Nov. 13, 1956 L. H. HORSLEY ET AL 2,770,664

AROMATIC HYDROCARBONS BY SOLVENT EXTRACTION WITH A SOLVENT OF DIETHYLENE GLYCOL AND WATER

Filed Nov. 9, 1951

3 Sheets-Sheet 1

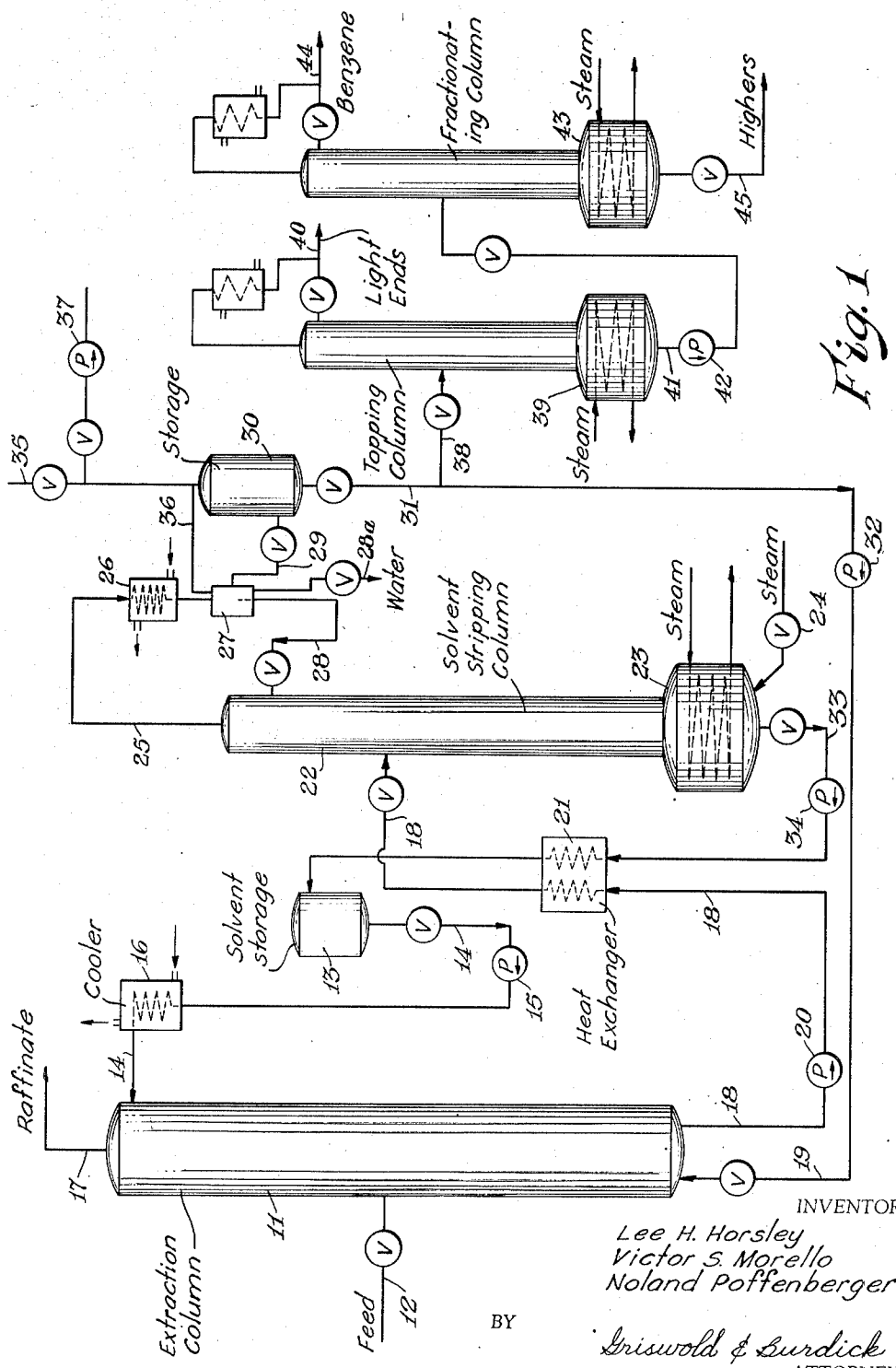


Fig. 1

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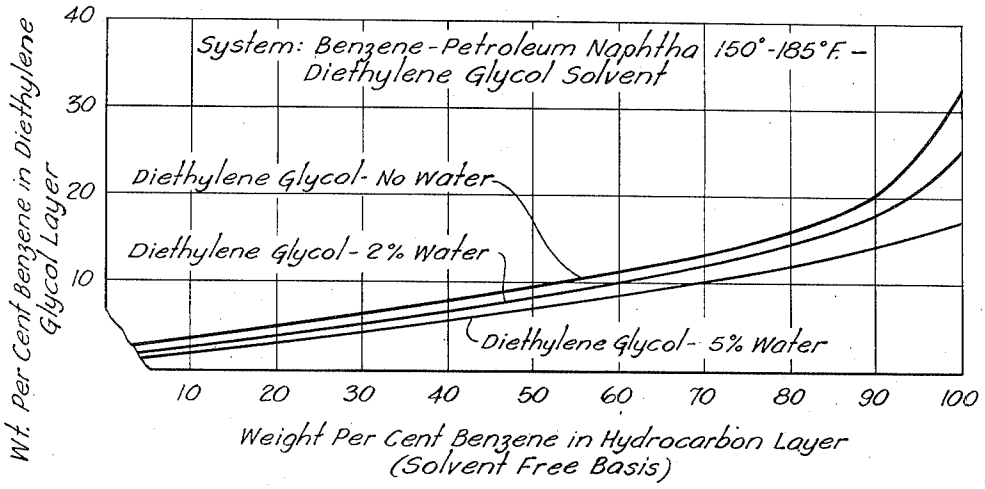


