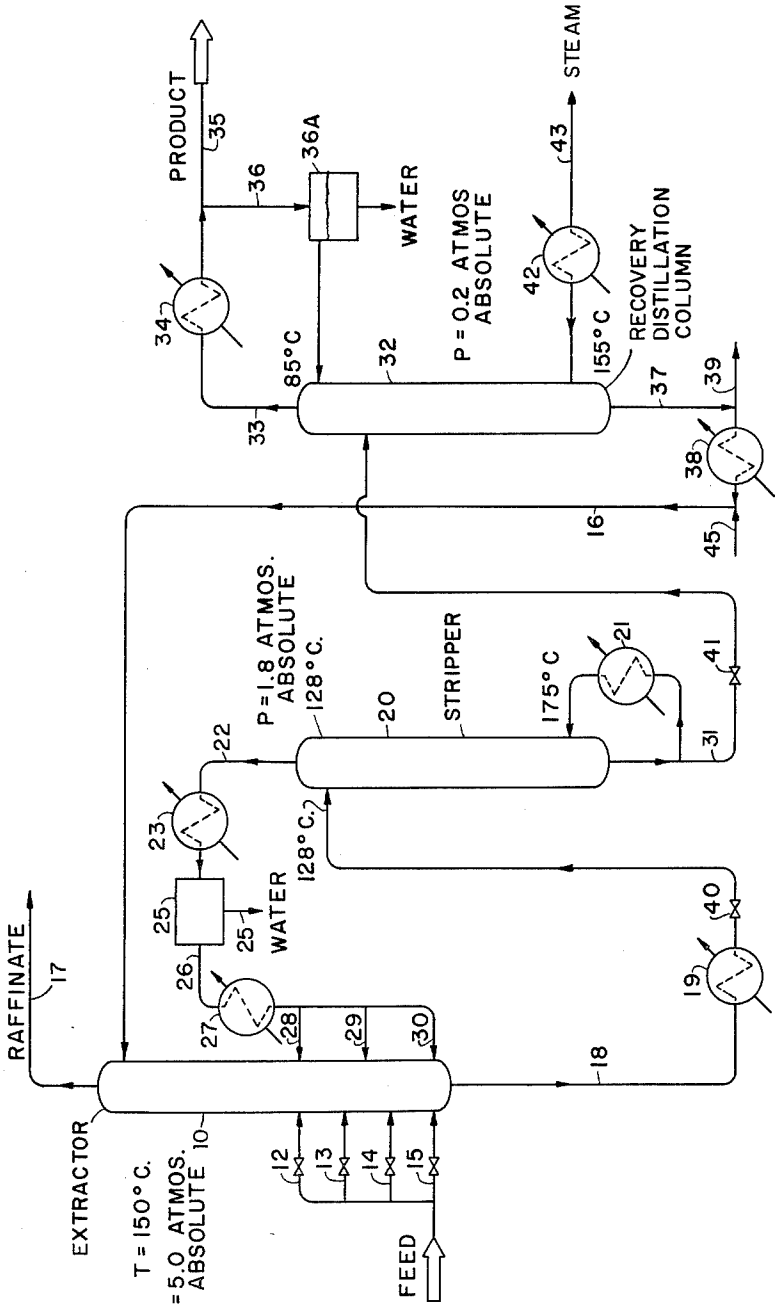
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PROCESS FOR SEPARATING AROMATIC HYDROCARBONS

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PROCESS FOR SEPARATING AROMATIC HYDROCARBONS

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This invention relates to a process for the extraction and recovery of aromatic hydrocarbons from a liquid hydrocarbon mixture.

