METHOD OF RECOVERING NAPHTHALENE

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8 Claims

ABSTRACT OF THE DISCLOSURE

A method for recovering naphthalene from a coal-tar naphthalene-oil fraction comprising washing the fraction sequentially with dilute and then with concentrated aqueous caustic solution and then distilling the fraction at a first absolute pressure to separate the forerunnings from the naphthalene and residue, and then distilling the naphthalene and residue at a second absolute pressure substantially less than the first absolute pressure to separate naphthalene from residue, whereby said naphthalene has a crystallizing point of at least 78° C.

This application, which is a continuation-in-part of our co-pending application Ser. No. 345,279, filed Feb. 17, 1964, and now abandoned relates to an improved method for recovering naphthalene from coal-tar fractions. More particularly, the improved method permits a higher recovery of available naphthalene from a coal-tar fraction than has been possible heretofore.

Crude coal tar derived from the carbonization of coal at elevated temperatures comprises largely naphthalene and tar acids in a naphthalene-oil fraction boiling between about 200° and 250° C. Minor quantities of other constituents, boiling below and above naphthalene, can interfere with the recovery of this naphthalene by fractional distillation. Coke plants faced with this problem have cooled these fractions, separated naphthalene crystals therefrom and sequentially distilled the crystals to a product from forerunnings and residue.

It is an object of our invention to provide a method for recovering 78° C. naphthalene from a caustic-washed, coal-tar naphthalene-oil fraction by means of a sequential distillation to separate forerunnings, naphthalene and residue at two different pressures.

A further object is to obtain an enhanced yield of 78° C. naphthalene from a caustic-washed naphthalene-oil fraction by distilling the fraction to separate the forerunnings from naphthalene and residue at an absolute pressure substantially higher than the absolute pressure at which the naphthalene and residue are separated.

Yet another object is to obtain an enhanced yield of 78° C. naphthalene by washing a naphthalene-oil fraction with a dilute caustic solution to remove substantially all of the tar acids, then washing with a strong caustic solution, and then fractionally distilling the so-washed fraction.

A still further object is to obtain an enhanced yield of 78° C. naphthalene from a naphthalene-oil fraction by washing the fraction with a strong caustic solution and then distilling the washed fraction to separate the forerunnings from naphthalene and residue at an absolute pressure appreciably higher than the absolute pressure at which the naphthalene and residue are separated.

We have found that, in the sequential distillation of a caustic-washed, naphthalene-oil fraction, the naphthalene yield is inversely proportional to the distillation pressure, in the range from atmospheric pressure to 100 mm. Hg absolute pressure. Surprisingly, and of greater significance, however, is the effect of conducting the distillation in two stages at different pressures. Removal of forerunnings or fores at atmospheric pressure, before the naphthalene heart cut is distilled at a reduced pressure, gives higher yields of 78° C. product than can be obtained by conducting the entire sequential distillation at either atmospheric or reduced pressures.

We further found that the difference between the boiling points of fores and naphthalene increases with increasing pressures. Conversely, the difference between the boiling points of naphthalene and tails or residue increases with decreasing pressures. As a result, a purer naphthalene and greater yields thereof are obtained as the boiling point differences become greater. Boiling points decrease when distilling at decreasing pressures. We have found that in a range including superatmospheric, atmospheric and sub-atmospheric pressures, the boiling points of the forerunnings and residue are on essentially straight, parallel lines. The boiling point line for naphthalene, however, is at a diagonal therebetween said lines and somewhat asymptotic thereto, providing the above-described results. Hence, the overall pressure range for our two-stage, sequential distillation may extend from a super-atmospheric pressure to a pressure below about 100 mm. Hg absolute.

While the selling price of naphthalene is relatively low, more expensive equipment to distill off forerunnings at super-atmospheric pressures and high-vacuum equipment to distill off naphthalene from residue at pressures below 100 mm. Hg absolute would not appear to be justified. Hence, it is preferred commercially, however, to remove fores at about atmospheric pressure and to separate naphthalene from tails at a substantially lower pressure, between about 100 and 300 mm. Hg absolute. More specifically, in a first-stage distillation at atmospheric pressure, forerunnings may be removed up to a vapor temperature at the column head between about 213° C. and 215° C. Thereafter in a second-stage distillation, for example at 200 mm. Hg absolute pressure, naphthalene may be removed up to a vapor temperature at the column head between about 165° C. and 168° C.

