

# PATENT SPECIFICATION

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## (54) PROCESS FOR SEPARATING HIGH PURITY AROMATIC HYDROCARBONS FROM MIXTURES CONTAINING THEM

(71) We, SNAMPROGETTI S.P.A., formerly SNAM PROGETTI S.P.A., an Italian Company, of Corso Venezia, 16, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a process for separating one or more aromatic hydrocarbons from mixtures containing the same and at least one non-aromatic hydrocarbon. More particularly, the present invention relates to the separation of aromatic hydrocarbons from mixtures containing the aromatic hydrocarbons at high concentrations.

According to the present invention, there is provided a process for recovering at least one aromatic hydrocarbon from a feed mixture of at least one aromatic hydrocarbon and at least one non-aromatic hydrocarbon, in which the total concentration of the aromatic hydrocarbon(s) is at least 80% by weight, which process comprises the following steps:—

(a) subjecting the feed mixture to extractive distillation in a first zone at a temperature in the range from 50 to 200° C in the presence of a solvent mixture of water and an organic solvent, in order to separate, as overhead products, non-aromatic hydrocarbon(s) and water and, as bottom products, the purified aromatic hydrocarbon(s) and a mixture of the organic solvent and water;

(b) rectifying in a second zone the bottom products from step (a), in order to separate, as second overhead products, aromatic hydrocarbon(s) and water and, as a bottom product, the said solvent mixture;

(c) recycling to the first zone the solvent mixture of step (b); and

(d) condensing and separating the overhead products of step (a), and recycling all

or substantially all of the separated water and a portion of the separated non-aromatic hydrocarbon(s) to the first zone at one or more points above the points at which feed mixture and the solvent mixture are fed to the first zone.

The feed mixture is introduced preferably halfway up an extractive distillation column working at a temperature of from 50 to 200° C in the presence of the solvent mixture; the non-aromatic hydrocarbons are discharged from the column top while the aromatic hydrocarbons, free from non-aromatic hydrocarbons, and the organic solvent and water are obtained from the bottom.

The bottom product of the extractive distillation is then fed to a rectification column for the separation of the solvent mixture, obtaining from the top of the rectification, high purity aromatic hydrocarbons.

The extractive distillation and rectification can be carried out in two separate columns; alternatively, they can be carried out in an upper portion and a lower portion, respectively, of the same column.

The solvent mixture is preferably fed some plates beneath the top of the extractive distillation zone or column, and at least a portion of the reflux is in the form of an external reflux because in such a case the overhead product does not contain solvent and does not require further treatments.

The external reflux is constituted by water and a portion of the non-aromatic hydrocarbon.

In the rectification zone or column there is preferably a reflux constituted by water obtained by separating into two phases the aromatic-containing stream; moreover, a portion of the same water is preferably sent to the bottom of the column, after vaporization at the expense of the hot solvent

mixture leaving the rectification column or zone.

The solvent mixture (of organic solvent and water) can be any one of those known in the art; use can be made also of mixtures of various organic solvents; preferably the organic solvent is selected from morpholine and aldehydic, ketonic and alkyl derivatives of morpholine, such as N-formyl morpholine, 2-formyl morpholine, 3-formyl morpholine and morpholine acetone.

By working with a solvent mixture containing water at a concentration of from 0.5 to 25% by weight, it is possible to obtain the following advantages:

- (1) the aromatics are substantially completely recovered regardless of their molecular weight;
- (2) the temperature at the bottom of the extractive distillation column is at such levels that medium or low pressure steam can easily be used as a heating means, the column top being at atmospheric pressure; and
- (3) the heat consumption, for a given aromatic recovery, is lower than when an anhydrous solvent is employed; the amount of heat to be recovered is small and it is therefore possible to recover the same with apparatuses of small dimensions.

For a better understanding of the present invention and to show how the same may be carried into effect, reference will now be made, by way of example, to the accompanying drawings in which:

Figure 1 illustrates a plant suitable for carrying out the process of the present invention; and

Figure 2 illustrates another plant suitable for carrying out the process of the present invention.

Referring firstly to Figure 1, there is shown a plant which includes a pipe 1 for introducing a feed mixture into an extractive distillation column 2. Higher up the column 2 than the pipe 1 is a pipe 19 for introducing a solvent mixture of water and an organic solvent into the column 2. At the head of the column 2 is a pipe 3 through which can be withdrawn non-aromatic hydrocarbons and water, and which leads to a heat exchanger 4 for condensing the stream in the pipe 3.

