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DRAWINGS ATTACHED.

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COMPLETE SPECIFICATION.

Separating Hydrocarbons by a Solvent Extraction Process.

We, UNIVERSAL OIL PRODUCTS COMPANY, a Corporation organised under the laws of the State of Delaware, United States of America, of No. 30 Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a solvent extraction process for the recovery of an aromatic component from a hydrocarbon mixture containing aromatic and non-aromatic hydrocarbons. More particularly this invention relates to a process wherein such hydrocarbon mixture is contacted in an extraction zone with a solvent composition which selectively dissolves the aromatic component of the hydrocarbon charge mixture and which contains water and an organic solvent boiling above the aromatic component, resulting raffinate and an extract phase containing dissolved aromatic component are separately removed from the extraction zone, the extract phase is thereafter subjected to a distillation in a distilling zone, and an overhead distillate vapor stream containing only a portion of the extracted aromatic component and a vaporous side cut stream containing steam and aromatic hydrocarbon vapor are separately removed from the distilling zone, followed by recovery of aromatic hydrocarbon from this side cut stream.

In the solvent extraction of aromatic hydrocarbons from a hydrocarbon mixture utilizing a solvent selectively miscible with the aromatic component of this mixture, the solvents utilized for this purpose generally contain a definite proportion of water in order to increase the selectivity of the solvent for the aromatic component of the hydrocarbon charge and to increase the capacity of the solvent to reject the non-aromatic charge components which accumulate and are removed from the extraction process as the so-called "raffinate" stream. By the inclusion of water in the solvent composition, the solubility of aromatic hydrocarbons in the solvent, although somewhat reduced in comparison with a non-aqueous solvent, greatly decreases the solubility of raffinate components in the solvent and also reduces the solubility of solvent in the raffinate stream. Solubility of solvent in the raffinate, however, cannot be completely eliminated and consequently, the raffinate stream inherently contains more or less solvent, depending upon the proportion of water in the solvent composition. Although the quantity of solvent in the raffinate at any instant is relatively small, the cumulative effect of such small amounts of solvent in a stream removed from the process flow and thus otherwise lost, greatly reduces the efficiency and economy of the solvent extraction process. Accordingly, it is desirable that the solvent dissolved in the raffinate stream be recovered therefrom. Such recovery is usually accomplished by countercurrently washing the raffinate with water in a separate washing zone from which an aqueous wash effluent is recovered containing dissolved therein the solvent recovered from the raffinate.

Although the aqueous solvent composition selectively extracts the aromatic components from the hydrocarbon feed stock, it nevertheless dissolves a small but significant quantity of raffinate components having essentially the same boiling point as the aromatic extract hydrocarbon. If these are

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not removed from the extract phase or rich solvent prior to the recovery of the aromatic component therefrom in the subsequent extract phase distillation or so-called stripping stage, dissolved raffinate components tend to distill from the rich solvent with the aromatic product, and since these hydrocarbons have essentially the same boiling point as the desired aromatic extract, they are not readily removed from the aromatic product by distillation. When the aromatic product is desired in a high state of purity, as, for example, in the production of benzene of nitration grade quality, containing 99+ per cent benzene, a slight contamination of the aromatic product with raffinate produces a non-acceptable product which generally cannot be readily purified by supplemenaary methods of purification. For this reason, the rich solvent stream is usually contacted (preferably under counter-current flow conditions), prior to the recovery of the aromatic extract therefrom in the extract phase distillation or so-called stripping stage, with a light paraffin-aromatic mixture recovered as overhead distillate from the rich solvent stripping column. During such counter-current contact of the rich solvent with the light paraffin-aromatic mixture, known in the art as reflux, the raffinate dissolved by the solvent is displaced from the extract phase or rich solvent prior to the removal of the latter from the solvent extraction zone, the raffinate thus being replaced by the light paraffin and aromatic components of the reflux. The rich solvent leaving the solvent extraction zone, thereby, contains dissolved aromatic extract and light paraffin present therein by virtue of the contact between the light paraffin-aromatic reflux and rich solvent stream in the lower portion of the solvent extraction zone.

In the subsequent distilling or stripping stage of the process the hydrocarbon solute is stripped from the rich solvent with the aid of steam formed by distillation of the aqueous solvent composition and/or by the injection of water into the lower or so-called reboiling section of the stripping zone which is maintained at a temperature above the boiling point of the solvent; the overhead produot from the stripping zone will then contain substantially all of the light paraffins of the reflux as well as a portion of the aromatic component of the rich solvent stream. When the aromatic component of the hydrocarbon charge consists of various aromatic hydrocarbons of different boiling points, the reflux will contain a portion of the most volatile aromatic component of the rich solvent stream. The remaining portion of the aromatic component of the extract phase is then discharged from the distilling or stripping zone as a vaporous side cut stream containing also vaporized water and organic solvent while the distillation residue obtained from the reboiling section of the distilling or stripping zone will contain organic solvent denuded of aromatic hydrocarbon and may contain water in an amount depending on the conditions of temperature, pressure and water or steam injection employed in the reboiling section. By appropriate selection of these conditions it is possible in the known solvent extraction process and desirable also in the process of the present invention to reconstitute the solvent composition in the distilling or stripping zone so that the effluent from the bottom portion of the reboiling section thereof contains the same proportion of water and organic solvent as the solvent composition which is brought into contact with the hydrocarbon charge mixture in the extraction zone.

A principal object of the present invention is a simplified and highly economical recovery of a solvent-free aqueous phase from the vaporous side cut stream of the extract phase distillation step of the process so as to permit a most effective washing of solvent from the raffinate and extract streams. Another object of the invention is the elimination of the necessity for separately distilling aqueous condensate ordinarily obtained in condensing the vaporous effluent of a conventional extract phase distillation. A further object of this invention is the reduction of the need of water from extraneous sources to a minimum in the recovery of a substantially pure, solvent-free aromatic extract and a solvent-free non-aromatic raffinate from a mixture of aromatic and non-aromatic hydrocarbons with the aid of a water-containing solvent composition.

