component (aromatic product) being vaporized overhead therewith because the heavy non-aromatic hydrocarbons have been displaced from the extract or rich solvent before the aromatic solute is recovered therefrom by stripping. Since the overhead fraction from the stripping operation is generally recycled to the solvent extraction zone to recover aromatic component vaporized into the overhead fraction, the volume of recycle fraction and the corresponding load on the extraction zone is substantially less when utilizing the process flow herein provided. Furthermore, the resulting reduction of heat load on the stripping column represents a substantial economy in operation of the entire process and permits the recovery of a pure aromatic extract product.

In a preferred embodiment of the present process, the extract or rich solvent phase from which the residual non-aromatic feed stock components have been substantially displaced by the more volatile paraffinic displacing agent is removed from the extraction zone and introduced into the top portion of a stripping zone, wherein substantially all of the volatile paraffin is vaporized from the extract phase (i.e., in the presence of the solvent), the vapor stream being removed from the top portion of the distillation zone, returned to the extraction zone, and charged ino the bottom of the extractor to obtain maximum countercurrent contact thereof with the rich solvent stream. Aromatic extract product substantially free of both feed stock non-aromatics and light paraffin displacing agent, as well as from selective solvent is removed as a side stream from the stripping zone and the rich solvent residue comprising the solvent from which the volatile components have been distilled is removed from the bottom portion of the stripping zone and is recycled to the extraction zone for repeated use therein as extractant.

The present method of separation is particularly suitable for recovering a single aromatic hydrocarbon such as benzene or a mixture of two or more aromatic hydrocarbon species, such as benzene, toluene and xylene, from a hydrocarbon mixture containing aromatic and non-aromatic hydrocarbons. A preferred method of extracting such a hydrocarbon mixture comprises introducing the hydrocarbon feed stock comprising a mixture of said aromatic and non-aromatic components into a countercurrent liquid-liquid phase extraction zone with a selective solvent which preferentially dissolves the aromatic component, one of the preferred solvents for this purpose consisting of an aqueous oxy-diethylene glycol solution containing from about 5 to about 15% by weight of water and from about 85 to about 95% by weight of glycol said selective solvent being introduced into the upper portion of the extraction zone to form a downwardly flowing, rich solvent stream, the mixed hydrocarbon feed stock being introduced at an intermediate portion of the extraction zone which is maintained at a temperature of from about 100° to about 250° C. and at a superatmospheric pressure sufficient to provide substantially liquid phase conditions in the extraction zone, forming thereby a raffinate comprising the non-aromatic hydrocarbon component of the feed stock, and

a liquid extract or rich solvent comprising solvent and the one or more aromatic hydrocarbon components of the feed stock, introducing a non-aromatic hydrocarbon fraction, which is more volatile than the aromatic component of the hydrocarbon mixture in the presence of the solvent into the bottom portion of the extraction column in counter-current flow relationship with the extract and in an amount sufficient to displace the non-aromatic hydrocarbon feed stock component from the rich solvent, removing the raffinate from the top of the extraction column and an extract rich solvent stream from the bottom of the column, introducing the latter stream at substantially the aforementioned temperature and pressure into the top portion of a stripping zone, isothermally reducing the pressure on the rich solvent in the upper portion of said stripping zone, whereby at least the volatile hydrocarbons dissolved in said rich solvent vaporize, separating a vapor fraction comprising volatile non-aromatic hydrocarbons dissolved in the rich solvent stream, returning the resulting vapor fraction to the bottom portion of the extraction zone to countercurrently mix therein with the downwardly flowing rich solvent stream, isothermally separating at a further reduced pressure a higher boiling fraction from a lower level of said stripping zone consisting essentially of water and said aromatic hydrocarbon component and separately recovering the water and aromatic hydrocarbon.

The process of the present invention is particularly distinguished by its economy and great flexibility of operation, yielding a product of high purity at a relatively high throughput rate of feed stock. The particular economy of operation realized in the preferred embodiment of the present separation method is the result of operating both the extraction zone and the stripping zone at substantially isothermal conditions. Except for the small heat load required for vaporizing the residue of aromatic solute from the rich solvent stream in the final stages of the stripping step, the process may be operated without substantial additional heat input, an especially important factor in the adaptation of the process to commercial use. The great industrial demand for starting materials of high purity in product synthesis, such as "nitration grade" toluene of 99+% purity and essentially 100% pure benzene has been met in the present separation process by providing a special reflux recycling technique in which the process is made more selective for the recovery of these hydrocarbons.

Typical hydrocarbon mixtures utilizable as charging stock in the present process include distillate fractions of catalytically cracked naphthas, specific boiling range fractions of natural or straight run petroleum distillates, and especially, certain reformed or hydroformed naphthas which are generally relatively rich in aromatic hydrocarbons and which comprise a particularly valuable source of benzene, toluene, and the xylenes, as well as the polynuclear aromatics in the higher boiling fractions. In the case of charge stocks comprising hydrocarbon mixtures containing components of different structural classes, the solubility of the components in the present solvents decreases in the general order: aromatic, cyclo-olefinic, cyclo-paraffinic, and aliphatic paraffinic hydrocarbons. Thus, any member or individual class in the fore part of the series may generally be separated from any succeeding member or class of the series, utilizing the present selective solvent and extraction procedure.

One of the outstanding and particularly useful applications of the present method of separation, providing a means of resolving a mixture of components not readily separable into its constituents by customary methods of separation, as for example by fractional distillation, is the separation of an azeotropic mixture of hydrocarbons such as a C_6 fraction of a petroleum distillate containing benzene, hexane and heptane isomers or a toluene-heptane-octane mixture. Such azeotropes boil over a considerable range of temperatures and contain varying proportions of the aromatic hydrocarbon constituent. By means of the present method of separation, an aromatic concentrate representing substantially all of the aromatic components present in the initial hydrocarbon mixture and of greater than 95% purity may be recovered as the primary product, although a product of such purity is separable, if at all, by other means such as fractional distillation only at great expense or by complex separation procedures. Although very small amounts of raffinate hydrocarbons in admixture with the desired extract hydrocarbon may accompany the rich solvent from the extraction zone, the proportion thereof in the ultimate product may be limited to extremely low concentrations when operating the process in accordance with one of the preferred procedures herein provided.

The selective solvent employed in the present separation process may be a single component liquid of essentially pure primary solvent or a two-component, normally liquid mixture, one of the components, herein designated as the primary solvent, exerting a selective solubilizing effect on the aromatic hydrocarbon to be recovered as product, and the other component, termed the secondary solvent, having a lower boiling point than the primary solvent and having little solubilizing effect on the raffinate component of the feed stock but soluble in all proportions with the primary solvent. Although the presence of the secondary solvent in the selective mixture employed in the process tends to reduce the solvent capacity of the solvent for the extract component of the feed stock and therefore tends to reduce the volume throughput of feed stock capable of being extracted in a column of given size, the secondary solvent has the effect of increasing the selectivity of the solvent mixture for aromatic hydrocarbons by reducing the solubility of raffinate-type compounds in the rich solvent, particularly when the final product is desirably a single individual compound as free of raffinate contaminants as possible. By maintaining the solvent to feed stock ratio charged into the extraction stage of the process at a high level in accordance with a preferred means of operating the present separation process, a relatively high rate of throughput and the desired objective of recovering a product highly concentrated in a single component substantially free of other contaminants may be realized.

