

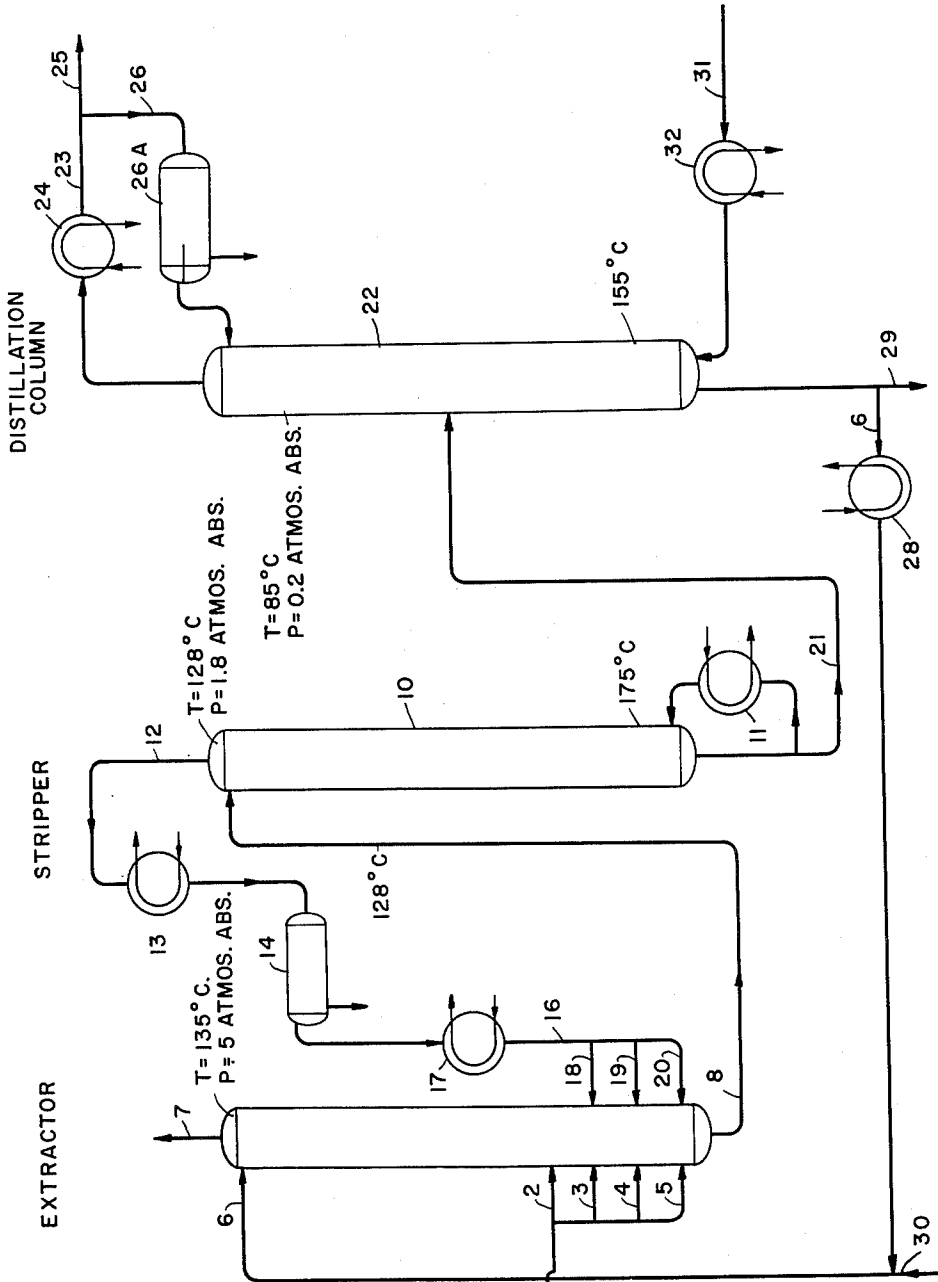
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PROCESS FOR SEPARATING AROMATIC HYDROCARBONS

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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 At the same end a raffinate poor in aromatics and in solvent is withdrawn, while at the other end an aromatic-rich extract phase is withdrawn and introduced into a column which is at a lower pressure than the extractor and wherein only part of the most volatile aromatics, together with non-aromatics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and after condensation are returned as reflux to the extractor at the end from which the aromatic rich extract is withdrawn.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 specification No. 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 invention will be illustrated with reference to the accompanying schematic drawing, wherein the sole FIGURE is a process flow diagram of a preferred embodiment of the improved process.

