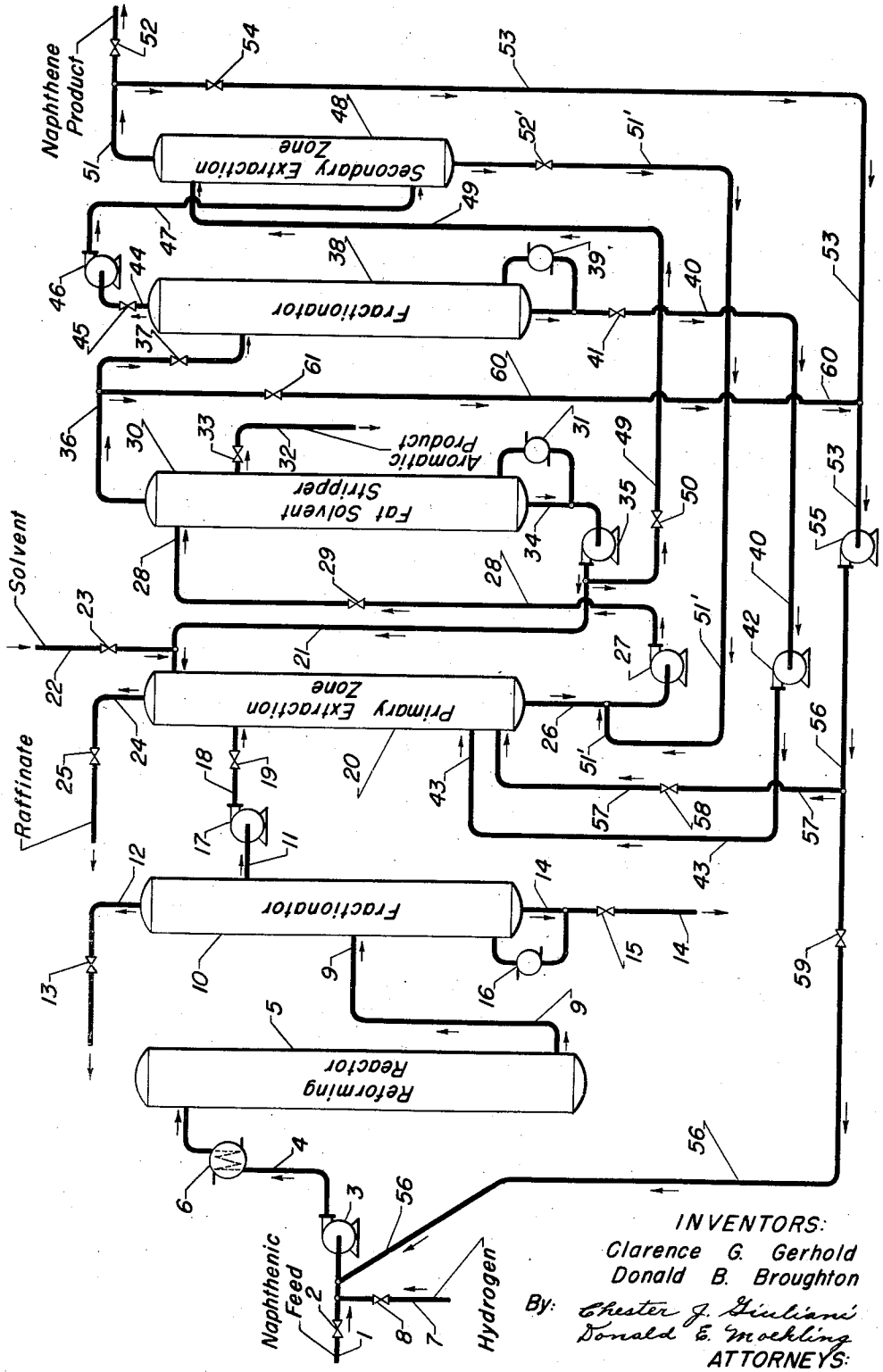
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SEGREGATION AND RECOVERY OF NAPHTHENIC HYDROCARBON CONCENTRATES

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SEGREGATION AND RECOVERY OF NAPHTHENIC HYDROCARBON CONCENTRATES

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This invention relates to a process for segregating naphthenic hydrocarbons from a hydrocarbon charging stock in a solvent extraction process. More specifically, the present invention concerns a two-stage solvent extraction process wherein a select hydrocarbon stream from the primary stage is employed as the charging stock to the secondary extraction stage and a product consisting essentially of the most volatile naphthenic hydrocarbons from the feed stock is recovered from the secondary extraction stage.

It is thus one object of this invention to prepare a naphthenic hydrocarbon concentrate employing a hydrocarbon mixture comprising paraffinic, naphthenic and aromatic hydrocarbons as starting material, effecting such separation by simple and expeditious means. Another object of this invention is to increase the conversion of naphthenic to aromatic hydrocarbons in a reforming process.