The solvent extraction process according the the present invention is characterized principally by the features of supplying the vaporous side cut stream from the distilling zone for the extract phase distillation directly to a separate rectifying zone and therein separating the vaporous side cut stream by fractionation into an aromatic extract fraction and an aqueous distillate substantially free from solvent, and washing the raffinate and the extract fraction with aqueous distillate thus obtained.

In a more specific embodiment of the process of this invention, aqueous distillate is supplied from the rectifying zone to the zone for washing the extract fraction and the resultant aqueous phase is separated from the washed extract fraction and then supplied to the zone for washing the raffinate. Preferably the aqueous phase resulting from the washing of the raffinate upon separation of this aqueous phase from the washed raffinate, is mixed with the overhead distillate obtained

from the distilling zone for the extract phase distillation, the resultant mixture is separated into a hydrocarbon phase and an aqueous phase substantially free from raffinate components, and the last-mentioned aqueous phase is supplied to the reboiling section of the distilling zone as a source of stripping steam in the latter zone.

In another specific embodiment of the process of this invention separate portions of the aqueous distillate are supplied from the rectifying zone to the zone for washing the extract fraction and to the zone for washing the raffinate. Most advantageously the aqueous phase resulting from the washing of the raffinate in this embodiment is separated from the washed raffinate and then mixed with the overhead distillate obtained from the extract phase distilling zone, the resultant mixture is separated into a hydrocarbon phase and an aqueous phase substantially free from raffinate components, the last mentioned aqueous phase is mixed with the aqueous phase separated from the washed extract fraction, and the resultant mixture of aqueous phases is supplied to the reboiling section of the extract phase distilling zone as a source of stripping steam therein.

Before the overhead distillate of the extract phase distilling zone is separated into an aqueous phase and hydrocarbon phase suitable for recirculation to the extraction zone for reflux purposes, the preferred embodiments of the present invention take advantage of the aromatic component present in this light distillate to displace the raffinate paraffin dissolved in the aqueous wash effluent of the raffinate water-washing step, and this aqueous wash effluent is thereafter charged into the rich solvent stripping zone as a source of stripping steam therein. Such additional processing technique will be hereinafter further described.

Typical hydrocarbon mixtures containing aromatic components and utilizable as the hydrocarbon charge to the present process include hydrocarbon distillate fractions (usually boiling within or near the gasoline boiling range) of natural gasoline or straight-run petroleum distillates, and especially, hydroreformed naphthas which are rich in aromatic hydrocarbons and are particularly valuable as a source of such mononuclear aromatic hydrocarbons as benzene, toluene and xylene.

Solvent compositions which have a preferential solubility for aromatic hydrocarbons generally contain one of more organic compounds containing in the molecule at least one polar group such as a hydroxyl, amino, cyano, carboxyl or nitro radical. In order to be effective in a system of extraction such as the process provided by the present invention, the solvent component having the polar radical must have a boiling point substantially greater than the boiling point of water which is included in the solvent composition for enhancing its selectivity, and in general, must also have a boiling point substantially greater than the end boiling point of the aromatic component to be extracted from the hydrocarbon charge. Preferably the organic polar compound used in the solvent composition boils above the end boiling point of the hydrocarbon mixture supplied as charge to the extraction zone. In most instances the solvent composition has a greater density than the hydrocarbon charge and is accordingly introduced into the uppermost portion of the solvent extraction zone, thereafter flowing downwardly, countercurrent to the rising hydrocarbon feed stock introduced into the extraction zone at its mid-point or in the lower portion thereof.

Organic compounds for use as the solvent component of the solvent composition preferably are selected from the group of those oxygen-containing compounds which include the aliphatic and cyclic alcohols, cyclic monomeric sulfones, the glycols and glycol ethers, as well as the glycol esters and glycol ether-esters. The mono- and polyalkylene glycols in which the alkylene group contains from 2 to 3 carbon atoms, such as ethylene glycol, diethylene glycol, triethylene glycol and tetraethylene glycol, propylene glycol, dipropylene glycol, and tripropylene glycol, as well as the methyl, ethyl, propyl and butyl ethers of the glycol hydroxyl groups and the acetic acid esters thereof constitute a particularly preferred class of organic solvents useful in admixture with water as the solvent composition for use in the present process. A particularly preferred cyclic monomeric sulfone is tetrahydrothiophene-1,1-dioxide. Various phenols, such as phenol and resorcinol and their alkyl ethers, such as for example para-cresol and thymol, are also effective solvents for aromatic hydrocarbons. Aliphatic nitriles and cyano-substituted ethers and amines of appropriate boiling point, such as acetonitrile, the di-alpha, di-beta, and di-gamma, propionnitriles and the diethers and polyalkylene polyamines constitute another group of useful solvents when combined with water in certain proportions to provide solvent compositions having the desired selectivity. The preferred polyalkylene glycols and especially, diethylene, triethylene and dipropylene glycols, containing from 2 per cent to about 25 per cent by weight of water, constitute especially desirable solvent compositions for use in the present process.

The improvement in the basic solvent extraction process to which the present invention is directed involves the rectification or

fractional condensation of the side-cut vapors removed from the extract phase distilling column, also called rich solvent stripping column, in a separate side-cut rectification column in order to produce an overhead distillate from the side-cut rectification column consisting essentially of pure water which is thereafter utilized for washing the extract and raffinate streams recovered from the solvent extraction process. In this manner, the heat present in the side-cut vapors is utilized for the separation of the distillate, from a residue of relatively non-volatile solvent and extract hydrocarbon, both of which are present in the side-cut vapors carried over to the water rectifying column. In this manner the aqueous phase recovered from the side-cut vapors is recovered in a form substantially free of solvent, that is a form in which it is most effective as a wash stream to remove solvent from the extract and raffinate product streams of the process. Contrasted with the methods heretofore utilized to accomplish solvent removal treatment the process flow of the present invention assures substantial savings in the amount of heating and cooling facilities required for effecting the desired recovery of solvent-free extract and raffinate products, as well as a substantial saving in the initial investment for equipment. The heat consumed in the process of the present invention is from 25 to 35 per cent less than the heat requirements of the process of the prior art utilizing vapor condensers in an otherwise similar system of solvent extraction, extract phase distillation, and product recovery and at the same rate of extract production. Thus, the present process eliminates the condensation of the side-cut vapors to a liquid stream in the manner formerly practiced, which would necessitate a redistillation of the aqueous condensate phase if an overhead distillate free of solvent were to be made available for purposes of washing the raffinate and extract streams with a minimum supply of water to the process.

