ABSTRACT OF THE DISCLOSURE

Extractive distillation process for simultaneously obtaining different aromatics with different boiling point ranges from a feedstock containing varied amounts of aromatics along with the desired aromatic compounds comprising in combination:

(a) Passing the feed stock through at least two extraction-distillation columns arranged in series after introducing the stock at a place in proximity to the vertical center of each column;

(b) Contacting the feed stock in each of said extractive distillation columns with an at least partially non-aromatic selectively active extraction agent containing aromatics other than the aromatics to be recovered, the said extraction agent being passed through the column from the top downwards;

(c) Each of said subsequent extraction-distillation columns being operated at a reduced pressure relative to the previous column;

(d) Withdrawing a mixture of aromatics and extraction agent from the bottoms of the said columns while withdrawing the nonaromatics in vapor form through the top of the columns;

(e) Then passing the said mixture of aromatics and extraction agent from the last extraction distillation column through a plurality of stripper columns arranged in series, one stripper column being provided for each desired type of aromatic;

(f) Withdrawing the aromatics to be recovered from the respective stripper columns at or in proximity to the top of the stripper column and withdrawing a nonaromatics containing product from a place above the place of introduction of the said mixture.

This invention relates to an extractive-distillation method which can be used mainly for the simultaneous extraction of aromatic substances of different boiling points from feedstocks that contain non-aromatic substances in addition to such aromatic substances.

The use of extractive-distillation for the extraction of pure aromatic substances from a feedstock mixture that also contains nonaromatic hydrocarbons has been disclosed in German DAS 1,206,414. According to the method disclosed therein, the feedstock is fed approximately in to the middle of an extractive-distillation column and thus brought into contact with an extraction agent which flows from top to bottom of the column and has a selective action on the aromatic substances, the aromatic substances being drawn off from the base of the column together with the extraction agent and being separated from each other and the extraction agent by subsequently distillation, while the non-aromatic substances are drawn off from the top of the column in the form of vapour.

This method has many advantages over liquid-liquid extraction. The following may be mentioned as examples: the omission of equipment for the recovery of the extractive distillation agent from the refined product, and the omission of large-scale mechanical equipment, such as a large number of circulating pumps and similar items. In addition, the viscosity of the extraction agent is greatly reduced in the extractive-distillation as a result of the fairly high temperatures used, so that the exchange of material between the extraction agent and the feedstock is substantially improved. This results in a better utilization of extraction agent so that smaller quantities of extraction agent can be used for a given yield. The dimensions of the extractor can also usually be reduced. The latter two measures thus also reduce the cost of extractive-distillation in comparison with liquid-liquid extraction.

Unfortunately, however, extractive-distillation has two disadvantages in comparison with liquid-liquid extraction. Firstly, the refined product of extractive-distillation installations sometimes contains very high proportions of extraction agent. Secondly, the extraction of extraction-product "cuts" having fairly wide boiling ranges by extractive-distillation is expensive.

Investigations have shown that, particularly in the case of extractive-distillation used for the separation of aromatic and nonaromatic substances, aromatic substances may appear in the refined product (paraffin fraction) in addition to the desired paraffins, even if extraction agents free from aromatic substances are used. Thus, for example, when propylene carbonate was used as an extraction agent, benzene contents of 10 to 30% by weight were found in the refined product phase, depending on the operating conditions. This high aromatic content of the refined product (paraffin fraction) is equivalent to an uneconomically low yield, particularly in the case of low aromatic contents in the feedstock. Extractive-distillation has therefore hitherto been used in practice only for feedstocks having a nonaromatic content of up to about 20% by weight, since the above-described disadvantages have no significance in these cases, or extractive-distillation has been carried out in combination with liquid-liquid extraction.

Investigations have now shown that the reason for the above-mentioned aromatic content in the refined product (paraffin fraction) is that two liquid layers form on the uppermost trays of extractive-distillation column, that is to say concentration conditions occur here so as to form a system with a miscibility gap.

The object of the invention is to obviate the disadvantages described; it is intended that the method developed should be suitable in particular for the simultaneous extraction of aromatic substances of different boiling points.