Fig. 2

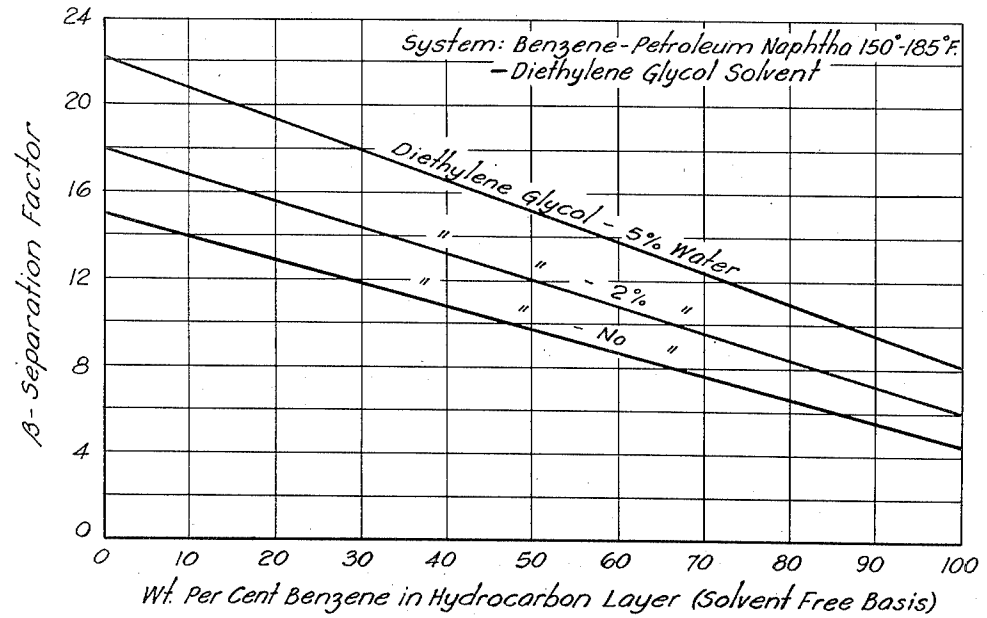


Fig. 3

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3 Sheets-Sheet 3

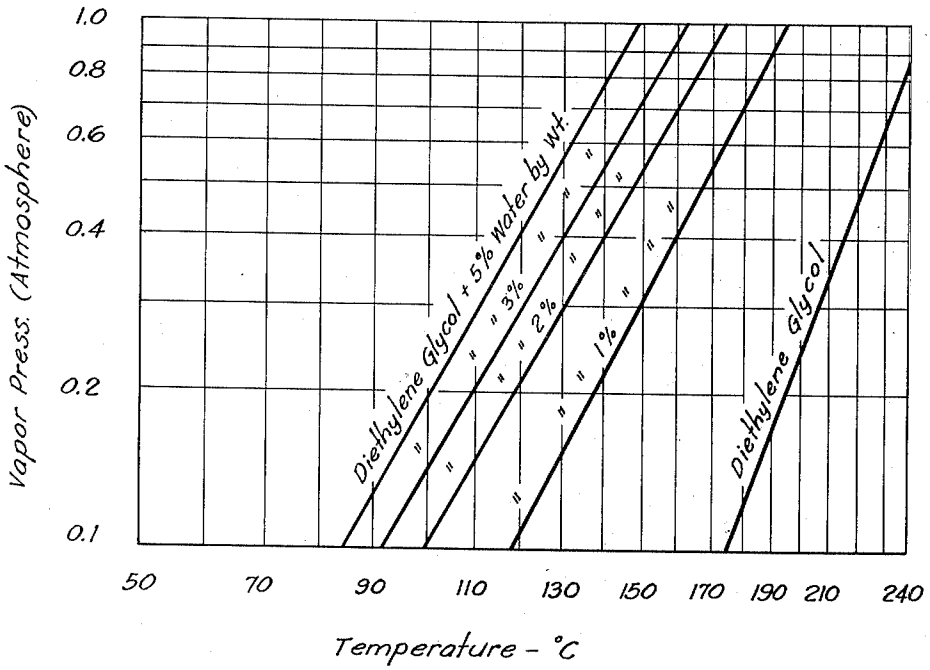


Fig. 4

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AROMATIC HYDROCARBONS BY SOLVENT EXTRACTION WITH A SOLVENT OF DIETHYLENE GLYCOL AND WATER

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Application November 9, 1951, Serial No. 255,688

7 Claims. (Cl. 260—674)

This invention relates to an extraction process for recovering individual aromatic hydrocarbons in high purity from liquid hydrocarbon mixtures, such as those produced by the reforming of gasolines. It particularly concerns the production of benzene, toulene, and the xylenes.

Aromatic hydrocarbons are found in quite small proportion in petroleum and in somewhat higher concentration in natural and straight-run gasolines. Richer sources of aromatic hydrocarbons can be produced by the catalytic reforming or aromatization of the naphtha cuts of petroleum and of natural gasolines. From all these sources, concentrated fractions of aromatic hydrocarbons can be separated by a number of known processes. The most common purpose in forming and concentrating such aromatic fractions is to provide blending stocks for upgrading motor fuels of low antiknock value. In this use, no effort is made to isolate single aromatic hydrocarbons, and many of the processes used or proposed to date are not suitable for doing so. There have been one or two industrial processes for the extraction and recovery of individual aromatics, particularly toluene, xylene, and higher hydrocarbons, from refinery cuts. However, these processes have largely proved complex, expensive, or otherwise unsuitable, especially when operated for the manufacture of pure benzene.

