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METHODS OF PRODUCING FUMARIC ACID

David Levin, Philadelphia, Pa., assignor to Chemical Concentrates Corporation, Fort Washington, Pa., a corporation of Pennsylvania

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This invention relates to the production of fumaric acid and more particularly to methods of producing fumaric acid from liquors containing maleic acid.

An object of this invention is to produce fumaric acid efficiently and economically.

Another object of this invention is to recover the values from maleic liquor in a usable form.

Another object of this invention is to obtain fumaric acid from liquors containing maleic acid which were ordinarily discarded.

In the production of phthalic anhydride, the scrub liquor contains maleic acid in addition to smaller quantities of other organic compounds. These liquors are frequently discarded because of the unavailability of a satisfactory method for the recovery of the maleic acid values from such liquor. Many methods have heretofore been proposed for this purpose, but they require elaborate equipment and are inefficient in operation or result in small yields. Likewise, in the production of maleic acid from benzol or other raw materials, maleic liquors are formed containing many impurities.

In accordance with this invention, methods are provided whereby the maleic acid values may be recovered in good yield efficiently and economically. The method in accordance with this invention comprises, in one aspect, reacting in an aqueous solution maleic acid with hydrochloric or hydrobromic acid in the presence of an alkali metal chloride, an alkali metal bromide, ammonium chloride or ammonium bromide. The amount of maleic acid employed in this process is desirably 0.1 to 10 mols and preferably 3 to 5 mols per liter of water present. The amount of hydrochloric or hydrobromic acid used is desirably 0.1 to 15 mols and preferably 1 to 4 mols per liter of water present, and the amount of the alkali metal chloride or bromide or ammonium chloride or bromide is desirably 0.1 mols per liter of water present to the solubility of the halide. Preferably, the amount of halide is 3 to 5 mols per liter of water present. The yield of fumaric acid is related to the molar concentration of the halogen acid and/or halide salt and/or maleic acid. However, if too high a concentration of maleic acid is used, then the separated fumaric acid forms too heavy a slurry to handle satisfactorily.

The reaction in the aqueous solution of the maleic acid with the hydrochloric or hydrobromic acid in the presence of the specified halides results in the production of fumaric acid. The resulting fumaric acid may be readily separated from the mixture by any suitable means, such as filtration, decantation or centrifugation.

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In accordance with another aspect of this invention, fumaric acid is produced from alkali metal maleates or ammonium maleates. In this aspect of the invention, the method is substantially the same, namely, the alkali metal maleate or ammonium maleate is reacted in an aqueous solution with hydrochloric or hydrobromic acid in the presence of an alkali metal chloride, an alkali metal bromide, ammonium chloride or ammonium bromide. The amount of alkali metal maleate or ammonium maleate used is the same molar amount as that of the maleic acid used in the production of fumaric acid heretofore described. The amount of hydrochloric or hydrobromic acid is also the same as employed when maleic acid is used as a starting material except that in addition there must be used an amount equivalent to the theoretical amount required for the conversion of the alkali metal maleate or ammonium maleate to maleic acid. The amount of alkali metal chloride, alkali metal bromide, ammonium chloride or ammonium bromide is also the same as that employed when maleic acid is used as a starting material. However, the amount of alkali metal halide or ammonium halide resulting from the reaction of the alkali metal maleate or ammonium maleate with the hydrochloric acid or the hydrobromic acid must be calculated as part of the alkali metal or ammonium halide present.