The method according to the invention for extractive-distillation is characterised in that the following features of the method are used individually or in combination:

(a) The extraction agent contains aromatic substances that are not to be extracted from the feedstock;

(b) Two or more extractive-distillation columns are installed one behind the other in series, the downstream extractive-distillation column(s) being operated at a reduced pressure in relation to the pressure of the preceding column(s);

(c) On the extraction-agent side, a number of stripping columns corresponding to the aromatic fractions to be extracted are installed behind each other in series, the aromatic substances (extracts) being drawn off from the top or some trays below the top and a product containing nonaromatic substances (refined product) being drawn off from the tray above the feedstock tray.
for example, may be added to the extraction agent in extractive-distillation in which benzene and xylene are to be extracted. Xylene or C₆ aromatic substances, which, for example, are not wanted extracts may be added to the extraction agent in an installation in which benzene is to be extracted from a feedstock. The proportion of the aromatic substances added to the extraction agent may be up to 20% by volume in relation to the extraction agent.

The proportion of the aromatic substances needed to be added to the extraction agent depends on the pressure at which extractive-distillation is carried out. The rule is that this addition can be correspondingly reduced as the operating pressure is increased above atmospheric. Such an addition may be made quite superficially by an appropriately high operating pressure.

The increase in the operating pressure of a first extractive-distillation column causes an increase in the solubility of the nonaromatic substances in the extraction agent. This measure somewhat impairs the selectivity of the extraction agent. But the resulting disadvantages can be compensated for by freeing the mixture of extraction agent and nonaromatic substances from the nonaromatic substances that are particularly difficult to remove in a downstream extractive-distillation column operated at a lower pressure (normal), or reduced pressure, that is, by the adoption of feature (b); thus features (a) and (b) are complementary and either may be employed individually, or both together.

According to the feature (c) of the method, the extraction of the individual extract products takes place in columns allotted to each pure-extract product. The nonaromatic substances that are difficult to separate and may still be present in the extract are withdrawn, according to the invention, from the tray above the feeding tray. Any low-boiling aromatic substances that may be present in this product can be stripped in a stripper.

For the substantial recovery of any portions of aromatic substances and extraction agent still present in the base products of this stripper, these products can be treated with distilled-off extraction agent, either together in a common small extraction-distillation column or in columns allocated to each product. If the various stripper-base products are treated in individual extractive-distillation processes, the losses of each of the aromatic substances treated may be kept as low as desired. If common extractive-distillation is used for all the stripper run-offs, only the losses of the highest-boiling aromatic substances can be kept as low as desired. The choice between these two possibilities should be made with a view to the economic and operational circumstances. The stripper run-offs may, of course, also be worked up by means of normal distillation instead of extractive-distillation.

The solubility of extraction agents in the condensate of the nonaromatic fraction (refined product) may sometimes be impaired by the addition of aromatic substances to the extraction agent. Some losses of extraction agent may then occur. But these can be easily avoided by not adding directly to the extraction agent a small part of the high-boiling aromatic additives to that agent, but by introducing these as a washing agent into the extractive-distillation column above the extraction-agent feeding point. These aromatic substances then cause the extraction agent to be washed out of the nonaromatic substances in the form of vapour.

Finally, it should be pointed out that the method of the invention is not bound to be a certain extraction agent, provided that the agent has a sufficient degree of selectivity for the separation of the aromatic substances. The method of the invention can also be used for the separation of any classes of substance with any desired extraction agents, if the attainable purity of the top product of the extractive-distillation is restricted by a miscibility gap.

The invention will be further explained with reference to the accompanying drawing which shows a flow-diagram of the basic equipment typically used in practice of the method, necessary equipment that is of only secondary importance for the implementation of the method such as boilers, condensers, heat-exchangers, pumps or valves being omitted from the drawing.

The equipment illustrated is that appropriate to refining of a feedstock comprising a hydrocarbon mixture of the following composition by weight.

