This invention relates to improvements in the process for producing motor fuels of high octane number involving a combination of catalytic reforming and solvent extraction wherein the highly knock-resistant aromatic components of the reformate product are extracted from unconverted non-aromatic hydrocarbons and the latter recycled to the reforming stage of the process, said improvements relating to the removal of undesirable hydrocarbons retained by the solvent prior to recycling the non-aromatic raffinate to the reforming zone. More specifically, this invention concerns the removal of polycyclic aromatic hydrocarbons from the lean solvent stream, following the extract stripping stage of the process, by a method which involves countercurrently washing the lean solvent with a non-aromatic hydrocarbon stream under liquid-liquid contacting conditions.

It is widely recognized that certain aromatic hydrocarbons, particularly aromatic hydrocarbon fractions (that is, monocyclic aromatic and alkyl aromatic hydrocarbons) are highly resistant to knocking when utilized as a component of a gasoline boiling range motor fuel for use in high compression engines. Benzene-type hydrocarbons, therefore, are desirable constituents of motor fuel blends in that they increase the octane number of paraffinic and naphthenic hydrocarbons with which they may be mixed in a typical petroleum-derived motor fuel. Processes have been developed for converting paraffinic gasolines boiling range fractions of petroleum, including fractions containing a large proportion of normal paraffins and/or naphthenes into hydrocarbon mixtures in which the proportion of aromatic constituents of the benzene series is increased, thereby increasing the octane number of the motor fuel fraction. These processes are generally referred to as "reforming" processes, one of the preferred methods of this type being the so-called catalytic reforming process whereby the gasoline boiling range feedstock, together with hydrogen, is passed over a reforming catalyst, as hereinafter described. In such reforming processes, the paraffinic and naphthenic components present in the feedstock undergo isomerization, hydrocracking, dehydrogenation and aromatization reactions, forming a relatively large yield of aromatic hydrocarbons of approximately the same average number of carbon atoms as the feedstock components. In order to isolate and recover the aromatic components of high knock-resistant value (that is the monocyclic aromatic hydrocarbons) from the resulting reformate, the latter is contacted at solvent extraction conditions with a solvent which is particularly selective for the aromatic constituents of the reformate product and thereafter stripping from the resulting rich solvent stream formed in the solvent extraction stage the desired aromatic extract utilizable as such for a motor fuel of high octane number or utilized as a blending stock for motor fuels of lower octane number to thereby upgrade the latter. The non-extracted portion of the reformate effluent, generally referred to as the hydrocarbon raffinate of the extraction process, contains paraffinic and naphthenic components subject to further conversion into aromatic hydrocarbons by the combined isomerization, dehydrogenation and cyclization reactions which occur during the reforming process and for this purpose the raffinate effluent from the solvent extraction column is preferably recycled to the reforming stage for further conversion into aromatic extract. It has been noted, however, that the lean solvent recovered from the extract stripping operation (being the solvent residue after removal of the aromatic extract therefrom) generally contains a small proportion of bicyclic and even higher polycyclic aromatic hydrocarbons which are not stripped from the rich solvent under the conditions generally employed for stripping the desired monocyclic extract from the rich solvent stream because of their greater solubility in the solvent and their substantially greater boiling point which is further increased by the presence of the solvent. As a consequence of such retention by the lean solvent, the polycyclic aromatic hydrocarbons remain dissolved in the lean solvent and enter the top of the solvent extraction zone when the lean solvent is recycled to the extraction zone for reuse therein. It has been found, however, that although these polycyclic aromatic hydrocarbons are not readily removed from the solvent stream in the stripping zone by vaporization therefrom, they are at least partially removed from the lean solvent in the top of the extraction zone by current contact of the lean solvent with the raffinate, as the latter contacts the incoming lean solvent stream, the raffinate thus freed of the polycyclic aromatics originally contained in the lean solvent being thereby recycled to the reforming stage of the process for further conversion into aromatics. The polycyclic aromatic hydrocarbons in the raffinate when the latter stream is recycled to the reforming zone constitute undesirable constituents of a suitable reforming zone feedstock inasmuch as they tend to undergo decomposition under the conditions maintained in the reforming zone, depositing catalyst deactivating residues such as coke and resins on the surface of the reforming catalyst particles. Any polycyclic aromatic components of the recycle raffinate which are sufficiently refractory to resist decomposition and deposition on the reforming catalyst, re-enter the solvent extraction zone and thus are continuously recycled in the process until they overload the solvent and necessitate special treatment of the solvent to remove at least a portion thereof from the recycle. By means of the present process, the lean solvent removed from the solvent stripping column and containing the polycyclic aromatic solute is washed with a liquid paraffinic hydrocarbon which extracts these polycyclic aromatics from the lean solvent and thereby permanently removes these polycyclic aromatics from the lean solvent prior to recycling the latter to the solvent extraction zone. Substantial advantages are thereby realized in that the life of the catalyst in the reforming stage of the process and the efficiency of the reforming reaction are both considerably enhanced and the necessity for separate treatment of the solvent to prevent build-up of polycyclic aromatic solute therein is also obviated.