In one of its embodiments the present invention relates to a process for separating in a countercurrent solvent extraction zone a mixture of hydrocarbons comprising paraffinic, naphthenic, and aromatic components employing a solvent more dense than said mixture and in which the naphthenic and aromatic components are at least partially soluble, removing from the lower portion of said zone a primary fat solvent stream, removing from the upper portion of said zone a raffinate comprising the paraffinic components of said mixture, introducing said mixture into said zone at a point between the raffinate and fat solvent outlets of said zone, vaporizing from said primary fat solvent a light overhead comprising aromatic and naphthenic hydrocarbon components of said mixture, subjecting at least a portion of said overhead to solvent extraction in a secondary extraction zone, recovering a secondary raffinate from said secondary zone, comprising the relatively low molecular weight naphthenic components of said mixture, recycling a reflux stream selected from (1) a portion of said secondary raffinate and (2) a portion of said light overhead to said primary extraction zone, and introducing said reflux into said primary extraction zone below the inlet of said mixture therein.

More specific embodiments of the invention relate to specific naphthenic hydrocarbons to be recovered as products, particular process flow arrangements to accomplish one or more of the aforementioned specific objectives, and particular operating conditions found to be most suitable for such objectives.

The process of this invention may be operated for the specific purpose of recovering a naphthenic hydrocarbon individual or a naphthenic hydrocarbon concentrate consisting essentially of a single naphthenic hydrocarbon which is valuable per se as a raw material or as a starting material in the preparation of other derivatives, such as naphthenic acids or aliphatic acids by oxidation thereof. The process may also be operated to recover a product comprising a mixture of naphthenes utilizable

as charge stock in a reforming process, wherein the naphthenes are subjected to dehydrogenation and isomerization to form aromatic hydrocarbons therefrom. The present separation process is also particularly applicable in combination with such reforming processes for the purpose of separating the unconverted naphthenes from the aromatic-containing product for further conversion in the reforming process to such aromatic product. In most naphthene-to-aromatic hydrocarbon reforming processes the conversion approaches an equilibrium state and the reformed product, by virtue of such equilibrium, contains a substantial proportion of unconverted naphthenes. Thus, in the conversion of cyclohexane and methylcyclopentane to benzene through the mechanism of dehydro-isomerization of such naphthenes in a reforming reaction, the product effluent from the reforming reactor generally contains a significant proportion of unconverted cyclohexane and methylcyclopentane. In the operation of such typical reforming processes a fraction representing all of the unconverted naphthenes in the product is separated from the reforming reactor effluent and recycled as feed stock to the reforming reactor for further reprocessing. Since any fraction thus separated by simple or fractional distillation contains benzene as an azeotrope with the methylcyclopentane and cyclohexane components in the mixture, recycle of the fraction to the reforming zone without prior separation of the benzene therefrom tends to reduce the desired conversion of the naphthenes to benzene by virtue of the mass action effect of the benzene on the equilibrium in the reforming process. By applying the principles of the present invention, that is, by separating the benzene from the recycle fraction and discharging the benzene from the recycle fraction, thereby providing a naphthene-rich recycle stream, the equilibrium is shifted in favor of the formation of benzene from the recycled naphthenes when the latter is subsequently recycled to the reforming zone.

The present invention, therefore, may be operated for the alternative objective of either producing a naphthene concentrate which in the case of cyclohexane may be utilized to provide the source of raw material for subsequent conversion to by-products such as adipic acid, for example, or the separation stage may be operated in combination with a reforming process for the ultimate production of benzene, toluene, xylene or a mixture of two or three of these aromatics, in accordance with the aforementioned principles affecting the equilibrium conversion of naphthenes to aromatic hydrocarbons.

Suitable hydrocarbon mixtures utilizable as feed stocks in the present process may be selected from any source of hydrocarbon mixtures containing paraffinic, aromatic, and naphthenic hydrocarbon components, and most appropriately from such mixtures which normally form azeotropic or constant boiling mixtures with each other. Thus, straight run gasoline fractions which boil over a relatively narrow boiling range and which contain C_5, C_6 and/or C_7 hydrocarbons of the paraffin, aromatic and naphthene series may be utilized as a charging stock in the present solvent extraction process. Since such mixtures are inherently present in the product formed from thermal or catalytic reforming processes, distillate fractions separated from the products of such reforming processes provide one of the most suitable sources of feed stock in the present separation process. Thus, a fraction separated from a reformed gasoline stock and containing C_6 hydrocarbons such as methylcyclopentane, cyclohexane, the normal and branched chain C_6 paraffins, and benzene may provide a suitable charging stock in the present process. Such fractions generally boil up to about 120° C. and are separated as a distillate fraction

from the liquid product of the hydroforming conversion process. The naphthene or naphthenes to be recovered from such a fraction may be cyclopentane, methylcyclopentane or cyclohexane. A feed stock having a higher end point may also be charged to the process for the recovery of cyclohexane or an alkylcyclohexane, for example, by charging a feed stock boiling up to about 140° C., such a fraction containing cyclohexane, the mono- and polymethylcyclohexanes, toluene and the normal and straight chain C_6 and C_7 paraffins. Broad and narrow boiling range fractions, including higher end boiling point mixtures, may also be utilized, the naphthene to be recovered generally being one or more of the lowest molecular weight naphthenes present in such a mixture.