The presence of the secondary solvent which has a boiling point below that of the primary solvent in the selective solvent mixture enables the solvent stripping stage of the process to be operated at a correspondingly lower temperature than in its absence and enables the recovery of all the aromatic hydrocarbon by stripping therefrom. The secondary solvent component of the selective solvent increases the vapor pressure of the extract dissolved in the solvent when the rich solvent is subjected to stripping. The resulting greater volatility of the aromatic extract permits recovery of the latter from the rich solvent at a lower temperature and more completely.

A particularly desirable arrangement for operation of the solvent stripper unit of the present process is to remove secondary solvent as a side-cut from the column and recycle the resulting stream of secondary solvent continuously, as separated, to the reboiling section of the column wherein it reduces the partial pressure of the dissolved extract component, thereby continuously and completely removing the extract from the rich solvent at a temperature below the decomposition temperature of the primary solvent.

Compounds utilizable as the primary solvent component of the present selective solvent composition are selected from the general group broadly characterized as oxygen-containing organic compounds. Particularly suitable primary solvents are the aliphatic and cyclic alcohols, glycols and glycol ethers (also referred to as the polyoxy-polyalkylene glycols) as well as the glycol esters and glycol ether-esters. Alkylene glycols and polyoxy-

polyalkylene glycols which are a particularly effective class of selective solvents include the di-, tri-, and tetra-oxy-ethylene glycols, particularly oxy-diethylene glycol, and mono-, di-, and tri-oxy-propylene glycols; certain glycol ethers, such as the Cellosolve series of compounds (defined structurally as the alkyl ethers of ethylene glycol), including methyl-, ethyl-, propyl-, and butyl Cellosolve; the Carbitols (defined structurally as the alkyl ethers of diethylene glycol), such as methyl-, ethyl-, propyl-, and butylcarbitols; the glycol and polyoxyalkylene glycol esters of low molecular weight organic acids such as the acetates and propionates; and other oxygen-containing organic compounds such as phenol, resorcinol, pyrocatechol, etc.; various alkyl phenols, such as the ortho-, meta-, and para-cresols, thymol, etc.; and the oxydialkylene-nitriles, such β,β'-oxydipropionitrile and others.

The secondary solvent which may optionally be utilized in admixture with the primary solvent to reduce the solubility of the raffinate component of the feed stock in the solvent and thus enhance the selectivity of the solvent for the extract component is a compound which is preferably substantially insoluble with or in the components of the feed stock. Its insolubility in the feed stock and solubility in the primary solvent enables the secondary solvent to be recycled to the top of the extraction column and to be there mixed with the effluent raffinate to remove the normally small amount of primary solvent which tends to dissolve in the raffinate as the latter flows countercurrently through the solvent in the liquid-liquid phase extraction column. In general, secondary solvents have the common characteristic of being insoluble or substantially insoluble in the raffinate. Normally liquid compounds having the above properties and preferably having a boiling point substantially below the boiling point of the primary solvent are such materials as water, furan, furfural, furfuryl alcohol, the poly-halogen substituted fatty acids, and the like, such as 1,2-dichloro-1,2-tetrafluoroethanol, perfluoroacetic acid and others. One of the preferred secondary solvents utilized in admixture with the primary solvents is water, present in the selective solvent in an amount sufficient to form a mixture containing from about 5% to about 75% by weight of water. In admixture with oxydiethylene glycol, the proportion of water is preferably from about 5 to about 35%, and preferably, from about 5 to about 10% by weight of the mixture. For the polypropylene glycols, the proportion of water in the mixed selective solvent is from about 8 to about 50%, and preferably from about 10 to about 40% by weight of the mixture. As the chain length of the alkylene group in the alkylene glycols increases, the selectivity of the solvent decreases and both the raffinate and extract hydrocarbons become more soluble in the solvent. It thus becomes essential to increase the proportion of secondary solvent such as water, in the solvent mixture (up to about 75% by weight of the mixture) to increase the selectivity of the solvent mixture as the primary solvent component becomes less selective.

Other embodiments of the invention and a correlation of the principles upon which the present separation process operates is further described in the accompanying diagram which represents a process flow typical of one of the preferred embodiments of this invention for the separation of a mixture of benzene, toluene, xylene and aliphatic paraffins containing from 6 to about 10 carbon atoms contained in a petroleum fraction such as a naphtha separated from the products of a catalytic reforming reaction, such as the Platforming process. The diagram is described on the basis of recovering benzene of 99+% purity, toluene of 98.5 to 99+% purity, and xylene of at least 95% purity, and for this purpose a particularly suitable solvent is a diethylene glycol-water mixture containing preferably, from about 5 to about 10% by weight of water or an aqueous triethylene glycol containing up to about 20% by weight of water. For the recovery of benzene, toluene and xylene the charge stock is a gasoline boiling range fraction boiling up to about 215° C., although for the recovery of benzene alone from a petroleum fraction, the latter preferably boils at an upper limit somewhat below the boiling point of toluene or about 110° C. and at a lower temperature limit above the boiling point of the benzene azeotropes in the fraction, which in the case of a hydroformed petroleum fraction containing paraffin homologs in admixture with benzene, is about 79–80° C.

Referring to the accompanying flow diagram, a gasoline boiling range petroleum distillate fraction boiling up to about 215° C. is charged into a fractionating column **1** through line **2**, and the feed stock is roughly fractionated therein into a vapor which leaves the top of column **1** as a light fraction consisting principally of gaseous hydrocarbons, such as butenes, butanes and some C_5 isomers. The vapor is removed from the column through line **3**, condensed, and discharged from the process to storage or other disposal. An intermediate fraction consisting of pentanes and hexanes as well as the corresponding C_5 and C_6 olefins, if any, and naphthenes is removed from column **1** through line **4**. The intermediate cut removed from column **1** through line **4** is directed into subsequent stages of the process for use as a light paraffin reflux fraction as hereinafter described. A bottoms fraction containing C_6 to about C_{10} hydrocarbons, including benzene, benzene azeotropes, toluene, xylene and paraffinic, naphthenic and olefinic hydrocarbons, if any, is removed from fractionating column **1** through line **5**, and charged as the aromatic-containing feed stock into the solvent extraction stage of the process. The latter fraction diverted into the process flow through line **5** is passed through heat exchanger **6** of sufficient heating capacity to raise the temperature of the feed stock to a level of from about 100° to about 250° C., preferably from about 125° to about 160° C. The fraction is maintained in liquid phase at the above temperature by compression to a superatmospheric pressure, generally within the range of from about 50 to about 150 lbs./in.^{2}, the fraction being pumped from heater **6** through line **7** by pump **8** and thereafter charged by way of line **9** into extraction column **10**.