The process of this invention is admirably adapted for the recovery of maleic acid values from scrub liquor resulting from the production of phthalic anhydride. In this process, the scrub liquor which contains appreciable amounts of maleic acid, such as of the order of 15 to 30% by weight, is ordinarily discarded. This situation results not only in an economic waste but may also involve a problem of stream pollution. The maleic acid values in such scrub liquor may be recovered as fumaric acid by the methods of this invention. The maleic acid in the scrub liquor is partially neutralized by the addition of sodium carbonate, sodium bicarbonate or sodium hydroxide until the pH of the liquor is within the range of 3.5 to 3.7. This partial neutralization converts the maleic acid to sodium acid maleate. The mixture is then cooled to below 25° C. and the precipitated sodium acid maleate is separated from the mixture by any suitable means, such as filtration, decantation or centrifugation. The resulting precipitated sodium acid maleate is then reacted in an aque-

ous solution with hydrochloric or hydrobromic acid in the presence of an alkali metal chloride, an alkali metal bromide, ammonium chloride or ammonium bromide. The sodium chloride or sodium bromide formed by the reaction of the sodium acid maleate with the hydrochloric or hydrobromic acid is calculated as part of the alkali metal chloride, alkali metal bromide, ammonium chloride or ammonium bromide present. The amounts of hydrochloric or hydrobromic acid and the amounts of halide employed in this phase of the process are the same as those heretofore described. The resulting fumaric acid formed is then separated by any suitable means, such as filtration, decantation or centrifugation. About 85 to 95% theoretical yields based upon the maleic acid equivalent of the purified crystals have been obtained in two hours of processing by the practice of this method.

The presence of the alkali metal chloride, the alkali metal bromide, ammonium chloride or ammonium bromide is essential for obtaining the maximum yield of fumaric acid, and from an economic standpoint, it is a marked advance over any of the methods heretofore proposed. Such alkali metal halides or ammonium halides accelerate substantially the reaction over methods in which the hydrochloric or hydrobromic acid alone is employed. For example, in tests conducted both with and without such alkali metal halides or ammonium halides under identical conditions and starting with recovered maleic acid, it was demonstrated that the yield of fumaric acid without such halides was 50% of the theoretical whereas with the halide up to 90% of the theoretical yield was obtained in the same period of time.

Examples of alkali metal maleates are sodium maleate, sodium acid maleate, potassium maleate, potassium acid maleate, lithium maleate and lithium acid maleate.

Examples of alkali metal chlorides and bromides are sodium chloride, sodium bromide, potassium chloride, potassium bromide, lithium chloride and lithium bromide.

A more comprehensive understanding of this invention is obtained by reference to the following examples:

Example 1.—Production of fumaric acid from scrub liquor containing maleic acid and obtained as a by-product in the production of phthalic anhydride

100 gals. of a scrub liquor obtained as a by-product in the production of phthalic anhydride and containing about 1 lb. per gallon of maleic acid was neutralized with caustic soda until the pH of the liquor was about 3.6. After the addition of the caustic soda, the temperature of the mixture was lowered to about 20° C. The precipitated sodium acid maleate formed was drained and washed with water. The precipitate amounted to 170 lbs. of wet crystals of sodium acid maleate which was equivalent to 120 lbs. of dry crystals of sodium acid maleate containing 3 molecules of water of crystallization. These wet crystals of sodium acid maleate were placed in a glass lined reaction kettle and to them were added 105 lbs. of 20° Baumé hydrochloric acid and the necessary water to adjust molar concentration. No additional water may be needed if crystals are sufficiently wet. The reaction mixture was boiled at about 110° C. for a period of two hours at atmospheric pressure during which time the fumaric acid was produced. Lower temperatures, such as temperatures between 90 and 100° C. may be employed but a longer time is required to produce the fumaric acid, depending upon the deviation from the temperature of 110° C. At higher than atmospheric pressures the reaction time is shortened due to higher operating temperatures. The reaction mixture in this example, represents the desired molar ratio of reactants and catalysts to achieve the most desirable result. In this example, 4 mols of sodium acid maleate per liter of water present was used and 6 mols of hydrochloric acid per liter of water present was used. The sodium acid maleate and hydrochloric acid produced 4 mols of sodium chloride leaving 2 mols of free hydrochloric acid per liter of water present.

Example 2.—Preparation of fumaric acid from maleic acid

464 grams of maleic acid are dissolved in 840 cc. of water, and 234 grams of sodium chloride and 200 cc. of 20° Baumé hydrochloric acid is added to the solution. The mixture is heated to boiling for a period of about two hours. The mixture is then cooled to about 25° C., and the precipitated fumaric acid was drained and washed.

