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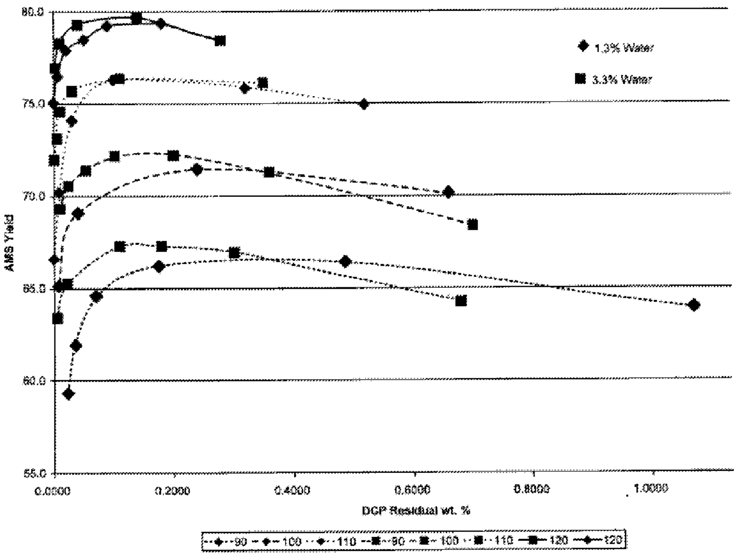

FIGURE 1

(57) Abstract: An improved method for the production of phenol, acetone and alpha-methyl styrene (AMS) from a cumene hydroperoxide and dimethylbenzyl alcohol (DMBA) mixture is described, wherein 0.5 - 5% additional water by weight is added prior to the final DMBA dehydration step, carried out in the presence of about 20 - 400 ppm mineral acid catalyst at 110 - 150 C for 0.5 to 40 minutes residence time. The use of additional water allows greater flexibility in maintaining optimum temperature in the second stage over a much broader turndown range with fixed equipment, decreases the residual dicumyl peroxide (DCP) at the yield optimum for a given temperature, and increases the overall yield of AMS at optimum conditions at a given temperature.

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METHOD FOR THE DECOMPOSITION OF CUMENE HYDROPEROXIDE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Patent Application 12/797,321, filed on June 9, 2010, the entire contents of which are incorporated herein by reference, for any and all purposes.

FIELD OF THE INVENTION

[0002] The present invention relates to an improved method for the production of phenol, acetone and alpha-methyl styrene (AMS) from a cumene hydroperoxide and dimethylbenzyl alcohol (DMBA) mixture.

BACKGROUND OF THE INVENTION

[0003] The dominant method for producing phenol and acetone is via air oxidation of cumene to cumene hydroperoxide (CHP), followed by acid catalyzed decomposition of the CHP selectively to phenol and acetone. Dimethylbenzyl alcohol (DMBA) is formed as the principal side product in the oxidation step, and is subsequently dehydrated to alpha-methyl styrene (AMS) in the same acid catalyzed decomposition step.

[0004] The acid catalyzed decomposition of CHP is well known, most modern processes utilizing a two step, continuous flow approach to optimize overall yield in this step, especially of DMBA to AMS. Examples of such prior art are U.S. Patent Nos. 7,482,493, 7,109,385, 6,307,112, 6,225,513, 6,201,157, 6,057,483, 5,998,677, 5,463,136, 5,430,200, 5,371,305, and 5,254,751, all of which are hereby incorporated by reference. These and other derivative approaches are based on the work of S. Sifniades et. al. as detailed in U.S. Patent No. 4,358,618, which is also hereby incorporated by reference.

[0005] A key to the two stage approach is to use a lower temperature first stage, targeting the selective decomposition of CHP into phenol and acetone while maximizing preservation of DMBA (and ultimately the AMS product from it) as dicumyl peroxide (DCP). The second stage is typically run shorter and hotter to selectively decompose the DCP into phenol, acetone and AMS, and dehydrate the residual DMBA from the first stage to AMS.