The liquid charge stock at the above indicated pressure is desirably charged into column **10** at a point intermediate the top and bottom of the column, between the respective rich solvent and raffinate outlet ports and substantially above the rich solvent outlet to provide sufficient space for countercurrent flow between a stream of the volatile paraffin displacing agent and the rich solvent stream, as hereinafter described. The mixture of aromatic and other hydrocarbons introduced as primary charge stock into solvent extraction column **10** is countercurrently contacted within the column with the aqeous glycol solvent, introduced into column **10** through line **11** having a solvent inlet port at approximately the upper end of the column. Extraction column **10** is a suitable arrangement of conventional liquid-liquid extraction equipment designed to intimately contact and mix two liquids at least partially immiscible with each other by countercurrent flow therethrough and may be a packed tower containing a packing with large superficial area such as Berl saddles or the like, or it may be a bubble plate extraction column of well known design and fabrication.

The hydrocarbon feed stock at its point of entry into extraction column **10** is of considerably lower density than the aqueous diethylene glycol solution admitted into the upper portion of column **10** and therefore tends to percolate upwardly through the downwardly-flowing, higher density stream of solvent when the two substantially immiscible liquids are introduced at the specified points in column **10**. Due to the selective solubility of the aromatic components of the feed stock in the present solvent, the aromatic hydrocarbons tend to dissolve in the glycol solvent phase, leaving a hydrocarbon raffinate

phase relatively lean in aromatics, and consisting primarily of paraffins present in the feed stock. Although the aromatic components are preferentially dissolved in the solvent and the latter contains sufficient water to selectively reject paraffinic, naphthenic, and olefinic components (if any) present in the feed stock, a small amount of the latter hydrocarbons also tend to dissolve in the selective solvent, and the resultant rich solvent stream containing a small quantity of the latter non-aromatic hydrocarbons gravitates downwardly through column **10** flowing upwardly against a stream of raffinate-type hydrocarbons into the lower portion of column **10**. The raffinate phase becomes progressively richer in aliphatic paraffins and olefins and relatively poor in aromatics as the raffinate phase flows upwardly through the column in countercurrent contact with the aqueous glycol solvent.

The raffinate comprising hydrocarbons substantially insoluble in the solvent also contains a minor proportion of dissolved solvent, which, although small in absolute amount, nevertheless when continuously removed from the process flow, represents a substantial loss in large scale operations if not recovered from the effluent raffinate. In order to accomplish this recovery, the make-up water required in the system to hydrate the primary solvent to its selective composition, in an amount sufficient to provide a selective solvent containing from about 5 to about 35% by weight of water, preferably, from about 5 to 10% by weight of water, is introduced into the extraction column at a point above the point of entry for the solvent, such that the upwardly flowing raffinate phase is washed with water just prior to removal of the raffinate from the system and beyond the point at which the raffinate last contacts solvent introduced into the system. The water thus introduced into the flow readily dissolves the diethylene glycol present in the raffinate hydrocarbons and thus recovers the primary solvent otherwise lost from the process flow.

The water introduced into the flow for this purpose is charged into column **10** through line **12** containing valve **13**, joins the glycol solvent introduced through line **11** and mixes therewith to form the selective solvent composition provided herein. A preferred means for introducing the water into column **10** is through a spray head such as **14** which distributes the water stream in the form of finely divided droplets into the raffinate phase with which it is intimately mixed. The water-washed raffinate from which the primary solvent has been substantially completely removed is withdrawn from extraction column **10** through line **15** and removed from the process flow to storage, or for other uses.

In the lower portion of the extraction column, below the point at which the feed stock enters the column, the rich solvent phase becomes progressively richer in benzene in its downward direction of flow. Although the normally raffinate paraffinic, naphthenic and olefinic hydrocarbon components dissolve with benzene in the solvent or extract phase in relatively small amounts when based on the total volume of the rich solvent stream, their amount when based on the volume or aromatics in the rich solvent is sufficient to contaminate the recovered benzene product to a less desirable and less economically valuable product, for example, to produce a product of less than nitration grade quality. Moreover, since these contaminants boil at temperatures corresponding to the boiling points of the individual aromatic azeotropes with these hydrocarbons and therefore tend to distill over with the aromatics in the stripping stage, they are inseparable from the aromatic product by merely simple fractional distillation. In accordance with one of the features of the present method of operation, a paraffinic fraction more volatile than benzene in the presence of the solvent is countercurrently contacted with the downwardly flowing rich solvent stream present in the lower portion of extraction column **10** to displace the feed stock raffinate components from the rich solvent and replace them with paraffins or naphthenes more volatile than benzene in the presence of the solvent. The displacing agent comprising more volatile raffinate-type compounds is preferably introduced into column **10** at a point closely contiguous to the outlet port for the extract phase, generally at the extreme bottom of the column. The volatile displacing agent may be derived from the initial reformed gasoline subjected to fractionation in column **1** as the side-cut fraction removed from column **1** through line **4**. Alternatively, the displacing agent may consist wholly or in part of the volatile overhead distillate from the stripping column recycled to the extraction column **10**, as hereinafter described. The volatile paraffins comprising the displacing agent replaces the heavier or less volatile paraffins, naphthenes and olefins derived from the feed stock which normally dissolve in the rich solvent stream in extraction column **10**. This embodiment of the present invention enables the production of an aromatic extract of high purity in that the contact of the countercurrently flowing rich solvent with the light paraffinic hydrocarbon fraction establishes a desirable liquid phase transfer of the light paraffins into the solvent phase and a simultaneous displacement of the less volatile, feed stock paraffins from the extract into the raffinate phase. The light paraffins are more readily vaporized from the benzene during the stripping stage of the process since they boil, in the presence of the solvent, sufficiently below the temperature of vaporization of the benzene from the solvent that they distill overhead from the rich solvent without appreciable quantities of benzene being vaporized therewith. The final benzene product recovered from the process, therefore, may, by the method of displacement herein provided, be substantially pure benzene depending upon the charging rate of volatile paraffin to the extraction column **10**. The less volatile, non-aromatic feed stock components, such as the heavy paraffins, displaced from the extract phase, as well as the excess of displacing agent, are removed from the process flow by inclusion in the effluent raffinate withdrawn from the flow through line **15**. It is evident that separation between the benzene and light paraffin displacing agent in stripping the rich solvent will be more readily obtained if the difference in boiling points between the components of the displacing agent and the extract is as broad as possible. The quantity of benzene which must be distilled overhead from the rich solvent in the stripping column for the purpose of eliminating the non-benzene impurities therefrom and providing a residue from which pure benzene may be distilled from a lower plate in the distillation column may be thereby substantially reduced.