In one of its embodiments the present invention relates to an improvement in the process for producing an aromatic concentrate by the method which comprises catalytically reforming a gasoline boiling range fraction at reforming conditions whereby at least a portion of said fraction is converted into monocyclic aromatic hydrocarbons, and the resulting reformate product is thereafter contacted with a solvent which selectively extracts the aromatic components therefrom to form a rich solvent containing said aromatic components in solution, said rich solvent is separated from a raffinate comprising non-aromatic hydrocarbons in said reformate, said rich solvent is stripped to recover said aromatic extract from a lean
solvent residue and said raffinate is recycled to said reforming step while said lean solvent is recycled to said contacting step, said improvement comprising washing said lean solvent prior to its recycle to said contacting step with a liquid, non- aromatic wash hydrocarbon of sufficient quantity to remove polycyclic aromatic hydrocarbons from said lean solvent and collecting said effluent comprising excess wash hydrocarbon and said polycyclic hydrocarbon from said lean solvent substantially free of polycyclic aromatics.

Specific embodiments of this invention relate to other aspects of the above process wherein particular boiling range hydrocarbon feed stocks, and specific solvent compositions are employed in the extraction stage of the process and specific sources of wash hydrocarbon are utilized in the lean solvent washing stage of the process.

Typical hydrocarbon mixtures utilisable as feed stocks in the present process include hydrocarbon mixtures derived from any source in which a substantial proportion (preferably, at least 20% by volume) of the hydrocarbon components have at least 6 carbon atoms per molecule and are hydrocarbons of the type which form monocyclic aromatic hydrocarbons by one or more of a combination of reactions, involving hydrogenation, dehydrogenation and aromatization. Thus, for example, suitable feed stocks include straight-run petroleum fractions, catalytically and thermally cracked petroleum products, particularly fractions thereof boiling in the gasoline boiling range, hydrogenated alcohols, products of Fischer-Tropsch synthesis, and hydrocarbon fractions from other sources, the components of which yield aromatic hydrocarbons by means of the present reforming stage of the process. Particularly suitable feed stocks contain an appreciable percentage of cyclopentane and cyclohexane derivatives which may be converted into benzene derivatives by dehydrogenation reactions such as methylecyclopentane, dimethylecyclopentane, cyclohexane, methylcyclohexane, dimethylcyclohexane, etc., as well as isoparaffins which undergo dehydrocracking-dehydrogenation reactions to form benzene and its derivatives, such as 2,2-dimethylbutane, 2-methylhexane, 2,2-dimethylhexane and other homologs and analogs.

The solvent utilisable in the extraction stage of the process is a normally liquid organic compound which preferentially dissolves aromatic hydrocarbons from hydrocarbon mixtures containing the same in admixture with aliphatic and naphthenic hydrocarbons. The solvent may be a single component organic liquid, or a mixture of normally liquid organic compounds, one component of which has a high solubility for aromatic hydrocarbons (termed the primary component) and a secondary component which increases the selectivity of the solvent for the aromatic components (termed the secondary solvent). Suitable organic compounds utilisable as the primary component of the solvent composition are preferably selected from the general group broadly characterized as oxygen-containing organic components and from certain nitriles and amines. Particularly suitable members of this group are the aliphatic and cycloalcohols, the glycols, glycol ethers (also referred to as the polyalkylene glycols), the glycol esters and the glycer ether esters. Alkylene glycols and polyalkylene glycols which are selective solvents particularly preferred herein are ethylene and propylene glycols, the di-, tri-, and tetra-ethyl ethers, particularly diethylene and triethylene glycols and the di- and tri-propylene glycols. The above mono- and poly-glycols which have their terminal hydroxyl groups etherified with short chain alkyl groups comprise another class of compounds useful as solvents, including the methyl-, ethyl-, propyl-, and butyl-Cello-solve ethers, the corresponding monomethyl-, ethyl-, and propyl-ethers of diethylene glycols, referred to as the corresponding alkyl Carbitols. The mono- and poly-alkylene glycol esters of short chain aliphatic acids, such as the acetates and propionates, also constitute a desirable class of solvents. Still other types of compounds useful as solvents are the aliphatic alcohols, such as methanol, ethanol, propanol, and homologs thereof, up to and including octanol; various phenols, such as phenol, resorcinol, pyrocatechol, the ortho-, meta-, and para- cresols, thymol; certain ketones, such as acetone, methyl ethyl ketone; certain esters, such as acetaldehyde, propionaldehyde, butyraldehyde, furfural, etc.; the amines and alkanol amines, such as ethanol amine, diethanol amine, triethanol amine, phenylethanol amine, propanol amine, butanol amine, pentanol amine, phenylenediamine, N,N'-dimethyl phenylenediamine, etc.; the nitriles, such as acetonitrile, succinonitrile, adiponitrile, beta,beta'-oxy-dipropionitrile, alpha,alpha'-oxy-di propionitrile, gamma,gamma'-oxy-dipropionitrile, benzonitrile, styryl nitrile etc. and other classes of organic compounds as well as other individual specific organic compounds.