The present invention and the improvements effected thereby are explained in greater detail in connection with the accompanying diagram which illustrates a typical process flow in conformity with this invention. It is not intended however to limit the scope of the invention to the specific solvent, specific process conditions, and particular apparatus arrangement described with reference to this drawing.

Referring to the accompanying diagram, an aromatic hydrocarbon-containing charge, such as the product of a gasoline reforming process containing benzene, toluene and xylenes as aromatic components, is introduced into the process flow through line 2 at a superatmospheric pressure which is sufficient to maintain the charge in substantially liquid phase at the particular temperature maintained within the extraction zone and which may be in the range of from about 0.7 to about 20 atmospheres or higher. Depending upon the water content of the solvent composition, the temperature of the extraction may be varied to increase or decrease the selectivity and solubility relationships between the solvent and the hydrocarbon feed stock. Utilizing a polyalkylene glycol solvent, for example, containing from 2 to about 25 per cent by weight of water, the process may be operated at temperatures of from about 100° to about 300° C. In order to increase the solubility of aromatics in the solvent, while maintaining the selectivity at a high level, the extraction stage of the process is preferably operated at a temperature in the range of from about 125° to about 200° C. with maintenance of liquid phase contact in the extraction zone. For polyethylene glycol solvents, such as triethylene glycol, containing from 5 to about 15 per cent by weight of water, the preferred extraction conditions for the present process are temperatures of from about 110° to about 150° C., utilizing solvent to hydrocarbon charge ratios of from about 5 to 1 to about 15 to 1 volumes per volume.

Referring again to the accompanying diagram, the hydrocarbon charge at the foregoing temperature and pressure conditions is introduced from line 2 into extraction column 1 at an intermediate point below the solvent inlet (which generally is at the upper portion of the column) and above the rich solvent outlet in the lowermost portion of the column. Lean solvent composition from which hydrocarbon solute has been removed in the stripping stage of the process, is charged through line 3 at the desired temperature and pressure into the upper portion of solvent extraction zone 1.

Solvent extraction zone 1 may be of any type suitable for effecting countercurrent contact between two liquid phases at least partially miscible in each other and wherein the relatively more dense solvent may be brought into intimate contact with the relatively less dense hydrocarbon phase. Thus, extraction zone 1 may be a packed column or may contain a series of horizontal, perforated plates through which the liquid solvent flows in dispersed form and in countercurrent flow relationship to an ascending hydrocarbon stream. The recycle reflux stream consisting in part, preferably predominantly, of a portion (usually the lightest portion) of the aromatic extract component present in the hydrocarbon charge, is introduced into zone 1 at a point below the charge line 2 through line 4. This reflux stream usually is the stream recovered as overhead distillate from the solvent stripping zone,

As the hydrocarbon charge and reflux flow upwardly through column 1 in countercurrent relationship to the descending solvent composition, the solvent selectively extracts the more soluble aromatic hydrocarbon components of the charge and selectively rejects the paraffinic and other non-aromatic components which make up the raffinate. The non-extracted residue, herein referred to as "raffinate", comprises predominantly paraffinic hydrocarbons substantially free of the aromatic hydrocarbons to be recovered as extract product of the process; thus raffinate is withdrawn from the top of extraction zone 1 through line 5, which discharges the raffinate stream into raffinate washing zone 6 for recovery of the normally small but significant quantity of solvent dissolved in the effluent raffinate hydrocarbon stream. Since this stream is customarily employed for blending into gasoline motor fuels, the presence of the solvent therein is detrimental to its use and must accordingly be removed therefrom prior to its use as a motor fuel. Moreover, if the solvent dissolved in the raffinate effluent, even though the quantity of this dissolved solvent is generally small, were not recovered therefrom, its continuous removal from the process in the raffnate would represent a substantial loss on a continuously operating basis, since the raffnate stream does not re-enter the process flow. Accordingly, raffinate washing zone 6 is incorporated into the process flow in order to recover the solvent removed from the extraction zone in the raffinate.

In order to effect such recovery of solvent from the raffinate on an efficient basis, however, the aqueous stream used to wash the raffinate must be free of solvent and must be confined to the smallest possible quantity sufficient for the purpose, since excess water must be removed from the recovered solvent solution in order that it may be utilized again in the extraction zone. The most effective aqueous wash stream for this purpose is that recovered from the vaporous side-cut of the stripping column in the operation according to the present process which produces a substantially pure water stream containing no dissolved solvent therein.

As the rich solvent stream containing dissolved aromatic extract flows downwardly through extraction zone 1, it countercurrently contacts the light aromatic reflux introduced into the lower portion of extraction zone 1 through line 4. The reflux, in its countercurrent contact with the descending rich solvent, displaces raffinate paraffins which have a tendency to dissolve in the rich solvent stream to a small extent; in effect, the rich solvent prior to its removal from the extraction zone is countercurrently washed with light, more soluble aromatics which replace the raffinate solute from the rich solvent into the upwardly flowing hydrocarbon phase and thus ultimately into the raffinate effluent from the extraction zone. The resulting rich solvent, which now contains dissolved aromatic extract and reflux components and is free from raffinate hydrocarbons boiling in the same range as the aromatic solute is removed from the bottom of extraction zone 1, through line 7, and is transferred by means of pump 8 through line 9, and at a rate controlled by valve 10, into the upper portion of stripping zone 11, for the recovery of hydrocarbon solute therefrom. Stripping zone 11 generally contains a reboiler 12 in the lower portion of the column which supplies additional heat to the rich solvent residue for stripping the last traces of aromatic solute from the solvent prior to removal of the latter from the stripping zone.