Referring again to the accompanying diagram, the volatile paraffin fraction recovered as a side cut from fractionating column **1** may contain various pentane and hexane isomers, such as n-pentane, isopentane 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, naphthenes such as cyclopentane, methylcyclobutane, and may contain some heptanes when a wide boiling range fraction is utilized as feed stock. In addition, the fraction may contain various olefin isomers boiling from about 40° to about 65° C. The more volatile paraffiin side cut removed through line **4** is passed through heater **16** and compressor **17** to increase the temperature and pressure of the latter paraffin fraction to the extraction conditions existing in solvent extraction column **10**, in general to temperatures of from about 90° to about 250° C. (preferably, from about 100 to about 150° C.) and to a superatmospheric pressure of from about 5 to about 150 lbs./in.^{2} and is thereafter transferred through line **18** into the bottom of extraction column **10** wherein the volatile paraffins are countercurrently contacted with the downwardly flowing rich solvent phase before the latter is removed from column **10** through line **19**. The rich solvent stream at the bottom of column **10**, consisting principally of the aqueous oxydiethylene glycol solvent and containing the aromatic

components of the feed stock dissolved therein as well as a small amount, relative to the quantity of aromatics contained therein, of said volatile paraffin hydrocarbons which are present by virtue of having displaced the less volatile, raffinate paraffins and other non-aromatic hydrocarbons of the feed stock, is transferred through line 19 containing valve 20 into the top of stripping column 21. This column is preferably designed to operate at substantially the same temperature as extraction column 10, but at a somewhat reduced pressure, sufficient to vaporize the components of the extract more volatile than the diethylene glycol solvent, advantageously at pressures reduced stepwise to atmospheric pressure in the upper portion of column 21, with pressure seals between the several stages. The lighest and most volatile components in the liquid rich solvent charged into the top portion of column 21 are isothermally flashed distilled at the reduced pressure maintained in the first pressure reduction stage in the top of the column, the resulting vapors being removed through vapor overhead line 22. These vapors comprise essentially the volatile paraffin hydrocarbon displacing agent dissolved in the rich solvent as described above since these hydrocarbons boil at a lower temperature in the presence of the solvent than the dissolved aromatic hydrocarbon solute, but may also comprise a substantial proportion of benzene when the pressure reduction in the first stage of the stripping is substantial. In accordance with one method of operating column 21, solvent is recycled through line 23 and valve 24 to the top of the column 21, above the point at which the rich solvent stream is introduced into the column. Even in the absence of such recycling of the solvent, however, the presence of the solvent in the extract phase from line 19 decreases the volatility of the dissolved aromatic component relative to that of the light paraffinic component also present in the extract phase, and thereby minimizes the proportion of the aromatic hydrocarbon tending to vaporize into the vapor overhead fraction flash-distilling from the rich solvent as a result of the first pressure reduction.

The vapor stream removed from column 21 through line 22 is cooled in condensor 25 in order to liquefy the water vapor and hydrocarbons present in this stream. The liquid condensate is charged through line 26 into receiver vessel 27 wherein the liquefied hyrocarbon upper layer containing the volatile paraffin is decanted from the lower layer aqueous condensate which is withdrawn from vessel 27 through line 28 and valve 29. The hydrocarbons comprising the upper layer in receiver 27 and comprising the paraffin hydrocarbon displacing agent are removed from receiver 27 through line 30 and desirably recycled by means of pump 31 to the extraction column 10 through line 32 which connects with line 4. The light paraffin overhead is thereby commingled with the volatile paraffin fraction distilled from the initial reformate charging stock, as aforesaid. The commingled volatile paraffins thus introduced into heat exchanger 16 and compressed by means of pump 17 are admitted into the bottom of column 10 at the desired operating conditions hereinbefore specified.

The volume of the paraffin fraction charged into column 10 is preferably as large as practicable to obtain the greatest possible quantitative displacement in column 10 of the less volatile paraffins dissolved in the extract therein and thereby produce a purer ultimate aromatic product. It may under some circumstances be preferred, however, to obtain a larger throughput of charging stock and a higher production rate of recovered product on a volumetric basis, as for example, when a greater tolerance for paraffin contaminants in the aromatic product is permissable. The liquid volume load on column 10 may be reduced in such instances by reducing the volume of volatile paraffins charged into the column for the purpose of displacing the less volatile, feed stock raffinate paraffins from the rich solvent. The volatile paraffin recycle from column 21 to column 10 may be omitted and the sole source of these paraffins charged into the bottom of column 10 may be the light paraffins fractionated from the gasoline in fractionating column 1 and removed therefrom through line 4, as described above.

The introduction of the rich solvent recovered from solvent extraction column 10 into solvent stripping column 21 at a superatmospheric pressure and at a temperature considerably above the boiling points of the volatile components present in the rich solvent, enables column 21 to be operated isothermally and substantially adiabatically when the spread in boiling points between the primary and secondary solvents is sufficient to obtain flash distillation of the most volatile components from the rich solvent without substantial vaporization of the relatively higher boiling glycol solvent component thereof. The reduction in pressure on the rich solvent as it passes into the column 21 through line 19 is preferably sufficient only to obtain the desired complete vaporization of the light paraffinic components as an overhead fraction in one stage of the pressure reduction, an intermediate fraction of somewhat higher boiling point comprising the aromatic solute and water as another distinct fraction which vaporizes as a result of a further stepwise reduction in pressure, and a high boiling distillation residue substantially free of volatile hydrocarbon components and comprising lean diethylene glycol solvent. The intermediate fraction consisting exclusively of aromatic hydrocarbons and water vapor, recovered from column 21 is removed as a side-cut through line 33 containing condensor 34 wherein the vapors are condensed into a liquid condensate comprising benzene, toluene, xylene, other aromatics extracted from the feed stock, and water. The condensate is run into receiver vessel 35 wherein the immiscible liquids separate into an upper layer comprising essentially aromatic hydrocarbons and a lower aqueous phase which is withdrawn from receiver vessel 35 through line 36 and valve 37. The aromatic product is removed from receiver 35 through line 38 and valve 39 to storage, drying equipment and fractionating equipment, not illustrated, for separating the mixture of aromatic hydrocarbons into substantially pure fractions of benzene, toluene, xylene, and a residue of higher boiling aromatics, if present in the extract. The aromatic products thus recovered are substantially pure products, free of paraffinic and other hydrocarbon impurities.

In order to free the rich solvent of substantially all of its hydrocarbon solute in stripping column 21, the rich solvent residue which accumulates in the bottom portion of column 21 is heated, for example, by reboiling coil 40 positioned in the bottom of stripping column 21 through which a high temperature fluid heated in heat exchanger 41 is circulated. In order to reduce the temperature required in the reboiling section to vaporize the last trace of extracted hydrocarbon (dissolved aromatics) from the rich solvent, and to maintain the water content and boiling point of the solvent at a substantially constant level, steam is charged into the reboiling section of column 21 wherein the water vapor exerts its own partial pressure to increase the vapor pressure of the residual aromatic component present in the rich solvent bottoms. One of the preferred sources of steam for this purpose in the present operation is vaporized water distilled from the rich solvent with the hydrocarbon side cuts and collected in receivers 27 and 35. The water distillate removed from side-cut receiver 35 through line 36 and valve 37 may be partially or wholly recycled by transfer through line 42 leading into the reboiling section of column 21. The water condensate from side-cut receiver 35 may be joined with the water condensate from receiver vessel 27 and the two streams combined by juncture of line 36 with line 42 and by suitable adjustment of valves 43 and 37; the combined aqueous streams may be pumped by means of pump 44 into heat exchanger 45, vaporized therein and the resulting vapor, preferably at a temperature of from about 100° to about 250° C., charged

through line 46 into the reboiling section of column 21. The resulting water vapor contacted with the rich solvent residue in the reboiling section of column 21 increases the vapor pressure of the dissolved aromatics present in the rich solvent residue and accompanies the benzene-water intermediate fraction removed from column 21 through line 33 and which is again collected in receiver 35.