The above solvents are particularly satisfactory for the separation of hydrocarbon mixtures to recover a substantially pure extract when the compounds are mixed with an anti-solvent, selected from certain polar materials which increase the selectivity of the solvent composition towards the desired component. Particularly suitable anti-solvents for use in combination with a water-soluble organic primary solvent, such as the above, preferred polyalkylene glycols, is water, which may be present in the solvent composition in amounts of from about 0.5 to about 20%, and preferably from about 2% to about 15% by weight. An advantageous anti-solvent composition. One of the most suitable highly polar anti-solvents which enhance the selectivity of the solvent composition for the extract are such materials as methanol, certain dicarboxylic acids, such as oxalic and malonic acids and other highly polar compounds.

The liquid hydrocarbon herein referred to as a "wash liquid" is mixed with the stock to be extracted under pressure in a conventional manner to constitute a raffinate-type component in the usual hydrocarbon feed stock mixture and is preferably a paraffinic or mixture of paraffinic hydrocarbons of relatively straight chain structure, such as a normal paraffin of only slight solubility in the solvent. It is also a hydrocarbon which differs in boiling point from the polycyclic aromatic hydrocarbon to be removed from the lean solvent stream by at least 10° C. and preferably by at least 40-50° C., boiling either above or below the boiling point of the polycyclic aromatic hydrocarbon present in the lean solvent. A particularly preferred liquid wash hydrocarbon is the volatile, paraffinic fraction separated from the feed stock as an overhead distillate, boiling substantially below the initial boiling point of the extractor feed, normally comprising Cs and C6 normal and isoparaffins. However, a paraffinic fraction boiling above the boiling point of the polycyclic aromatic contained in the lean solvent may also be utilized, such as a kerosine boiling range fraction having a boiling range above about 325° F., up to about 500° F., preferably above about 415° F.

Other embodiments of this invention will be further described with reference to the accompanying diagram which illustrates a particular process flow in combination with a simple arrangement of apparatus for the separation and recovery of a mixture of benzene, toluene, xylens and ethylbenzene, as well as higher monocyclic aromatic hydrocarbons, which mixture is useful as a blending agent for the production of a typical high octane gasoline blend.

Referring to the accompanying diagram a crude, straight-run petroleum fraction, constituting one of the preferred sources of the initial charge stock in the present process, is charged into the process flow through line 1 and valve 2, being charged into a suitable feed preparation zone 3, such as a fractional distillation column, containing a reboiler 4 for heating the feed stock to its distillation temperature. A light fraction comprising the most volatile components present in the feed stock, and preferably having a sufficiently broad boiling range to in-
clude C₅ normal and isoparaffins, is taken overhead from column 3 through line 7 and diverted by means of pump 6 into subsequent stages of the process for use as a liquid wash hydrocarbon for the purpose hereinafter described. An intermediate fraction boiling within the gasoline range, and containing the components which may be catalytically reformed into aromatic hydrocarbons by means of the reforming catalyst in the present process and having, for example, an end boiling point up to about 425°F. is separated as a side cut from said feed preparation column 3 through line 7 and diverted into the reforming stage of the process, as hereinafter described. A liquid bottoms residue, comprising components of the aromatic components from the charge stock point of the gasoline fraction is removed from the bottom of column 3 through line 8 in amounts controlled by valve 9 and discharged from the process flow.