In the preferred manner of operating the present extraction process, zone 1 is maintained at a temperature above the boiling point of the rich solvent and at a pressure sufficient to maintain the rich solvent substantially in liquid phase at the particular extraction temperature. Thereafter, the resulting rich solvent, in essentially liquid phase, is transferred into stripping zone 11, wherein the pressure on the rich solvent is reduced (preferably in several stages), while maintaining substantially the same temperature in zone 11 by means of reboiler 12. Hydrocarbon solute, including particularly a portion, respectively light portion, of the aromatic component thereof, is flashed from the rich solvent at the resulting substantially isothermal stripping conditions. The composition of the overhead vapor is a mixture of the light paraffins and the light aromatics together with a small amount of solvent and water vaporized from the rich solvent, the proportion of the latter components increasing as the boiling points of the respective overhead and side-cut vapors increase.

In any event, the reduction in pressure between the extraction and stripping column is sufficient to vaporize almost completely the paraffinic component of the rich solvent stream and if necessary, sufficient heat is introduced into the reboiling section of the column to supply the heat of vaporization required to completely remove all of the paraffin from the rich solvent into the overhead vapor and to effect such vaporization on a substantially isothermal basis. Overhead vapor is removed from the top of the stripping column through line 13, into overhead condenser 14, which liquefies the vaporized components for withdrawal therefrom through line 15 and discharge into overhead receiver 16. The upper hydrocarbon layer accumulating in receiver vessel

16 (comprising a mixture of the light paraffins distilled from the rich solvent and a portion of the aromatic component, respectively, a large proportion of the lightest aromatic component of the extract phase) is withdrawn from the top of receiver vessel 16 through line 4 and valve 17 for use as the aforementioned recycle reflux. The aromatic component present in the reflux stream, recovered therefrom in extraction zone 1, increases as the amount of reflux recycled to the extraction zone increases; thus, greater proportions of the lightest aromatic are forced into the higher boiling fraction separated from the stripping zone as side-cut and ultimately all of the light aromatic component present in the charge is recovered as a portion of the extract product.

The aqueous phase obtained as a distinct lower layer in the receiver 16 contains solvent dissolved therein and also contains dissolved aromatic component. Another stream which enters the overhead condensate receiver 16 is the aqueous wash effluent recovered from the raffinate washing column 6. This wash effluent, after contacting the raffinate to recover solvent dissolved therein, contains a small amount of raffinate, which if it were introduced into the stripping column, would contaminate the extract product with paraffins boiling in the same boiling range as the aromatic extract and normally not recoverable therefrom. In accordance with a preferred feature of the present process, this aqueous wash effluent is mixed with the contents of the overhead receiver where the aromatics present in the receiver vessel 16 displace the raffinate from the wash effluent and the displaced raffinate mixes with the reflux layer recycled to the extraction zone. The lower aqueous layer in the receiver vessel 16, now containing dissolved aromatic extract instead of raffinate may be charged into the reboiling section of the stripping column without danger of contaminating the extract product by paraffins or other non-aromatic hydrocarbons.

The aqueous phase accumulating in the settling leg of receiver vessel 16 is drained therefrom through line 18, into water receiver vessel 19. Water accumulating in vessel 19 and containing dissolved solvent recovered from the various water washing and stripping stages of the present process is withdrawn, as required, through line 20, and valve 21, and preferably is charged into heat exchanger 22, in which the water is transformed by indirect heating at least partially into superheated steam which together with the solvent, is injected through line 23, into the reboiling section of stripping zone 11. Alternatively, the water in vessel 19 may be charged directly into the reboiling section, in which case the duty on reboiler 12 is greater. The steam thereby generated in the bottom of the stripping zone is injected into the rich solvent residue, stripping the residual hydrocarbons from the solvent and rehydrating the solvent to the level of water content required for the solvent composition for recycling to extraction zone 1. Thus, the solvent contained in the various sources of aqueous streams in the process is reintroduced into the lean solvent composition, thereby recovering the solvent for reuse in the process. Heating medium for use in heat exchanger 22 is introduced through line 24, and withdrawn through line 25. Although not shown in the drawing, hot lean solvent on its way from the stripping zone 11 to the extraction zone 1 or hot rich solvent on its way from the extraction zone 1 to the stripping zone 11 may be used, if so desired, as heating medium in the exchanger 22.

The lean solvent composition from which the hydrocarbon solute has been completely stripped and which has been rehydrated to the water content required for use in the extraction zone is withdrawn from the bottome of stripping zone 11, through line 26, at a rate controlled by valve 27, and is transferred by means of pump 28, through line 3, into the top of extraction zone 1 for reuse in the solvent extraction system. Any solvent required for make-up, due to losses in the system, is charged into line 3, from storage, through line 29, at the rate required by the process.

A side-cut which contains substantially all of the aromatic extract hydrocarbons present in the rich solvent stream, except for the portion of aromatic component removed in the overhead vapor (ultimately recovered in the side-cut vapor) and which is free of all paraffinic raffinate is withdrawn from column 11 in vaporous state through line 30, and valve 31. In accordance with the invention herein provided this vaporous side-cut is discharged into water rectifying column 32, wherein the heat contained in the side-cut vapors is utilized to distill a substantially pure water overhead from the rectifying column, and the rectifier overhead distillate is utilized as wash water in the separate raffinate and extract washing columns.