The rich solvent residue comprising diethylene glycol or lean solvent stream from which the volatile hydrocarbon components have been substantially completely removed is withdrawn from column 21 through line 47 containing valve 48 and is recycled through line 50 at the operating pressure existing in extraction column 10 by means of pump 49 to the upper portion of column 10 where line 50 is joined with the lean solvent charging line 11. A predetermined portion of the recycled solvent may be diverted from line 50 into line 23, through valve 24 and charged into the top of stripping column 21, as hereinbefore described.

The solvent recycled to column 10 is rehydrated to the the critical concentration of water required for selective solvent extraction of aromatics from the feed stock in accordance with the present process by the water introduced through line 12 into the top of extraction column 10 and the latter quantity of water required to increase the water content of the selective solvent to the appropriate critical level within the range of from about 5 to about 10% by weight of the solvent composition is obtained by continuously recycling at least the requisite make-up portion of the liquid water condensate removed from column 21 and accumulated in receivers 27 and 35 through line 42 containing valve 51 and pump 52 into water charging line 12, pump 52 increasing the pressure of the recycled water to the level at which column 10 operates.

Although the operation of the process as described above with reference to the accompanying diagram utilizes a diethylene glycol-water solution as the selective solvent, it is apparent that an operable and practical system of separation, albeit less selective and less efficient and productive of a less desirable product, may be provided by utilizing a solvent consisting only of the primary solvent component, such as diethylene glycol, free of secondary solvent component, such as the aforementioned water.

This invention is further illustrated with respect to certain specific embodiments thereof in the following examples, which however, are not intended to unduly limit the scope of the invention necessarily in accordance therewith.

Example I

A selective solvent extraction system embodying the preferred flow of the accompanying diagram is provided to recover benzene from a hydroformed straight-run gasoline fraction. The hydroformate is fractionally distilled to separate a fraction having a boiling range of from about 40° to about 81° C. and the latter distillate is further fractionated into a light paraffin fraction boiling from 40° to about 65° C. and a feed stock fraction boiling from about 65° to about 81° C., the latter fraction containing C_6 and C_7 isomeric paraffins and about 36% by weight of benzene. This feed stock fraction is charged in liquid phase at a pressure of approximately 6.5 atmospheres and at a temperature of 150° C. into the mid-point of a selective solvent extraction column at a rate of 1662 gallons per hour. The column is a vertical sieve deck extraction column approximately 67 feet high, 4 feet internal diameter and containing 62 sieve decks, the liquid phase hydrocarbon feed being charged into the column on the 20th sieve deck. The selective solvent consisting of an aqueous solution of diethylene glycol containing about 7.5% by weight of water is introduced at a rate of 11,840 gallons per hour into the top of the column. The volatile paraffin fraction boiling from 40° to about 65° C. and separated from the initial reformate charged to the fractionator is introduced at a temperature of 130° C. and at about 6.5 atmospheres gage pressure, and at a rate of 52 gallons per hour into the bottom of the extraction column at a point adjacent to the outlet port for the rich solvent formed in the column. A recycle light paraffin overhead fraction from the rich solvent stripping tower, hereinafter described, is charged with the light paraffins into the extraction column at a rate of 2,414 gallons per hour. The combined stream is percolated upwardly through the sieve deck plates against the downwardly flowing stream of solvent.

The rich solvent stream (14,579 gallons per hour) leaving the extraction column contains selective solvent having dissolved therein 2,380 gallons per hour of benzene and 374 gallons per hour of light paraffins. The rich solvent is removed from the bottom of the solvent extraction column at a temperature of 135° C. and at a pressure of 6.5 atmospheres and is transferred into a bubble plate stripping column having a primary flashing section operated at a gage pressure of 50 pounds per square inch, a secondary flashing section operated at 3 pounds per square inch gage and a distillation section operated at substantially atmospheric pressure, the rich solvent being fed into the primary flashing section, the residue thereafter flowing successively into the secondary flashing and distillation sections which are vapor sealed from each other. A reboiling section is contained in the lower portion of the stripping column which maintains the liquid rich solvent bottoms accumulating in the lower portion of the column at a temperature of approximately 155° C. A light vapor fraction is flash-distilled from the primary flashing section of the stripping column and passed through a heat exchanger which condenses the vapor to a liquid; water is drawn off from the condensate and charged as steam into the bottom, reboiler section of the stripping column.

The vapor from the secondary flashing section is also condensed and the water layer withdrawn and combined with the water stream to the reboiler section. The hydrocarbon condensate from the primary flashing contains 690 gallons per hour of benzene and 282 gallons per hour of light paraffin. The vapor condensate from the secondary flashing operation contains 1240 gallons per hour of benzene and 91 gallons per hour of light paraffin. The combined primary and secondary flash condensates are recycled as reflux to the bottom of the solvent extraction column.

An intermediate fraction removed from the distillation section of the stripping column is condensed into a liquid fraction which separates into a water layer containing a small amount of dissolved benzene and a benzene layer containing about 99.9+% benzene, the latter benzene product, which exceeds nitration grade standards, being recovered at a rate of 337 gallons per hour. The total recovery of benzene represents 100% of that present in the initial feed stock. The aqueous stream recovered from the intermediate fraction condensate is recirculated to the reboiling section of the stripping column. Diethylene glycol solvent containing 7.5% by weight of water is removed from the bottom of the solvent stripping column at a rate of 11,705 gallons per hour and is recycled, together with an additional 135 gallons per hour of make-up solvent, to the solvent inlet port of the solvent extraction column where it is re-used as the present selective solvent. The heat consumption for the process is 12,570,000 B.t.u. per hour.

In an operation similar to the above process for the recovery of benzene from a hydroformed straight run gasoline fraction, except that the volatile paraffin fraction boiling from 40° to 65° C. is not charged into the bottom of the solvent extraction column, the process yields 340 gallons per hour of a recovered benzene product containing about 98% by weight of benzene. This benzene product does not pass nitration grade test specifications because of

its low melting point. The vapor flashed from the solvent stripping column is a benzene-hexane-heptane azeotrope which is recycled to the bottom of the solvent extraction column but is materially less effective for the purpose of displacing the paraffin hydrocarbons of the feed mixture from the rich solvent than the operation hereinabove described. The heat consumption for the process is approximately 19,600,000 B.t.u. per hour for the same rate of benzene production, which, moreover, is of lower quality (lesser purity).