In particular, the known extraction processes have not been capable of isolating individual aromatic hydrocarbons in both high purity and high yield. If a product at least 98 percent pure is to be made directly, not more than perhaps 80 percent of the total available hydrocarbon is recovered. On the other hand, if nearly complete recovery is achieved, the product is rarely over 90 percent pure, and must be cleaned up by elaborate treatment, such as washing with sulfuric acid. Indeed as Claussen et al. state in U. S. Patent 2,404,902, "No known solvent is sufficiently selective to recover by a simple operation all of an aromatic compound from admixture with the associated paraffinic and naphthenic materials in a petroleum distillate and at the same time to recover it in a state of sufficiently high purity that it may be subjected directly to nitration as, for instance, in the preparation of explosives, or may be used directly as raw material in other specific chemical processes."

An additional problem in known extraction processes is that, even when operation is such as to isolate a single aromatic hydrocarbon in a purity of 98 to 99 percent, the product still does not meet standard U. S. specifications for a nitration grade, or even an industrial grade, hydrocarbon (A. S. T. M. specification D835 to D850). The product is frequently discolored and becomes more so on storage. It may also react peculiarly in certain organic syntheses. There have been hints that olefinic hydrocarbons in the naphtha or other feedstock are in some measure responsible for these difficulties (c.f. Trans. Amer. Inst. Chem. Engrs. 40, 211 (1944)). During solvent extraction, the olefins are not cleanly separated from the aromatic hydrocarbons, but in part accompany the latter even through multi-stage extractions

with solvents of high selectivity. In the final product, the olefins tend to form gums and colored bodies which, even in minute proportions, seriously affect the quality. Further, the presence of the olefins also seem to render the solvent less capable of making a complete separation of aromatic from naphthenic and paraffinic hydrocarbons. No adequate way of dealing with the olefin problem has heretofore been available.

It is therefore the principal object of the present invention to provide a process for the isolation of individual aromatic hydrocarbons in both high yield and high purity from hydrocarbon feedstocks containing them, even when such stocks contain appreciable proportions of olefins. A related object is to provide a process capable of isolating benzene, as well as toulene and zylenes, from refinery fractions in purity sufficient to meet all standard specifications entirely by the physical steps of solvent extraction, stripping, and fractionation, and without the need for any chemical treatment. A similar object is to provide a process for making virtually pure benzene in good yield from gasoline, natural or straight-run.

These objects are realized, according to the invention, by an extraction process in which benzene and other aromatic hydrocarbons are separated from mixtures thereof with non-aromatic hydrocarbons by means of a selective solvent consisting essentially of diethylene glycol, or mixtures thereof with water. The benzene-containing hydrocarbon mixture is introduced into a counterflow multi-stage extraction system near the middle, while diethylene glycol is introduced into one end of the system into extractive contact with the hydrocarbon phase therein. Substantially aromatic hydrocarbon-free raffinate is withdrawn from the system at the same end. Diethylene glycol rich in benzene and other aromatic hydrocarbons is withdrawn from the other end of the system, and is stripped to separate the aromatic hydrocarbon portion therefrom. A part of this latter portion is returned to the system at this other end as reflux. The remainder of the aromatic hydrocarbon portion is withdrawn as product, and may be subjected to fractionation to isolate the benzene and other individual aromatic hydrocarbons.

The success of the new process depends mainly upon the exceptional behavior of diethylene glycol as a selective solvent. It was long ago suggested that various glycols, including diethylene glycol, might be used to extract aromatic hydrocarbons from naphthas (British specification 456,958). However, it has not heretofore been appreciated that, in extracting the particular hydrocarbon benzene, the particular glycol diethylene glycol is almost uniquely advantageous, even as compared to closely-related glycols, both with respect to its physicochemical properties in an extraction system and to the economics of the process. These advantages of diethylene glycol are also observed in the extraction of toluene and to a considerable degree in that of the xylenes and ethyl benzene.

Unlike many selective solvents, diethylene glycol exhibits phase equilibria with benzene and non-aromatic hydrocarbons in ternary mixtures thereof which impose no physical limit on the maximum purity of benzene obtainable. The solvent is highly selective, with good solvent power for benzene and such low solvent power for non-aromatics that the solvent loss in the raffinate is exceedingly small. Further, this selectivity remains high over the entire range of concentrations existing in a multi-stage counterflow system, even in the enriching stages where the concentration of aromatic hydrocarbon is highest. On the other hand, the solvent power for aromatics is not high enough to reach complete miscibility, so that it is possible to maintain two separate phases at every stage in the sys-

tem. Hence, with diethylene glycol, a separation of benzene from other hydrocarbons which is complete for all practical purposes can be achieved in a finite, and in fact a comparatively small, number of extraction stages, at high-efficiency even with moderate reflux to product ratios.

In addition, the physical properties of diethylene glycol are such as to allow design of an extraction process which operates at or near atmospheric pressure in conventional equipment at temperatures attainable with ordinary process steam heating. The low volatility of diethylene glycol makes easy the stripping of aromatic hydrocarbons from the glycol extract phase by simple distillation or steam distillation, leaving the diethylene glycol as bottoms. The thermal stability of diethylene glycol and its noncorrosiveness toward metals make it possible to operate the entire process in ordinary steel equipment. Further, the relatively high density of diethylene glycol and its high surface tension allow ready liquid-liquid separation of the extract phase from the hydrocarbon phase in the extraction system and eliminate the emulsion problems often encountered in extraction processes.

Another characteristic of diethylene glycol as a selective solvent for isolating benzene and other light aromatic hydrocarbons from naphthas is in its effect on whatever olefins may be present in such stocks. Like other selective solvents, diethylene glycol does not effect complete separation of aromatics from olefins. The latter appear partly in the raffinate and partly in the extract. However, in unprecedented manner, diethylene glycol drastically alters the relative distribution of the individual olefins between raffinate and extract to the point that what olefins do remain in the aromatic extract are easily separated from it by simple rectification. This heretofore unknown property of diethylene glycol, further demonstrated in the examples to follow, is to a considerable degree responsible for the success of the invention in producing high purity benzene and other aromatic hydrocarbons meeting all standard quality specifications.