[0006] A variety of improvements have been demonstrated by changing the conditions of the CHP decomposition, essentially through dilution with acetone, water, phenol or cumene, separately or in various combinations, though some improvements focus on the equipment, such as the use of multitudinous reaction stages. Zakoshansky et. al. references and summarizes these various approaches in U.S. Patent No. 5,254,751, including one of the more innovative approaches where the acid is partially neutralized with amines prior to the second stage.

[0007] All of these approaches have plusses and minuses, typically requiring recycling of significant amounts of product material back to this part of the process, higher levels of acid catalyst (thus requiring more base to neutralize the reaction product prior to distillation) and/or additional complexity in both equipment count and control, for what in most cases is a marginal gain in selectivity over commonly practiced optimized approaches. Many approaches do not consider potential detrimental downstream impacts in terms of yield, energy, product quality and equipment count/complexity.

[0008] It has been found that adding only water, an additional 0.5 to 5 wt.%, just to the feed of the second stage, allows the temperature in the second stage to be fixed in a much narrower, more optimal range, independent of overall process rate. However, since DMBA, water and AMS are in equilibrium in the second stage, it was expected that the DMBA concentrations would be significantly higher at the same optimum DCP range, resulting in a slight yield penalty. Adding water to the feed of the second stage did significantly increase the maximum DMBA and DCP to AMS yield obtainable; however, it was surprising to find this optimum at essentially the same DMBA residual and a much lower DCP residual. The much lower DCP residual in particular has yield and product quality implications in the purification part of the process.

SUMMARY OF THE INVENTION

[0009] The present invention relates to a method for the production of phenol, acetone, and alpha-methyl styrene from a mixture of cumene hydroperoxide and dimethylbenzyl alcohol wherein the first stage is carried out with an acetone to phenol mole ratio of 1.0 - 1.5, water content of 0.5 to 1.5 wt.%, sulfuric acid concentration of 20 - 400 ppm, a reactor pressure of

500 - 760 mmHg, and a temperature of 60 - 85 °C, being optimized to maximize the yield of dicumyl peroxide from cumene hydroperoxide and dimethylbenzyl alcohol under any specific set of feed and operational conditions. Additional water, 0.5 to 5 wt.%, is then added prior to the second stage which is maintained preferably at 130 - 140 °C, regardless of residence time by controlling the rate of water addition. Water addition at a fixed temperature is then further refined to minimize residual dicumyl peroxide and maximize overall dimethylbenzyl alcohol to alpha-methyl styrene yield.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Figure 1 is a graph of AMS yield and second stage residual DCP versus temperature, with and without approximately 2% additional water added.

DETAILED DESCRIPTION OF THE INVENTION

[0011] In accordance with the present invention, the decomposition process, especially the second stage, is run at higher temperatures, e.g., 110 - 150 °C, most preferably in the range of 130 - 140 °C, and shorter times to balance maximum yield against the rate of organic fouling and the thermal decomposition of DCP, so as to give additional DMBA equivalents. Yield is optimized in the second stage by monitoring residual DCP and DMBA and targeting levels that have been established as representing optimum yield at a given feed composition to, and operation of, the first stage. However, most processes have fixed equipment in the decomposer second stage in terms of residence time, and so at slower overall process rates, or with other changes in the process ahead of the decomposition stage, the temperature should be decreased in the second stage of decomposition, which inherently will adversely affect AMS from DMBA yield. Even if one is at the proper DCP and DMBA levels for that particular temperature, that optimum is inferior to those at higher temperatures and the optimum residual DCP level is higher (see Figure 1), which can affect yield and product quality downstream of decomposition.