Example II

An operation similar to the process described in Example I is conducted for the recovery of toluene from a feed stock consisting of the fraction boiling from about 103° to about 111° C., separated from the hydroformed straight run gasoline fraction indicated in Example I, above. A volatile paraffin fraction boiling from about 81° to about 100° C. is also separated from the hydroformate starting material and is utilized as the volatile paraffin fraction charged into the solvent extraction column for displacement of the less volatile, azeotrope-forming paraffins from the toluene-containing rich solvent in the extraction column.

The toluene product recovered from the rich solvent by stripping in accordance with the procedure described in Example I, above, is substantially pure toluene and the product recovered represents approximately 95% of the toluene contained in the initial straight run gasoline reformate product.

Example III

Benzene, toluene and xylene are recovered from a petroleum-derived hydrocarbon fraction containing these aromatic hydrocarbons in admixture with paraffinic, olefinic and naphthenic hydrocarbons by subjecting the hydrocarbon fraction to solvent extraction utilizing a solvent comprising an aqueous diethylene glycol solution containing about 7.5% by weight of water. In the following example the hydrocarbon mixture consisted of a gasoline boiling range fraction recovered from the normally liquid products of a catalytic reforming process in which a straight run gasoline fraction boiling from about 150° to about 270° F., was utilized as feed stock, the fraction being charged at hydroforming reaction conditions in admixture with hydrogen over a hydroforming catalyst consisting of platinum and halogen supported on alumina. The products of the hydroforming conversion were separated into a liquid fraction having an initial boiling point of about 150° F. (65° C.) and an end boiling point of about 310° F. (154° C.). This fraction, utilized as charging stock to the present solvent extraction run, contained approximately 7.0% benzene, 25.6% toluene and 30.6% by weight of xylene.

The above liquid hydroformate was charged at the rate of 1635 bbls./day, at a pressure of 100 p.s.i., and at a temperature of 290° F. onto the 37th tray (from the bottom) of a vertical, countercurrent extraction column containing 60 actual plates of the sieve deck type, corresponding to about 15 to about 20 theoretical plates. As the above feed stock mixture was charged into the extraction column, the aqueous diethylene glycol solvent, being the lean solvent stream recovered from the stripping stage of the present combined process, rehydrated to its 7.5% water content by combination with raffinate wash-water, as hereinafter described, was charged at the rate of 24,780 bbls./day at a temperature of 300° F. and at a pressure of 100 p.s.i. into the top of the extraction column, thereafter percolating downwardly through the subadjacent perforated trays of the column against a rising stream of the mixed hydrocarbon charging stock introduced into the column on the 37th tray.

Another hydrocarbon stream comprising a mixture of paraffinic and aromatic hydrocarbons containing approximately 26% by volume of benzene, recovered from the subsequent stripping operation as a light overhead vapor fraction, as hereinafter described, together with 300 bbls./day of a C_5–C_6 fraction supplied from extraneous sources was charged into the lower portion of the extraction column wherein it acts as a reflux stream to displace into the raffinate higher molecular weight paraffins dissolved in the rich solvent stream from the feed stock and boiling it approximately the same temperatures as the aromatic components. This stream made up of the combined light vapor overhead and extraneous C_5–C_6 fraction was charged into the column in the manner described at a rate of 2,102 bbls./day at a pressure of 100 p.s.i. and at a temperature of 285° F.

The countercurrently flowing hydrocarbon and solvent streams in the extraction column produced a resultant rich solvent stream comprising the aqueous diethylene glycol solvent containing dissolved therein the aromatic hydrocarbon constituents of the feed stock and accumulate in the lower portion of the extraction column from which it is removed and charged at the temperature and pressure maintained within the extraction column into a solvent stripping column containing a flashing section in its uppermost portion wherein the pressure is initially reduced to one-half the level maintained in the extraction zone, that is, to a pressure of about 50 p.s.i. in order to flash distill the light paraffinic hydrocarbon displacing agent which is present in the rich solvent stream by virtue of having displaced the heavy paraffins therefrom in the extraction zone. The boiling point of the light paraffins contained in the rich solvent stream are not affected by the presence of the solvent, whereas the boiling point of the aromatic constituents (also dissolved in the rich solvent stream), is increased by virtue of the presence of the solvent. However, with the vaporization of the light paraffins by reducing the pressure on the rich solvent stream in the uppermost portion of the stripping zone, a portion of the lowest boiling aromatic component present, that is, the benzene solute, also vaporizes with the light paraffin flash distilled from the rich solvent. The overhead vapors also contain a portion of the water present in the rich solvent stream and these combined vapors are lead into a water-cooled condenser having a receiver vessel attached thereto for accumulation of the condensed liquid overhead. The liquid condensate collected in receiver vessel separates into two phases, an upper layer comprising a mixture of benzene and light paraffins, containing approximately 22 volume percent of light paraffins and a lower aqueous phase which contains a small amount of diethylene glycol accompanying the light vapor overhead. The upper, aromatic-paraffin hydrocarbon phase accumulating in the overhead vapor receiver is withdrawn at a rate of 1,233 bbls./day and charged into the reflux line leading into the bottom of the extraction column to displace heavy paraffins from the rich solvent stream in the extraction column. A lower aqueous layer in the amount of 242 bbls./day is circulated to the bottom of the stripping column and charged into the reboiling section thereof to generate steam which act as a stripping agent in the column. The rich solvent residue accumulating in the uppermost flashing section is passed into a secondary flashing zone wherein the pressure on the rich solvent residue is reduced to 2 p.s.i.g. The hydrocarbons and water further flash distilled from the rich solvent residue by virtue of the pressure reduction at isothermal conditions are liquefied at atmospheric pressure in a water-cooled side condenser, the liquid condensate being collected in a receiver vessel attached to the condenser. The lower aqueous phase was withdrawn from the receiver at a rate of 378 bbls./day and combined with the aqueous stream recovered from the light overhead vapor fraction for generation of steam charged into the bottom portion of the stripping column to vaporize the aromatic solute in the rich solvent.

The upper, hydrocarbon layer accumulating in the secondary flash receiver, in the amount of 569 bbls./day comprises predominantly benzene mixed with a small

amount of light paraffins which is combined with the primary flash distillation overhead and recycled for reflux to the extraction column together with the primary flash overhead and the C_5–C_6 extraneous paraffin stream. The secondary rich solvent residue within the stripping column thereafter flows from the secondary flash section into the extractive distillation portion of the stripping column wherein the remaining hydrocarbon solute is vaporized from a rich solvent residue, the required heat for the latter distillation being supplied by a reboiler in the lower portion of the stripping column.

A side-cut fraction is removed from the stripping column by withdrawing the vapors from the 31st plate of the stripping section of the column, condensing the vapors in a water-cooled, side-cut condenser and passing the resulting mixture of water and aromatic hydrocarbon condensate into a receiving vessel. The lower aqueous layer separating in the receiving vessel is withdrawn and transferred to the raffinate water-washing column adjacent to the extraction tower for removing the small amount of dissolved solvent in the raffinate, the resulting washed raffinate containing less than 0.01% by weight of solvent. The aqueous phase is recovered and charged into the top of the extraction column, thereby returning the solvent in the washer washings to the system.