Water rectifier 32 is a fractional distillation column containing side-to-side pans, bubble deck plates or a packing material, such a quartz chips, wherein contact between vapor and liquid phases may be obtained and thereby fractionation is realized. Although ordinarily the latent and sensible heat content of the vapors entering water rectifier 32 provides sufficient heat for fractionation purposes in column 32, a reboiler 33 may be provided for introducing additional heat into column 32 to the extent

needed for satisfactorily effecting the desired rectification or fractionation in this column.

Accompanying the water and hydrocarbon extract portions of the side-cut vapor is a small but significant proportion of solvent. This solvent is carried in the side-cut vapor in spite of its relatively high boiling point because it has sufficient vapor pressure at the distillation temperature or is entrained due to foaming. During the fractionation in water rectifier 32, high boiling components of the side-cut vapor, including aqueous solvent and extract, condense while a major proportion of the water present in the side-cut vapor distills overhead through line 34, into condenser 35, from which the resulting liquid distillate flows through line 36 into receiver vessel 37.

The rectifier bottoms or residue remaining in column 32 after separation of water and aromatic hydrocarbon therefrom as overhead vapor, is predominantly aromatic extract admixed with a concentrated aqueous solution of the solvent. This residue is withdrawn from column 32 through line 38, at a rate controlled by valve 39, and is discharged from line 38 into the bottom of extract washing column 40.

The overhead distillate from column 32, which collects as liquid phase in receiver vessel 37, separates on standing into two layers, an upper hydrocarbon layer consisting of aromatic extract or light aromatic extract which is withdrawn from the top of receiver vessel 37 through line 41 and is at least partly refluxed back to the top of the rectifying column 32. A portion of this hydrocarbon stream may be withdrawn through line 42 and valve 43 as a net product if it is necessary to raise the hydrocarbon partial pressure at the top of the column 32 in order to take over more water. The aromatic extract product is thereafter conveyed by line 38 into the bottom of water washing column 40.

The lower layer accumulating in receiver vessel 37 is substantially pure, solvent-free water (contaminated only with dissolved aromatic extract). This aqueous distillate thus constitutes an especially preferred source of water for countercurrently washing the raffinate and extract products formed in the present process. For this purpose, the water is withdrawn from settling leg 44 of receiver vessel 37 through line 46, which conveys separate portions of the aqueous stream into the upper sections of columns 40 and 6, wherein extract and raffinate, respectively, are individually washed with a countercurrent stream of the water. The flow of water into extract washing column 40 is controlled by valve 47, and the flow of water into the raffinate washing column 6 is controlled by valve 48. In each column the water descends through a rising stream of the hydrocarbon phase, thereby countercurrently washing the latter and removing dissolved solvent therefrom. Washed raffinate substantially free of solvent and suitable for gasoline use or recycling to other process units in the refinery, such as a catalytic reforming reactor, is removed from the top of column 6, through line 49. Washed aromatic extract, substantially free of solvent, is removed from the top of column 40 through line 50, to storage, drying units, or to fractionators for recovery of the individual aromatic hydrocarbons by fractionation. The excess portion of the water condensed from the overhead which is not required for use in the extract and raffinate wash columns is withdrawn from line 45 through line 51 at a rate controlled by valve 52, and is charged directly into water receiver vessel 19, for storage prior to being charged into the stripping column 11 for generation of steam therein.

The aqueous wash stream recovered from extract washing zone 40, containing both the solvent dissolved from the extract product and the solvent residue obtained from the water rectifying column 32, is removed from column 40, through line 53 at a rate controlled by valve 54, and thereafter is preferably discharged from line 53 into water receiver vessel 19. A small amount of extract hydrocarbons has a tendency to dissolve in the aqueous solution of solvent, but since this stream is to be utilized in the stripping zone 11, the stream may be discharged from line 53 directly into the reboiling section of the stripping zone.

The aqueous wash effluent from the raffinate water washing column 6, is an aqueous solution of the solvent recovered from the raffinate. However, due to the contact of the aqueous solution with the raffinate stream, a small but significant proportion of the raffinate hydrocarbons are dissolved in the aqueous solvent solution and therefore this stream should not be discharged into the water receiver vessel 19 or the reboiler section of the stripping zone 11 where the raffinate components present in this aqueous phase could cause contamination of the extract product recovered as side stream from the stripping zone. In the preferred embodiment of the present invention, therefore, the aqueous wash effluent from the raffinate water washing column is treated in a separate stage of the process to displace raffinate hydrocarbons from the aqueous wash stream with aromatic hydrocarbons, prior to being introduced into the stripping zone. For this purpose, the aqueous wash effluent recovered from the raffinate washing column 6 is passed through line 55 and valve 56 into line 15 which conveys the stripper overhead into receiver vessel 16. As indicated further above, the stripper over-

head product from column 11 consists to a large extent of aromatic component of the hydrocarbon charge and this aromatic hydrocarbon material accumulates as an upper layer in receiver vessel 16. It has been found that by mixing the aqueous wash effluent from the raffinate wash column with the overhead hydrocarbons recovered from the stripping zone 11 the raffinate components are displaced from the aqueous wash effluent by means of the aromatic hydrocarbons contained in the stripper overhead product. The resultant aqueous wash effluent which settles into the lower portion of receiver vessel 16, now contains aromatic hydrocarbons instead of raffinate component, the aromatic component being more soluble in the aqueous wash effluent than the raffinate hydrocarbon. Since the hydrocarbon layer accumulating in receiver vessel 16 is to be recycled to the extraction zone, the raffinate components enter the extraction column in the bottom thereof, flow upwardly through the column and are ultimately recovered from the process as a portion of the raffinate stream withdrawn from the process as one of the products thereof. The raffinate-free aqueous wash effluent collects in the bottom of receiver vessel 16 and is removed therefrom through line 18, into water receiver vessel 19 from which the aqueous solution is withdrawn and ultimately utilized as stripping steam for stripping zone 11.