The method of separating naphthenic hydrocarbons from mixtures of the same with other hydrocarbons provided by the present invention involves a two-stage solvent extraction process wherein the fat solvent stream formed during the solvent extraction is subjected to a stripping operation to separate a light overhead comprising a mixture of the desired naphthene product and its aromatic analogs and thereafter subjecting the resulting light overhead to a secondary extraction to segregate the naphthenes from the aromatic hydrocarbons. The process for effecting such separation, comprising this invention, is further described in the accompanying diagram which illustrates the method in conjunction with a reforming process, the combination being one of the preferred embodiments of the present invention.

Referring to the accompanying drawing, a suitable mixed hydrocarbon feed stock containing naphthenic precursors of aromatic hydrocarbons is charged into a combined reforming-solvent extraction process comprising one of the embodiments of this invention through line 1 in amounts controlled by valve 2 and is thereafter transferred by means of pump 3 and line 4 at a suitable hydroforming reaction temperature and pressure into reforming reactor 5. The desired reaction pressure, usually from about 50 to about 2000 p. s. i. g. is determined by the pressure developed by pump 3 and the reaction temperature, usually from about 800 to about 1200° F., is determined by the temperature at which the feed stock is heated in furnace 6 which is placed in the feed line to the reforming reactor 5. The preferred operating temperatures and pressures are fixed by the process requirements for effecting the reforming reaction; that is, whether the reaction is effected by exclusively thermal means or with the aid of a suitable reforming catalyst. In order to suppress carbon formation during the reforming reaction, hydrogen may be admitted with the charge stock, for example, through line 7 in controlled amounts determined by valve 8. Such mixed hydrogen-hydrocarbon feed stocks are particularly desirable when the reforming reaction is effected in the presence of a catalyst such as a metal selected from group VIII of the periodic table supported on an inert or acidic support, such as platinum or palladium deposited on alumina containing a small amount of combined halogen, or an iron, nickel and/or cobalt metal or metal oxide, deposited on alumina or on alumina-silica composite. Other suitable catalysts include the group VI metal or metal oxides composited with an inert support such as alumina, including, for example, chromia-alumina composites, molybdena-alumina composites, etc. Following the required period of residence of the feed stock in reforming reactor 5, during which time the naphthenic hydrocarbon components of the feed stock undergo dehydrogenation and isomerization reactions to form, in part, the analogous aromatic hydrocarbons therefrom, the products are removed from reactor 5 through line 9 and thereafter discharged into fractional distillation column 10. Because of the equilibrium relationships between the aromatic and naphthenic hydrocarbon components of the feed stock and the resulting incomplete conversion of naphthenes to the analogous aromatic hydrocarbons, the product of the reforming

reaction contains an appreciable quantity of unconverted naphthenes, which in the case of benzene production, may consist of methylcyclopentane, cyclohexane, and polyalkylated cyclopentanes which form benzene by dehydrogenation and isomerization, and which may be accompanied by cracking of one or more alkyl groups from the cyclopentyl nucleus. In the case of the ultimate production of toluene from the naphthenic hydrocarbon feed stock, the toluene precursors may consist of dimethylcyclopentane, methylcyclohexane and other polyalkylcyclopentanes and cyclohexanes. The naphthenic precursors of xylene may consist of trialkylcyclopentanes and di- and polyalkylcyclohexanes. These hydrocarbons may be present individually or in admixture in the hydrocarbon feed stock, depending upon the boiling point range of the latter; the product of the reforming reaction may therefore contain benzene, toluene, xylene and polyalkyl-substituted benzenes, either individually or in admixture, as well as the unconverted naphthene precursors.

The reforming reaction product charged into fractionator **10** is preferably segregated into select fractions whose boiling ranges depend upon the product desired in the present process. Thus, when the aromatic primary product to be recovered is benzene, a fraction boiling up to about 200° F. is separated from the reforming reaction product in fractionator **10** and thereafter utilized as feed stock in the subsequent stages of the present process. If the desired primary product is toluene, and only toluene, a fraction boiling from 200° to 270° F. is separated in fractionator **10**. A correspondingly higher end point boiling fraction for recovery of xylene or a broad boiling range fraction, boiling up to about 300° F. for the recovery of a mixture of aromatic hydrocarbons, including benzene, toluene and xylene, may be selected as a side-cut from fractionator **10** for use as feed to the subsequent extraction stage of the process. One or more of these fractions may be separated in fractionator **10** as side-cuts, removed from the column through side-cut draw-offs, such as line **11**. The light gaseous components of the reformed product, such as recycle hydrogen may be removed from fractionator **10** through line **12** and valve **13** while the bottoms comprising material boiling above the end point of the desired side cut is removed from column **10** through line **14** and valve **15** to storage or other disposition. Heat required for the fractionation may be supplied by means of reboiler **16**.