Several processes for the extraction and recovery of aromatic hydrocarbons from liquid hydrocarbon mixtures have already been proposed. Various high boiling, aromatic selective solvents have been suggested, among these are diethylene glycol, dipropylene glycol, and sulfolane. Because of the light-heavy selectivity of these solvents, the hydrocarbons in the mixture are extracted in the following order: light aromatics, heavy aromatics, light paraffins, and heavy paraffins. It has developed in the use of these high boiling solvents that when the process is operated to obtain a high yield of aromatics, contamination with light paraffinic material is usually experienced. A procedure for increasing the purity is described in British Patent No. 739,200 wherein a hydrocarbon mixture containing aromatic hydrocarbons is introduced into a multi-stage extractor at an intermediate point and a glycolic, water-containing selective solvent for aromatic hydrocarbons is introduced into one end of the extractor. At the same end a raffinate poor in aromatics and in solvent is withdrawn, while at the other end an aromatic-rich extract phase is withdrawn and introduced into a column which is at a lower pressure than the extractor and wherein only part of the most volatile aromatics, together with non-aromatics of equivalent volatility, are removed as the top products and after condensation are returned as reflux to the extractor at the end from which the aromatic rich extract is withdrawn. From the remainder of the extract phase the aromatics are separated from the solvent by distillation in a distilling column at atmospheric or subatmospheric pressure, direct steam being injected near the bottom of the distilling column. It is stated in the example of the British patent that by using this process the purity of the recovered aromatics may amount to 97.5% and that this value may be increased to about 98% by using a more complex recovery system for the extract phase comprising three columns instead of two, and using two different reflux streams instead of one single reflux stream. This addition of a further column together with all its auxiliary equipment to the recovery system which is obviously a very costly measure, clearly demonstrates the extreme difficulties encountered in attempting to increase the products purity in extraction processes of the present type.

In this connection it should be noted that the specifications for nitration grade toluene require a very high aromatics content, viz. of at least 98.5% by volume (cf. ASTM specification D841–50).

It has now been found that by introducing certain changes in the process as described in British Patent 739,200 and by adhering to certain specific operating conditions, it is possible to obtain aromatics having a purity of 97.5–99% or even higher, while using a simple recovery system that involves two columns only. The process of the invention will be illustrated with reference to the accompanying drawing, wherein the sole FIGURE is a process flow diagram of a preferred embodiment of the improved process.

The combination of the following conditions has been found to give the aforesaid improved results:

(1) The solvent employed is a high boiling, aromatic selective material having an atmospheric (normal) boiling temperature within the range of 225° C. to 295° C., and should contain not more than 2% by weight of water. Suitable solvents include diethylene glycol, dipropylene glycol, sulfolane, and mixtures thereof.

(2) The temperature in the extraction zone should be between 140 and 170° C.

(3) The extract phase from the extraction system should be cooled by at least 15° C. to a temperature between 115 and 150° C. before entering the stripping zone.

(4) The pressure in the stripping zone should be lower than the pressure in the extraction system, but not so low as to cause appreciable flash vaporization (i.e. vaporization by pressure reduction without heating) and should be at least 1.5 atmospheres absolute.

(5) The top temperature in this stripping zone should be between 115 and 150° C. and the bottom temperature should be at least 165° C.

(6) The condensed top vapors from the stripping zone should be freed from substantially all water present as a second liquid phase before being returned to the extraction system.

(7) The pressure in the distilling zone should be below 0.5 atmospheres absolute.

(8) The bottom temperature in the distilling zone should be at least 145° C., but should be at least 10° C. below the bottom temperature in the stripping zone.

(9) Direct steam should be injected into said distilling zone in order to enable the hydrocarbons to be distilled off at not too high bottom temperatures.

Thus, according to the present invention a process for the extraction and recovery of aromatic hydrocarbons from a liquid hydrocarbon mixture containing one or more aromatic hydrocarbons, comprises introducing the mixture into a counterflow multi-stage extraction system wherein the temperature is maintained between 140 and 170° C.; introducing, at one end of the extraction system, a high boiling, aromatic selective solvent having an atmospheric boiling temperature within the range of 225° C. to 295° C. and which contains dissolved water in the proportion of not more than 2% by weight; cooling the aromatic-rich extract phase withdrawn from the extraction system by at least 15° C. to a temperature between 115° C. and 150° C.; introducing the thus cooled extract phase without appreciable flash vaporization into a stripping zone, which is operated at a pressure of at least 1.5 atmospheres absolute, at a top temperature between 115° C. and 150° C. and at a bottom temperature of at least 165° C.: condensing the vapors from said stripping zone and recycling them to the extraction system after removing substantially all water present as a second liquid phase, the condensed vapors being introduced into the extraction system at the end at which the extract phase is withdrawn and/or at an intermediate point; and separating the solvent from the hydrocarbons in the remainder of extract phase at a pressure of less than 0.5 atmospheres absolute in a distilling zone having a bottom temperature of at least 145° C., said bottom temperature being at least 10° C. lower than the bottom temperature in the stripping zone.