The gasoline boiling range fraction of the crude feed stock, separated as an intermediate cut in column 3, removed therefrom through line 7 and valve 8 is transferred into catalytic reforming zone 9 by means of pump 10, being increased to the proper temperature and pressure conditions for the reforming conversion by means of said pump 10 which transfers the fraction at the desired pressure through line 11 into heater 12 and thereafter through reforming reactor 9. In the preferred method of effecting catalytic reforming reactions, the conversion is accomplished in the presence of hydrogen, generally in the presence of sufficient hydrogen to provide a molar ratio of hydrogen to hydrocarbons of from about 0.5 to 1 to about 20 to 1, and preferably from about 2 to 1 to about 10 to 1. Hydrogen for this purpose is introduced into the process flow through line 14 in the required amount determined by valve 15, the hydrogen mixing with the gasoline fraction in line 11 by connecting line 14 therewith.

Depending upon the specific reforming catalyst employed in zone 9, the desired conversion of paraffinic and naphthenic hydrocarbons into aromatic derivatives is obtained at generally superatmospheric pressures and at temperatures in the range of from about 500°F. to about 1200°F. and preferably at from about 500°F. to about 800°F. Suitable pressures may be within the range of from slightly superatmospheric to 100 atmospheres or more, preferably from about 10 to about 50 atmospheres. One of the preferred reforming catalysts known to the petroleum refining art is a catalyst comprising a composite of metal selected from the group consisting of platinum, palladium and iridium, preferably platinum, and a halogen selected from fluorine and chlorine combined with an alumina support, the latter catalyst being generally known in the refining art as a "plating" catalyst. Particularly active catalysts of this type contain from 0.001 to about 1.0% by weight of platinum and from 0.01 to about 3% by weight of combined halogen. By virtue of the reforming conditions maintained in catalytic reforming zone 9, a substantial proportion of the aliphatic and cyclic paraffins contained in the intermediate or gasoline boiling range feed stock is converted into aromatic hydrocarbons, the remaining components being of saturated paraffinic character. The effluent product of the reforming reaction may be separated into a normally gaseous fraction and a normally liquid material and the normally liquid material may be further fractionated into a select cut containing monocyclic aromatic hydrocarbons, the remaining components being of saturated paraffinic character. The products of the reforming conversion are removed from reforming zone 9 through line 16 and the normally liquid portion thereof discharged in liquid phase into solvent extraction zone 17 wherein the hydrogen feed stock is contacted with a solvent which selectively dissolves the aromatic components from the charge stock under liquid-liquid, preferably countercurrent, solvent extraction conditions. Since the solvent is generally the phase of greatest density in the extraction zone, it is preferably introduced into the top of the extraction column when a countercurrent extraction system is desired. Solvent for this purpose, such as an aqueous diethylene glycol solution, is initially introduced into the process flow and make-up portions of the solvent are charged into the process through line 18 in amounts controlled by valve 19 at a pressure suitable for effecting the solvent extraction stage of the process, the solvent being conveyed through line 19 and heater 20 which raises the temperature of the solvent to the desired extraction temperature. The solvent stream at the latter temperature and pressure of the solvent charge is introduced at a lower level in column 17, preferably at a point substantially in the mid-section of the column rises countercurrently to the dense solvent stream introduced into the top of the column, the solvent preferentially dissolving the aromatic hydrocarbon components of the feed stock contacted therewith. At the point of entry of the solvent into the extraction zone, the hydrogen solvent stream is substantially free of aromatic constituents, being removed as a raffinate stream from the column through line 24 in amounts controlled by valve 25. This stream contains a large proportion of paraffinic hydrocarbons which may be converted in the reforming zone into aromatic hydrocarbons of high octane number, and thus they constitute a suitable recycle stream to the reforming reaction zone. For this purpose, the raffinate stream removed from extraction zone 17 through line 22 may be returned to reforming zone 7 and mixed therein with fresh hydrogen feed comprising the intermediate gasoline boiling range fraction separated in column 3, aforesaid.

The raffinate stream removed from extraction zone 17 through line 22 may also contain hydrogen, if the latter is not separated from the raffinate effluent prior to discharge of the raffinate feed stock into extraction column 17. By thus recycling the raffinate directly into the hydrogen feed line, the hydrogen constituent present in the raffinate is also recovered for recycling purposes.

