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# SEPARATION OF HYDROCARBONS

Harry Clough and John Allan Smith, Norton-on-Tees, England, assignors to Imperial Chemical Industries Limited, a corporation of Great Britain

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This invention relates to the separation of hydrocarbons.

It is known broadly to separate aromatic hydrocarbons from non-aromatic hydrocarbons by extractive distillation using various solvents such as anilines and phenols.

It is commonly desired to separate fractions having an increased xylene and a reduced ethyl benzene content from complex mixtures of xylenes with ethyl benzenes and aliphatic and/or naphthenic hydrocarbons, but this has been found to be difficult. The boiling points at atmospheric pressure of ethyl benzene, o-xylene, m-xylene and p-xylene, lie within a relatively narrow temperature range. The application of fractional distillation, azeotropic distillation or extractive distillation to the aforesaid complex mixtures has not previously been found to give altogether satisfactory results from the aspects of efficiency and economy, and this no doubt is largely attributable to the proximity of the boiling points and the similarity in chemical properties, of the components.

It is important to be able to separate m- and p-xylenes from ethyl benzene in order to provide a suitable feedstock for isomerisation of the xylenes, a process of growing importance for the production of p-xylene. The presence of ethyl benzene in such feedstock results in degradation, reduces the total output of the isomerisation unit, leads to the production of impure xylenes, and, if it is desired to separate the xylenes inter se, interferes with that separation. Moreover, separation of the ethyl benzene is additionally advantageous since it is a valuable intermediate for the production of styrene. The present invention provides an efficient process for obtaining an aromatic fraction enriched in xylenes and impoverished in ethyl benzene from hydrocarbons containing non-aromatics, ethyl benzene and xylenes.

According to the present invention there is provided a process for the production of a fraction having an increased xylene content and an increased weight ratio xylenes:ethyl benzene, and of a fraction having an increased weight ratio ethyl benzene:xylenes, from mixtures comprising ethyl benzene, xylenes and aliphatic and/or naphthenic saturated hydrocarbons which comprises subjecting the mixture to extractive distillation with a polar solvent having a boiling point at least 50° C. higher than that of o-xylene, taking off as overhead product a fraction containing substantially all the non-aromatic hydrocarbons and only a minor proportion of xylenes, and as bottom product a solution of aromatic hydrocarbons substantially free from non-aromatics and having an increased xylene content and an increased weight ratio, xylenes:ethyl benzene.

It is preferred that the percentage by weight of xylenes in the overhead fraction from the extractive column be kept as low as possible, and in any case it should not exceed 10%, and preferably should not exceed 5%.

Examples of suitable polar solvents are alkyl phenols,



alkyl anilines, nitro-aromatic hydrocarbons, and polyhydric alcohols and alkyl esters thereof.

The preferred polar solvent is a phenol cut boiling within the range 215°–255° C.

The process may be conducted in the usual types of column, viz. bubble cap or sieve plate or one provided with packing e. g. Raschig rings.

A convenient method of operation is to employ two columns, of which the first is employed in extractive distillation and the second in stripping. The solvent is introduced near the top of the extractive distillation column, the feed at a point below this, a mixture of non-aromatic hydrocarbons and ethyl benzene containing a small amount of xylenes is taken off as overheads, and a solution of xylenes in solvent as bottoms. This last mentioned solution is delivered to the stripping column, in which mixed xylenes are taken off as overhead, and the solvent is obtained as bottoms and returned to the extractive distillation column. There is a reflux of overheads to the extractive column to scrub out solvent from the vapours, and a reflux of bottoms to the extractive column to scrub out non-aromatics from the liquid product. In order to increase the concentration of xylenes in the bottom product it is desirable to permit a minor proportion of xylene to remain in the overhead.

It is convenient to operate both columns at atmospheric pressure, but reduced or elevated pressure may also be used.

