

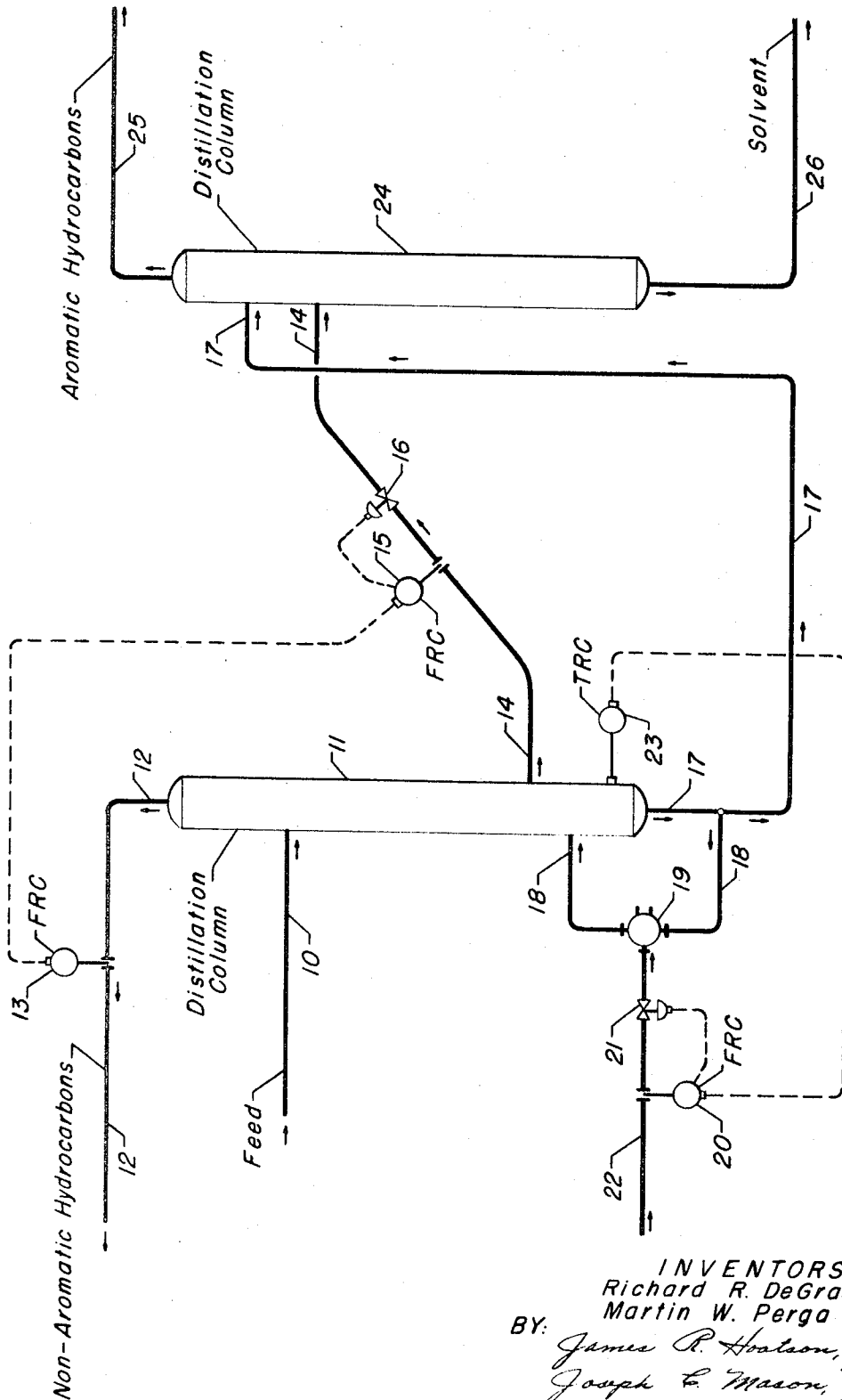
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METHOD FOR CONTROL OF SOLVENT SEPARATION PROCESSES

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**METHOD FOR CONTROL OF SOLVENT
 SEPARATION PROCESSES**

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ABSTRACT OF THE DISCLOSURE

Method of solvent extracting aromatic hydrocarbons from a suitable feedstock such as catalytic reformat. Solvent extract is fractionated to recover aromatic hydrocarbons in a two-tower system comprising first extractive distillation and then fractionation. The extractive distillation column is controlled to provide optimum preheat to the subsequent aromatic recovery fractionation column.