The rich solvent stream flowing downwardly through extraction zone 17 contains substantially all of the aromatic components present in the gasoline boiling range feed stock charged into column 17, but also contains a minor amount of feed stock raffinate constituents because of the lack of complete selectivity of the solvents for aromatic hydrocarbons. These raffinate hydrocarbons, usually of paraffinic nature, are advantageously separately recovered and converted into additional yield of aromatic hydrocarbons of high octane rating. For the purpose of displacing these raffinate components from the rich solvent stream into the raffinate effluent from column 17 the rich solvent is contacted, preferably under countercurrent flow conditions, with a suitable wash hydrocarbon stream comprising components preferentially soluble in the rich solvent. A material particularly suitable for this purpose (that is, for displacing feed stock raffinate components dissolved in the rich solvent) is a light paraffinic fraction (that is, a fraction made up of low molecular weight paraffins) which dissolve more readily in the
solvent than the feed stock raffinate paraffins or a portion of the aromatic extract recovered from the rich solvent stream in the subsequent stripping stage of the process, the portion thus recovered being herein referred to as a "recycle reflux stream." The latter is introduced preferably into the lowermost portion of the column to provide mixing with the current component of the rich solvent stream. In the present process, the recycle reflux is charged in controlled amounts into the bottom of solvent extraction zone 17 through line 24, being derived from the upper portion of the stripping column, as hereinafter described. The aromatic and light paraffin components present in the recycle reflux contact the rich solvent in the lower portion of the extraction zone, displacing therefrom the feed stock paraffins which combine with the raffinate removed from the top of the column.

The resulting washed rich solvent containing light paraffins and/or aromatics in place of the displaced raffinate paraffins is withdrawn from the bottom of column 17 through line 25, valve 26 and transferred by means of pump 27 into line 28 which discharges the rich solvent into solvent stripping zone 29. Zone 29 is generally operated at a lower pressure than that maintained in extraction zone 17, such that a major proportion of the dissolved hydrocarbons contained in the rich solvent vaporize therefrom by merely reducing the ambient pressure on the rich solvent streams; that is, at substantially isothermal conditions. The remaining monocyclic aromatic solute is stripped from the rich solvent by means of heat introduced into the solvent residue in the lower portion of zone 29 through reboiler 30. The light paraffins and a substantial proportion of the most volatile aromatic constituent of the rich solvent stream (generally benzene) are flashed overhead from stripping zone 29 through line 31, valve 32 and constitutes the portion of extract returned to the bottom of extractor 17 as recycle reflux for displacing feed stock paraffins from the rich solvent stream. For this purpose, the light vapor overhead is pumped from line 31 into recycle charge line 24 by means of pump 33 which increases the pressure on the recycle stream to the pressure maintained in extraction zone 17.

A higher boiling extract product is vaporized from the rich solvent as a side cut from stripping zone 29, being removed therefrom through line 34 and valve 35 into side condenser 36 wherein the predominantly aromatic extract vapors are liquefied and the liquid condensate drained to receiver line 37 into upper liquid layer therein. When utilizing a solvent composition in the process which contains water, such as the aforementioned aqueous diethylene glycol solution, at least a small portion of the water as well as a small portion of the solvent distills with the aromatic extract into receiver vessel 38 and collects as a lower liquid layer therein. This portion of condensate may be drained from the receiver for recycle purposes through line 39 and valve 40. For example, this aqueous stream may be charged into stripping zone 29 (preferably into the reboiling section) to provide a source of stripping steam in zone 29, not illustrated, however, in the accompanying diagram. The liquefied, monocyclic aromatic hydrocarbon extract collects as an upper liquid layer in receiver vessel 38 and may be drained from the vessel through line 41 and valve 42 into storage or transferred into suitable blending equipment for mixing with a gasoline fraction as a high octane blending stock.