While diethylene glycol alone has exceptional merit as a selective solvent for benzene, further great advantage may be realized in the invention by incorporating water, preferably from 0.5 to 10 percent by weight, in the diethylene glycol, although higher amounts of water may be used if desired. The selectivity of diethylene glycol as a preferential solvent for benzene can be increased from two to four fold by the addition of as little as one percent water, without serious loss in total benzene solubility. Adding water within the preferred range permits operation at atmospheric pressure and also effects a significant reduction in the viscosity of the solvent, allowing easier handling, and decreases its boiling point, permitting lower stripping temperatures. There is little if any tendency for the water to separate from the diethylene glycol at any stage of the extraction process, so that the solvent is, for practical purposes, of the single-component type.

It is also important, in the invention, to select or to prepare, as by catalytic treatment, hydrocarbon feedstocks which admit of high recoveries of purfied benzene. Aromatic mixtures produced by the catalytic reforming of vaporized gasoline fractions in the presence of hydrogen under cyclizing conditions, e.g. over a platinum-containing catalyst, are particularly suitable, as will be further explained. Such mixtures, even those having wide boiling ranges, can be separated cleanly into aromatic and nonaromatic portions according to the invention, without the elaborate predistillations or careful segregation of refinery stocks so essential in prior processes.

The invention may be described in detail with reference to the accompanying drawings, in which

Fig. 1 is a schematic diagram of apparatus for carrying out a preferred form of the new process, showing the flow of materials;

Fig. 2 is an equilibrium diagram at 25° C. for the two-phase system benzene: petroleum naphtha (boiling range 150° to 185° F.): diethylene glycol solvent, showing the solubility of benzene in the diethylene glycol layer as a function of the benzene concentration in the hydrocarbon layer. Curves are given for anhydrous diethylene glycol and for diethylene glycol containing 2 percent and 5 percent by weight of water.

Fig. 3 is another equilibrium diagram for the same system at 25° C., showing the variation of the separation factor β (a measure of the selectivity of the diethylene glycol solvent for benzene) as a function of the benzene content of the hydrocarbon layer; and

Fig. 4 is a graph showing the vapor pressures (in atmospheres) at different temperatures of diethylene glycol and several diethylene glycol-water mixtures.

In operating the system shown in Fig. 1, the liquid feed to be processed may, for instance, be a benzene-rich fraction of a catalytically reformed naphtha. The extractant is diethylene glycol, preferably containing a small proportion of water.

The extraction step is carried out in a column **11** designed for multi-stage countercurrent liquid-liquid contact. The hydrocarbon-feed is introduced as a continuous stream through a valved inlet **12** about half way up the column. The diethylene glycol solvent, from storage **13**, enters the column **11** near the top by way of a valved line **14**, pump **15**, and indirect water cooler **16**. Raffinate, virtually free of benzene, and consisting of naphthenes and paraffins, together with part of any olefins in the feed, leaves the column through a top outlet **17**. This raffinate contains virtually no diethylene glycol. The extract, consisting of benzene and other aromatic hydrocarbons, if any, and part of any olefins in the feed, together with the diethylene glycol, is withdrawn from the bottom of the column through a line **18**. To insure complete separation of naphthenes and paraffins, and to allow concentration of the aromatic hydrocarbons, a stream of reflux, consisting of essentially solvent-free extract, is returned to the column **11** at the bottom through a valved inlet line **19**.

The benzene-containing extract from the column **11** is forwarded by the pump **20** through a heat exchanger **21**, where it is warmed somewhat, and fed into the center of the fractionating column **22** of a conventional stripping still **23** heated by a steam coil. In the still **23**, the benzene and any other aromatic hydrocarbons are vaporized from the diethylene glycol solvent. A small flow of steam may be injected into the still through a line **24** to assist in the vaporization, if needed, and to control the water content of the diethylene glycol. The hydrocarbon vapors leave the still through a top outlet line **25** leading to a condenser **26**. The condensate, consisting of crude benzene, other aromatic hydrocarbons, traces of olefins, and whatever water was vaporized in the still, flows into a gas separator and decanter **27**. A part of the hydrocarbon distillate is fed back to the column **22** through a valved line **28**; the water layer is removed through a bottom drain **28***a*. The remainder of the distillate is led through a line **29** to storage **30**. From the latter, a valved line **31** and pump **32** return a portion of the benzene-rich condensate as a continuous stream to the line **19** leading to the bottom of the extractor **11**. The stripped diethylene glycol solvent, free of benzene, leaves the still **23** at the bottom through valved line **33**, and is forwarded by a pump **34** through the heat exchanger **21** back to storage **13**. For atmospheric pressure operation of the still **23**, the storage tank **30** is open through a valved vent **35**, which is open to the separator **27** through a line **36**. However, if distillation at reduced pressure, e. g. at 0.5 atmosphere, is desired, the still and auxiliary equipment may be exhausted by a pump **37**.

A portion of the benzene-containing distillate from the receiver **30** is continuously led to a finishing system through the line **38**. This stream enters the center of a fractionating column of a topping still **39**, in which a small overhead of light ends boiling lower than benzene and con-

taining most of any olefins in the extract, is removed through a line **40**. Bottoms are withdrawn through a line **41** and pump **42** and sent to the center of the fractionating column of a finishing still **43**. Here benzene is produced as overhead through a product line **44**. Hydrocarbons boiling higher than benzene, mainly toluene, leave through a bottom line **45**. If desired, the light ends from line **40** and highers from line **45** may be blended and used to up-grade gasoline of low antiknock value. Alternatively the highers from line **45** may be rectified to isolate toluene, the xylenes, and some ethyl benzene, if present, as purified products.

The apparatus just described is flexible and admits of considerable variation in operating conditions without adverse consequences. In general, however, it is preferred to run the column **11** at about atmospheric pressure and at temperatures up to about 60° C. Under these conditions, a feedstock containing a relatively modest portion of benzene, e. g. 10 to 30 percent by weight, can easily be separated into a finished benzene of high purity.