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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 130 and 155° C.
- (3) The extract-phase from the extraction system should enter the stripping zone with a temperature between 125 and 155° C.
- (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.
- (5) The top temperature in this stripping zone should be between 125 and 155° 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.
- (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.
- (10) The bottom product from the distilling zone should be cooled by at least 15° C. to a temperature between 130 and 155° C. before being reintroduced into the extraction zone.

Thus, according to the present invention there is provided a process for the extraction and recovery of aromatic hydrocarbons from a liquid hydrocarbon mixture containing one or more aromatic hydrocarbons; by introducing the mixture into a counterflow multi-stage extraction system, introducing, at one end of the extraction system a high boiling, aromatic selective solvent having an atmospheric boiling temperature within the range of 225° to 295° C. and containing dissolved water; maintaining the extraction system under pressure sufficient to keep the flowing contents liquid and maintaining the flowing contents at an elevated temperature; withdrawing a raffinate poor in aromatics and in solvent from the same end of the system as that at which the solvent is introduced; withdrawing an aromatic-rich extract phase from the other end of the system, stripping said extract phase in a stripping zone to liberate a mixture of aromatic and non-aromatic hydrocarbons, said stripping being effected at a pressure lower than that prevailing in the extraction system; condensing the so liberated vapors and returning the condensate to the extraction zone; conducting the remainder of the extract phase to a distilling zone operating at a subatmospheric pressure, in which distilling zone separation is effected between hydrocarbons and solvent, with direct steam being introduced into said zone; and returning substantially hydrocarbon-free solvent containing dissolved water to the extraction system. The temperature in the extraction system is maintained between 130 and 155° C.; the solvent supplied to one end of the extraction system contains not more than 2% by weight of water. The extract-phase withdrawn from the extraction system is introduced into the stripping zone at a temperature between 125° C. and 155° C. without the occurrence of appreciable flash vaporization. The stripping

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 zone is operated at a pressure of at least 1.5 atmospheres absolute, at a top temperature between 125° C. and 155° C. and at a bottom temperature of at least 165° C. The vapors from said stripping zone are condensed and recycled to the extraction system after removing substantially all water present as a second liquid phase. The condensed vapors are introduced into the extraction system at the end at which the extract phase is withdrawn and/or at an intermediate point of the extraction zone. The bottom product from the stripping zone is passed to the distilling zone which is maintained at a pressure of less than 0.5 atmospheres absolute and at a bottom temperature of at least 145° C., the bottom temperature being at least 10° C. lower than the bottom temperature in the stripping zone. The bottom stream from the distilling zone is cooled by at least 15° C. to a temperature between 130 and 155° C. and then reintroduced into the extraction system.

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 reforming gasolines, such as hydroformates and platformates, or from fractions thereof. The feed stocks should have an ASTM final boiling point of not higher than 220° C. Preferably the upper cutting point should be not higher than 160° C. When using a reformat 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° C. 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 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 extraction phase end of the system may be useful under specific circumstances.

The stream of hydrocarbons and solvents 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 aromatic-rich extract phase is withdrawn. It is preferred to introduce this stream at or near the end of the system (i.e. at the

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 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 130 and 155° C. 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 introduced in the stripping zone, at or near its top, with a temperature between 125 and 155° C., which implies that there will be no or substantially no intentional cooling of this stream between extraction system and stripping zone.

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. 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 gravimetric 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 125 and 155° C., and the bottom temperature should be at least 165, the difference between top and bottom temperature being at least 40° C. The top product contains substantially all water and non-aromatic hydrocarbons present in the extract phase, and, in addition, some solvent and aromatic hydrocarbons.

In order to substantially reduce or prevent deterioration of the solvent when applying high bottom temperatures in the stripping zone it is generally advisable that the solvent should contain a minor proportion, e.g. between 0.05 and 1% by weight of phenothiazine or of a substituted phenothiazine. The use of these compounds for the purpose referred to is described in greater detail in the copending United States application Serial No. 862,761, of Philip J. Garner, filed December 30, 1959.