Downstream of the heat exchanger 4 is a separator 5 for separating the condensed products into two phases. The non-aromatic hydrocarbon phase is discharged through a pipe 6, and a portion of this phase is recycled to the head of the column 2 through a pipe 7. The condensed aqueous phase is conveyed through the pipe 8 to the pipe 7 and is recycled completely to the column 2.

At the foot of the column 2 is a pipe 9 for conducting the bottom product (of

aromatic hydrocarbons and solvent mixture) via a heat exchanger 10 (where heat is recovered) to a solvent separation column

11. Water in the vapour phase is introduced into the column 11 through a pipe 16.

At the head of the column 11 is a pipe 20 through which the overhead product (of aromatic hydrocarbons and water) is conveyed to a heat exchanger 12 in which the overhead product is condensed. Downstream of the heat exchanger 12 is a separator 13 where the condensed products separate into two phases. The aromatic hydrocarbon phase is discharged through a pipe 14.

Some of the water in the lower region of the separator 13 is recycled in the liquid state to the head of the column 11 through a pipe 15; and another portion of the water is conveyed through a pipe 21 to a heat exchanger 18 where it is vaporized; the resulting water vapour is re-introduced into the column 11 via the pipe 16.

At the bottom of the column 11 is a pipe 17 through which the solvent mixture is passed to the heat exchanger 18 and from there via the pipe 19 to the heat exchanger 10 and the column 2.

A different plant is shown in Figure 2. This plant includes a pipe 33 for introducing feed into an extractive distillation column 31 at a point one third of the way down the column 31, which has a plurality of plates. A few plates below the top of the column 31 is a pipe 32 for introducing the solvent mixture into the column 31.

Approximately one third of the way up the column 31 is a pipe 34 for conveying a high purity aromatic hydrocarbon stream (containing some water) in the vapour phase to a scrubbing column 39; any organic solvent in the stream is removed by scrubbing in the column 39 in the vapour phase in countercurrent with water. The water necessary for the scrubbing is introduced into the column 39 through a pipe 40. The overheads of the column 39 are conveyed in a pipe 43 to a heat exchanger 44 where they are condensed. Downstream of the heat exchanger 44 is a separator 45 where the aromatic phase is above the aqueous phase. The aromatic phase is withdrawn through a pipe 38. The aqueous phase is recycled through the pipe 40.

Water is conveyed from the bottom of column 39 in a pipe 41 to a heat exchanger 42, where it is vaporized; the water in the vapour phase is recycled to the column 31 via the pipe 46.

Lean solvent mixture leaves the bottom of column 31 in a pipe 47 which passes through the heat exchanger 42 where it heats and vaporizes the water in the pipe 41. The cooled lean solvent mixture is then recycled to the column 31 in the pipe 32.

At the head of the column 31 is a pipe 48 for conveying the overhead product (non-aromatic hydrocarbons and water) to a heat exchanger 49 where the overhead product is condensed. The condensed product is separated in a separator 50. Part of the non-aromatic hydrocarbon phase is discharged through a pipe 37 and another part is recycled to the top of the column 31 through a pipe 36. All of the aqueous phase is recycled through a pipe 35 to the top of the column 31.

The following Examples illustrate the present invention.

#### EXAMPLE 1

The process of this example was carried out in a plant as shown in Figure 1. There was used an artificial feed constituted by:

|                   |               |
|-------------------|---------------|
| benzene           | 95% by weight |
| <i>n</i> -heptane | 5% " "        |

To the column 2 having 45 plates with a single bubble cap of the stage type was fed:—

on the 20th plate from the bottom 1 kg/h (kilogram per hour) of feed; and

on the 40th plate from the bottom *N*-formyl morpholine as organic solvent with 6% water, at a flow rate of 2.50 kg/h; the temperature of the solvent mixture was maintained equal to that of the feed plate (98°C) in order to avoid an internal reflux.

The distillate in pipe 3 was constituted by *n*-heptane with 2% of benzene and about 10% of water: to the 45th plate of column 2 were refluxed 0.050 kg/h of hydrocarbon in pipe 7 and all the 0.010 kg/h of water obtained in the distillate.

In the distillate the organic solvent was not analytically detectable; the temperature at the bottom of the column 2 was 115°C.

As bottom product, there was obtained a mixture of solvent mixture and benzene which was fed to the 20th plate from the bottom of the second column 11 having 30 plates with a single bubble cap of the stage type; from the top of column 11 were obtained 0.949 kg/h of benzene and 0.1 kg of water; the latter was completely refluxed. The bottom temperature of column 11 was 145°C.