BACKGROUND OF THE INVENTION

This invention relates to a method and a system for separating an essentially binary feed mixture containing a small amount of a third component.

This invention relates to the recovery of aromatic hydrocarbons via the solvent extraction of aromatic components from a suitable feedstock. It particularly relates to the recovery of aromatic hydrocarbons from the extract phase from such a solvent extraction operation. It specifically relates to a method for controlling the preheat requirements for an aromatic hydrocarbon recovery distillation column.

It is known in the art that a conventional process for the recovery of high purity aromatic hydrocarbons from various feedstocks including catalytic reformat is liquid-liquid extraction utilizing a solvent such as diethylene glycol or sulfolane, each of which has high selectivity for the aromatic components present in the feedstock. Typically, in the practice of a prior art process, the hydrocarbon feed mixture containing aromatic and non-aromatic hydrocarbons is contacted in an extraction zone with an aqueous solvent composition which selectively dissolves the aromatic component from the feedstock thereby forming a raffinate phase comprising one or more non-aromatic hydrocarbons and an extract phase comprising solvent having aromatic hydrocarbons dissolved therein. The separated extract phase is then distilled, yielding an overhead distillate containing only a portion of the extracted aromatic component, a sidecut fraction or intermediate stream comprising aromatic hydrocarbons and a bottoms fraction comprising lean solvent suitable for reuse in the extraction zone. Frequently, to prevent losses of the solvent the raffinate phase is washed with water in a washing zone in order to remove solvent from the raffinate phase.

Also, not infrequently, the extract phase is subjected to extractive distillation in the presence of added solvent in order to remove a contaminating quantity of nonaromatic hydrocarbons from the extract phase. This extractive distillation operation is normally performed to make possible the recovery of nitration grade aromatic hydrocarbons such as benzene and toluene. Therefore, a typical prior art process for the recovery of aromatic hydrocarbons encompasses a solvent extraction step, an extractive distillation step, and a final distillation step for the recovery of the aromatic hydrocarbons from a solvent phase.

In the extractive distillation operation it is common practice to add to the extract phase considerable quantities of additional solvent so that the relative volatilities

between a nonaromatic hydrocarbon component and an aromatic hydrocarbon component are substantially increased in order to effectuate an almost complete separation between the two via distillation. This, of course, requires a distillation column of some complexity utilizing large quantities of utilities such as steam for heat input so that the distillation operation may be properly performed. However, the extractive distillation column is severely limited in the amount of heat input which is possible because care must be taken to minimize the quantity of aromatics in the overhead fraction which would represent a loss in yield of desirable aromatic hydrocarbons by virtue of adding inefficiencies to the extraction operation to which the overhead stream from the extractive distillation column is normally returned. Accordingly, the extractive distillation operation achieves a balance between the desire to remove nonaromatic hydrocarbons from the aromatic hydrocarbons and the desire to maximize the recovery of the aromatic hydrocarbons.

In similar fashion, the operation of the aromatic recovery column is one of achieving proper thermal and material balance. It would be desirable to have the feed to the aromatic recovery column as high as possible in temperature so that a minimum amount of reboiler heat may be added to the column. It is also desirable to control the temperature of the feed since relatively small changes in temperature have a large effect on the heat balance of the column.

In copending application Ser. No. 641,773 filed on even date herewith, there is disclosed a method for achieving the optimum thermal balance in the aromatic hydrocarbon recovery column. In said copending application the method taught embodies the removal of not only an overhead fraction and a bottoms fraction from the extractive distillation column, but here is also taught a requirement for the removal of a sidecut vapor fraction containing aromatic hydrocarbons which combination effectuates a significant increase in the preheat available to the subsequent aromatic hydrocarbon recovery column.

SUMMARY OF THE INVENTION

It is therefore an object of this invention to provide a system for separating an essentially binary feed mixture containing a small amount of a third component.