Example 3.—Preparation of fumaric acid from sodium maleate

324 grams of sodium maleate are dissolved in 270 cc. of water. To this solution is added 1205 grams of 40% hydrobromic acid. The mixture is heated to a temperature of about 110° C. for a period of two hours. The mixture is then cooled to about 25° C., and the fumaric acid formed is drained from the mixture and washed free of acid and salt. It then may be dried, if desired.

The terms and expressions which I have employed are used as terms of description and not of limitation, and I have no intention, in the use of such terms and expressions, of excluding any equivalents of the features shown and described or portions thereof, but recognize that various modifications are possible within the scope of the invention claimed.

What is claimed is:

1. The method of producing fumaric acid which comprises reacting, in an aqueous solution, 0.1 to 10 mols per liter of water present of maleic acid with 0.1 to 15 mols per liter of water present of free hydrohalogen acid selected from the class consisting of hydrochloric acid and hydrobromic acid in the presence of 0.1 mol per liter of water present to the solubility limit of a halide selected from the class consisting of alkali metal chlorides, alkali metal bromides, ammonium chloride and ammonium bromide and separating the resulting fumaric acid from the mixture.

2. The method of producing fumaric acid which comprises reacting, in an aqueous solution, 3 to 5 mols per liter of water present of maleic acid with 1 to 4 mols per liter of water present of free hydrohalogen acid selected from the class consisting of hydrochloric acid and hydrobromic acid in the presence of 3 to 5 mols per liter of water present of a halide selected from the class consisting of alkali metal chlorides, alkali metal bromides, ammonium chloride and ammonium bromide and separating the resulting fumaric acid from the mixture.

3. The method of producing fumaric acid which comprises reacting, in an aqueous solution, about 4 mols of maleic acid per liter of water present with about 2 mols per liter of water

present of free hydrohalogen acid selected from the class consisting of hydrochloric acid and hydrobromic acid in the presence of about 4 mols per liter of water present of a halide selected from the class consisting of alkali metal chlorides, alkali metal bromides, ammonium chloride and ammonium bromide and separating the resulting fumaric acid from the mixture.

4. The method of producing fumaric acid which comprises reacting, in an aqueous solution, 0.1 to 10 mols per liter of water present of a member selected from the class consisting of alkali metal maleates and ammonium maleates with a hydrohalogen acid selected from the class consisting of hydrochloric acid and hydrobromic acid in the presence of a halide selected from the class consisting of alkali metal chlorides, alkali metal bromides, ammonium chloride and ammonium bromide, and separating the resulting fumaric acid from the mixture, the amount of said hydrohalogen acid being 0.1 to 15 mols per liter of water present above that theoretically required to convert maleate to maleic acid, and the amount of said halide being 0.1 mol per liter of water present to the solubility limit of said halide.

5. The method of producing fumaric acid which comprises reacting, in an aqueous solution, 3 to 5 mols per liter of water present of a member selected from the class consisting of alkali metal maleates and ammonium maleates with a hydrohalogen acid selected from the class consisting of hydrochloric acid and hydrobromic acid in the presence of a halide selected from the class consisting of alkali metal chlorides, alkali metal bromides, ammonium chloride and ammonium bromide, and separating the resulting fumaric acid from the mixture, the amount of said hydrohalogen acid being 1 to 4 mols per liter of water present above that theoretically required to convert the maleate to maleic acid, and the amount of said halide being 3 to 5 mols per liter of water present.

6. The method of producing fumaric acid which comprises reacting, in an aqueous solution, about 4 mols per liter of water present of a member selected from the class consisting of alkali metal maleates and ammonium maleates with a hydrohalogen acid selected from the class consisting of hydrochloric acid and hydrobromic acid in the presence of about 4 mols per liter of water present of a halide selected from the class consisting of alkali metal chlorides, alkali metal bromides, ammonium chloride and ammonium bromide, and separating the resulting fumaric acid from the mixture, the amount of said hydrohalogen acid being about 2 mols per liter of water present above that theoretically required to convert the maleate to maleic acid.