The hydrocarbon phase separated as an upper layer in the side-cut receiver is a mixture of benzene, toluene and xylene containing less than 0.3% by weight of hydrocarbons other than monocyclic benzene derivatives (these being generally of polycyclic types). The aromatic mixture was fractionally distilled into a benzene fraction boiling from 80.0° to 80.1° C., containing 99.99% benzene, a separate toluene fraction of greater than 99% purity and a C_8 aromatic hydrocarbon fraction. A material balance of the process as a whole, based upon the aromatic content of the feed stock, indicates that over 99% of the benzene, from 98 to 98.5% of the toluene and from 87 to 89% of the xylene contained in the original feed stock mixture was recovered by the above combination of solvent extraction and rich solvent stripping stages of the process.

The lean solvent residue accumulating in the lower portion of the stripping column in contact with the reboiler coil and containing approximately 7.5% by weight of water and nil percent hydrocarbons is withdrawn from the bottom of the reboiler at a temperature of about 300° F. and recycled to the top of the extraction column at the aforesaid rate of 24,780 bbls./day and at a temperature of approximately 290° C. (the temperature being reduced somewhat after the addition of the water layer of the raffinate wash thereto).

The hydrocarbon raffinate stream comprising components of the original hydrocarbon feed stock mixture not extracted by the selective solvent, as well as the excess light paraffins contained in the reflux stream charged to the extractor is removed from the top of the extraction column at a rate of 926 bbls./day, is washed with the aforesaid stream of water to remove the small amount of diethylene glycol solvent dissolved therein and thereafter diverted to storage. The raffinate contains less than 0.01% benzene, approximately 0.5% toluene and approximately 3% by weight of xylenes.

I claim as my invention:

1. A process for the separation of a hydrocarbon mixture containing non-aromatic hydrocarbons and at least one aromatic hydrocarbon selected from the group consisting of benzene, toluene and xylene, which comprises introducing said mixture to an intermediate point in the height of an extraction zone, countercurrently contacting said mixture in the zone with a solvent which is selective for aromatic hydrocarbons at an elevated temperature and at a pressure sufficient to maintain said solvent and said mixture in substantially liquid phase, thereby forming a liquid raffinate phase and a liquid extract phase, removing the raffinate phase from the upper portion of said zone, commingling with the extract phase in the lower portion of said zone a light paraffinic hydrocarbon which boils in the presence of the solvent at a temperature below the boiling point of the aromatic hydrocarbon being extracted, but which remains in the liquid state at said temperature and pressure, said light paraffin being introduced into the lower portion of the extraction zone in sufficient amount to replace the non-aromatic hydrocarbons of said mixture in the extract phase with said light paraffins, thereafter removing from the lower portion of said zone the extract phase containing the light paraffinic hydrocarbon, transferring said extract phase into a separate fractional distillation zone and vaporizing from said extract the light paraffin and said aromatic hydrocarbon at a reduced pressure and at substantially said elevated temperature and at substantially isothermal conditions.

2. The process of claim 1 further characterized in that said light paraffin displacing agent is vaporized from said extract in said distillation zone by sufficiently reducing the pressure on said extract to vaporize substantially all of said light paraffin displacing agent therefrom and thereafter further reducing the pressure on said extract sufficiently to vaporize substantially all of said aromatic hydrocarbon from said extract, separately collecting the resulting paraffin-containing and aromatic-containing fractions.

3. The process of claim 1 further characterized in that said extract phase is distilled in said distillation zone by sufficiently reducing the pressure on said extract to vaporize at substantially isothermal conditions a light paraffin fraction from a first extract residue and separately withdrawing said fraction, thereafter, further distilling said first residue at substantially isothermal conditions by reducing the pressure in the distillation zone sufficiently to vaporize a mixed light paraffin-aromatic fraction from a second extract residue and separately withdrawing said mixed fraction from the distillation zone and finally distilling at substantially isothermal conditions a relatively pure aromatic fraction from a third extract residue and separately withdrawing the aromatic fraction from the distillation zone.

4. The process of claim 1 further characterized in that said hydrocarbon mixture is extracted with said solvent in said extraction zone at a pressure of from about 5 to about 20 atmospheres.

5. The process of claim 1 further characterized in that said light paraffin fraction distilled from said extract is recycled to the extraction zone and introduced therein as said light paraffin commingled with the light extract phase in the lower portion of the extraction zone.

6. The process of claim 1 further characterized in that said light paraffin fraction and said light paraffin-aromatic fraction vaporized from the extract in said distillation zone are recycled to said extraction zone as the light paraffin commingled with the extract phase in the lower portion of said extraction zone.

7. The process of claim 3 further characterized in that said third extract residue is distilled by the addition of heat thereto at substantially atmospheric pressure.

8. The process of claim 3 further characterized in that said third extract residue is distilled to remove residual aromatic hydrocarbons therefrom by reducing the pressure on said third residue at substantially isothermal conditions.

9. The process of claim 3 further characterized in that said third extract residue is returned to said extraction zone as said selective solvent.

10. A process for recovering an aromatic concentrate from a reformed gasoline product which comprises fractionally distilling said product to separate therefrom a light paraffinic fraction of lower boiling point than benzene and a heavier fraction containing aromatic and paraffinic hydrocarbons, countercurrently contacting said heavier fraction with a selective solvent for aromatics in

an extraction zone, thereby forming a heavy paraffinic raffinate and an extract comprising said solvent, dissolved aromatic hydrocarbon and a small proportion of relatively heavy paraffins, removing the raffinate from the upper portion of said zone, introducing to the lower portion of said zone a sufficient amount of said light paraffinic fraction to displace said relatively heavy paraffins substantially completely from said extract, thereafter removing the extract from the lower portion of the extraction zone, and in a separate fraction distillation zone, reducing the pressure on the extract to vaporize at substantially isothermal conditions substantially all of the light paraffin from said extract and thereby form an extract residue containing said aromatic hydrocarbon dissolved therein, thereafter further reducing the pressure on said extract and vaporizing at substantially isothermal conditions said dissolved aromatic hydrocarbon from the solvent residue and separately withdrawing the last-mentioned aromatic fraction from the distillation zone.

11. The process of claim 10 further characterized in that said light paraffinic fraction vaporized from said extract is combined with said light paraffinic fraction separated from said gasoline product and the combined mixture thereafter introduced into the lower portion of said extraction zone.

12. A process for the separation of organic materials of different chemical constitution by solvent extraction, which process comprises contacting a mixture of such materials with a solvent selective for one of said materials so as to extract said one of said materials, said contacting being conducted at elevated temperature under substantially isothermal conditions; passing the mixed solvent and extracted organic material without substantial change in temperature to a separation zone; and separating the solvent and extract in said separation zone by vaporization at substantially the temperature of the contacting step under reduced pressure and isothermal conditions.