It is another object of this invention to provide a method for the recovery of aromatic hydrocarbons from the extract phase of a solvent extraction operation in a more facile and economical manner.

It is still another object of this invention to provide a method for fractionating a sulfolane solvent having dissolved therein aromatic and nonaromatic hydrocarbons in a facile and economical manner.

It is a specific object of this invention to provide a method for controlling the preheat requirement for an aromatic hydrocarbon recovery distillation column.

Thus, according to one embodiment of this invention there is provided a method for controlling the preheat requirements for an aromatic hydrocarbon recovery distillation column which comprises the steps of: (a) introducing a feed stream comprising solvent, aromatic hydrocarbons, and nonaromatic hydrocarbons into a prefractionation zone; (b) maintaining fractionation conditions in said zone including a predetermined bottoms temperature, said temperature controlling heat input to bottoms reboiler means; (c) withdrawing from said prefractionation zone at a predetermined rate an overhead stream comprising non-aromatic hydrocarbons, withdrawing a bottoms stream comprising solvent and aromatic hydrocarbons at said temperature, and withdrawing a vapor sidecut stream containing aromatic hydrocarbons at a rate responsive to said predetermined rate of overhead stream withdrawal; and, (d) introducing said bottoms

stream and said vapor sidecut stream into an aromatic hydrocarbon recovery distillation column maintained under conditions sufficient to produce a distillate fraction comprising aromatic hydrocarbons and a bottoms fraction comprising solvent.

Another embodiment of this invention includes a system for separating an essentially binary feed mixture containing a small amount of a third component comprising in combination a first fractionation column, a second fractionation column, means for introducing said feed mixture into an intermediate section of said first column, means for withdrawing an overhead product from the top of said first column, means for withdrawing a bottoms fraction from the bottom of said first column, means for withdrawing a sidecut fraction from the lower portion of said column, means for measuring the temperature in the bottom of said first column, means for controlling the rate of withdrawal of said overhead product stream from said first column, first control means for the rate of withdrawal for said sidecut fraction responsive to said rate of overhead product withdrawal, second control means for controlling the rate of heat input to said first column responsive to said temperature measurement means for the bottom of said first column, means for introducing said bottoms fraction from said first column into said second column as one feed thereto, means for introducing said sidecut fraction from said first column into said second column as another feed thereto, means for withdrawing an overhead product from the top of said second column, and means for withdrawing a bottoms product from the bottom of said second column.

It is noted from the hereinabove brief description of the present invention both from its method aspects and its system aspects, relative to the prior art, that significant improvement in control and significant economies of operation are achieved by the expedient of fixing the rate of withdrawal of the overhead from the extractive distillation column, which rate then controls the amount of withdrawal of a vapor sidecut fraction from the column. Complementing this first control means is the second control means for heat input into the bottom of the column. Operating and controlling the column in accordance with the practice of this invention results in a significant increase in the temperature of both the liquid and vapor streams passing into the subsequent aromatic recovery column. Thus, the capital expenses, particularly for the aromatic recovery column, are significantly decreased.

The hydrocarbon feed mixture which may be separated by the improved method and system of the present invention comprises many different aromatic-nonaromatic mixtures. Typically, feedstocks applicable to the solvent extraction step include hydrocarbon distillate fractions (usually boiling within or near the gasoline boiling range) of natural gasoline or straight-run petroleum distillates, and especially comprises reformed naphthas which are rich in aromatic compounds and which are particularly valuable as a source of mononuclear aromatic hydrocarbons such as benzene, toluene, and xylene. Thus, the desired aromatic hydrocarbons which are ultimately recovered in the practice of this invention may comprise benzene; toluene; benzene and toluene; toluene and xylene; and benzene, toluene, and xylene. In each case, however, it is understood that the feedstock which is to be separated by the practice of this invention contains nonaromatic hydrocarbons as well as aromatic hydrocarbons; that is, the aromatic extract from the solvent extraction step comprises solvent having aromatic hydrocarbons dissolved therein, but this extract is also contaminated with a small amount of nonaromatic hydrocarbons. Thus, in a broad aspect, the feedstock consists essentially of a binary feed mixture containing a small amount of a third component. However, the process of the present invention is specifically directed to the separation of hydrocarbon feed mixtures comprising benzene and toluene and to feed mixtures comprising toluene and xylene as the aromatic hydrocarbon. Typi-

cally, the feedstocks of the present invention, as charged to the aromatic extractive step, rather than as charged to the fractionation system, will contain from about 30% to about 60% by weight aromatic hydrocarbons; although, aromatic concentrations as high as 95% by weight may be used in some cases. The quantity of added solvent is directly proportional to the aromatic content of the feed.