The side-cut to be utilized as feed stock in the subsequent extraction stages of the process, removed from column **10** through line **11**, is transferred by means of pump **17** in the liquid phase through line **18** in amounts controlled by valve **19** into primary solvent extraction zone **20** for effecting the desired separation of unconverted naphthenes from the aromatic primary product. A suitable selective solvent for the aromatic and naphthenic components of the feed stock, generally of higher density than the hydrocarbon feed, is introduced into the upper portion of extraction zone **20** through line **21**, the solvent generally consisting of the lean, regenerated solvent recycled from subsequent stages of the process. Make-up portions of the solvent, designed to replace losses of solvent from the system, may be introduced into the process flow from storage through line **22** in controlled amounts determined by valve **23**. The particular solvent composition for use in the present process is selected on the basis of its selective solvent action for the aromatic component of the feed stock, a more limited solvency for the naphthenic hydrocarbon components, and the least solvency for aliphatic hydrocarbon components of the mixture. Solvents of this type may be selected from a wide variety of organic compounds, including the alcohols, glycols, polyglycols, glycol ethers, alcohol esters of organic acids, certain organic nitriles and others well recognized in the solvent extraction art for their selectivity toward aromatic hydrocarbons. The selectivity of the

solvent for aromatic hydrocarbons may be enhanced by the inclusion of an anti-solvent, such as water, in the composition, the latter further reducing the solubility of non-aromatic hydrocarbons in the solvent. One of the preferred classes of such selective solvents are the glycols and the polyalkylene glycols containing from about 0.5 to about 25%, and preferably from 2 to about 10% by weight of water, such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, mixtures of one or more of the aforesaid glycols or the mixed ether-glycols, such as trimethyl ether of glycerol.

The mixed hydrocarbon feed stock is introduced into extraction zone 20 below the point of introduction of the solvent composition and flows upwardly in countercurrent relationship to the more dense solvent, the aromatic hydrocarbon components of the feed stock being removed therefrom by the selective solvent action of the solvent in contact therewith. Under the countercurrent contacting conditions maintained in the column the solvent becomes progressively richer in aromatic components and leaner in paraffinic components of the feed stock, which may initially tend to dissolve in the solvent as a result of the initially low concentration of aromatic hydrocarbons therein. Although the solvent tends to dissolve aromatic hydrocarbons more readily than naphthenes, and naphthenic hydrocarbons more readily than aliphatic hydrocarbons, and although the aromatics and naphthenes tend to displace paraffins from the solvent, a small proportion of the paraffins contained in the mixed hydrocarbon feed stock remain dissolved in the fat solvent stream leaving the bottom of the extraction zone, unless such paraffinic components are completely displaced therefrom by a stream of such aromatic and/or naphthenic hydrocarbons contacted with the fat solvent just prior to removal of the latter from the extraction zone. In order to effect such displacement of aliphatic hydrocarbons from the fat solvent stream a reflux stream containing such aromatic and/or naphthenic hydrocarbons is introduced into the lower portion of the primary extraction zone 20 and countercurrently contacted with the fat solvent stream just prior to its removal from the extraction zone, thereby displacing the dissolved paraffins into the raffinate flowing from the top of the column. The reflux stream, derived from a recycle fraction as hereinafter indicated, is introduced into the extraction zone, preferably in the lowermost portion thereof, in order to provide the greatest countercurrent contact in the extractor with the fat solvent stream. By virtue of such selective displacement action of aromatic and naphthenic hydrocarbons on the paraffins normally dissolved in small amounts in the fat solvent, the paraffinic contaminants are displaced into the rising hydrocarbon raffinate stream removed from the uppermost portion of the extraction zone through line **24** and valve **25**. In order to provide the aforementioned countercurrent contacting action between the hydrocarbon feed and solvent and the displacement action in the lower portion of the extraction zone, the feed stock mixture is generally introduced into the column between the points of removal of the paraffinate at the top of the column and the extract phase at the bottom of the extraction zone, the reflux stream being charged into the extraction zone at a point just above the outlet port of the fat solvent stream. The fat solvent or extract phase containing the aromatic and naphthenic hydrocarbon components dissolved in the solvent is removed from the extraction zone through line **26** and is transferred by means of pump **27** and line **28** in controlled amounts determined by valve **29** into the upper portion of fat solvent stripping column **30**, wherein the hydrocarbon solute components of the fat solvent stream are vaporized therefrom by distillation with heat supplied to the stripping column by reboiler **31** or by a jet of steam, not illustrated, introduced into