An advantage connected with the use as solvent of the aforesaid phenol cut boiling within the range 215°–255° C. is that it makes possible an improved separation of p- and m-xylenes from ethyl benzene, which is surprising since the boiling points at atmospheric pressure of the three compounds are very close, being 138.5, 138.8 and 136.2° C., respectively. Other advantages attending the use of this solvent are: it does not azeotrope to a serious degree with any of the components of the aforesaid type of hydrocarbon mixture; it is non-corrosive; the toxic hazard with it is low; it is stable; its cost is low; and it can be easily recovered in a sufficiently pure condition for recycling.

The following table illustrates the low azeotroping power of this solvent as compared with other solvents that have been examined. The method of test was to fractionate synthetic mixtures of solvent (i) with non-aromatics and (ii) with aromatics and determine the composition of the overhead product:

| Solvent | (i) Azeotrope with non-aromatic hydrocarbons | (ii) Azeotrope with aromatic hydrocarbons |
|---|---|---|
| Phenol | Azeotrope containing about 8.5% phenol. | Azeotrope containing about 5.5% phenol. |
| metacresylic acid | Azeotrope containing about 3% cresols. | Azeotrope containing 0.7% cresols. |
| 230–250° C. cut of tar acids. | Azeotrope containing about 1% tar acids. | No azeotrope is formed. |

It is preferred to use a phenol cut of the aforesaid boiling range which contains at most only a small proportion, preferably 10% by weight at most, of compounds in which both the 2- and 6-positions relative to the hydroxy group are occupied by alkyl radicles.

The invention is illustrated by the following examples in which the preferred solvent, a phenol cut boiling within the range 215°–255° C. at atmospheric pressure, was employed.

The advantages of the process of the present invention over methods employing azeotropic distillation are that for a given throughput: fewer stills and less equipment are needed; the heat consumption is considerably less;

the product is purer; the solvent is cheaper; and operation is simpler and easier.

The concentration of non-aromatic hydrocarbons is determined chromatographically, and of xylenes by infra red spectroscopy.

## EXAMPLE 1

The mixture of hydrocarbons to be treated had the following composition.

| | Percent by weight |
|---|---|
| p-Xylene | [1] 7.0 |
| m-Xylene | [1] 16.4 |
| o-Xylene | [1] 2.9 |
| Ethyl benzene | 7.0 |
| Non-aromatics | 66.7 |

[1] Xylenes : ethyl benzene = 3.8 : 1.

The non-aromatics contained about 30% by weight of naphthenes.

The extractive distillation column was 53 inches long by 1 inch internal diameter, was packed with 1/16 inch stainless steel gauze ferrules, and in hydrocarbon fractionation had an efficiency equal to 53 theoretical plates.

A phenol cut having the following boiling characteristics as determined by Stanard Methods for Testing Tar and its Products published by the Standardisation of Tar Products Tests Committee:

| | ° C. |
|---|---|
| Initial boiling point | 218.5 |
| 95% had distilled at | 245.5 |

was fed at a rate of 283 grams per hour to the extractive distillation column at a point 7½" below the top of the column, and the aforesaid hydrocarbon mixture at a point 31½" below the top of the column at a rate of 67.9 grams per hour.

A mixture having the composition:

| | Percent by weight |
|---|---|
| Non-aromatics | 89.00 |
| Ethyl benzene | 5.54 |
| Xylenes (total) | 5.46 |
| p-Xylene | 2.42 |
| m-Xylene | 3.04 |

was taken off as overheads at the rate of 50.8 grams per hour; and a phenol solution of xylene concentrate together with a small proportion of non-aromatics and a reduced content of ethyl benzene having the relative composition:

| | Percent by weight |
|---|---|
| o-Xylene | [1] 14.0 |
| m-Xylene | [1] 55.8 |
| p-Xylene | [1] 20.0 |
| Ethyl benzene | 10.0 |
| Non-aromatics | 0.2 |

[1] Xylenes : ethyl benzene = 9 : 1.

was taken off as bottoms. The column was run under the following equilibrium conditions:

| | ° C. |
|---|---|
| Still head temperature | 130 |
| Phenols inlet temperature | 148 |
| Hydrocarbon inlet temperature | 131 |
| Boiler temperature | 208 |

Approximately 84.5% by weight of the xylenes present in the original mixture was recovered in the bottom product.