Solvent compositions which may be utilized in the practice of this present invention are those selected from the classes which have high selectivity for aromatic hydrocarbons. These aromatic selective solvents generally contain one or more organic compounds containing in their molecule at least one polar group such as hydroxyl, amino, cyano, carboxyl, or nitro radical. In order to be effective the organic compounds of the solvent composition having the polar radical must have a boiling point substantially greater than the boiling point of water which preferably 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 feed mixture.

Organic compounds suitable for use as part of the solvent composition preferably are selected from the group of those organic 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 poly-alkylene 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 satisfactory class of organic solvents useful in admixture with water as the solvent composition for use in the present invention. An illustrative glycol comprises triethylene glycol.

Additionally, excellent results may be obtained utilizing the cyclic monomeric sulfone, such as tetrahydrotriophene-1,1-dioxide. Still further, an organic compound particularly useful in the practice of this invention is a sulfolane which may be made by condensing a conjugated diolefin with sulfur dioxide and then subjecting the resulting product to hydrogenation, alkylation, hydration and/or other substitution or addition reactions. Typically, organic compounds belonging to the sulfonane class are 2-sulfolene, 2-methylsulfolane, 2,4-dimethylsulfolane, 2,4-dimethyl-4-sulfolane, methyl-3-sulfonyl ether, ethyl-3-sulfonyl sulfide, and others.

The apparatus embodied in the practice of the present invention may be any conventional or convenient type known to those skilled in the art. Also, the operating conditions suitable for the practice of this invention are conventional and well known to those skilled in the art, with exception of the precise temperatures and pressures for operating the extractive distillation column and the aromatic recovery column according to the teachings of this invention. In any event, from the teachings presented and from a general knowledge of the art those skilled in the art will be able to choose the proper operating conditions to achieve the benefits ascribed to the practice of the present invention. The amount of solvent composition utilized should be at least sufficient to dissolve the constituent to be extracted. It may be desirable to use a considerable excess over the theoretical amount of solvent composition necessary, especially when maximum purity and maximum recovery of the aromatic hydrocarbons are desired. Usually, in the extraction step the solvent composition to feed ratios will range from about 1:1 to about 20:1 by volume, preferably from about 5:1 to about 15:1 by volume. A summary of the conditions necessary for the practice of the sulfolane type of operation may be found in *Petroleum Refiner*, volume

38, No. 9, September 1959, pages 185-192, the entire disclosure of which is incorporated herein by reference.

The solvent extraction step, as previously mentioned, is well known and may utilize apparatus of any type suitable for effecting counter-current contact between two liquid phases, at least partially, but not wholly miscible with each other and wherein the relatively more dense solvent may be brought into intimate contact with the relatively less dense hydrocarbon phase. Thus, the extraction zone which produces the solvent extract which is used as feedstock to the practice of the present invention may comprise a packed column or may contain a series of horizontal plates through which the liquid solvent flows in dispersed form and in counter-current flow relationship to the ascending hydrocarbon stream.

The invention may be more fully understood with reference to the appended drawing.

DESCRIPTION OF THE DRAWING

The appended drawing is a schematic representation of apparatus for practicing one embodiment of the invention.

Referring now to the drawing, and extract phase from a conventional solvent extraction zone, such as one using a sulfolane type solvent, is passed into the system via line 10. The extract phase is an essentially binary feed mixture containing a small amount of a third component; that is, it has aromatic hydrocarbons dissolved therein and due to inherent inefficiencies of any commercial solvent extraction step the extract phase is also contaminated with a small amount of non-aromatic hydrocarbons. The feed in line 10 may be mixed with an added solvent stream (source not shown), depending on feed composition, so that an extractive distillation operation may be performed. The combined extract feed stream plus added solvent is passed into extractive distillation column 11 which is maintained under distillation conditions more fully discussed hereinafter.