The present process can be applied to feed stocks having a wide or a narrow boiling range. It is especially suitable for separating aromatics from catalytically reformed gasolines, such as hydroformates and platformates, or from fractions thereof. The feed stock should have an ASTM final boiling point not higher than 220° C. Preferably the upper cutting point should be not higher than 160° C. When using a reformate fraction as starting material the upper cutting point should advantageously be approximately the same as the upper cutting point of the feed stock for the reforming operation. The lower

cutting point of the feed stock should preferably be about 100° C.

When carrying out the process according to the invention the volumetric ratio of solvent to hydrocarbon feed should be between 3:1 and 8:1, preferably between 4:1 and 6:1, whereas the ratio of the amount of top product returned from the stripping zone to the extraction system to the amount of hydrocarbon feed should be between 0.2:1 and 0.7:1, preferably between 0.3:1 and 0.5:1.

Various high boiling solvents may be used in the present process. Among these are diethylene glycol, dipropylene glycol and sulfolane. Diethylene glycol is preferred. The suitable solvents boil within the temperature range of 225 to 295° C. The solvent used in the extraction system may contain a small amount, not exceeding 2% by weight, of water.

The extraction system should be a countercurrent multistage extraction system, e.g., a column containing packing material, or sieve plates, a "rotating disc contactor," a multiplicity of mixer-settler combinations, and the like. The number of theoretical stages should preferably be at least 5.

The feed to the extraction system may be introduced at an intermediate point, but it is generally preferred to introduce it at or at least near that end of the extraction system at which the aromatic-rich extract phase is withdrawn, because in that case the best compromise between product purity and recovery (yield) is usually realized. Suitable inlet points are at said end of the extraction system (viz. at the first theoretical stage) or at the second theoretical stage, the latter embodiment being somewhat preferred because in that case the purity is distinctly higher whereas the recovery is only slightly decreased. Feed introduction at a plurality of points between the middle and the extract phase end of the system may be useful under specific circumstances.

The stream of hydrocarbons and solvent that is obtained as top product from the stripping zone and (after condensation and after removing substantially all water separating as a second liquid phase in the condensing operation) is returned to the extraction system, should also be introduced at one or more points at or near the end of the extraction system at which the extract phase is withdrawn. It is preferred to introduce this stream at or near the end of the system (i.e. at the first or second theoretical stage of the system) because in these cases the best compromise between product purity and recovery is realized. The recycle material may in some instances be advantageously returned to the extraction system in a plurality of streams between the middle and the extract phase end of the system. If necessary, the recycle stream may be heated before entering the extraction system.

The temperature in the extraction system should be between 140 and 170° C., because in this range the best compromise is realized between selective aromatic extraction, heat economy and solvent stability. There may be a certain temperature gradient over the system provided that the above limits are adhered to.

The extract phase leaving the extraction system is cooled by at least 15° C. to a temperature between 115 and 150° C. and then introduced in the stripping zone, at or near its top.

The stripping zone is operated at a pressure that is lower than that prevailing in the extraction system but that is at least 1.5 atmospheres absolute. The difference in pressure in the extraction system and in the stripping zone should be not so large as to cause appreciable flash vaporization. In fact, if there is any vaporous material present in the extract phase when entering the stripping zone, the weight ratio of this vaporous material to the fresh feed to the extraction system should not exceed 1:10. Preferably this ratio should be below 5:100, and in the most preferred embodiment no vaporous material will be present at all. In this zone the top temperature should be between 115 and 150° C., and the bottom temperature should be at least 165° C., the difference between top and bottom temperature being at least 40° C. The top product contains substantially all water and nonaromatic hydrocarbons present in the extract phase, and, in addition, some solvent and aromatic hydrocarbons.