As heretofore indicated, the rich solvent stream even after substantially complete removal of the monocyclic extract product therefrom by distillation in stripping zone 29 still contains a small proportion of dissolved polycyclic aromatics (mostly naphthalenes) which are not removed from the lean solvent by the aforementioned stripping, even at the relatively high temperatures to which the lean solvent is heated in the reboiling section of stripping zone 29. Hence, under the usual method of operating a combined solvent extraction-solvent stripping process, these polycyclic aromatic hydrocarbons remain dissolved in the stripped solvent and are necessarily recycled in the lean solvent stream to the top of the extraction column. As previously indicated, however, the polycyclic aromatic solute is removed with ease from the lean solvent when it is contacted in the upper section of solvent extraction zone 17 with the raffinate stream, the raffinate washing the polycycles from the lean solvent and carrying them in solution with the paraffinic constituents of the raffinate into the reforming zone. The presence of the polycyclic aromatics in the lean solvent may result in rapid deactivation of the reforming catalyst and if not removed from the hydrocarbon stream in the reforming zone (for example, by conversion to coke or resins which form a deactivating deposit on the reforming catalyst), the polycycles are again extracted in the solvent extraction zone, gradually building up in total quantity and over-burdening the solvent with a constantly increasing load of polycyclic aromatic solute. In accordance with the process of this invention the lean solvent stream removed from the bottom of stripping zone 29 and containing dissolved polycyclic aromatics is withdrawn therefrom through line 43, valve 44 and transferred by means of pump 45 through line 46 into the top of a lean solvent washing zone, designated on the accompanying diagram as column 47 and countercurrently contacted therein with a liquid, non-aromatic hydrocarbon wash stream which selectively removes the polycyclic aromatic solute from the lean solvent. As heretofore indicated, the wash hydrocarbon may comprise the light fore ends of the crude feed stock (C₅-C₇ paraffins) fractionally distilled in feed preparation zone 3, being recovered as an overhead from the latter column and transferred by means of pump 6 into wash hydrocarbon feed line 48 which introduces the light paraffins at sufficient pressure to maintain the same in liquid phase into the lower portion of lean solvent wash zone 47 in controlled amounts determined by valve 49. A portion or substantially all of the wash hydrocarbon may be derived from recycle sources, as hereinafter described, and/or further supplemented from external sources, for example, from extraneous sources through line 54 and valve 55. In order to operate the present combined process on an economical basis the solvent stream is desirably maintained at least at a constant temperature throughout the entire system in order to avoid substantial heating costs occasioned by changing the temperature of the solvent stream. The wash hydrocarbon therefore, is desirably charged into contact with the lean solvent in zone 47 at substantially the temperature of the solvent withdrawn from the solvent stripping zone 29 and at sufficient pressure to maintain the wash hydrocarbon in substantially liquid phase. The liquefied wash hydrocarbon rising countercurrently through the lean solvent descending downwardly through wash zone 47, removes the polycyclic aromatic hydrocarbon solute from the solvent the resulting stream of combined polycyclic aromatics and excess light paraffinic wash hydrocarbon being withdrawn from the top of zone 47 through line 50 and valve 51 into storage or into a suitable fractionating column for recovery of the wash hydrocarbon from the polycyclic aromatics dissolved therein. The volume ratio of liquid wash hydrocarbon to solvent required to effect the substantially complete removal of the polycyclic solute from the lean solvent is generally greater than 0.1 to 1 and may be as high as 2.0 to 1 depending on the composition of the wash hydrocarbon. The preferred volume ratio of wash hydrocarbon to lean solvent charged into zone 47 is from about 0.5 to 1 to about 2 to 1 volumes per volume. The washed lean solvent, substantially free of polycyclic aromatic solute, containing dissolved wash hydrocarbon solute is desir-
ably flashed before the washed lean solvent is recycled back to the extraction zone 17 for reuse of the solvent composition therein. Removal of the latter contains wash the aromatic-containing feed stock in solvent extraction zone 17. To accomplish such distillation the flashed wash lean solvent is removed from the bottom of column 47 and charged into distillation zone 56 containing reboiling coil 57 which introduces sufficient heat into the lean solvent to vaporize a substantial proportion of the paraffinic wash hydrocarbon solute therefrom. Alternatively, ambient pressure on the lean solvent charged into zone 56 may be reduced in order to flash the hydrocarbons therefrom adiabatically. The wash hydrocarbons thus flashed from the lean solvent are taken overhead from condenser 58, condensing in heat exchanger 59 and the resulting liquefied wash hydrocarbons transferred from condenser 59 through line 60 by means of pump 61 into line 62 connecting with line 48 for recycle of the liquid wash hydrocarbon into the bottom of the column 47. Lean solvent substantially free of wash hydrocarbon and containing only a small quantity of hydrocarbon solute from the lean solvent stream is not necessarily an essential step in the process.

The process of this invention is further described in the following illustrative example, which, however, is not intended to limit the scope of the invention necessarily in accordance therewith.