These data show that operating as described it is possible to obtain overhead a fraction enriched in ethyl benzene, and as bottoms a solution of aromatics in phenol substantially free from non-aromatics and showing an increased content of xylenes, and a lower ethyl benzene: xylenes ratio. It is a simple matter to treat the bottoms in a stripping column and obtain as overhead a xylene mixture having only small amounts of non-aromatics and a lower ethyl benzene:xylenes ratio than the starting material. The use of the aforesaid phenol cut as solvent in the extractive distillation facilitates the separation.

In this extractive distillation, the ratio of ethyl benzene to p-xylene has been raised from 50:50 in the feed to 70:30 in the distillate. The normal relative volatility of ethylbenzene with respect to p-xylene is 1.07 and the above degree of separation would have required a reflux ratio of over 10:1 even with an infinite number of plates. In the presence of the solvent and the non-aromatics, however, the separation was in fact achieved in a length of column corresponding to 24 theoretical plates at a reflux ratio of less than 5. This means that the effective relative volatility of ethyl benzene to p-xylene must have been increased to at least 1.25.

A similar enhancement of relative volatility was obtained in the extractive distillation of the same initial mixture using the same phenol cut in a 56 inches long by 1.25 inches internal diameter column packed with 1/8 inch gauze rings. Here operation at a 2:1 reflux ratio gave an overhead product having an aromatic hydrocarbon content of which 70% by weight was ethyl benzene, a concentration which, in the absence of the added polar solvent, could have been achieved only by the use of reflux ratios greater than 10:1 and of a very much longer column. The benefits in heat economy are evident.

## EXAMPLE 2

A similar extractive distillation was carried out on a hydrocarbon mixture having the following composition:

| | Percent by weight |
|---|---|
| p-Xylene | [1] 4.3 |
| m-Xylene | [1] 8.6 |
| o-Xylene | [1] 6.9 |
| Ethyl benzene | 4.1 |
| Non-aromatics | 76.1 |

[1] Xylenes : ethyl benzene = 4.8 : 1.

The extractive distillation column was 56 inches long by 1.25 inches internal diameter, was packed with 1/8" stainless steel gauge ferrules and in hydrocarbon fractionation had an efficiency of 36 theoretical plates. The characteristics of the extractive solvent were:

Initial boiling point, 221° C.
95% had distilled at 250° C.

The extractive distillation column was operated so that 83% by weight of the feed was taken off overhead, the still head temperature being 134° C., the boiler temperature 211° C., and the feed inlet and solvent inlet temperatures 118° C. and 150° C. respectively.

The compositions of the hydrocarbons taken off from the extractive column as overheads, and, as bottoms, in solution in phenol, were respectively:

*Overhead fraction*

| | Percent by weight |
|---|---|
| Non-aromatics | 91.1 |
| Ethyl benzene | 3.2 |
| Xylenes (total) | 5.7 |
| p-Xylene | 2.0 |
| m-Xylene | 3.4 |
| o-Xylene | 0.3 |

*Bottom fraction*

| | Percent by weight |
|---|---|
| o-Xylene | [1] 33.8 |
| m-Xylene | [1] 36.7 |
| p-Xylene | [1] 15.5 |
| Ethyl benzene | 6.7 |
| Non-aromatics | 7.3 |

[1] Xylenes : ethyl benzene = 12.8 : 1.

Approximately 78% by weight of the xylenes present in the original mixture was recovered in the bottom product. The lower recovery of xylenes is attributable to the leanness in xylenes of the starting material.