The foregoing description with respect to Fig. 1 is illustrative only, it being obvious that there are a variety of other apparatus arrangements and operating procedures within the scope of the invention, as will be further explained. For instance, the stripper **23** may be operated without reflux or fractionation by entering the feed **18** at the top of the column **22**. Figs. 2 to 4 present physico-chemical data to permit working out the operating details of many such variations.

The diagram of Fig. 2 summarizes the results of a large number of solubility determinations at 25° C. in the two-phase system diethylene glycol: benzene: petroleum naphtha (boiling range 150° to 185° F.). The latter component, which was benzene-free, was chosen as typical of the non-aromatic hydrocarbon portion of feedstocks used in the invention. In the diagram, in which all percentages are by weight, the percent of benzene in the diethylene glycol layer is given as a function of the benzene in the hydrocarbon layer (solvent-free basis). Curves are given for anhydrous diethylene glycol as the solvent and also for systems in which the diethylene glycol contains 2 percent and 5 percent of water, respectively.

The diagram of Fig. 3 summarizes additional data obtained in the same solubility determinations reported in Fig. 2. In this case, the separation factor β is plotted as a function of the percent of benzene in the hydrocarbon layer. This coefficient β, sometimes termed selectivity factor, was calculated according to the equation

$$\beta=\frac{Y_B}{Y_N}\times\frac{X_N}{X_B}$$

where Y_B and Y_N represent the concentration, in weight percent, of the benzene and petroleum naphtha, respectively, in the glycol-rich phase, and X_B and X_N represent the corresponding concentrations in the hydrocarbon-rich phase. Curves are given for anhydrous diethylene glycol and for diethylene glycol containing 2 and 5 percent water. It will be noted that the coefficients β are larger when the diethylene glycol contains water, indicating that the water-containing glycol is more selective a solvent for benzene than the dry glycol.

As will be appreciated from Figs. 2 and 3, both the selectivity and solvent power of the diethylene glycol can be maintained at any desired value within wide limits merely by adjusting the concentration of water in the solvent. While the two graphs show conditions at 25° C., the selectivity and solubility change only slightly with temperature, so the graphs serve as rough guides to operation at any temperature.

Fig. 4 presents vapor pressure data for diethylene glycol and several diethylene glycol-water mixtures. This figure is of assistance in planning the operation of the solvent stripper **23**, which must be held at a temperature sufficient to vaporize the extracted hydrocarbons almost completely. To this end, the temperature in the base of the still should approximate the boiling point at the existing pressure of benzene-free solvent, i. e. diethylene glycol or diethylene glycol-water mixture. As the data shows, the addition of water to the glycol lowers the temperature at which the still **23** need be operated to produce effective stripping into a range easily obtainable with ordinary process steam heating.

The data in Figs. 2 to 4 were determined by careful physico-chemical measurement and are believed largely new to the literature.

As previously mentioned, the process of the invention is applicable generally to the separation of benzene, toluene, and other light aromatic hydrocarbons from admixture with non-aromatic hydrocarbon liquids, both paraffinic and naphthenic. The process also effects a partial separation of benzene from olefinic hydrocarbons, and further redistributes the olefins so that those not extracted are easily removed from the benzene by simple rectification. Hence, the process is capable of operation on feedstocks of wide boiling range, even in the presence of substantial proportions of olefins. On the other hand, since olefins do complicate operation somewhat, it is economically advantageous, in making benzene, not only to select a feed which is rich in that hydrocarbon, containing at least 10 to 30 percent benzene, but which also is relatively free of olefins, e.g. containing not over 2 to 3 percent.

Among suitable ultimate sources of benzene for the process of the invention are aromatic-containing naphthas and gasolines produced from petroleum during refining or catalytic conversion processes. Natural gasolines or naphthas recovered from natural gas in the Texas Gulf Coast and South Texas areas are particularly desirable. To avoid burdening the extraction step, these source materials are ordinarily subjected to a preliminary fractional distillation to effect a concentration of the C_6 and C_7 hydrocarbons and to exclude high-boiling materials. In general, a comparatively broad still cut, boiling in the range of 60° to 95° C., may be taken, and will be found to contain most of the benzene and parent materials for benzene. When toluene, xylenes, and ethyl benzene are also to be recovered, broader fractions may be employed.

In many respects, the more desirable feedstocks for extraction of benzene according to the invention are the liquid hydrocarbon products of vapor-phase catalytic reforming and cyclization of C_6 and C_7 hydrocarbon fractions in the presence of hydrogen. Typical of these reforming processes are "hydroforming," i. e. the reforming of naphthas over a molybdena-alumnia catalyst under pressure at 900° to 1000° F. in the presence of excess hydrogen (Trans. Amer. Inst. Chem. Eng. 42, 611 (1946), and "platforming," i. e. the reforming of gasolines over a platinum-containing catalyst under pressure in the presence of hydrogen at 800° to 900° F. (Ind. Eng. Chem. 42, 582 (1950)). The "platforming" process makes perhaps the most satisfactory benzene source material in that the product is exceptionally rich in aromatic hydrocarbons and contains little olefinic hydrocarbons. Optimum yields of high-grade benzene appear to be realized when C_6-rich fractions of natural gasoline are "platformed," and then extracted according to the invention. High-purity benzene is produced simply by extraction and distillation, without the need for any chemical purification.

As previously explained, in operating on feedstocks containing a substantial portion of olefins, a part of the olefins remain in the crude benzene after in it stripped from the diethylene glycol solvent. Such olefins as persist may usually be separated almost completely by fractional distillation of the crude extract during which they tend to concentrate in fractions boiling lower than benzene, between benzene and toluene, and between toluene and any xylenes. If, with some exceptional feedstock, complete removal of olefins is not effected in this way, final traces may be removed by treatment by concentrated sulfuric acid or by a chlorination step, followed by rectification, or by

simple clay treatment similar to that used on gasoline.