Example 1

In the following run an aromatic extract product useful for blending purposes for producing high octane motor fuel is prepared in accordance with the process of this invention, as follows. Mid-Continent petroleum crude is separated into three specific cuts by fractional distillation, (1) an overhead light paraffinic cut containing C₄-C₇ hydrocarbons having an ending boiling point above about 110° F. is taken from the top tray of the distillation column at the rate of 35 bbls./hr. and diverted, together with an additional quantity of n-pentane from an external source, into a lean solvent wash tower for purposes hereinafter described to remove polyaromatics from the lean solvent feed stream (2). An intermediate cut consisting of an initial boiling point of about 150° F. and an end boiling point of about 420° F. is separated from the feed preparation column at a rate of 108 bbls./hr. and charged, together with 64 bbls./hr. of a recycle fraction recovered as raffinate from the solvent extraction stage of the present catalytic reforming unit, hereinafter more fully described; (3) a bottoms residue from the feed preparation column consisting of components boiling above the gasoline boiling range is removed from the column and discharged from the present process flow. The 172 bbls./hr. of catalytic reforming reactor feed (made up of 108 bbls./hr. of straight-run distillate and 64 bbls./hr. of recycle raffinate) is charged, together with 189 ft³/m³ of hydrogen (approximately 6 moles of hydrogen per mole of hydrocarbon feed) at a temperature of 752° F., at a pressure of 200 p.s.i. and at a rate sufficient to provide a space velocity of 1.0 into a catalytic reforming reactor packed with a platinum supported on a combined alumina-halogen composite, the catalyst being of the type referred to in the petroleum refining art as a "plating-forming" catalyst, which is capable of converting the paraffinic and naphthenic components of the feed stock into aromatic derivatives. The reformate effluent from the catalytic reforming zone is flashed in the condenser 18 and the liquid hydrocarbon fraction recovered as an overhead of 164 bbls./hr., containing 21% by volume of aromatic hydrocarbons consisting predominantly of benzene, toluene and C₈ aromatics, and some unconverted paraffins is charged into the mid-section of a liquid-liquid countercurrent solvent extraction column containing eleven-deck trays for effecting intimate contact between the hydrocarbon feed stock and solvent charged into the top of the column. The solvent, comprising recycled diethylene glycol containing 7.5% by weight of water is charged at a rate of 16,000 bbls./hr. into the top of the extraction column at a temperature of 298° F. and at 100 p.s.i.g. A light paraffinic aromatic hydrocarbon fraction recovered from the overhead of the stripping column, hereinafter described and consisting predominantly of C₈ paraffins and benzene is charged at a rate of 78 bbls./hr. into the bottom of the extraction column at the aforementioned temperature and pressure conditions. A raffinate stream comprising non-extracted paraffins and hydrocarbons is removed from the top of the extraction column at a rate of 64 bbls./hr. and after water-washing and drying, is fed into the platforming reactor in admixture with the straight-run distillate, as aforesaid. A rich solvent stream containing dissolved aromatic hydrocarbons is removed from the bottom of the extraction column at a temperature of 290° F. and at a pressure of 100 p.s.i. and charged into the flashing section of a stepwise pressure reduced stripping column for recovery of the hydrocarbon solute from the rich solvent. The pressure is reduced in this flashing section to 50 p.s.i.g., resulting in the vaporization of the aforementioned 78 bbls./hr. of light vapor overhead containing 88% by volume of benzene. The rich solvent residue from the flashing section is allowed to flow into a secondary flashing section wherein the pressure is reduced to atmospheric pressure and the rich solvent residue is heated in the reboiling section to a temperature of 304° F. Stream is injected into the reboiling section at a rate of 4.5 bbls./hr. (equivalent) of water, the combined distillation effects removing 35 bbls./hr. of aromatic extract consisting of a 99.9% aromatic fraction containing 78% benzene, 14% toluene and the remainder C₈ aromatics. This extract is reserved for blending with gasoline to form a high octane motor fuel.

The lean solvent stream removed from the bottom of the rich solvent stripping zone at a temperature of 304° F. and atmospheric pressure contains approximately 0.016% by weight of polyaromatic aromatics. In accordance with the present process, this stream is fed into the top of a countercurrent, liquid-liquid lean solvent wash column into which a combined stream comprising the light paraffin overhead from the feed preparation column (consisting of 35 bbls./hr. of C₄ and C₅ paraffins) and 2860 bbls./hr. of C₆ hydrocarbon motor fuel part from recycle sources and the remainder from externally supplied n-pentane is fed into the bottom of the column. The overhead from the lean solvent wash column, at a rate of 940 bbls./hr. is fractionated to recover 4.6 bbls./hr. of a mixture of naphthalene, mono- and dimethyl naphthalenes and a small amount of higher naphthalene homologs. The light paraffin overhead from this column is diverted into a gasoline blending tank for mixing with the monocyclic aromatic hydrocarbon extract hereinafter indicated. The washed, lean solvent substantially free of polyaromatic aromatics removed from the bottom of the wash column at a rate of 17,000 bbls./hr. and at 298° F. is passed into a packed distillation column 100 for its further treatment.
11 column operated at atmospheric pressure. Heat is supplied to the column through a reboiler in the bottom of the column. Approximately 1240 bbls./hr. of light hydrocarbon overhead is removed from the top of the column and recycled to the wash hydrocarbon make-up supply, as indicated above. The lean solvent residue from the bottom of the distillation column is pumped at 100 p.s.i. into the top of the solvent extraction column as recycled lean solvent at a rate of 16,000 bbls./hr., as previously described.