EXAMPLE 3

A similar extractive distillation was carried out employing the same column and extractive solvent as in Example 2, on a hydrocarbon mixture having the composition:

| | Percent by weight |
|---|---|
| p-Xylene | [1] 6.6 |
| m-Xylene | [1] 12.0 |
| o-Xylene | [1] 12.0 |
| Ethyl benzene | 10.0 |
| Non-aromatics | 59.4 |

[1] Xylenes : ethyl benzene=3.1 : 1.

The compositions of the hydrocarbons taken off from the extractive column as overheads and, as bottoms, in solution in phenol, were respectively as follows:

*Overhead fraction*

| | Percent by weight |
|---|---|
| Non-aromatics | 87.7 |
| Ethyl benzene | 7.1 |
| Xylenes (total) | 5.2 |
| p-Xylene | 1.9 |
| m-Xylene | 3.0 |
| o-Xylene | 0.3 |

*Bottom fraction*

| | Percent by weight |
|---|---|
| o-Xylene | [1] 34.0 |
| m-Xylene | [1] 32.0 |
| p-Xylene | [1] 16.0 |
| Ethyl benzene | 15.0 |
| Non-aromatics | 3.0 |

[1] Xylenes : ethyl benzene=5.5 : 1.

The column was operated so that 61.7% by weight of the feed was taken overhead, the still head temperature being 134°, the boiler temperature 194°, and the feed inlet and solvent inlet temperatures 118° C. and 150° C. respectively.

Approximately 85% of the xylenes present in the original mixture was recovered in the bottom product.

The invention is of particular value in its application to complex hydrocarbon mixtures of the specified type boiling between 125° and 155° C.

Preferably, because more effective separation results, the starting material should contain at least 40%, and more preferably at least 60%, by weight of non-aromatic hydrocarbons. The invention is applicable with considerable advantage to such mixtures in which the proportion of ethyl benzene amounts to from 5 to 30% by weight of the total xylenes, since thereby more valuable ethyl benzene and xylene concentrates are obtained. Preferably, for similar reasons, the xylene content of the starting material should not be less than 5% by weight, and more preferably not less than 20% by weight thereof.



The invention may also be applied to hydrocarbon mixtures which are deficient in saturated aliphatic and/or naphthenic hydrocarbons by making up the deficiency by the addition of saturated aliphatic and/or naphthenic hydrocarbons before applying the extractive distillation.

We claim:

1. Process for the production of a fraction with an increased xylene content and an increased weight ratio of xylene:ethyl benzene and a fraction with an increased ethyl benzene:xylene weight ratio from feed mixtures containing ethyl benzene, xylenes and at least one non-aromatic hydrocarbon selected from the group of saturated hydrocarbons consisting of aliphatic and naphthenic hydrocarbons, characterized in that said feed mixture contains at least 40% of non-aromatic hydrocarbons, which comprises subjecting said feed mixture to extractive distillation with an excess of a substituted mono-hydroxy phenol cut having a boiling point within the range of from 215° to 255° C. at atmospheric pressure and containing not more than 10% by weight of phenols in which the 2- and 6-positions, relative to the hydroxy group, are occupied by alkyl radicals, and taking off as overhead product a fraction containing substantially all of said non-aromatic hydrocarbons, a major proportion of said ethyl benzene and only a minor proportion of xylenes, and as bottom product a solution of aromatic hydrocarbons substantially free from said non-aromatic hydrocarbons and comprising the major proportion of said xylenes and only a minor proportion of said ethyl benzene, so that said bottom product has a substantially increased weight ratio of xylenes:ethyl benzene relative to the ratio in said feed mixture.

2. A process as claimed in claim 1 in which the non-aromatic content by weight of the starting material is less than 40% and prior to the extractive distillation there is introduced there into sufficient non-aromatic hydrocarbon to raise the non-aromatic content by weight to at least 40% by weight of the resulting mixture.

3. The process of claim 1 wherein said minor proportion of xylene in said overhead product is maintained below about 5%.

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