the column. The presence of the solvent in the stripping zone tends to increase the boiling point of the aromatic component dissolved therein relative to the naphthenic components and in order to provide a fat solvent residue containing only dissolved aromatic hydrocarbons for subsequent vaporization from the residue in pure form, sufficient heat is introduced into the fat solvent stream to strip the latter completely of non-aromatic hydrocarbons prior to vaporization of the aromatic solute therefrom. In thus stripping the non-aromatic solute from the fat solvent, however, a portion of the aromatic dissolved in the fat solvent necessarily distill over the light vapor overhead before the fat solvent residue is free of non-aromatic solute components because of the partial vapor pressure of these aromatics. The aromatic components, free of non-aromatic hydrocarbons, are removed from zone **30** as a side-cut through line **32** and valve **33** into storage or for further treatment, not illustrated. In the case of a feed stream to the solvent extraction zone containing a mixture of homologous aromatic hydrocarbons, a greater proportion of the more volatile aromatic component, such as benzene, will be distilled out of the fat solvent in the light overhead vapor, and a greater proportion of the homologous aromatic, such as toluene and xylene, will be stripped from the fat solvent as the side-cut product. The solvent residue from which the aromatic solute components have been more or less completely vaporized is removed as a bottoms stream from the lower portion of stripping zone **30** through line **34** and is transferred by means of pump **35** into regenerated solvent recycle line **21** for reuse as lean solvent in extraction zone **20**.

The light vapor overhead stripped from the fat solvent and containing all of the non-aromatic as well as a portion of the aromatic components of the fat solvent stream is removed from zone **30** through line **36** containing valve **37** and introduced into fractionating column **38** for separation of the aromatic and non-aromatic components of this stream. In the absence of the solvent which normally would otherwise increase the boiling point of the aromatic hydrocarbon component if distilled in its presence, the naphthenic and aromatic hydrocarbons present in the essentially hydrocarbon light vapor overhead boil at their normal boiling points, or at the boiling point of the azeotrope thereof, making a preliminary partial separation between the aromatic and naphthenes feasible by fractional distillation. Because of the presence of naphthenes of the same number of carbon atoms as the aromatic present in the light vapor overhead, however, the lightest fraction distilled from the hydrocarbon mixture is an azeotropic mixture of the lightest aromatic, and the analogous naphthenic components present in the overhead. The overhead from fractional distillation column **38** is, however, richer in naphthenes than the equilibrium mixture remaining in the column, the aromatics tending to concentrate through loss of overhead naphthenes in the higher boiling residue within column **38**. The latter residue, heated by reboiler **39**, and containing a major proportion of the aromatics charged into column **38**, provides a desirable source of hydrocarbon reflux to extraction zone **20**, the use of column **38** bottoms as the latter reflux stream also providing a means of recovering the aromatic components in the system. The aromatics ultimately recovered from the fat solvent stream formed in zone **20** also recover the aromatics present in the aromatic bottoms of column **38** by virtue of such recycle of column **38** bottoms as reflux to primary extraction zone **20**. The bottoms residue of column **38** is accordingly desirably recycled as a reflux stream through line **40** and valve **41** into the lower portion of extraction zone **20**, pump **42** and line **43** being employed for this purpose.

As indicated, the overhead fraction from column **38** is predominantly a mixture of light naphthenes and aromatics which distill over from column **38**, in the

absence of the solvent, as an azeotropic mixture, the overhead vapors being removed from column 38 through line 44 and valve 45 and transferred by means of pump 46 and line 47 into secondary extraction zone 48. Selective solvent extraction of the secondary overhead in zone 48 in accordance with this invention effects the separation of the naphthenic from the aromatic components of this fraction and thereby provides a means of recovering the naphthenic concentrate of this process. Solvent extraction as a method of segregating the aromatic from the naphthenic components of the secondary overhead provides the most convenient and readily operable means for effecting such separation because of the relative solubilities of the two classes of hydrocarbons in the solvent, the solubility of the aromatic components comprising the secondary overhead in the solvent being substantially greater than the naphthenic hydrocarbon components. Therefore, the mere contact of the secondary overhead with the selective solvent, preferably in a countercurrent flow arrangement, will form a fat solvent stream containing the aromatic components and a raffinate stream consisting substantially of pure naphthenic product. Any naphthenes dissolving in the secondary fat solvent are returned to the process flow, and thereby ultimately recovered because of the provision herein for recycling the secondary fat solvent stream to the primary fat solvent stripping column. The solvent for the secondary extraction zone 48 may be the same as or different from the solvent utilized in primary extraction zone 20 and is preferably the same solvent to enable a single fat solvent stripping column to be utilized for both the primary and secondary fat solvent streams, the product recovered from both streams being the aromatic component of the feed stock. A preferred arrangement for this purpose is to utilize the regenerated solvent recovered as the lean solvent stream from stripping column 30 as the source of lean solvent for secondary extractor 48, and for this purpose a side stream of solvent is removed from regenerated solvent return line 21 and is thereafter transferred by pump 35 into secondary solvent feed line 49 in controlled amounts determined by valve 50. The solvent stream is conducted in to the upper portion of secondary extraction zone 48, and permitted to flow downwardly in countercurrent relation shop to the rising hydrocarbon stream introduced into zone 48 through line 47. The secondary overhead stream comprising the feed to extraction zone 48 is admitted into column 48 at a point substantially below the solvent inlet and preferably in the lowermost portion of the column. The naphthenic hydrocarbon component or components, constituting the lightest naphthenes present in the initial feed stock do not dissolve to any substantial degree in the presence of aromatic hydrocarbon in the solvent and therefore may be removed from the upper portion of zone 48 as a raffinate stream through line 51 and valve 52 to product storage or for further fractionation to separate individual naphthenes therefrom. The aromatic hydrocarbons which selectively dissolve in the solvent stream charged into secondary extractor 48 may be recovered from the resulting fat solvent in a secondary stripper, not illustrated, but preferably are recovered with the aromatics present in the primary fat solvent stream in stripper 30; for this purpose the fat solvent from the secondary extractor 48 is removed through line 51' and valve 52' and charged into line 26 leading to stripper 30. The aromatic product stream removed through line 32 from stripper 30 thereby contains all the aromatics present in the system.