The diethylene glycol used as the extractant in the process of the invention may be the ordinary commercial product, and may contain small proportions of non-interfering solvents without serious consequence. As already explained, real advantage is realized by adding to the diethylene glycol a small proportion of water, i. e. 0.5 to 10 percent by weight. At values below 0.5 percent, the effect of water is not pronounced, while above 10 percent the solubility of benzene in the extractant is reduced unduly and other adverse effects begin to appear. For atmospheric pressure operations, optimum concentration of water is in the range of 1 to 5 percent, with 1.0 to 2.0 percent being a good working value. As already mentioned, the water tends to remain with the diethylene glycol throughout the process, and nowhere appears as a separate phase, except with the benzene product of the stripper. Here it is trapped and may be returned to the still. However, since water loss may occur during prolonged operation, is may be necessary to test the diethylene glycol at intervals and to add water as needed to maintain the desired concentration. Such addition may conveniently be made in the form of steam supplied to the stripper, as at line **24** in Fig. 1.

In the operation of the countercurrent multistage extraction according to the invention, the temperature should preferably be controlled below 60° C. by cooling the solvent and feedstock, if necessary, to insure maximum efficiency and to minimize hazard due to the presence of volatile hydrocarbon. The pressure in the extractor should be sufficient to maintain all phases liquid. Atmospheric pressure is ordinarily adequate, and, even under extreme conditions, only low superatmospheric pressures are required. The details of extractor design and operation for any particular set of conditions chosen may be worked out from the data of Figs. 2 to 4 by known engineering principles. In general, however, there should be efficient counter-current extraction, with usually a minimum of five or more theoretical stages. The solvent: feedstock ratio used is, of course, dependent on the composition of the stock, the number of extraction stages, and the purity of product and the recovery desired. Several volumes of solvent per volume of feed, e.g. at least a 4:1 ratio, are usually used. Likewise, one or more volumes of solvent-free extract are desirably recycled as reflux to the extraction system per volume subjected to fractionation, such reflux serving to insure virtually complete exclusion of non-aromatic hydrocarbons from the extract.

In an alternative mode of operating the process described with respect to Fig. 1, the heat-exchangers **16** and **21** may be eliminated and the system operated almost isothermally. In this case, the extractor **11** is operated at the same temperature as the stripper reboiler **23**. To achieve this equilibrium, the water content of the diethylene glycol must be controlled carefully at the value required to maintain the other conditions chosen, in accordance with the data in Figs. 2 to 4. For instance, if the extractor and stripper are both operated at 150° C., with moderate pressure in the extractor, about 7.5 percent by weight of water should be present in the diethylene glycol. Such operation reduces heating and cooling to a minimum, significantly lowering costs.

The following examples will further illustrate the invention.

Example 1

The feedstock was a benzene-rich mixture of aromatic, naphthenic, paraffinic, and olefinic hydrocarbons, produced by passing a vaporized natural gasoline fraction together with hydrogen over a platinum-containing catalyst at a temperature of 800° to 900° F. according to the "platforming" process (Oil and Gas. J. 48 (47), 83 (1950); Petr. Refiner 29 (4), 131 (1950)). It contained about 20 to 30 percent by weight of aromatic hydrocarbons, primarily benzene. The olefin content corresponded to a bromine index of 2660. (The bromine index is the bromine measured as milliliters of N/100 bromate-bromide solution absorbed by 100 milliliters of olefin-containing material, according to the procedure described by Johnson et al., Anal. Chem. 19, 869 (1947)).

For purpose of analysis, a sample of this feedstock was subjected to careful fractional distillation in a three-foot Podbielniak column at 40:1 reflux ratio. The amount of the fraction, weight per cent aromatic hydrocarbon in the fraction (as measured by refractive index), and bromine index of each fraction were determined as follows:

Boiling Range, °C.	Wt. Percent of Feed	Aromatic Content, Percent	Bromine Index
29.5–50.5	5.7	0	
50.5–61.5	7.4	0	
61.5–70.0	21.8	0	1950
70.0–81.0	17.2	39.0	2720
81.0	6.8	74.5	1820
81.0–91.0	2.9	18.0	2260
91.0–94.0	12.3	0.7	1780
94.0–110.0	16.2	26.5	2970
Residue	9.7		

From these values, it is apparent that the olefins occurred in all boiling ranges and could not be separated from the non-olefinic material by fractionation.

The main body of the feedstock was then extracted according to the invention with diethylene glycol at room temperature in a laboratory countercurrent multistage extraction unit according to the general scheme shown in Fig. 1. The raffinate phase from the top of the extraction column contained only 1.0 percent aromatic hydrocarbon and had a bromine index of 2820. The extract phase from the bottom of the column, after separation from the diethylene glycol solvent, contained 97 percent aromatic hydrocarbons and had a bromine index of 1440. The extraction thus made a clean separation of the aromatic from the non-aromatic portions of the feedstock. However, the olefins of the feed were distributed in both extract and raffinate.

The aromatic-rich extract was then subjected to a fractional distillation to separate the fraction boiling at temperatures up to 80° C. This fraction, which represented about 80 percent by weight of the total extract, was then subjected to fractional distillation through a three-foot Podbielniak column at 15:1 reflux ratio. The amount of each fraction, aromatic content, bromine index, and freezing point of the fractions were determined as

Boiling Range, ° C.	Wt. Percent of Feed	Aromatics, Percent	Bromine Index	Freezing Point, ° C.
28.5–71.0	3.7	31	9500	
71.0–78.0	4.4	73	4300	
78.0–78.5	30.7	98	950	3.8
78.5–79.0	57.5	98	275	4.9
Residue	3.7			

It will be evident that, in fractional distillation, virtually all the olefinic impurities were removed as forerunnings, leaving final fractions which were at least 98 percent benzene and which met standard specifications for that material.