13. A process for separating hydrocarbons of different chemical structure and solubilities which comprises effecting liquid-liquid contacting of a mixture of such hydrocarbons with a high-boiling thermally stable solvent at a temperature in the range of about 90° to about 250° C. so as to separate an extract phase and a raffinate phase; passing said extract phase at substantially the contacting temperature to a vaporizing zone; reducing the pressure in said zone while supplying heat thereto in sufficient amount to prevent substantial temperature change therein so as to vaporize extract hydrocarbon from liquid solvent; recovering vaporized extract hydrocarbon from said zone; and returning stripped solvent without substantial temperature change to the extraction step.

14. A process for separating hydrocarbons of different chemical structure and solubilities which comprises effecting liquid-liquid contacting of a mixture of such hydrocarbons with a high-boiling thermally stable solvent at a temperature in the range of about 90° to about 250° C. under substantially isothermal conditions so as to separate an extract phase and a raffinate phase; passing said extract phase at substantially the contacting temperature to a vaporizing zone; maintaining said vaporizing zone under reduced pressure so as to cause vaporization of extract hydrocarbon from solvent while supplying sufficient heat to maintain said zone substantially under isothermal conditions and substantially at aforesaid contacting temperature; and recovering vaporized extract hydrocarbon from said zone.

15. A process according to claim 13 wherein the solvent is selected from the group consisting of polyethylene glycols and alkyl ethers of polyethylene glycols.

16. A process according to claim 13 wherein the extract hydrocarbon comprises a xylene, the raffinate comprises a non-aromatic hydrocarbon, the temperature is in the range about 100° to about 150° C., and the solvent is triethylene glycol.

17. A process according to claim 13 wherein the extract hydrocarbon is benzene and the raffinate hydrocarbon is a non-aromatic hydrocarbon.

18. A process according to claim 13 wherein the separated extract phase is maintained at gage pressure not greater than 50 pounds per square inch.

19. A process according to claim 13 wherein the solvent is a polyalkylene glycol.

20. A process according to claim 13 wherein part of the recovered extract hydrocarbon is recycled to a lower part of the extraction zone.

21. A process according to claim 13 wherein the extract hydrocarbon is an aromatic hydrocarbon and a low-boiling paraffin hydrocarbon is passed into the lower part of the extraction zone.

22. A process according to claim 13 wherein the hydrocarbon feed is a benzene concentrate and from about 5% to about 10% by weight of water is maintained in the solvent during the extraction step.

23. A process according to claim 13 wherein said solvent is selected from the group consisting of polyalkylene glycols and alkyl ethers thereof.

24. The process of claim 14 further characterized in that said mixture comprises at least two hydrocarbons selected from the group consisting of aromatics, cyclo-olefins, cyclo-paraffins and aliphatic paraffins.

25. The process of claim 14 further characterized in that said mixture comprises aromatic and non-aromatic hydrocarbons.

26. The process of claim 14 further characterized in that said mixture comprises cyclo-paraffinic and aliphatic paraffinic hydrocarbons.

27. The process of claim 14 further characterized in that said mixture comprises an aromatic hydrocarbon selected from the group consisting of benzene, toluene and xylene.

28. The process of claim 1 further characterized in that both said extraction zone and said fractional distillation zone are maintained at substantially isothermal conditions.

29. A process for separating an aromatic hydrocarbon from a hydrocarbon mixture containing the same which comprises contacting the mixture with a selective solvent for said aromatic hydrocarbon at an elevated temperature and at substantially isothermal conditions, separating undissolved non-aromatic hydrocarbons from the resultant extract comprising said solvent and aromatic hydrocarbon, and vaporizing the aromatic hydrocarbon from the solvent in said extract at substantially said elevated temperature and under reduced pressure and substantially isothermal conditions.

30. In the separation by distillation of components of a phase resulting from selective solvent extraction of hydrocarbons, wherein said selective solvent consists of a pair of ingredients, one of said pair being miscible with said hydrocarbons contacted therewith and the other of said pair being immiscible with said hydrocarbons and having a boiling point lower than that of said miscible solvent, the improvement comprising introducing additional immiscible component into the zone of said distillation in an amount sufficient to distill said immiscible component and said hydrocarbons from said zone as overhead, while maintaining the conditions in the distillation zone to recover as bottoms therefrom a substantially hydrocarbon-free solvent pair containing its components in a proportion suitable for re-use in said selective solvent extraction, said proportion being substantially the same as the proportion present in said selective solvent consisting of said pair of ingredients.

31. In the separation by distillation of components of a phase resulting from selective solvent extraction of hydrocarbons, wherein said selective solvent consists of a pair of ingredients, one of said pair being miscible with

said hydrocarbons contacted therewith and the other of said pair being immiscible with said hydrocarbons and having a boiling point lower than that of said miscible solvent, the improvement comprising introducing additional immiscible component into the zone of said distillation in an amount sufficient to distill said immiscible component and said hydrocarbons from said zone as overhead substantially free of said hydrocarbon-miscible component, while leaving and recovering as bottoms substantially hydrocarbon-free solvent having substantially the same composition of said selective solvent consisting of said pair of ingredients.

32. In the separation by distillation of components of a phase resulting from selective solvent extraction of hydrocarbons, wherein said solvent is a mixture of diethylene glycol monomethyl ether and water, the improvement comprising introducing additional proportions of water into the zone of said distillation in an amount sufficient to distill said water and said hydrocarbons from said zone as overhead substantially free of said diethylene glycol monomethyl ether while leaving and recovering as bottoms substantially hydrocarbon-free solvent having a ratio of diethylene glycol monomethyl ether to water substantially the same as present in said mixture.

33. The method of claim 31 wherein hydrocarbon-immiscible solvent component distilled from the zone of said distillation is recycled as at least a portion of the said hydrocarbon-immiscible liquid added to the said zone, whereby any hydrocarbon-miscible solvent component therein is re-used in said distillation.

34. The method of claim 32 wherein water distilled from said distillation zone is recycled as at least a portion of said water added to said zone, whereby any diethylene glycol monomethyl ether in said overhead is re-used in said distillation.

35. The method of claim 32 wherein said hydrocarbon subjected to solvent extraction is a straight-run gasoline.

36. The method of claim 32 wherein said hydrocarbon subjected to solvent extraction is a mixed aromatic fraction.

37. In the separation by distillation of components of a phase resulting from selective solvent extraction of hydrocarbons, wherein said selective solvent consists of a pair of ingredients, one of said pair being miscible with said hydrocarbons contacted therewith and the other of said pair being immiscible with said hydrocarbons and having a boiling point lower than that of said miscible solvent, the improvement comprising introducing additional immiscible component into the zone of said distillation in an amount sufficient to distill said immiscble component and said hydrocarbons from said zone as overhead, while maintaining the conditions in the distillation zone to recover as bottoms therefrom a substantially hydrocarbon-free solvent pair containing its components in a proportion suitable for re-use in said selective solvent extraction, said proportion being substantially the same as the proportion present in said selective solvent consisting of said pair of ingredients, at least part of said additional immiscible component introduced into said distillation zone being recycled from distillate obtained from said distillation.

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