Operating under proper conditions, a non-aromatic hydrocarbon upper stream is withdrawn from column 11 via line 12 and passed through flow recorder controller (FRC) 13 which has indicator point means for fixing the withdrawal rate of the upper stream in a predetermined manner. A lower stream comprising solvent and aromatic hydrocarbons is withdrawn, preferably, from the bottom of column 11 via line 17 and passed directly into aromatic recovery distillation column 24. A critical feature of this invention is the withdrawal of a vapor sidecut fraction from distillation column 11 via line 14. The locus for withdrawal is selected so that the material in line 14 contains a concentration of aromatic hydrocarbons and is of sufficient purity from an aromatics standpoint so that no contaminating non-aromatic hydrocarbons will appear in the distillate fraction from distillation column 24, more fully discussed hereinafter. The vapor sidecut fraction from distillation column 11 is passed via line 14 through control valve 16 at a rate responsive to the rate set by FRC 13. Flow recorder (FR) 15 is utilized in order that the rate of withdrawal of the vapor sidecut may be known. The manner of operating extractive distillation column 11 with respect to this first control means is that an increase in the rate of withdrawal of the material in line 12 will create a corresponding decrease in the rate of withdrawal of the vapor sidecut stream, all other factors remaining the same.

Referring now to the lower section of extractive distillation column 11, temperature recorder controller (TRC) 23 comprises suitable means for measuring the temperature of the material in the bottom of said column. As used herein the term "temperature in the bottom" is intended to embody a measurement of temperature physically within the lower portion of the column, the temperature of the material withdrawn in line 17, and/or the temperature of the material being returned to the lower portion of the column from reboiler 19. A portion of the material in line 17 is diverted via line 18, passed

through reboiler 19, and back into column 11. Reboiler 19 may be heated by any suitable means such as by steam or hot oil which is passed via line 22 through control valve 21 and through reboiler 19 wherein the heating medium gives up heat to the material in line 18. FRC 20 controls valve 21 which in turn regulates the amount of heat input into column 11 in a manner responsive to the temperature measured by TRC 23.

As a practical mode of operation, the material injected into column 24 from line 17 in liquid phase may be introduced at a locus, for example of two (2) fractionating trays higher in column 24 than the locus for the introduction of the vapor phase stream in line 14. In some cases, however, it may be preferable to introduce this fraction at a locus lower than the vapor stream locus or to admix the streams and feed them together into column 24.

Distillation column 24 is operated in conventional manner for the separation of aromatic hydrocarbons from the selective solvent. Depending upon the volatility characteristics of the solvent, the operating conditions are chosen so that extremely high purity aromatic hydrocarbons may be withdrawn from distillation column 24 via line 25. Lean solvent suitable for reuse in an extraction process is withdrawn from distillation column 24 via line 26.

Typical operating conditions for distillation column 24 when utilizing sulfolane as the solvent and desiring to recover benzene and toluene as the aromatic hydrocarbons include an overhead temperature from 120° F. to 306° F., a bottoms temperature from 300° F. to 350° F., and a column pressure from 90 mm. Hg to 760 mm. Hg. Those skilled in the art, from the general knowledge and from the teachings presented herein will know how to choose the proper operating conditions depending upon the composition of the feed to effectuate recovery of high purity aromatic hydrocarbons from the solvent.

Referring again to extractive distillation column 11, suitable operating conditions for this column are conventional in that sufficient heat must be added to the column in order for separation to take place between the non-aromatic hydrocarbons and the aromatic hydrocarbons dissolved in the solvent. Typical operating conditions for distillation column 11 for the use of a sulfolane type solvent include a pressure from 90 mm. Hg to 15 p.s.i.g., an overhead temperature from 140° F. to 330° F., and a bottoms temperature from 170° F. to 350° F., preferably, as high as 350° F. Compatible with these conditions, the sidecut vapor fraction in line 14 is withdrawn at a temperature generally from 170° F. to 350° F.