The naphthenic hydrocarbon recovered from secondary extraction zone 48 through line 51 consists of substantially pure light naphthenes present in the initial stock and is recovered as an individual only by virtue of the use of a portion of the naphthenic product as a reflux stream in primary extraction zone 20, the light naphthenic product displacing heavier naphthenes, and paraffins contained in the feed stock from the fat solvent in the lower portion of extraction zone 20. The portion of naphthenic product reserved for use as reflux is removed from product line 51 through line 53 in controlled amounts determined by valve 54 and is transferred by means of pump 55 into line 56 from which the reflux portion is removed through line 57 and valve 58 for discharge into primary extraction zone 20. The reflux stream is preferably charged into the lowermost tray of zone 20, immediately above the fat solvent outlet, in order to accomplish countercurrent contact with the fat solvent stream just prior to removal of the latter from the extraction zone and transfer to the stripping column. By thus contacting the fat solvent stream with the light naphthenes just prior to stripping the fat solvent, maximum effective displacement of heavy naphthenes and paraffins is thereby accomplished.

When the ultimate purpose of the present process is the conversion of naphthenes to aromatic hydrocarbons in the aforementioned reforming stage, rather than the recovery of a substantially pure naphthenic hydrocarbon product, the naphthenes removed from product line 51 through line 53 may be transferred by means of pump 55 through line 56 and valve 59 into line 1 which feeds into reforming reactor 5, whereby the naphthene to aromatic molar ratio in the reforming zone is increased, likewise increasing the conversion of naphthenes to aromatics. By manipulation of valve 58 and 59, either a minor proportion or a major proportion of the naphthenic product may be either recycled to the reforming reactor or returned to the primary extraction zone as a reflux stream therein. It is to be noted however that at least a portion of the light naphthenes recovered as product must be diverted into line 57 for use as reflux in order to obtain the aforementioned selective displacement of heavy naphthenes and paraffins from the primary fat solvent stream. Since both the aromatics and light naphthenes are useful as a source of reflux in the primary extraction zone to displace heavy paraffins and naphthenes from the fat solvent prior to stripping, an alternate supply of the reflux stream which contains both of said aromatic and naphthenic components is the light overhead from the stripping zone, the latter being recycled to reflux line 53 from overhead line 36 through conduit 60, the amount thereof being controlled by valve 61.

Other modifications of the process are obviously feasible and the preferred method of operation which is selected herein for illustrative purposes only in the following example is not intended to limit the generally broad scope of the invention in strict accordance therewith.

Example

A naphthene-base petroleum stock boiling from an initial boiling point of about 65° F., up to an end boiling point of about 400° F. and containing the following classes of hydrocarbons in their indicated proportions:

	Percent
Paraffins	63
Olefins	1
Naphthenes	28
Aromatics	8.3

is utilized as the feed stock in a Platforming process in which the naphthenic hydrocarbon components are selectively dehydro-isomerized in the presence of a solid catalyst comprising platinum supported on an alumina-halogen composite. Hydrogen under pressure is charged into the reforming reactor with the hydrocarbon feed stock to inhibit carbon formation and assist in the reforming reaction. The conversion of naphthenic to aromatic hydrocarbons is an equilibrium conversion which is determined at least in part by the concentration of aromatics in the feed stock to the Platforming reactor.

The reformed product contains the following classes of hydrocarbons in their indicated proportions:

	Percent
Paraffins	63.5
Olefins	0.0
Naphthenes	2.4
Aromatics	34.1

The normally liquid portion of the product is subjected to solvent extraction under countercurrent flow conditions in a column into which the feed stock is introduced on approximately the center plate of the column, the solvent, consisting of a 7.5% aqueous solution of diethylene glycol, being charged onto the top tray of the column and allowed to percolate downwardly through the column against the rising stream of liquid hydrocarbon feed stock. A raffinate stream composed almost exclusively of the paraffinic components of the feed stock is removed from the top tray of the column and discharged from the process flow. The naphthenes present in the raffinate, as shown by analysis of this stream were C_7, C_8, and higher molecular weight alkylcyclohexanes and cycloheptanes, there being substantially no cyclopentane, methylcyclopentane or cyclohexane present in this stream.