7. The method of producing fumaric acid which comprises reacting, in an aqueous solution, 0.1 to 10 mols per liter of water present of maleic acid with 0.1 to 15 mols per liter of water present of free hydrochloric acid in the presence of 0.1 mols per liter of water present to the solubility limit of sodium chloride, and separating the resulting fumaric acid from the mixture.

8. The method of producing fumaric acid which comprises reacting, in an aqueous solution, 3 to 5 mols per liter of water present of maleic acid with 1 to 5 mols per liter of water present of free hydrochloric acid in the presence of 3 to 5 mols of sodium chloride per liter of water present, and separating the resulting fumaric acid from the mixture.

9. The method of producing fumaric acid which

comprises reacting, in an aqueous solution, about 4 mols per liter of water present of maleic acid with about 2 mols per liter of water present of free hydrochloric acid in the presence of about 4 mols per liter of water present of sodium chloride, and separating the resulting fumaric acid from the mixture.

10. The method of producing fumaric acid which comprises reacting, in an aqueous solution, 0.1 to 10 mols per liter of water present of sodium acid maleate with hydrochloric acid in the presence of sodium chloride and separating the resulting fumaric acid from the mixture, the amount of hydrochloric acid being 0.1 to 15 mols per liter of water present above that theoretically required to convert the maleate to maleic acid and the amount of sodium chloride being 0.1 mols per liter of water present to the solubility limit of sodium chloride.

11. The method of producing fumaric acid which comprises reacting, in an aqueous solution, 3 to 5 mols per liter of water present of sodium acid maleate with hydrochloric acid in the presence of sodium chloride and separating the resulting fumaric acid from the mixture, the amount of hydrochloric acid being 1 to 4 mols per liter of water present above that theoretically required to convert the maleate to maleic acid, and the amount of sodium chloride being 3 to 5 mols per liter of water present.

12. The method of producing fumaric acid which comprises reacting, in an aqueous solution, about 4 mols of sodium acid maleate per liter of water present with hydrochloric acid in the presence of 4 mols per liter of water present of sodium chloride, and separating the resulting fumaric acid from the mixture, the amount of hydrochloric acid being about 2 mols per liter of water present above that theoretically required to convert the maleate to maleic acid.

13. The method of producing fumaric acid from a liquor containing maleic acid which comprises partially neutralizing the waste liquor by the addition of a member selected from the class consisting of sodium carbonate, sodium bicarbonate and sodium hydroxide until the pH of said liquor is within the range of 3.5 to 3.7, cooling the mixture to below 25° C., separating the precipitated sodium acid maleate from the mixture, reacting in an aqueous solution 3 to 5 mols per liter of water present of the separated sodium acid maleate with hydrochloric acid in the presence of sodium chloride, and separating the resulting fumaric acid from the mixture, the amount of hydrochloric acid present being 1 to 4 mols per liter of water present above that theoretically required to convert the maleate to maleic acid, and the amount of sodium chloride being 3 to 5 mols per liter of water present.

14. The method of producing fumaric acid from a liquor containing maleic acid which comprises partially neutralizing the waste liquor by the addition of a member selected from the class consisting of sodium carbonate, sodium bicarbonate and sodium hydroxide until the pH of said liquor is within the range of 3.5 to 3.7, cooling the mixture to below 25° C., separating the precipitated sodium acid maleate from the mixture, reacting in an aqueous medium about 4 mols per liter of water present of the separated sodium acid maleate with hydrochloric acid in the presence of about 4 mols of sodium chloride per liter of water present and separating the resulting fumaric acid from the mixture, the amount of hydrochloric acid being about 2 mols per liter of

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water present above that theoretically required to convert the maleate to maleic acid.

DAVID LEVIN.

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