By the aforementioned recovery means, all of the solvent contained in the various hydrocarbon streams and aqueous distillates is recovered in the process for recycling to the extraction zone, thereby providing a complete, cyclic flow of the solvent utilized in the process. Only very small quantities of the solvent are required for make-up purposes. By the aforementioned method, furthermore, an extract product of 99+ percent aromatic hydrocarbon component is recovered as the product of the process in a more effective manner than hitherto known and a raffinate product in which the proportion of aromatic components is substantially nil is also recovered as a major product of the process.

The following illustrative examples describe several runs of a cyclic, solvent extraction operation under various conditions and serve to demonstrate the advantages which are realized by operating the process in accordance with the present invention. In each case a catalytically reformed fraction of gasoline boiling range is utilized as hydrocarbon charge for the recovery of a mixture of benzene, toluene, and xylene with the aid of a diethylene glycol solvent composition containing about 8 percent by weight of water in a countercurrent solvent extraction operation effected in an extraction column comprising a series of horizontal perforated plates. The extraction stage of the process results in the formation of a rich solvent composition which is thereafter stripped in the presence of steam to recover the aromatic hydrocarbon extract. In the operation of the rich solvent stripping column a benzene-light paraffin overhead stream containing vapors of diethylene glycol and water is separated as the lightest fraction from the process by stepwise reduction in the pressure on the extract phase or rich solvent. A middle distillate comprising the aromatic hydrocarbon extract, together with diethylene glycol solvent and water is separated as a vaporous side-cut fraction from the stripping column by the introduction of heat and steam into the lower portion of the stripping zone, and the vapors recovered as side-cut from the stripping column are treated in one of two different methods herein referred to as runs A and B; run A does not involve all features of the present invention whereas run B is carried out in accordance with the present invention.

In run A the side-cut vapor recovered from the stripping column is charged into a water-cooled condenser and is condensed therein, the liquid condensate is passed into a receiver vessel and therein is allowed to accumulate and separate into a hydrocarbon layer and an aqueous layer, and these layers are decanted and separately treated. In run B the hot side-cut vapors are charged from the stripping column into a rectivying column comprising a fractionating still with perforated trays known by the trade name "FRI DUAL-FLOW" wherein a solvent-free water is separated as overhead distillate from a mixture of extract hydrocarbon and aqueous solvent removed as bottoms from the rectifying column. Each of these cuts are separately treated in accordance with the procedure hereinafter described.

In each of the above indicated runs the catalytic reformate is fractionally distilled to separate a fraction having a boiling range of from 65° to 155° C. This fraction, which is used as hydrocarbon charge to the extraction treatment, contains approximately 7.0 percent by weight of benzene, 25.6 percent by weight of toluene and 30.6 percent by weight of C_8 xylenes and ethylbenzene, the remainder consisting of non-aromatic, mostly paraffinic hydrocarbons in C_6—C_9 range. This charge is passed at the rate of 2600 hectoliters per day, at a superatmospheric pressure of 6.8 atmospheres and at a temperature of 144° C. into the mid-section of a countercurrent solvent extraction column of the aforementioned type containing 60 actual plates. As the feed stock is charged at these conditions into the solvent extraction zone, the aqueous diethylene gly-

col solvent composition, recovered from the reboiling section of the solvent stripping zone is charged at the rate of 39,400 hectoliters per day and at a temperature of 144° C. and at a pressure of 6.8 atmospheres into the top of the extraction column, thereafter percolating downwardly through the perforations in the horizontal plates against a rising stream of the hydrocarbon charge. Another stream, herein referred to as a recycle reflux, enters the extraction column below the hydrocarbon charge inlet, namely in the lowermost portion of the extraction column; this reflux is a mixture of benzene and light paraffins containing approximately 88 percent by volume of benzene in admixture with C_5 and C_6 aliphatic paraffins derived from the hydrocarbon layer of the stripper overhead condensate. The reflux is charged into the bottom of the solvent extraction column at a rate of 3342 hectoliters per day and at the extraction temperature and pressure maintained within the extraction zone.

The raffinate (non-extracted portion of the hydrocarbon charge) is removed from the top of the solvent extraction zone at a rate of 1218 hectoliters per day and is diverted into the bottom of a counter-current raffinate washing zone into the top of which 946 liters per hour of the recovered lower aqueous phase of the side-cut stripper condensate, recovered as indicated hereafter, is charged to remove the small quantity of solvent dissolved in the raffinate stream (approximately 270 liters per day). The recovered, washed raffinate, removed from the top of the raffinate washing column contains less than 0.2 percent by weight of benzene, approximately 0.5 percent by weight of toluene and about 6 percent by weight of xylene. The recovered aqueous wash effluent from the raffinate wash column is separately treated in accordance with the procedure designated herein as run B, to provide a comparative basis of examination for the different runs.

The rich solvent stream recovered from the bottom of the solvent extraction column is charged at the temperature and pressure maintained in the extraction column into a solvent stripping zone wherein the hydrocarbon solute in the rich solvent is allowed to flash-distill in the upper section of the stripping column while steam generated by heating the aqueous wash effluent streams is injected into the lower portion of the stripping column to recover the aromatic solute dissolved in the rich solvent. The rich solvent upon entering the stripping column is flash-distilled by successive reductions of the pressure from 6.8 atmospheres down to substantially atmospheric pressure; the resulting flashed overhead vapors are condensed in a water-cooled overhead vapor condenser and collected as overhead liquid condensate in the receiver vessel attached to the condenser. This receiver vessel also receives approximately 946 liters per hour of aqueous wash effluent recovered from the raffinate washing zone and containing raffinate paraffins dissolved therein which are displaced from the aqueous stream by virtue of the benzene dissolved in the aqueous phase of the ovehead stripper condensate. The liquid charged into the overhead vapor condensate receiver separates into two phases, the upper layer comprising a mixture of benzene (about 85 percent by volume) and paraffinic hydrocarbons, including the light paraffins present in the rich solvent and derived from the recycle reflux stream and heavy paraffins displaced from the aqueous raffinate wash effluent. The lower layer in the condensate receiver is predominantly water which contains a small amount of dissolved diethylene glycol solvent vaporized from the rich solvent in the stripper overhead, together with a small quantity of dissolved benzene. The upper layer is withdrawn and charged at the aforementioned rate of 3342 hectoliters per day into the bottom of the extraction column as recycle reflux. The lower aqueous layer of the overhead condensate, in the amount of 384 hectoliters per day is separately withdrawn therefrom and charged into an aqueous condensate receiver in which the aqueous stream utilized as the source of stripping steam is stored, as hereinafter indicated.