A reflux fraction comprising cyclopentane, methylcyclopentane and cyclohexane, recovered as a product stream in the subsequent stages of the process, as hereinafter indicated, was charged into the bottom of the extraction column at a rate of approximately 8% by volume of the charging stock feed rate.

A fat solvent stream removed from the bottom of the extraction column at a temperature of 280° F. and at a pressure of 90 p. s. i. g. was fed into a fat solvent stripper comprising a fractional distillation column containing a reboiler, and a steam inlet on the lowermost tray into which steam at 20 pounds pressure was admitted for the purpose of stripping the last traces of hydrocarbon solute from the fat solvent. The stripper operates at essentially atmospheric pressure, except that the uppermost trays containing liquid seals between successive plates, were operated at successively reduced pressures from a maximum of 90 p. s. i. g. on the uppermost tray. An overhead vapor stream containing 35% by volume of aromatics (predominantly benzene) and 65% by volume of light naphthenes (cyclopentane, methylcyclopentane and cyclohexane) was removed from the top of the stripper and discharged in vapor state into a fractional distillation column. A side stream removed from a lower tray of the stripper consisted of water, benzene, toluene and xylene, the hydrocarbon content of which was 99.9% aromatic. A regenerated lean solvent stream, reconstituted to 7.5% water was pumped from the reboiler section of the stripper to the top of the primary extraction column, a small side-stream being separately removed for diversion to a secondary extraction column, hereinafter described.

The stripper overhead when fractionally distilled yielded a fractionator overhead consisting predominantly of benzene and about 38% by volume of a mixture of cyclopentane, methylcyclopentane and cyclohexane. The bottoms from the column contained no naphthenes and was composed primarily of benzene, toluene and xylene which was recycled as a reflux stream to a lower plate of the primary extraction column, being introduced into the column into an inlet approximately two plates above the inlet for the light naphthene reflux which was introduced into the bottom of the primary extraction column and which was derived by further extraction of the fractionator overhead, as hereinafter described.

The napthenic-aromatic hydrocarbon fractionator overhead was charged into the bottom of a secondary extraction column of similar design but of substantially smaller size than the primary extractor. The raffinate stream from the top of the column upon analysis contains no aromatic components and contains none of the heavy naphthenes present in the initial feed stock. The small bleed stream of regenerated glycol solvent removed from the bottom of the stripper was charged into the top of the secondary extractor and allowed to flow downwardly therein, countercurrent to the liquid phase hydrocarbon mixture (fractionator overhead). A fat solvent stream removed from the bottom of the secondary extractor contained the aromatic components present in the fractionator overhead, that is, all of the benzene distilled overhead with the light naphthenes from the fractionator. A small amount (approximately 12% of the total hydrocarbon solute present in the fat solvent stream) of light naphthenes was also dissolved in the secondary extractor fat solvent stream. The latter stream was pumped into the supply line leading into the primary fat solvent stripper.

The light naphthenes contained in the secondary extractor raffinate stream contained no aromatic or paraffinic components and its analysis indicated that it is made up of approximately the following amounts of each of the indicated light naphthenes:

	Percent
Cyclopentane	About 65
Methylcyclopentane	About 22
Cyclohexane	About 13

The above naphthenic product is divided into two portions, an amount representing approximately 55% of the total volume of naphthenes recovered is recycled to the bottom of the primary extraction column as a reflux stream for the column, and the remaining 45% is further fractionated to separate the benzene precursors: methylcyclopentane, and cyclohexane from the cyclopentane product, the former mixture comprising the bottoms from the fractionation, being recycled to the Platforming reactor for use therein as supplement for the feed stock to the process, which thereby increases the total conversion of naphthenes to aromatic product (benzene) by displacement of the naphthene-to-benzene equilibrium in the reforming reaction zone.

We claim as our invention:

1. In a process for separating in a counter-current primary solvent extraction zone a mixture of hydrocarbons comprising paraffinic, naphthenic and aromatic components, employing a solvent more dense than said mixture and in which the naphthenic and aromatic components are at least partially soluble, removing from the lower portion of said zone a primary fat solvent stream, and removing from the upper portion of said zone a raffinate comprising the paraffinic components of said mixture, the method which comprises introducing said mixture into said zone at a point between the raffinate and fat solvent outlets of said zone, vaporizing from said primary fat solvent a light overhead comprising aromatic and naphthenic hydrocarbon components of said mixture, subjecting at least a portion of said overhead to solvent extraction in a secondary extraction zone and therein separating naphthenic from aromatic components, recovering a secondary raffinate from said secondary zone comprising the relatively low molecular weight naphthenic components of said mixture, and recycling a reflux stream selected from the group consisting of (1) a portion of said secondary raffinate and (2) a portion of said light overhead to said primary extraction zone, and introducing said reflux into said primary extraction zone below the inlet of said mixture therein.