[0012] In an embodiment of the present invention, a method for the production of phenol, acetone and alpha-methyl styrene from a mixture of cumene hydroperoxide and dimethylbenzyl alcohol is described wherein the first stage is carried out with an acetone to phenol mole ratio of about 1.2 - 1.5, a water content of about 1.0 - 1.5 wt.%, sulfuric acid concentration of about 300 - 350 ppm, a reactor pressure of about 500 - 600 mm Hg, a temperature of about 75 - 81 °C, and a 5 - 6 minute residence time, mixing being provided via vigorous boiling of the mixture and return of the subsequently condensed volatiles. Additional water, about 1 - 2% was added to the product mixture obtained under the aforementioned conditions, and the resulting material fed to a plug flow reactor operating at 125 - 135 °C, the temperature being adjusted as high as possible such that 0.16 - 0.22 wt.% DMBA and 0.01 - 0.03 wt.% DCP were realized in the second stage product effluent. The detailed data described in Example 1 below yielded Figure 1, and the concept was validated in a commercial unit as described in the subsequent Examples, showing the improvement in yield maximum versus residual DCP to lower DCP levels, and the yield benefit of both higher temperature use and additional water added to the second stage feed.

EXAMPLES

Example 1:

[0013] The results in Figure 1 were generated using a well stirred glass reactor that was charged with 15 ml of a solution of 1/1 molar phenol/acetone spiked with approximately 8.2% DCP, 1.3% DMBA, 1.4% AMS, 12% cumene, and sufficient water added to give either 1.3% or 3.3% water content. The solution was brought to target temperature, and 8 1.it of 0.5 molar sulfuric acid added (approximately 25 ppm in the bulk reaction) to start the reaction. Samples were taken at various times, neutralized with a small amount of base, and analyzed for a complete component profile.

Example 2:

[0014] A CHP-containing stream with 80% CHP, 3.6% DMBA, 0.4% acetophenone (AP), and the residual cumene, was fed to the back mixed first stage of a commercial CHP decomposer operating under conditions of vigorous boiling at 550 - 600 mm Hg pressure, 78 - 80 °C, a 1.25 - 1.35 mole ratio of acetone to CHP, 5 - 6 minute residence time, 300 - 350 ppm of sulfuric acid, and 1.0 - 1.3 wt.% water under optimum conditions. With no additional water added ahead of a plug flow second stage with 0.8 - 1.0 minutes of residence time, an average AMS yield of 80.8% was obtained at 108 C, with 0.09 to 0.12 wt.% DCP, and 0.16 to 0.18% DMBA residuals exiting the second stage.

Example 3:

[0015] Conditions were as in example 2 with 1.5 wt.% additional water added ahead of the second stage. An optimal average AMS yield of 82.1% was obtained at 122 °C with 0.02 to 0.04% DCP, and 0.16 to 0.18 wt.% DMBA exiting the second stage.

Example 4:

[0016] Conditions were as in example 2, but at a 10% higher overall process rate. With no additional water added ahead of a plug flow second stage with 0.7 - 0.9 minutes of residence time, an average optimal AMS yield of 80.1% was obtained at 108 °C, with 0.09 to 0.11 wt.% DCP, and 0.16 to 0.17% DMBA exiting the second stage.

Example 5:

[0017] Conditions were as in example 4 with 1.5 wt.% additional water added ahead of the second stage. An average optimal AMS yield of 81.0% was obtained at 123 °C with 0.02 to 0.04% DCP, and 0.18 to 0.19 wt.% DMBA exiting the second stage.

Example 6:

[0018] Conditions were as in example 5, an average optimal AMS yield of 81.6% was obtained at 127 °C with 0.01 to 0.02% DCP, and 0.17 to 0.18 wt.% DMBA exiting the second stage.

Example 7:

[0019] Conditions were as in example 5 with 1 wt.% additional water added ahead of the second stage. An average optimal AMS yield of 79.6% was obtained at 124 °C with 0.01 to 0.02% DCP, and 0.17 to 0.18 wt.% DMBA exiting the second stage.