One of the advantageous features discovered in the practice of the embodiments of this invention is the achievement of a considerably elevated temperature in the bottom of distillation column 11. By utilizing the vapor sidecut feature control by the rate of withdrawal of the overhead product from this extractive distillation column, a considerable increase in the temperature of the bottoms may be achieved without increasing the loss of aromatic hydrocarbons in the non-aromatic hydrocarbon fraction removed from the column via line 12. It is also to be noted that this increased bottom temperature may be controlled at a predetermined level by the use of TRC 23 operating to control the heat input to reboiler 19. Thus, the increase in temperature in the bottom of the column reflected by the interaction of TRC 23 on control valve 21 and the withdrawal rate of the material in line 14. By operating at a considerably increased and essentially constant temperature in the bottom of the extractive distillation column, considerably less heat is required in final aromatic recovery column 24.

The control instruments as described herein are commercially available items of manufacture, and it is not intended to limit the invention to any specific types of

instruments; although, in many cases instruments of this type provide a pneumatic signal. It is within the scope of this invention to utilize control systems which are hydraulic, electrical, electronic, or mechanical or may constitute a mixture of these types. A preferred control system would utilize an electrical signal, in which case electrically operated valves would be used.

PREFERRED EMBODIMENT

From the teachings presented hereinabove, the preferred embodiment of the method aspects of this invention includes the broad method previously mentioned wherein the solvent comprises sulfolane.

Another preferred embodiment of the method aspects of this invention includes the broad method utilizing sulfolane as the solvent wherein said predetermined temperature is from 170° F. to 350° F.

Still, a further preferred embodiment of the system aspects to this invention includes the broad system previously mentioned wherein said means for introducing said bottoms fraction into said second column is at a locus below the locus for introducing said sidecut fraction into said second column.

The invention claimed:

1. Method for controlling the preheat requirements for an aromatic hydrocarbon recovery distillation column which comprises the steps of:

(a) introducing a feed stream comprising solvent, aromatic hydrocarbons, and nonaromatic hydrocarbons into a prefractionation zone;

(b) maintaining fractionation conditions in said zone including a predetermined bottoms temperature, said temperature controlling heat input to bottoms reboiler means;

(c) withdrawing from said prefractionation zone at a predetermined rate an overhead stream comprising nonaromatic hydrocarbons, withdrawing a bottoms stream solvent and aromatic hydrocarbons at said temperature, and withdrawing a vapor sidecut stream containing aromatic hydrocarbons at a rate responsive to said predetermined rate of overhead stream withdrawal; and

(d) introducing said bottoms stream and said vapor sidecut stream into an aromatic hydrocarbon recovery distillation column maintained under conditions sufficient to produce a distillate fraction comprising aromatic hydrocarbons and a bottoms fraction comprising solvent.

2. Method according to claim 1 wherein said solvent comprises sulfolane.

3. Method according to claim 2 wherein said predetermined temperature is chosen to optimize added heat

input to said recovery column, the upper limit being a temperature below the decomposition temperature of said solvent.

4. Method according to claim 3 wherein said predetermined temperature is from 170° F. to 350° F.

5. Method according to claim 2 wherein said aromatic hydrocarbons are selected from the group consisting of benzene, toluene, benzene and toluene; and benzene, toluene, and xylene.

6. System for separating an essentially binary feed mixture containing a small amount of a third component comprising in combination a first fractionation column, a second fractionation column, means for introducing said feed mixture into an intermediate section of said first column, means for withdrawing an overhead product from the top of said first column, means for withdrawing a bottoms fraction from the bottom of said first column, means for withdrawing a sidecut fraction from the lower portion of said first column, means for measuring the temperature in the bottom of said first column, means for controlling the rate of withdrawal of said overhead product from said first column, first control means for the rate of withdrawal for said sidecut fraction responsive to said rate of overhead product withdrawal; second control means for controlling the rate of heat input to said first column responsive to temperature measurement means for the bottom of said first column, means for introducing said bottoms fraction from said first column into said second column as one feed thereto, means for introducing said sidecut fraction from said first column into said second column as another feed thereto, means for withdrawing an overhead product from the top of said second column, and means for withdrawing a bottoms product from the bottom of said second column.

7. System according to claim 6 wherein said means for introducing said bottoms fraction into said second column is at a locus below the locus for the means for introducing said sidecut fraction into said second column.

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HERBERT LEVINE, *Primary Examiner*.

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