The bottom product from the stripping zone is passed to the distilling zone operating at a pressure below 0.5 atmosphere absolute, preferably 0.2 atmosphere absolute and at a bottom temperature of at least 145° C., which temperature should always be at least 10° C. and preferably at least 20° C. lower than the bottom temperature in the stripping zone.

Whereas the stripping zone will be operated without introduction of direct steam near or in the bottom part, this measure should be taken in the distilling zone because otherwise the temperatures required to obtain a substantially hydrocarbon-free solvent as the bottom product would be so high as to cause decomposition of the glycolic solvent.

As a consequence of this introduction of steam in the distilling zone the solvent leaving the distilling zone contains a certain amount (less than 2% by weight) of dissolved water.

If necessary, there may be cooling of the solvent stream that is recycled to the extraction system.

In view of the simplicity of the operation it is generally preferred that there is no intentional heating or cooling, otherwise than by expansion, of the stream flowing from the stripping to the distilling column.

In the preferred embodiment of the present process the following operating conditions are adhered to:

Temperature in extraction system °C.	150
Temperature of aromatic-rich extract phase on entering stripping zone °C.	128
Top temperature in stripping zone °C.	128
Bottom temperature in stripping zone °C.	175
Top temperature in distilling zone °C.	85
Bottom temperature in distilling zone °C.	155
Pressure in extraction system atm. abs.	5
Pressure in stripping zone atm. abs.	1.8
Pressure in distilling zone atm. abs.	0.2

Under these conditions the water content of the solvent leaving the distilling column will be about 0.6% by weight.

It should be realized that the present approach, in which there is a cooling between extraction system and stripping column, substantially no flash vaporization between extraction system and stripping zone, a rather large temperature drop over the stripping zone and a distinctly higher bottom temperature in the stripping zone than in the distilling zone, is fundamentally different from the approach of U.K. Patent 739,200, already mentioned above, in which there is obviously no external cooling between extraction system and stripper, in which the temperature drop over the stripping zone is rather small (as reflected by a statement that it is usually not necessary to add heat to the stripping zone by means of a reboiler) and in which the main heat input in the recovery system is obviously in the bottom of the distilling zone and not in that of the stripping zone.

As a consequence of this essentially different situation the present process has the advantage that a greater proportion of the nonaromatics still present in the extract-phase is removed in the overhead of the stripping zone, which results in a higher purity of the final extract as compared with the previous process.

The invention will now be illustrated with reference to the accompanying schematic drawing.

A liquid hydrocarbon mixture containing both aromatic and nonaromatic hydrocarbons, is extracted in a multistage countercurrent extractor 10, which operates under pressure and at a temperature between 140 and 170° C. For this purpose the feed is introduced into the extractor

through one or more of the feed inlet lines 12 to 15, whereas the selective solvent, containing dissolved water, is introduced into the extractor 10 at or near its top through line 16.

The raffinate phase, which contains only relatively small amounts of water, solvent and aromatic hydrocarbons, is withdrawn from the top of the extractor 10 through line 17 and further processed to remove substantially all solvent present therein.

The aromatic-rich extract phase is withdrawn from the bottom of the extractor through line 18 and passes through a cooler 19 and a reducing valve 40 to the stripper column 20, the cooled extract phase being introduced at or near the top of the stripper. The pressure in column 20 is at least 1.5 atmospheres absolute but lower than the pressure in extractor 10.