[0020] Thus and in accordance with the present invention, disclosed is a method for the production of phenol, acetone and alpha-methyl styrene from a mixture of cumene hydroperoxide and dimethylbenzyl alcohol, which comprises a first stage reaction with an acetone to phenol mole ratio of about 1.0 - 1.5, a water content of about 0.5 to 1.5 wt.%, a sulfuric acid concentration of about 20 - 400 ppm, a reactor pressure of about 450 - 760 mm Hg, a temperature of about 60 - 85 °C, and a residence time of 4 - 45 minutes, with about 0.5 to 3 wt.% additional water then being added prior to a plug flow, and a second stage reactor maintained at about 110 - 150 °C with a residence time of 0.5 to 30.0 minutes. In a preferred embodiment, the first stage reaction conditions are about 300 - 350 ppm sulfuric acid, about 450 - 500 mm Hg operating pressure, about 78 - 80 °C operating temperature, and a 5 - 6 minute residence time, the acetone to phenol mole ratio being about 1.25 to 1.35, and the water content being about 1.0 - 1.2 wt.% in the first stage, and the second stage reaction conditions are a residence time of 0.7 to 1.0 minutes, about 1 - 2 wt.% additional added water, and a temperature of about 120 - 140 °C.

[0021] In a further preferred embodiment of the present invention, exit concentrations of dicumyl peroxide are maintained at about 0.01 - 0.15 wt.%., the first stage reaction conditions are an acetone to phenol ratio of about 1.0, a sulfuric acid concentration of about 20 - 50 ppm, atmospheric to slightly negative pressure, and a residence time of 15 - 45 minutes, and the second stage reaction conditions are a residence time of 5 to 20 minutes, about 1 - 2 wt.% additional added water, and a temperature of about 120 - 140 °C, with a temperature of 134 - 138 °C particularly preferred. In another preferred embodiment, exit concentrations of dicumyl peroxide are maintained at about 0.06 to 0.10 wt.%, with about 0.02 - 0.03 wt.% being particularly preferred.

[0022] While the present invention has been described with respect to particular embodiments thereof, it is apparent that numerous other forms and modifications of the invention will be obvious to those skilled in the art. The appended claims and the present invention generally should be construed to cover all such obvious forms and modifications which are within the true spirit and scope of the present invention.

What is claimed is:

1. A method for the production of phenol, acetone and alpha-methyl styrene from a mixture of cumene hydroperoxide and dimethylbenzyl alcohol, which comprises:

a first stage reaction with an acetone to phenol mole ratio of about 1.0 - 1.5, a water content of about 0.5 to 1.5 wt.%, a sulfuric acid concentration of about 20 - 400 ppm, a reactor pressure of about 450 - 760 mm Hg, a temperature of about 60 - 85 °C, and a residence time of 4 - 45 minutes, with about 0.5 to 3 wt.% additional water then being added prior to a plug flow, and a second stage reactor maintained at about 110 - 150 °C with a residence time of 0.5 to 30.0 minutes.

2. The method of claim 1, wherein the first stage reaction conditions are about 300 - 350 ppm sulfuric acid, about 450 - 500 mm Hg operating pressure, about 78 - 80 °C operating temperature, and a 5 - 6 minute residence time.

3. The method of claim 2, wherein the acetone to phenol mole ratio is about 1.25 to 1.35, and the water content is about 1.0 - 1.2 wt.% in the first stage.

4. The method of claim 3, wherein the second stage reaction conditions are a residence time of 0.7 to 1.0 minutes, about 1 - 2 wt.% additional added water, and a temperature of about 120 - 140 °C.

5. The method of claim 4, wherein exit concentrations of dicumyl peroxide are maintained at about 0.01 - 0.15 wt.%.

6. The method of claim 1, wherein the first stage reaction conditions are an acetone to phenol ratio of about 1.0, a sulfuric acid concentration of about 20 - 50 ppm, atmospheric to slightly negative pressure, and a residence time of 15 - 45 minutes.

7. The method of claim 6, wherein the second stage reaction conditions are a residence time of 5 to 20 minutes, about 1 - 2 wt.% additional added water, and a temperature of about 120 - 140 °C.