Example 2

In a semi-plant operation, benzene was produced from a charging stock by catalytically reforming a selected fraction to increase its benzene content, and extracting the product according to the invention.

The charging stock was a blend of natural gasolines collected mainly from the Texas Gulf and South Texas areas and having A. P. I. gravity of 74.1, and a boiling range of 90° to 328° F. (A. S. T. M. specification D–850–47). This stock was distilled to separate it into

a light overhead cut, an intermediate naphtha, and a heavy naphtha. The intermediate naphtha, representing 31.4 percent by volume of the feedstock, had an A. P. I. gravity of 65°, and an A. S. T. M. boiling range of 162° to 207° F. It is consisted mainly of paraffinic and cycloparaffinic hydrocarbons of 6 and 7 carbon atoms per molecule, together with some benzene.

The latter fraction was vaporized and passed together with an excess of hydrogen over a platinum-containing catalyst at a temperature of 800° to 900° F. and at a pressure of 500 to 900 p. s. i. g. according to the "platforming" process, and the resulting reformed product was condensed. The liquid condensate had an A. P. I. gravity of 56.0°, a Reid vapor pressure of 4.3 pounds, and an A. S. T. M. boiling range of 140° to 284° F., and contained 17.0 percent by weight of benzene.

This condensate was then fractionally distilled to separate a light overhead, a middle cut representing 56.4 percent by volume of the total and containing virtually all the benzene in the condensate, and heavy ends. The middle cut had a specific gravity of 0.765, a boiling range of 154° to 200° F., and contained, by infra-red analysis, 27.6 percent by weight of benzene. It had a bromine index of 2280.

The middle cut was then forwarded as the feedstock into the extraction and recovery system illustrated in Fig. 1. The extractor was of the vertical mixer-settler type and was equivalent to about 10 theoretical extraction stages. The solvent was commercial diethylene glycol to which 1.0 percent by weight of water had been added. Operation was at 40° C. with a solvent to feed ratio of 4:1 and a solvent-free benzene return to the base of the extractor column of 4 volumes per volume forwarded to the finishing stills. The raffinate from the top of the extractor contained less than 0.1 percent benzene. The solvent-free aromatic hydrocarbon mixture produced as overhead in atmospheric pressure operation of the solvent stripper contained 97 percent by weight of benzene, in a quantity corresponding to 99 percent overall recovery efficiency in the solvent-extraction.

For analytical purposes, a sample of this solvent-free overhead was subjected to fractional distillation in a three-foot Podbielniak column at a reflux ratio of 15:1. The amount of each fraction, aromatics content, bromine index, and freezing point were determined as follows:

Boiling Range, ° C.	Wt. Percent of Feed	Wt. Percent Aromatics	Bromine Index	Freezing Point, ° C.
74.5–79.0	6.5	71	----------	----------
79.0	25.5	99	200	4.6
79.0–79.5	25.2	100	----------	5.3
79.5–80.5	25.5	100	45	5.4
80.5	9.1	100	----------	5.5
Residue	8.2	99	----------	----------

The solvent-free extract having this analysis was processed through the finishing stills, yielding benzene having a freezing point of 5.3° to 5.5° C., a boiling range varying less than 2° C. from beginning to end, and an acid wash color of 3. It met all specifications for industrial grade benzene (A. S. T. M.-specification: D836–47). The yield of high-purity benzene thus isolated represented 96.5 percent of the total benzene content of the "platformed" condensate.

The process of the invention is intended primarily for the production of pure benzene from hydrocarbon mixtures, and is most effective therewith. However, the extraction step with diethylene glycol, or with mixtures thereof with water, may also be used in the separation of toluene and other aromatic hydrocarbons from mixtures thereof with paraffinic and cyclo-paraffinic hydrocarbons, even in the absence of benzene.

This application is a continuation-in-part of our application Serial No. 198,578 filed December 1, 1950, now abandoned.

What is claimed is:

1. A continuous process for isolating benzene in a substantially pure state from the liquid hydrocarbon product of the vapor-phase catalytic reforming and cyclization in the presence of hydrogen of a gasoline fraction containing mainly hydrocarbons of six and seven carbon atoms per molecule, such product containing at least 10 percent by weight of benzene and an appreciable proportion of olefins not exceeding about 3 percent, which comprises introducing a stream of the hydrocarbon product into a counterflow multistage extraction system near the middle, introducing a stream of diethylene glycol containing 0.5 to 10 percent by weight of water into one end of the system into extractive contact with the hydrocarbon phase therein, withdrawing a stream of substantially aromatic hydrocarbon-free raffinate containing part of the olefins from the system at the same end, withdrawing a stream of benzene-containing extract containing the other part of the olefins from the other end of the system, subjecting the extract to evaporative conditions to distill a benzene-rich hydrocarbon portion therefrom, returning part of the said separated hydrocarbon portion as a reflux stream to the extraction system at this other end, and subjecting the remainder of the separated hydrocarbon portion to fractional distillation to separate the olefins therefrom and to isolate the benzene therein in a substantially pure state.

2. A process according to claim 1 wherein at least 4 volumes of diethylene glycol-water mixture are introduced into the extraction system per volume of liquid hydrocarobn feed and wherein at least half of the benzene-rich hydrocarbon portion distilled from the extract is returned to the extraction zone as reflux.

3. In a process for isolating light aromatic hydrocarbons of the class consisting of benzene, toluene, ethylbenzene and the xylenes from a mixture thereof with close-boiling paraffins and naphthenes, such mixture also containing an appreciable proportion of olefins boiling in the same temperature range and not separable by fractional distillation, the steps which comprise introducing a stream of the mixture into a counterflow multistage extraction system near the middle, introducing a solvent consisting essentially of diethylene glycol and containing from 0.5 to 10 percent by weight of water into one end of the system into extractive contact with the hydrocarbon phase therein, withdrawing from the system at the same end a stream of substantially aromatic hydrocarbon-free raffinate containing most of the paraffins, naphthenes, and that part of the olefins not separable from the aromatic hydrocarbons by fractional distillation, withdrawing a stream of aromatic hydrocarbon-rich extract containing the other part of the olefins from the other end of the system, evaporatively stripping the extract to separate the hydrocarbon portion therefrom, returning part of the separated hydrocarbon portion as a stream to the extraction system at this other end, and subjecting the remainder of the separated hydrocarbon portion to fractional distillation to separate the remaining olefins from the aromatic hydrocarbons and to isolate individual aromatic hydrocarbons in the substantially pure state.