The stripper 20 is provided with a reboiler 21 and is operated with a fairly high temperature drop over the column. In the stripper, separation is effected into a top product containing some solvent, part of the aromatic hydrocarbons and most of the water and non-aromatic hydrocarbons present in the extract phase leaving the extractor 10, and a bottom product that contains only a small amount of water and contains solvent and aromatic hydrocarbons and at most a minor amount of non-aromatic hydrocarbons. The top vapors are passed through line 22 to the condenser 23 and the resulting liquid passed to the settler 24, wherein separation in two layers, viz. a water-rich layer and a layer consisting mainly of solvent and hydrocarbons, takes place. The water layer is removed via line 25, whereas the solvent-hydrocarbon layer is passed through line 26 and heater 27, to one or more of the lines 28 to 30, through which it enters the extractor in its lower part.

The bottom product from the stripper is passed through line 31, provided with a reducing valve 41 to distilling column 32, no intentional heating or cooling of this bottom product being effected other than the cooling caused by the expansion in the reducing valve. In column 32, which operates at sub-atmospheric pressure, separation is effected into a top product containing aromatic hydrocarbons and substantially free from solvent, and into a bottom product, that is substantially free from aromatic hydrocarbons.

The top vapors are withdrawn through line 33, provided with condenser 34 and the condensate is partly withdrawn via line 35, as the aromatic-rich product, and partly passed through line 36 equipped with the settler 36A, wherein separation in two layers, viz. a lower water-rich layer and an upper layer consisting mainly of hydrocarbons, takes place. The upper layer is recycled as reflux to distilling column 32. The bottom product from this distilling column is withdrawn through line 37 and returned to the extractor through line 16, if necessary after cooling in cooler 38. If desired, part of the bottom product may be withdrawn through line 39 for purification or rejection, and fresh or purified solvent may be introduced through line 45. Distilling column 32 is operated without a reboiler, hot steam being introduced into the bottom of this column via line 43 and heater 42 to strip dissolved hydrocarbons from the descending liquid.

It should be realized that the drawing and its above description are schematic and that many auxiliary features such as valves and pumps, have not been represented or discussed.

The invention will now be further illustrated with reference to an example.

EXAMPLE

A platformate fraction with a boiling range from 90 to 150° C. (cutting points) have the following composition (in mole percent):

C_6 aromatics	0.4
C_7 paraffins	22.0
C_7 aromatics	40.2
C_8 paraffins	12.3
C_8 aromatics	23.3
C_9 aromatics	1.8
	100.0

was extracted in a so-called rotating disc contactor of such dimensions as to be equivalent to 5 theoretical stages. An extraction and recovery system as represented in the accompanying schematic drawing was used, the preferred operating conditions already mentioned, viz.:

Temperature in extraction system	° C.	150
Temperature of extract phase on entering stripping zone	° C.	128
Top temperature in stripping zone	° C.	128
Bottom temperature in stripping zone	° C.	175
Top temperature in distilling zone	° C.	85
Bottom temperature in distilling zone	° C.	155
Pressure in extraction system	ata.	5
Pressure in stripping zone	ata.	1.8
Pressure in distilling zone	ata.	0.2

were adhered to as much as possible.

The feed was introduced at the bottom (i.e. in the first theoretical stage) and the diethylene glycol solvent was introduced at the top (i.e. in the fifth theoretical stage) of the extractor.

The point of introduction of the recycle stream from the stripping zone in the extractor was varied, this stream being introduced into the first, the second and the third theoretical stage, respectively.

Table I gives the aromatics contents of the final streams and the aromatics recovery figures, obtained in these experiments with varying point of inlet of the recycle stream.

Table I

	Introduction of recycle stream into theoretical stage No.		
	1	2	3
Aromatics content, mole percent:			
in raffinate	1.8	2.6	4.6
in extract	97.8	98.3	98.6
Aromatics recovery (percent of aromatics from feed recovered in extract)	99.1	98.6	97.5

From the above table it follows that the extract purity increases and that the aromatics recovery decreases when the recycle stream from the stripper is introduced at a higher numbered stage.

In a further series of experiments, the recycle stream from the stripping column was always introduced at the bottom of the extractor (i.e. at the first theoretical stage), whereas the point of introduction of the feed was varied, this stream being introduced at the first, the second and the third theoretical stage, respectively.