Benzene obtained in this way contained less than 200 ppm of *n*-heptane and the solvent content was below the analytically detectable value.

Because of the high temperature difference between the two column bottoms it was convenient to exchange heat between the feed for the second column and the bottom product of the second column, reducing in this way the heat consumption in the second column. The lean solvent mixture in pipe 19 was cooled from 145°C to 120°C in the

heat exchanger and from 120°C to 98°C by cooling with water.

#### EXAMPLE 2

The process was carried out in a plant as shown in Figure 1 of the drawings, with the extractive distillation carried out at a temperature in the range from 50 to 200°C. There was used an artificial feed constituted by:

|         |               |
|---------|---------------|
| benzene | 70% by weight |
| toluene | 20% " "       |
| xylene  | 5% " "        |

non-aromatic hydrocarbons 5% " "

For the first column there were used the same amounts as in the preceding example, except that the solvent mixture contained 4% water.

From the top of the second column there was obtained 0.699 kg/h of benzene, 0.199 kg/h of toluene and 0.045 kg/h of xylene, together with 0.200 kg/h of water; 0.100 kg of water were refluxed and 0.100 kg were subjected to heat exchange with the solvent from the column bottom in order to produce a stripping stream, thereby lowering the solvent mixture temperature to 115°C; the solvent mixture was fed to near the top of the first column.

#### WHAT WE CLAIM IS:—

1. A process for recovering at least one aromatic hydrocarbon from a feed mixture of at least one aromatic hydrocarbon and at least one non-aromatic hydrocarbon, in which the total concentration of the aromatic hydrocarbon(s) is at least 80% by weight, which process comprises the following steps:—

(a) subjecting the feed mixture to extractive distillation in a first zone at a temperature in the range from 50 to 200°C in the presence of a solvent mixture of water and an organic solvent, in order to separate, as overhead products, non-aromatic hydrocarbon(s) and water and, as bottom products, the purified aromatic hydrocarbon(s) and a mixture of the organic solvent and water;

(b) rectifying in a second zone the bottom products from step (a), in order to separate, as second overhead products, aromatic hydrocarbon(s) and water and, as a bottom product, the said solvent mixture;

(c) recycling to the first zone the solvent mixture of step (b); and

(d) condensing and separating the overhead products of step (a), and recycling all or substantially all of the separated water and a portion of the separated non-aromatic hydrocarbon(s) to the first zone at one or more points above the points at which feed mixture and the solvent mixture are

At the head of the column 31 is a pipe 48 for conveying the overhead product (non-aromatic hydrocarbons and water) to a heat exchanger 49 where the overhead product is condensed. The condensed product is separated in a separator 50. Part of the non-aromatic hydrocarbon phase is discharged through a pipe 37 and another part is recycled to the top of the column 31 through a pipe 36. All of the aqueous phase is recycled through a pipe 35 to the top of the column 31.

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(b) rectifying in a second zone the bottom products from step (a), in order to separate, as second overhead products, aromatic hydrocarbon(s) and water and, as a bottom product, the said solvent mixture;

(c) recycling to the first zone the solvent mixture of step (b); and

(d) condensing and separating the overhead products of step (a), and recycling all or substantially all of the separated water and a portion of the separated non-aromatic hydrocarbon(s) to the first zone at one or more points above the points at which feed mixture and the solvent mixture are



fed to the first zone.

2. A process according to claim 1, wherein the second overhead products of step (b) are condensed and separated, and a portion of the thus separated water is recycled to the second zone at a point above that at which the bottoms product from step (a) is fed to the second zone, and another portion of the thus separated water is vaporized and then recycled to the second zone at a point below that at which the bottoms product from step (a) is fed to the second zone.

3. A process according to claim 2, wherein the water is vaporized by heat taken from the solvent mixture being recycled to the extractive distillation.

4. A process according to any preceding claim, wherein the organic solvent is selected from morpholine and the aldehydic, ketonic and alkyl derivatives of morpholine.

5. A process according to claim 4, wherein the organic solvent is selected from N-formyl morpholine, 2-formyl morpholine, 3-formyl morpholine and morpholine acetone.

6. A process according to any preceding claim, wherein the concentration of water in the solvent mixture is in the range from

0.5 to 25% by weight.

7. A process according to claim 1, substantially as hereinbefore described with reference to Figure 1 of the accompanying drawings.

8. A process according to claim 1, substantially as hereinbefore described with reference to Figure 2 of the accompanying drawings.

9. A process according to claim 1 substantially as described in either of the foregoing Examples.

10. An aromatic hydrocarbon whenever recovered by a process according to any preceding claim.

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