Utilizing the indicated combination of catalytically reforming, solvent extraction and lean solvent wash procedure, the catalyst in the reforming zone remains active for long periods of time, having an average life of approximately 530 days. In a similar process, except that the lean solvent stream recovered from the stripping column is recycled directly to the solvent extraction zone without washing with light paraffin fraction, the reforming catalyst life is of substantially shorter duration, averaging about 105 days. In the latter type of operation, furthermore, the quantity of polycyclic aromatics contained in the lean solvent stream gradually increases to a level at which the lean solvent must be regenerated after 56 hours of recirculation in the process, effected by removing 2% by volume of the solvent circulation per hour and redistilling the solvent to recover the diethylene glycol. The polycyclic aromatics thus removed are separated in an impure and unsatisfactory condition.

I claim as my invention:

1. A process for producing an aromatic concentrate which comprises catalytically reforming a gasoline boiling range fraction at reforming conditions whereby at least a portion of said fraction is converted into monocyclic aromatic hydrocarbons contacting the reformate product with a solvent which selectively extracts the aromatic components therefrom to form a rich solvent containing aromatic components in solution, separating said rich solvent from a raffinate comprising non-aromatic hydrocarbons in said reformate, stripping said rich solvent to recover an aromatic extract from a lean solvent residue, recycling said raffinate to said reforming step, washing said lean solvent with a liquid, non-aromatic wash hydrocarbon of sufficient quantity to extract polycyclic aromatic hydrocarbons from said lean solvent, separating wash hydrocarbon effluent comprising excess wash hydrocarbon and said polycyclic hydrocarbon from lean solvent substantially free of polycyclic aromatics, and recycling the thus washed lean solvent to said contacting step.

2. The process of claim 1 further characterized in that said wash hydrocarbon is substantially paraffinic.

3. The process of claim 1 further characterized in that said wash hydrocarbon comprises C₅ paraffinic hydrocarbons.

4. The process of claim 1 further characterized in that said wash hydrocarbon is a paraffinic hydrocarbon fraction boiling at a temperature above the end boiling point of said gasoline boiling range fraction.

5. The process of claim 4 further characterized in that said wash hydrocarbon is a fraction boiling in the kerosene range.

6. The process of claim 1 further characterized in that said wash hydrocarbon is mixed with said lean solvent at substantially the same temperature as said contacting step.

7. The process of claim 7 further characterized in that said wash hydrocarbon comprises C₅ paraffins and said washing step is effected at a pressure sufficient to maintain the wash hydrocarbon in substantially liquid phase.

8. The process of claim 7 further characterized in that the wash hydrocarbon effluent is subjected to distillation to thereby recover wash hydrocarbon solute from washed lean solvent.

9. The process of claim 1 further characterized in that said solvent is a polyethylene glycol.

10. The process of claim 1 further characterized in that the washed lean solvent separately recovered from the wash hydrocarbon effluent is subjected to distillation and recycling the thus washed lean solvent to the solvent extraction step.

11. The process of claim 10 further characterized in that the wash hydrocarbon overhead from said distillation is recycled to said washing step.

12. A process which comprises fractionating a gasoline distillate to separate therefrom a light fraction containing C₅ paraffins and a heavier fraction, catalytically reforming said heavier fraction, subjecting resultant reformed products to solvent extraction with a selective solvent for aromatics, separating the aromatic-rich solvent from paraffinic raffinate and supplying the latter to the forming step, stripping monocyclic aromatics from the solvent, washing the stripped solvent with a sufficient quantity of said light fraction to extract polycyclic aromatic hydrocarbons from the solvent, and recycling the thus washed solvent to the solvent extraction step.

References cited in the file of this patent

UNITED STATES PATENTS

2,241,430 Snow, May 13, 1941
2,415,700 Meier, Feb. 11, 1947
2,697,684 Hemminger et al., Dec. 21, 1954
2,711,433 Poffenberger, June 21, 1955
2,721,164 Fenske, Oct. 18, 1955
2,727,848 Georgian, Dec. 20, 1955
2,745,790 Manley, May 15, 1956

2,938,858