Substantially no 78° C. naphthalene is recoverable by our two-stage distillation from a naphthalene-oil fraction having a crystallizing point of about 70° C., unless it has been caustic washed. After washing the fraction with a dilute aqueous caustic solution to substantially completely remove the tar acids therefrom, the washed fraction has a crystallizing point of about 73° C. and, upon distillation in accordance with our method, yields about 87% of the contained naphthalene as 78° C. product. In a preferred method of processing, the dilute-caustic washed naphthalene oil is washed again using a strong caustic solution, for example 50% caustic solution, after which the washed naphthalene oil has about the same crystallizing point, 73° C. Surprisingly, however, we
found that our subsequent distillation method, when applied to the 50% caustic-washed naphthalene oil, resulted in an increase in yield of 73% to about 87% to about 93% of the available naphthalene.

From a consideration of the commercial aspects of our process, the preferred caustic is caustic soda. When describing caustic concentrations or concentrations of caustic in aqueous solutions in this application, the concentration is expressed as a percentage by weight of sodium hydroxide. From a laboratory standpoint only, there may be used the caustic alkalis or alkali metal hydroxides of the family including cesium, lithium, potassium and rubidium hydroxides as well as sodium hydroxide.

The concentration of a dilute caustic solution may be between about 4% and 15% sodium hydroxide by weight, a concentration between about 8% and 10% being preferred. The strong caustic solution may have a concentration between about 25% and 75% by weight, the preferred concentration being about 50% sodium hydroxide. Below about 35% concentration, the above-described effectiveness gradually diminishes. Use of solutions stronger than about 50% concentration requires such small volumes of caustic solution relative to naphthalene-oil volumes that effective contact with the oil is difficult to achieve, so that the above-described effectiveness gradually diminishes.

In washing the naphthalene-oil fraction with a caustic solution more concentrated than about 15% would not ordinarily be practiced, since subsequent distillation provides an adequate yield of 78° C. product. More importantly, a reason for not using a caustic solution stronger than 15% is related to tar-acid recovery. If stronger caustic is used, some tar bases and neutral oils are extracted into the aqueous phase, and the tar bases particularly are later found as contaminants in the tar-acid products. However, by sequentially washing a naphthalene oil with dilute- and then with strong-caustic solution, the tar acids can be substantially completely recovered by the dilute caustic without contamination of the tar-acid products. In a particularly desirable method of sequentially washing the naphthalene oil, the strong-caustic extract is subsequently diluted with water to a concentration of about 8% to 10% caustic, which is used as the dilute caustic solution to extract substantially all of the tar acids from the succeeding batch of naphthalene oil.

Sequentially washing a naphthalene-oil fraction with dilute caustic with assurance of the yield of naphthalene in any subsequent fractional distillation of the so-washed fraction, as contrasted with the yield from a naphthalene oil washed only with dilute caustic. If tar-acid recovery is not a factor, then the naphthalene oil need be washed only with a strong-caustic solution to enhance the yield of 78° C. naphthalene in any subsequent fractional distillation.

An understanding of the invention may be obtained from the following detailed description and explanation while referring to the accompanying drawing illustrating the preferred practice. The single figure of the drawing is a diagrammatic representation of a system for carrying out the method of our invention.

Referring now in detail to the drawing, a crude naphthalene-oil fraction is introduced by a pipe 10 to a caustic washer 11, supplied through a pipe 12 with an aqueous solution containing about 8% sodium hydroxide by weight. After the washing step, the naphthalene oil is separated from the caustic solution which contains substantially all the tar acid formerly present in the oil. The washed oil flows through a pipe 13 to a second caustic washer 14. The caustic extract solution flows through a pipe 15 to a means for recovery of tar acids (not shown). Caustic washer 14 is supplied by means of a pipe 16 with an aqueous solution containing about 50% sodium hydroxide by weight.

After the second washing step, the naphthalene oil is separated from the caustic solution. The twice-washed oil flows through a pipe 18 to a distillation column 19. The 50% caustic solution flowing from washer 14 through pipe 12 has sufficient water from a pipe 17 admixed therewith to yield it to about 8% caustic for use in washer 11. In column 19, operated at atmospheric pressure, forerunnings are distilled off overhead and flow from the column through a pipe 20 for further disposal. The residue from this distillation flows through a pipe 21 to a second distillation column 22 operated at subatmospheric pressure between about 100 and 300 mm. Hg absolute. In column 22, naphthalene is distilled off overhead and flows from the column through a pipe 23 to an indirect condenser 24. The naphthalene is condensed to a liquid by means of hot water from a pipe 25 and is discharged through a barometric pipe 26. The vacuum is sustained by a steam jet ejector 27. The residue or tails flows from column 22 through a pipe 28 for further disposal.