Table II gives the results obtained:

Table II

	Introduction of feed into theoretical stage No.		
	1	2	3
Aromatics content, mole percent:			
in raffinate	1.8	5.4	11.8
in extract	97.8	98.9	99.6
Aromatics recovery, percent	99.1	97.1	93.2

This table shows that the extract purity is greatly increased by introducing the feed at a higher numbered

stage, but that this method greatly impairs the aromatics recovery.

From the two tables it is evident that introducing the feed at the second theoretical stage and introducing the recycle stream at the second one, yields a quite satisfactory compromise between product purity and aromatics recovery, which explains why this embodiment is a preferred one.

It should be observed that all values for the aromatics content of the extract are greater than the value (97.5%), mentioned in U.K. Patent 739,200 as the upper value when using a two-stage recovery system.

We claim as our invention:

1. A process for the extraction and recovery of aromatic hydrocarbons from a liquid hydrocarbon mixture containing aromatic and non-aromatic hydrocarbons comprising (1) introducing the mixture into a counter-flow multi-stage extraction system wherein the temperature is maintained between 140 and 170° C.; (2) introducing, at one end of the extraction system, a high boiling, aromatic selective solvent having a normal boiling temperature within the range of 225° C. to 295° C. and which solvent contains dissolved water in the proportion of not more than 2% by weight; (3) passing the solvent in countercurrent flow to the hydrocarbon mixture to obtain a solvent extract phase enriched in aromatics; (4) cooling the aromatic-rich extract phase withdrawn from the other end of the extraction system by at least 15° C. to a temperature between 115° C. and 150° C.; (5) introducing the thus cooled extract phase without appreciable flash vaporization into a stripping zone, which is operated at a pressure of at least 1.5 atmospheres absolute, at a top temperature between 115° C. and 150° C. and at a bottom temperature of at least 165° C. to separate overhead a vapor phase enriched in non-aromatic hydrocarbons; (6) condensing the vapors from said zone and recycling them to the extraction system after removing substantially all water present as a second liquid phase, with the condensed vapors being introduced into the extraction system between the intermediate point of the system and the end at which the extract phase is withdrawn; (7) withdrawing the liquid remainder of the extract phase from the stripping zone and separating the solvent from the hydrocarbons thereof in a distilling zone at a pressure of less than 0.5 atmosphere absolute, said zone having a bottom temperature of at least 145° C., which is at least 10° C. lower than the bottom temperature in the stripping zone.

2. A process in accordance with claim 1 wherein the aromatic selective solvent is selected from the group consisting of diethylene glycol, dipropylene glycol, sulfolane, and mixtures thereof.

3. A process according to claim 1 in which the feed mixture is a catalytically reformed gasoline, or a fraction thereof.

4. A process according to claim 1 in which the feed stock has an upper cutting point not higher than 160° C.

5. A process according to claim 1 in which the feed to the extraction system is introduced near that end of the extraction system at which the extract phase is withdrawn.

6. A process according to claim 5 in which the feed is introduced to one of the first two theoretical stages of the extraction system.

7. A process according to claim 1 in which the condensed vapors substantially free from water are introduced to one of the first two theoretical stages of the extraction system.

8. A process according to claim 1 in which the extract phase is introduced in the stripping zone near the top of said zone.

9. A process according to claim 1 in which the weight ratio of the vaporous material present in the extract phase on entering the stripping zone to the fresh feed to the extraction system is less than 5:100.

10. A process according to claim 9 in which no vapors are present in the extract phase on entering the stripping zone.

11. A process according to claim 1 in which the temperature in the extraction system is 150° C., the temperature of the aromatic-rich extract phase entering the stripping zone is 128° C., the top temperature in the stripping zone is 128° C., the bottom temperature in the stripping zone is 175° C., the top temperature in the distilling zone is 85° C., and the bottom temperature in the distilling zone is 155° C.; the pressure in the extraction system is 5 atmospheres absolute, the pressure in the stripping zone is 1.8 atmospheres absolute, and the pressure in the distilling zone is 0.2 atmosphere absolute, and the selective solvent is diethylene glycol.

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