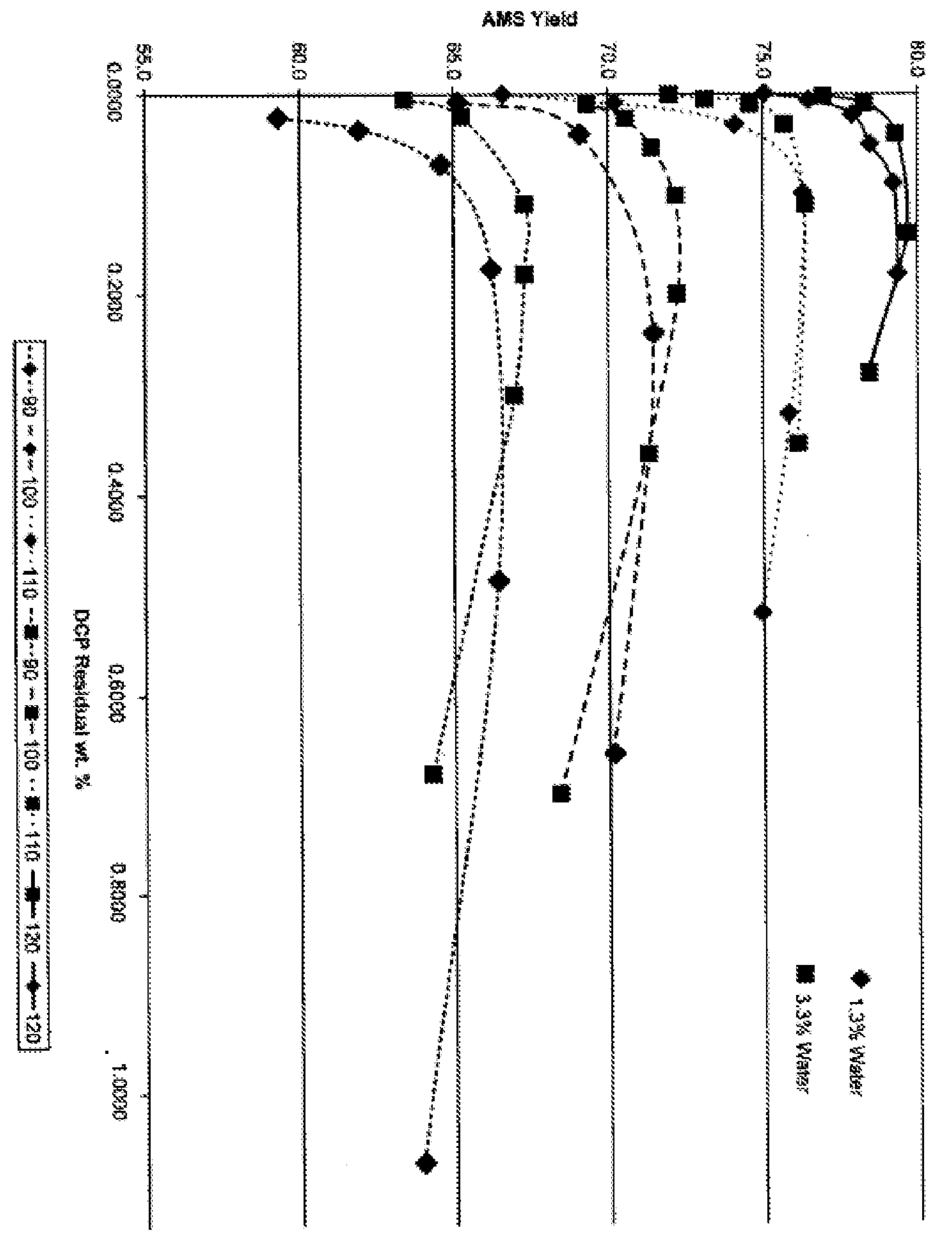
8. The method of claim 4, wherein the temperature is 134 - 138 °C.

9. The method of claim 5, wherein exit concentrations of dicumyl peroxide are maintained at about 0.02 - 0.03 wt.%.

10. The method of claim 7, wherein the temperature is about 134 - 138 °C.

11. The method of claim 5, wherein exit concentrations of dicumyl peroxide are maintained at about 0.06 to 0.10 wt.%.

FIGURE 1


AMS Yield
55.0
60.0
65.0
70.0
75.0
80.0
0.0000
0.2000
0.4000
0.6000
0.8000
1.0000
DCP Residual wt. %
1.3% Water
3.3% Water
90
100
110
90
100
110
120
120