The bottom product leaving the stripping zone is passed to the distilling zone operating at a pressure below 0.5 atmospheres, preferably 0.2 atmospheres 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. There should be no or substantially no other cooling of the stream passing from the stripping zone to the distilling zone otherwise than by expansion.

Whereas the stripping zone will be operated without introduction of direct steam near or in the bottom part, direct steam should be introduced into 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.

The bottom product from the distilling zone is cooled by at least 15° C. to a temperature between 130 and 155° before being recycled to the extraction system.

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

Temperature in extraction system.....° C.----- 135  
 Temperature of extract phase on entering stripping zone.....° C.----- 128  
 Top temperature in stripping zone.....° C.----- 128

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Bottom temperature in stripping zone.....° C.....	175
Top temperature in distilling zone.....° C.....	85
Bottom temperature in distilling zone.....° C.....	155
Temperature of bottom stream from distilling zone after cooling.....° C.....	140
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.

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

As a consequence of this essentially different situation the present process has the advantage that a greater proportion of the non-aromatics 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.

A liquid hydrocarbon mixture containing both aromatic and non-aromatic hydrocarbons, is extracted in a multi-stage countercurrent extractor 1, which operates under pressure and at a temperature between 130 and 155° C. For this purpose the feed is introduced into the extractor through one or more of the feed inlet lines 2 to 5, whereas the selective solvent, containing a small amount of dissolved water, is introduced into the extractor 1 at or near its top through line 6.

The raffinate phase, which contains only relatively small amounts of water, solvent and aromatic hydrocarbons, is withdrawn from the top of the extractor 1 through line 7 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 8 and passes through a reducing valve (not shown) to the stripper column 10, the cooled extract phase being introduced at or near the top of the stripper. The pressure in column 10 is at least 1.5 atmospheres, but lower than the pressure in extractor 1.

The stripper 10 is provided with a reboiler 11 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 1, 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 12 to the condenser 13 and the resulting liquid passed to the settler 14, 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 15, whereas the solvent-hydrocarbon layer is passed through line 16 and heater 17, to one or more of the lines 18 to 20, through which it enters the extractor in its lower part.

The bottom product from the stripper is passed through line 21, and reducing valve (not shown) to distilling column 22. In column 22, which operates at subatmospheric pressure, separation is effected into a top product

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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 23, provided with condenser 24 and the condensate is partly withdrawn via line 25, as the aromatic-rich product, and partly passed through line 26 equipped with the settler 26A, 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 column 22. The bottom product from this column is withdrawn through line 27 and returned to the extractor through line 6 after cooling in cooler 28. If desired, part of the bottom product may be withdrawn through line 29 for purification or rejection, and fresh or purified solvent may be introduced through line 30. Distilling column 22 is operated without a reboiler, hot steam being introduced into the bottom of this column via line 31 and heater 32 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.

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 counterflow multi-stage extraction system wherein the temperature is maintained between 130 and 155° 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) withdrawing the extract phase from the extraction system and introducing the said extract phase at a temperature between 125° and 155° C. without appreciable flash vaporization into a stripping zone, which is operated at a pressure of at least 1.5 atmospheres absolute and at a top temperature between 125° C. and 155° C. and at a bottom temperature of at least 165° C. to separate overhead a vapor phase enriched in non-aromatic hydrocarbons; (5) condensing the vapors from said zone and forming a first liquid phase consisting essentially of hydrocarbons along with a second liquid phase and recycling them to the extraction system after removing substantially all water present as the 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; (6) 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 atmospheres 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; and (7) withdrawing the stripped solvent from the distilling zone, cooling said stripped solvent by at least 15° C. to a temperature between 130° and 155° C., and returning the cooled solvent to the extraction system.

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.

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6. A process according to claim 1 in which the condensed vapors substantially free from water are introduced near that end of the extraction system at which the extract phase is withdrawn.

7. A process according to claim 1 in which the extract phase is introduced in the stripping zone near the top of said zone. 5

8. 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

9. A process according to claim 8 in which no vapors are present in the extract phase on entering the stripping zone.

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