It will be apparent that caustic washers 11 and 14, columns 19 and 22, the indirect condenser 14 and other hereinafore-described equipment may be of any design known to effect the desired results. Preferably, distillation columns 19 and 22 are bubble-cap or perforated-tray columns containing 40 or more trays.

The following are typical examples of our process.

EXAMPLES 1–7

A sample of 300 g. of a naphthalene-oil fraction having a distillation range between about 210° and 230° C. was washed with about 110 cc. of an aqueous caustic solution containing about 8% by weight of sodium hydroxide. After separation of the oil and caustic solution, the oil was washed with about 12 cc. of an aqueous caustic solution containing about 50% by weight of sodium hydroxide. After separation of the oil and caustic solution, the oil was transferred to distillation apparatus comprising a flask, a packed column, 4' long and 3/4" diameter, and reflux means. Operating at a reflux ratio of about 19 to 1 and at atmospheric pressure, forerunnings were distilled from the sample to a vapor temperature in the column head of about 213° C. By means of a vacuum pump, the column pressure was reduced to about 100 mm. Hg absolute. In Example 2, the reflux ratio was adjusted to about 4:1 and the distillation continued, to distill off naphthalene to a column head temperature of about 146° C. The naphthalene product, weighing 218 g., had a crystallizing point of 78° C. and represented a recovery of 96.2% of the naphthalene in the original sample.

This procedure of Example 1 was repeated as Examples 2-4, with similar fractions, to illustrate the effect of sequential distillations on other fractions. In Example 2, the preferred pressure conditions were used: the forerunnings were distilled off at atmospheric pressure and the naphthalene was separated from the residue at 200 mm. Hg absolute. To demonstrate the flexibility of operation in using our pressure effect, pressures of 600 mm. Hg absolute and 100 mm. Hg absolute were used in Example 3. In Example 4, the preferred pressure conditions were reversed; namely, the forerunnings were distilled off at 200 mm. Hg absolute pressure and the naphthalene was separated from residue at atmospheric pressure. This reversal of the preferred pressure combination resulted in a drop in 78° C. product recovery to 84.3% from 93.0% for the preferred pressure combination.

In Examples 5–7, with similar oil fractions, a single pressure was used to distill off both forerunnings and the naphthalene to illustrate the generally lower yields of product as compared to the preferred method.

While it is preferred to operate our two-stage distillation with a naphthalene-oil fraction that has been sequentially washed first with a dilute, then with a concentrated caustic solution, the benefits of the two-stage distillation are obtainable where the fraction has been washed only with a dilute caustic solution, namely, 8% solution as illustrated in Examples 2, 4, 6 and 7. Examples 6 and 7
demonstrate the benefit to prior-art, single-pressure fractional distillations for the recovery of naphthalene by sequentially washing with a distillate, then with a strong caustic solution. The results obtained in Examples 1-7 are summarized in Table I.

<table>
<thead>
<tr>
<th>Example</th>
<th>Operating pressure, mm. Hg absolute</th>
<th>Weight percent contained naphthalene recovered in 78°C product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>700-100</td>
<td>69.2</td>
</tr>
<tr>
<td>2</td>
<td>700-200</td>
<td>69.0</td>
</tr>
<tr>
<td>3</td>
<td>600-300</td>
<td>91.6</td>
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<tr>
<td>4</td>
<td>600-700</td>
<td>84.2</td>
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<tr>
<td>5</td>
<td>500</td>
<td>90.0</td>
</tr>
<tr>
<td>6</td>
<td>200</td>
<td>87.1</td>
</tr>
<tr>
<td>7</td>
<td>700</td>
<td>84.4</td>
</tr>
</tbody>
</table>

EXAMPLES 8-13
In Examples 8-13, the Example 2 distillation combination was repeated, namely, removing forerunnings at 760 mm. Hg absolute pressure, then separating naphthalene from residue at 200 mm. Hg absolute pressure with similar oil fractions. These examples illustrate the effect of different predistillation caustic washes and are summarized in Table II. Where tar-acid recovery is not a problem, the dilute caustic wash may be omitted and only a concentrated caustic wash used to achieve the above-described benefits in fractional distillations to recover naphthalene, as shown by Example 12.