2. In a process for separating in a counter-current primary solvent extraction zone a mixture of hydrocarbons comprising paraffinic, naphthenic and aromatic components, employing a solvent more dense than said mixture and in which the naphthenic and aromatic components are at least partially soluble, removing from the lower portion of said zone a primary fat solvent stream and removing from the upper portion of said

zone a raffinate comprising the paraffinic components of said mixture, the method which comprises introducing said mixture into said zone at a point between the raffinate and fat solvent outlets of said zone, vaporizing from said primary fat solvent in a vaporizing zone a light overhead comprising aromatic and naphthenic hydrocarbon components of said mixture, segregating at least a portion of said overhead and subjecting said portion to solvent extraction in a secondary extraction zone and therein separating naphthenic from aromatic components, recovering a secondary raffinate stream from said secondary zone comprising the relatively low molecular weight naphthenic hydrocarbon components of said mixture, recovering a secondary fat solvent as bottoms from said secondary extraction zone and supplying the same to said vaporizing zone, and recycling a reflux stream selected from the group consisting of (1) a portion of said secondary raffinate and (2) a portion of said light overhead to said primary extraction zone, and introducing said reflux into said primary extraction zone below the inlet of said mixture therein.

3. The process of claim 1 further characterized in that said mixture of hydrocarbons contains a C_6 naphthenic hydrocarbon.

4. The process of claim 1 further characterized in that said mixture of hydrocarbons contains C_6 naphthenic and C_6 aromatic hydrocarbons.

5. The process of claim 1 further characterized by introducing said mixture at approximately the mid-point and said reflux stream into approximately the bottom of said primary extraction zone.

6. The process of claim 1 further characterized in that said light overhead is fractionated to segregate a relatively volatile fraction comprising a naphthenic hydrocarbon component of said mixture from a less volatile fraction comprising an aromatic hydrocarbon component of said mixture, recycling said less volatile fraction to said primary extraction zone as a reflux stream, and introducing said reflux into the lower portion of said primary zone.

7. The process of claim 1 further characterized by fractionating said light overhead fraction to segregate a relatively volatile fraction comprising a naphthenic hydrocarbon component of said mixture from a less volatile fraction comprising an aromatic hydrocarbon component of said mixture, recycling at least a portion of said relatively volatile fraction to said primary extraction zone as a reflux stream, and introducing said reflux into the lower portion of said primary zone.

8. A process for the conversion of naphthenic hydrocarbons to aromatic hydrocarbons which comprises subjecting a hydrocarbon mixture comprising a naphthenic hydrocarbon precursor of said aromatic hydrocarbon to reforming conditions whereby said naphthenic hydrocarbon is converted to an equilibrium mixture of aromatic and naphthenic hydrocarbons, subjecting the product of said reforming step to solvent extraction in a primary extraction zone with a solvent more dense than said mixture and in which the naphthenic and aromatic components are at least partially soluble, removing from the lower portion of the extraction zone a primary fat solvent stream, removing a raffinate comprising the paraffinic components of said mixture from the upper portion of said zone, introducing said mixture into the extraction zone at a point between the raffinate and fat solvent outlets of said zone, vaporizing from said primary fat solvent a light overhead comprising aromatic and naphthenic hydrocarbon components of said mixture, segregating at least a portion of said overhead and subjecting said portion to solvent extraction in a secondary extraction zone and therein separating naphthenic from aromatic components, recovering a secondary raffinate stream from said secondary zone comprising the relatively low molecular weight naphthenic hydrocarbon components of said mixture, recycling a reflux stream selected from the group consisting of (1) a portion of said secondary raffinate and (2) a portion of said light overhead to said primary extraction zone, introducing said reflux into said primary extraction zone below the inlet of said mixture therein, and recycling a portion of said secondary raffinate to said reforming step.

9. A process for recovering a naphthene concentrate from a mixture of paraffinic, naphthenic and aromatic hydrocarbons which comprises countercurrently contacting said mixture in a primary extraction zone with a solvent more dense than said mixture and in which the naphthenic and aromatic hydrocarbons are at least partially soluble, removing the resultant fat solvent from the lower portion of said zone and vaporizing aromatic and naphthenic hydrocarbons therefrom in a stripping zone, fractionating the resultant vapors to separate the same into relatively light and heavy fractions, introducing the heavier fraction to the lower portion of said primary zone as reflux therein, subjecting the lighter fraction to solvent extraction in a secondary extraction zone with a solvent for aromatics to separate the naphthenic from the aromatic components of the lighter fraction, and supplying the fat solvent from said secondary zone to said stripping zone for vaporization of the dissolved aromatics therein.

10. The process of claim 9 further characterized in that there is recovered as a side-cut from said stripping zone an aromatic product of higher boiling point than said vapors from the stripping zone.

11. The process of claim 9 further characterized in that separate streams of lean solvent from said stripping zone are introduced to the upper portions of said primary and secondary extraction zones.

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