A side-cut fraction is removed from an intermediate plate of the solvent stripping column at atmospheric pressure, liquified in a water-cooled condenser and collected in a side-cut receiver. A lower aqueous layer containing diethylene glycol, distilled together with the water from the rich solvent and containing a small amount of dissolved extract, is withdrawn from the receiver in the amount of 1945 liters per hour and charged into the water receiver vessel which accumulates for storage the water washings and aqueous phases separated in the process. The combined aqueous mixture, containing approximately 2.3 percent by weight of diethyleneglycol, is charged at a rate of 7760 liters per hour into a heat exchanger which transforms a major portion of the water in the aqueous mixture to steam at 1.36 atmospheres, the remainder of the aqueous mixture and steam being thereafter charged into the reboiling section of the solvent stripping zone. The steam thereby generated rises through the rich solvent in the stripping column, removing the hydrocarbon extract from the rich solvent by virtue of the resulting steam distillation.

The aromatic extract (upper layer, 1382 hectoliters per day), accumulating in the side-cut receiver vessel, after being washed

with water at the rate of 870 liters per hour was fractionally distilled. A benzene overhead boiling from 80.0 to 80.1° C., consisting of 99.99 percent benzene, is condensed and separately collected. A toluene fraction separated from the residue in a separate distillation column and consisting of 99.1 percent toluene is also separately collected. The residue of the latter distillation comprising xylene and ethylbenzene contains less than 1.5 percent by weight of impurities. The recovery of aromatic product is 98.6 percent of the aromatics initially present in the hydrocarbon feed stock charged to the process.

The aqueous layer drained as the bottom layer of the side-cut receiver vessel contains 2.65 percent by weight of diethylene glycol solvent distilled with the hydrocarbons and water in the side-cut vapor fraction. This aqueous condensate is charged into a secondary distillation column containing about 5 plates and heated in the lower portion thereof with a reboiler for distillation of the water from the aqueous mixture. The overhead, when separately condensed and collected is utilized as a source of water for washing the extract and raffinate streams, as aforesaid. The condensed overhead is substantially pure water containing only slight traces of diethylene glycol solvent.

In the following run B the aforementioned solvent extraction process is operated at the same solvent to feed stock charging rate, in the same equipment and in general the same procedure is utilized to effect the recovery of the desired aromatic extract, except that the side-cut vapors withdrawn from the stripping column are charged directly into a water rectifying column containing "FRI DUALFLOW" trays and having about 3 theoretical plates. In most cases no additional heat is required by the secondary distillation column to rectify the stripper side-cut vapors charged into the column. An overhead vapor is withdrawn from the top of the column and passed into a water-cooled condenser from which the condensate is collected and stored in a receiver vessel. An upper hydrocarbon layer consisting of light aromatics is refluxed to the top plate of the side-cut rectifier. The lower aqueous layer in the receiver, consisting essentially of water containing only traces of diethylene glycol solvent, is withdrawn from the receiver vessel as lower layer at the rate of 6975 liters per hour and charged in part into the top of the raffinate and extract water wash columns for use therein as the source of water for the removal of glycol from these hydrocarbons. 946 liters per hour of the rectifier overhead condensate are charged into the top of the raffinate washing column and 870 liters per hour are charged into the top of the extract water washing column. The raffinate removed from the top of the raffinate wash column contains about 2 ppm. (= parts per million) of glycol and the extract removed from the top of the extract water wash column contains less than 1 ppm. of ethylene glycol solvent. The aqueous washing recovered from the raffinate water wash column is mixed with the overhead distillate from the stripper, the aqueous phase separated from the resultant mixture is directed into the water receiver vessel which also receives the aqueous effluent of the extract water wash column and the remainder of the side-cut rectifier distillate, the entire mixture being thereafter charged into a heat exchanger which generates steam for introduction into the stripping zone of the rich solvent stripping column.

Utilizing the latter method of rectifying the side-cut vapors from the stripping stage of the process (that is, run B) the total heat required to operate the process is reduced by 28 percent and the quantity of cooling water for operating the condensers is likewise reduced by 28 percent.

WHAT WE CLAIM IS:—

1. A solvent extraction process wherein a hydrocarbon mixture containing aromatic and non-aromatic hydrocarbons is contacted in an extraction zone with a solvent composition which selectively dissolves the aromatic component of said mixture and which contains water and an organic solvent boiling above said aromatic component, resulting raffinate and an extract phase containing dissolved aromatic component are separately removed from said extraction zone, said extract phase is thereafter subjected to a distillation in a distilling zone, and an overhead distillate vapor stream containing only a portion of the extracted aromatic component and a vaporous side-cut stream containing steam and aromatic hydrocarbon vapor are separately removed from said distilling zone, characterized in that said vaporous side-cut stream is supplied from said distilling zone directly to a separate rectifying zone and therein is separated by fractionation into an aromatic extract fraction and an aqueous distillate substantially free from solvent, and said extract fraction and said raffinate are washed with said aqueous distillate.

2. Process as claimed in Claim 1, characterized in that a stream of the aqueous distillate is supplied from the rectifying zone to the zone for washing the extract fraction and the resultant aqueous phase is separated from the washed extract fraction and is then supplied to the zone for washing the raffinate.