TABLE II
<table>
<thead>
<tr>
<th>Example</th>
<th>Predistillation wash</th>
<th>Weight percent contained naphthalene recovered in 78°C product</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>None</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>5% caustic</td>
<td>87.4</td>
</tr>
<tr>
<td>10</td>
<td>8% and 50% caustic</td>
<td>80.0</td>
</tr>
<tr>
<td>11</td>
<td>9% and 50% caustic</td>
<td>80.0</td>
</tr>
<tr>
<td>12</td>
<td>50% caustic</td>
<td>80.1</td>
</tr>
<tr>
<td>13</td>
<td>5 and 15% caustic</td>
<td>80.2</td>
</tr>
</tbody>
</table>

EXAMPLES 14 AND 15
As hereinabove described, many tar plants processing naphthalene-oil fractions require a low-temperature crystallization step prior to fractionating the crystals to recover naphthalene. Traditionally, lower-boiling fractions containing naphthalene, for example, the naphthalene residue from fractionation of light oil, and a residue from fractionation of coal-tar benzol fractions, have been admitted with naphthalene oil to the crystallization step. The following examples were conducted to illustrate that our method may be used to recover naphthalene from such blends, which contain appreciably greater quantities of fores.

The procedure of Example 2 was repeated as Example 14 except that distillation Blend A comprised 88.8% of the same naphthalene-oil fraction, which had been sequentially washed with 8% and 50% caustic, and 11.2% of a light-oil naphthalene residue having a content of about 71% naphthalene. Example 2 was repeated as Example 15 except that distillation Blend B comprised 87.8% of the same naphthalene-oil fraction, 6.9% of the same light-oil naphthalene residue and 5.3% of a naphthalene residue from a coal-tar benzol fraction, having a content of about 67% naphthalene. The results are summarized in Table III. The results of Example 2 are cited for comparison.

While the above examples illustrate prefered methods of operation, changes therein may be made without departing from the spirit of the invention. The absolute pressures at which forerunnings are separated and at which naphthalene is separated from residue may be more or less than given in the examples. Thus forerunnings may be separated at superatmospheric pressure. Naphthalene may be separated from residue, for example at 50 mm. Hg absolute pressure. Commercial considerations would be important in determining relative pressure conditions, for example, capital costs, distillation costs, volume of throughput and the selling price of naphthalene.

Although we have disclosed herein the preferred practies of our invention, we intend to cover as well any change or modification therein which may be made without departing from the spirit and scope of the invention.

We claim:
1. A method for recovering naphthalene from a caustic-washed coal-tar naphthalene-oil fraction comprising distilling the fraction at a first absolute pressure to separate the forerunnings from the naphthalene and residue, and then distilling the naphthalene and residue at a second absolute pressure substantially less than the first absolute pressure to separate naphthalene from residue, said second absolute pressure being below atmospheric pressure whereby said naphthalene has a crystallizing point of at least 78°C.
2. A method as defined in claim 1 characterized by distilling forerunnings at about atmospheric pressure.
3. A method as defined in claim 1 characterized by separating naphthalene from residue at a pressure between about 100 and 300 mm. Hg absolute.
4. A method as defined in claim 1 characterized by washing said fraction prior to distillation with an aqueous caustic solution having a concentration between about 25% and 75% by weight.
5. A method for recovering naphthalene from a caustic-washed naphthalene-oil fraction boiling between about 210° and 230°C, comprising distilling said fraction at about atmospheric pressure and removing therefrom material boiling below about 215°C, further distilling the remaining portion at subatmospheric pressure and collecting a naphthalene-containing portion having a crystallizing point of at least 78°C.
6. A method as defined in claim 5 characterized by washing said naphthalene-oil fraction with an aqueous caustic solution having a concentration between about 4% and 15% by weight, then washing said caustic-washed fraction with a second aqueous caustic solution having a concentration between about 25% and 75% by weight.
7. A method for recovering naphthalene from a caustic-washed coal-tar naphthalene-oil fraction comprising distilling the fraction to sequentially separate forerunnings, naphthalene and residue, distilling the forerunnings at an absolute pressure appreciably higher than the absolute pressure at which naphthalene and residue are sepa-
rated, whereby said naphthalene has a crystallizing point of at least 78° C., characterized by distilling forerunings at about atmospheric pressure, and separating naphthalene from residue at a pressure between about 100 and 300 mm. Hg absolute.

8. A method for recovering naphthalene from a naphthalene-oil fraction boiling between about 210° and 230° C., comprising washing said fraction with a water solution containing about 8% by weight sodium hydroxide, then washing said fraction with a water solution containing about 50% by weight sodium hydroxide, distilling said caustic-washed fraction at about atmospheric pressure and removing therefrom material boiling below about 215° C., further distilling the remaining portion at about 200 mm. Hg absolute pressure and collecting a naphthalene portion boiling up to about 165° C.