4. In a process for isolating benzene and toluene in the substantially pure state from a liquid hydrocarbon mixture produced by catalytic reforming and containing mainly hydrocarbons of six and seven carbon atoms per molecule, such mixture containing 10 to 30 percent by weight of benzene together with paraffins, naphthenes, and an appreciable proportion of olefins boiling in the same temperature range and not separable from the benzene and toluene by fractional distillation, the steps which comprise introducing a stream of the mixture into a counterflow multistage extraction system near the middle, introducing a solvent consisting essentially of diethylene glycol and containing from 0.5 to 10 percent by weight of water into one end of the system into extractive con-

tact with the hydrocarbon phase therein, withdrawing from the system at the same end a stream of raffinate substantially free of benzene and toluene and containing substantially all the paraffins, naphthenes, and that part of the olefins not separable from the aromatic hydrocarbons by fractional distillation, withdrawing from the other end of the system an extract rich in benzene and toluene and containing the other part of the olefins, subjecting the extract to evaporate conditions to distill the hydrocarbon portion therefrom, returning part of this hydrocarbon portion to the extraction system at this other end, and fractionally distilling the remainder of this hydrocarbon portion to separate as individual fractions fore-runnings containing much of the olefins, substantially pure benzene virtually free of olefins, and intermediate fraction containing some olefins, and substantially purse toluene virtually free of olefins.

5. In a process for isolating light aromatic hydrocarbons of the class consisting of benzene, toluene, ethylbenzene and the xylenes from a mixture thereof with close-boiling paraffins and naphthenes, such mixture also containing an appreciable proportion of olefins boiling in the same temperature range and not separable by fractional distillation, the steps which comprise introducing a stream of the mixture into a counterflow multistage extraction system near the middle, introducing a solvent consisting essentially of diethylene glycol and containing a predetermined proportion of water from 0.5 to 10 percent by weight into one end of the system and passing it therethrough in extractive contact with the hydrocarbon phase therein while maintaining the said concentration of water substantially constant throughout the extraction system, withdrawing from the system at the same end a stream of substantially aromatic-hydrocarbon-free raffinate containing most of the paraffins, naphthenes, and that part of the olefins, not separable from the aromatic hydrocarbons by fractional distillation, withdrawing a stream of aromatic-hydrocarbon-rich extract containing the other part of the olefins from the other end of the system, subjecting the extract to evaporate conditions to distill the hydrocarbons therefrom in crude form together with at least part of the water in the solvent while injecting water into the extract undergoing distillation in a proportion sufficient to maintain the concentration of water therein throughout distillation at substantially the predetermined proportion aforesaid, separating the crude hydrocarbon distillate from the water distilled therewith, recycling part of the separated hydrocarbon portion as a stream to the extraction system near the solvent outlet end, and subjecting the remainder of the separated hydrocarbon portion to fractional distillation to separate the remaining olefins from the aromatic hydrocarbons and to isolate individual aromatic hydrocarbons in the substantially pure state.

6. In a process for separating light aromatic hydrocarbons of the class consisting of benzene, toluene, ethylbenzene and the xylenes from a feed mixture thereof with close-boiling non-aromatic hydrocarbons in a liquid-liquid counterflow multistage solvent extraction system followed by a solvent stripping zone, wherein the extraction system and the stripper are operated substantially isothermally at a predetermined temperature in the range corresponding to the boiling temperatures at atmospheric pressure of mixtures of diethylene glycol with from 0.5 to 10 percent by weight of water, the steps which comprise: introducing the feed mixture into the extraction system near the middle; introducing into one end of the system a selective solvent at the predetermined temperature and consisting essentially of diethylene glycol and containing from 0.5 to 10 percent by weight of water, and passing such solvent into extractive contact with the hydrocarbon phase in the system while maintaining the system under a moderate pressure sufficient to keep all phases liquid; withdrawing substantially aromatic hydrocarbon-free raffinate from the system at the solvent inlet end; withdrawing aromatic hydrocarbon-rich extract from the other end of the system, transferring it without substantial temperature change to the solvent stripping zone maintained at about atmospheric pressure and therein boiling it to strip therefrom the hydrocarbon portion and some of the water while injecting water into the boiling liquid in a proportion just sufficient to maintain the normal boiling temperature of the stripped solvent at the predetermined temperature aforesaid; withdrawing stripped solvent from the stripping zone and recycling it without substantial cooling to the extraction zone; returning part of the stripped hydrocarbon portion to the extraction zone at the solvent outlet end; and fractionally distilling the remainder of the hydrocarbon portion to separate the light aromatic hydrocarbons as product.

7. A process according to claim 6 wherein the predetermined temperature is about 150° C. and the concentration of water in the solvent is about 7.5 percent.

References Cited in the file of this patent

UNITED STATES PATENTS

2,246,297	Duncan et al.	June 17, 1941
2,302,383	Stratford et al.	Nov. 17, 1942
2,400,802	Arnold	May 21, 1946
2,407,820	Durrum	Sept. 17, 1946
2,409,695	Laughlin	Oct. 22, 1946
2,449,402	Lipkin et al.	Sept. 14, 1948
2,478,916	Haensel et al.	Aug. 16, 1949
2,492,787	Davis	Dec. 27, 1949
2,514,997	Floyd	July 11, 1950

FOREIGN PATENTS

456,958	Great Britain	Nov. 18, 1936