<table>
<thead>
<tr>
<th>Parts</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonaromatic substances</td>
<td>500</td>
</tr>
<tr>
<td>Benzene</td>
<td>290</td>
</tr>
<tr>
<td>Toluene</td>
<td>140</td>
</tr>
<tr>
<td>Xylene</td>
<td>70</td>
</tr>
</tbody>
</table>

For the purposes of this description it will be assumed that 1000 kg. of such feedstock is to be refined in unit time (e.g., per hour) and the amounts of materials quoted are those used or obtained in the same time unit.

The extraction agent used is 350 kg. of propylene carbonate with which 350 kg. of C₆ aromatic substances have been admixed, so that the total quantity of the circulating extraction agent is 3500 kg.

The feedstock is introduced on to a middle tray of a first extractive-distillation column 2, which is operating at a pressure of about 3.5 atmospheres, through pipe 1, 2000 kg. of the extraction-agent mixture is fed through a pipe 3 to one of the upper trays of the column 2, 450 kg. of nonaromatic substances escape from the top of the column through a pipe 4 in the form of vapour, and are fed into a collecting pipe 5.

The base product of the column 2, which contains the aromatic substances and the extraction-agent mixture in addition to a small residue of nonaromatic substances, is pumped through a pipe 6 into a second extractive-distillation column 7, which is operating at normal atmospheric pressure.

The base product is introduced on to one of the middle trays of the column 7, 1000 kg. of the extraction-agent mixture are fed through a pipe 8 on to one of the upper trays of the column 7 and 30 kg. of nonaromatic substances escape from the top of the column through a pipe 9 in the form of vapour and are also fed into the collecting pipe 5 after condensation.

The base product of the column 7 is conveyed into a first stripping column 11 through a pipe 10, being introduced on to one of the middle trays of the column 11. The column 11 is used for the refinement of the benzene, which is drawn off from the top through a pipe 12. At the same time, a product containing nonaromatic substances is drawn off from the tray above the feeding tray through a pipe 13, and freed from benzene residues in a stripper 14.

The base product of the column 14 is fed into a collecting pipe 16 through a pipe 15, while the base product of the column 11 is conveyed into a second stripping column 19, which is used for refining the toluene, through a pipe 17. The base product is introduced at all of the middle trays of the column 18 in this case as well, a side product containing nonaromatic substances also being drawn off through a pipe 20 from the tray above the feeding tray.

The toluene escapes from the top of column 18 through a pipe 19. A stripper 21 is used to strip aromatic residues from the side product. The base product of the column 21 is also conveyed through a pipe 22 into the collecting pipe 16, while the base product of the column 18 passes through a pipe 23 into a third stripping column 24, in which the xylene is stripped. The xylene escapes from the top of column 24 through a pipe 25, while a side product containing nonaromatic substances is drawn off through a pipe 26 from the tray above the feeding tray in the middle of the column.

A stripper 27 is used to strip aromatic residues from
the side product, the base product of the column 27 being conveyed into the collected pipe 16 through a pipe 28.

The product flows combined in the collecting pipe 16 and containing nonaromatic substances are conveyed into an extractive-distillation column 29 for after-refining.

These flows are introduced on to one of the middle trays of the column 29. 500 kg. of extraction-agent mixture are introduced through a pipe 30 onto one of the upper trays of the column 29. The base product of this column is drawn off through a pipe 32, whence it passes into the pipe 10 and is thereby returned into the downstream stripping columns, while 20 kg. of nonaromatic substances escape from the top of the column through a pipe 31; these nonaromatic substances are fed to the collecting pipe 5.

The extraction-agent mixture, freed from the aromatic substances, is drawn off from the base of the last stripping column 24 through the pipe 32 and returned to the extractive-distillation columns through the branch pipes 8 and 30. The extraction-agent mixture is introduced into the process through the pipe 33 when the installation is started up. The pipe sections 34, 35 and 36 are inlets to the extractive-distillation columns, which are situated above the inlet trays for the extraction agent and through which part of the aromatic substances is added to the extraction agent to be introduced into the process.