3. Process as claimed in Claim 1, characterized in that separate portions of the

with water at the rate of 870 liters per hour was fractionally distilled. A benzene overhead boiling from 80.0 to 80.1° C., consisting of 99.99 percent benzene, is condensed and separately collected. A toluene fraction separated from the residue in a separate distillation column and consisting of 99.1 percent toluene is also separately collected. The residue of the latter distillation comprising xylene and ethylbenzene contains less than 1.5 percent by weight of impurities. The recovery of aromatic product is 98.6 percent of the aromatics initially present in the hydrocarbon feed stock charged to the process.

The aqueous layer drained as the bottom layer of the side-cut receiver vessel contains 2.65 percent by weight of diethylene glycol solvent distilled with the hydrocarbons and water in the side-cut vapor fraction. This aqueous condensate is charged into a secondary distillation column containing about 5 plates and heated in the lower portion thereof with a reboiler for distillation of the water from the aqueous mixture. The overhead, when separately condensed and collected is utilized as a source of water for washing the extract and raffinate streams, as aforesaid. The condensed overhead is substantially pure water containing only slight traces of diethylene glycol solvent.

In the following run B the aforementioned solvent extraction process is operated at the same solvent to feed stock charging rate, in the same equipment and in general the same procedure is utilized to effect the recovery of the desired aromatic extract, except that the side-cut vapors withdrawn from the stripping column are charged directly into a water rectifying column containing "FRI DUALFLOW" trays and having about 3 theoretical plates. In most cases no additional heat is required by the secondary distillation column to rectify the stripper side-cut vapors charged into the column. An overhead vapor is withdrawn from the top of the column and passed into a water-cooled condenser from which the condensate is collected and stored in a receiver vessel. An upper hydrocarbon layer consisting of light aromatics is refluxed to the top plate of the side-cut rectifier. The lower aqueous layer in the receiver, consisting essentially of water containing only traces of diethylene glycol solvent, is withdrawn from the receiver vessel as lower layer at the rate of 6975 liters per hour and charged in part into the top of the raffinate and extract water wash columns for use therein as the source of water for the removal of glycol from these hydrocarbons. 946 liters per hour of the rectifier overhead condensate are charged into the top of the raffinate washing column and 870 liters per hour are charged into the top of the extract water washing column. The raffinate removed from the top of the raffinate wash column contains about 2 ppm. (= parts per million) of glycol and the extract removed from the top of the extract water wash column contains less than 1 ppm. of ethylene glycol solvent. The aqueous washing recovered from the raffinate water wash column is mixed with the overhead distillate from the stripper, the aqueous phase separated from the resultant mixture is directed into the water receiver vessel which also receives the aqueous effluent of the extract water wash column and the remainder of the side-cut rectifier distillate, the entire mixture being thereafter charged into a heat exchanger which generates steam for introduction into the stripping zone of the rich solvent stripping column.

Utilizing the latter method of rectifying the side-cut vapors from the stripping stage of the process (that is, run B) the total heat required to operate the process is reduced by 28 percent and the quantity of cooling water for operating the condensers is likewise reduced by 28 percent.

WHAT WE CLAIM IS:—

1. A solvent extraction process wherein a hydrocarbon mixture containing aromatic and non-aromatic hydrocarbons is contacted in an extraction zone with a solvent composition which selectively dissolves the aromatic component of said mixture and which contains water and an organic solvent boiling above said aromatic component, resulting raffinate and an extract phase containing dissolved aromatic component are separately removed from said extraction zone, said extract phase is thereafter subjected to a distillation in a distilling zone, and an overhead distillate vapor stream containing only a portion of the extracted aromatic component and a vaporous side-cut stream containing steam and aromatic hydrocarbon vapor are separately removed from said distilling zone, characterized in that said vaporous side-cut stream is supplied from said distilling zone directly to a separate rectifying zone and therein is separated by fractionation into an aromatic extract fraction and an aqueous distillate substantially free from solvent, and said extract fraction and said raffinate are washed with said aqueous distillate.

2. Process as claimed in Claim 1, characterized in that a stream of the aqueous distillate is supplied from the rectifying zone to the zone for washing the extract fraction and the resultant aqueous phase is separated from the washed extract fraction and is then supplied to the zone for washing the raffinate.

3. Process as claimed in Claim 1, characterized in that separate portions of the

aqueous distillate are supplied from the rectifying zone individually to the zone for washing the extract fraction and to the zone for washing the raffinate.

4. Process as claimed in Claim 2, characterized in that an aqueous phase is separated from the washed raffinate and is then mixed with the overhead distillate obtained from the extract phase distilling zone, the resultant mixture is separated into a hydrocarbon phase and an aqueous phase substantially free from raffinate components, and the last-mentioned aqueous phase is introduced into the reboiling section of said distilling zone.

5. Process as claimed in Claim 3, characterized in that the reboiling section of the extract phase distilling zone is supplied with an aqueous stream which is formed by commingling the aqueous phase which is separated from the washed raffinate with the overhead distillate of the extract phase distilling zone, separating the commingled materials into a hydrocarbon phase and an aqueous phase which is substantially free from raffinate components, and mixing the last-mentioned aqueous phase with the aqueous phase which is separated from the washed extract fraction.

6. Process as claimed in Claim 4 or 5 characterized in that a distillation residue free from raffinate components and having the same composition as the solvent composition introduced into contact with the hydrocarbon charge mixture in the extraction zone is formed in the distilling zone simultaneously with the formation of a vaporous side-cut stream free from raffinate components by returning the hydrocarbon phase, which has been separated from the mixture of aqueous phase from the raffinate washing step and of overhead distillate from the extract phase distilling zone, to the extraction zone at a point in proximity of the point of discharge of the extract phase therefrom and by introducing the aqueous phase recovered from the washing of the extract fraction and raffinate and from the overhead distillate of said distilling zone together with any remaining portion of the aqueous distillate recovered from the rectifying zone into the reboiling section of said distilling zone.

7. The solvent extraction process for the separation of aromatic hydrocarbon from its admixture with non-aromatic hydrocarbons substantially as described with reference to the accompanying drawing.

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