According to the method of the invention, the following yields were obtained:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Percent of feedstock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>98.97</td>
</tr>
<tr>
<td>Toluene</td>
<td>98.58</td>
</tr>
<tr>
<td>Xylene</td>
<td>100</td>
</tr>
</tbody>
</table>

The nonaromatic substances could also be drawn off practically entirely through the collecting pipe 5. The method of the invention is therefore characterised by extraordinarily good separating efficiency and high yields for all the fractions to be extracted. All the aromatic substances extracted have a good degree of purity.

The mixture of aromatic substances often contains still higher-boiling substances, e.g., \(C_9\) aromatic substances, in addition to benzene, toluene and xylene. If these aromatic substances are also to be extracted, the mixture drawn off from the base of the column 24 can be worked up appropriately as in the case of the preceding columns. If quantitative separation of the \(C_9\) aromatic substances is not planned, the base product of the column 24 can be worked up in a simple stripping column.

We claim:

1. Extractive-distillation process for simultaneously obtaining different aromatics with different boiling point ranges from a feed stock containing varied amounts of nonaromatics along with the desired aromatic compounds comprising, in combination,

(a) passing the feed stock through a first extractive-distillation column while contacting it in said column with an at least partially nonaromatic selectively active solvent containing aromatics other than the aromatics to be recovered;

(b) withdrawing a liquid extract of aromatics and solvent from said first extractive-distillation column while withdrawing the nonaromatics in vapor form from said column;

(c) then directly passing the said liquid extract of aromatics and solvent through at least one subsequent extractive-distillation column so as to further separate in said at least one subsequent extractive-distillation column nonaromatics from said extract and withdrawing the thus separated nonaromatics in vapor form from said extractive-distillation column,

said subsequent extractive-distillation column being operated at a reduced pressure relative to the preceding column;

(d) then directly passing the thus obtained extract of aromatics and solvent from the last extractive-distillation column through a plurality of stripper columns arranged in series, one stripper column being provided for each desired type of aromatics;

(e) withdrawing the aromatics to be recovered from the respective stripper columns and simultaneously also withdrawing nonaromatics from said stripper columns.

2. The extractive distillation process of claim 1 wherein in the first of said extract-distillation columns is operated at a pressure above atmospheric.

3. The extractive distillation process of claim 1 wherein the said nonaromatics containing product is passed from each stripper column to an auxiliary stripper column where residual boiling aromatics are eliminated.

4. The extractive distillation process of claim 3 wherein a substantially nonaromatic raffinate is withdrawn from the bottoms of each auxiliary stripper column and subjected to another extractive-distillation step.

5. The extractive distillation process of claim 3 wherein a substantially nonaromatic raffinate is obtained from each of said auxiliary stripper columns and all the raffinates are combined and processed in one common extractive-distillation column.

6. The extractive distillation process of claim 3 wherein a purified substantially nonaromatic raffinate is withdrawn from the bottom of each auxiliary stripper column and subjected to further processing by conventional distillation.

7. The extractive distillation process of claim 1 which includes the step of withdrawing from the bottoms of the last stripper column a mixture of said solvent and aromatics other than those to be recovered and feeding said mixture back into the extractive distillation operation.

8. The extractive distillation process of claim 1 which includes introducing a portion of the aromatics used in the said solvent into the extractive distillation column separate from the said solvent and at a place above the inlet for the remainder of the said solvent.

9. The extractive distillation process of claim 1 wherein in the amount of aromatics that is added to the said solvent is up to 20% by volume relative to the volume of the said solvent.

10. The extractive distillation process of claim 1 wherein in the sensible heat of the bottoms product of the last stripper column and of the high pressure operated extractive distillation column is employed for heating the lower pressure extraction-distillation columns and the stripper columns.

References Cited

UNITED STATES PATENTS

2,215,915 9/1940 Cope et al. 208—313
2,434,424 1/1948 Morris et al. 203—73
2,455,803 12/1948 Pierotti 203—51
2,834,822 5/1958 Worthington et al. 260—674
3,227,632 1/1966 Schmalenbach et al. 208—313

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208—313, 319