PROCESS FOR CLEAVAGE OF AN OXIDATION MIXTURE COMPRISING HYDROPEROXIDES

The present application relates to a process for cleaving an oxidation product comprising s-butyl benzene hydroperoxide and/or cumene hydroperoxide which reduces the production of non-recoverable by-products from dimethylbenzyl alcohol (DMBA) and ethyl methyl benzyl carbinol (EMBA).

In general, phenol is manufactured by oxidizing cumene to form the hydroperoxide of cumene, followed by cleavage of the cumene hydroperoxide with an inorganic acid such as sulfuric acid to form a cumene hydroperoxide cleavage product. Some processes oxidize s-butylbenzene, either alone or in combination with cumene, to produce s-butylbenzene hydroperoxide.

A cumene oxidation product generally contains dimethylbenzyl alcohol (DMBA). Where the oxidation feed comprises s-butylbenzene, the oxidation product also generally comprises ethyl methyl benzyl carbinol (EMBA). It is desirable to maximize conversion of DMBA in the oxidation product to α-methyl styrene (AMS), and to maximize conversion of EMBA in the oxidation product to α-ethyl styrene (AES) and 2-phenyl-2-butene (2P2B) because these compounds can be hydrogenated to produce cumene and s-butylbenzene for recycle back to the oxidation reactors, which increases overall conversion efficiency.

Unfortunately, many cleavage reactions are run at relatively high reaction temperatures. For example, the reaction temperature in typical boiling pot reactions is from 75 °C to 85 °C. At such high reaction temperatures, significant amounts of DMBA, EMBA, product AMS, product AES, and product 2P2B are converted to "non-recoverable by-products."

Methods are needed which decrease the loss of DMBA and EMBA to non-recoverable by-products.

It has been surprisingly found that by carrying out the cleavage reaction in a certain manner produces lower amount of non-recoverable by--products.

Accordingly, the present invention provides a process for cleaving one or more hydroperoxides selected from s-butylbenzene hydroperoxide, cumene hydroperoxide, and/or combinations thereof the process comprising the steps of:

feeding a cleavage reaction feed to a cleavage reactor to produce a cleavage reaction mixture comprising the one or more hydroperoxides; and

subjecting the cleavage reaction mixture to cleavage reaction conditions effective to produce a cleavage reaction product comprising phenol and one or more component selected from the group consisting of methyl ethyl ketone (MEK), acetone, and combinations thereof;

wherein the cleavage reaction conditions comprise a cleavage reaction temperature which is sufficiently high to cleave a majority of the one or more hydroperoxides but sufficiently low to produce a first quantity of non-recoverable byproducts from components selected from the group consisting of dimethylbenzyl alcohol (DMBA), ethyl methyl benzyl carbinol (EMBA), and combinations thereof (typically such cleavage reaction temperature is less than 75°C, preferably from 45°C to less than 75°C), the first quantity of said non-recoverable by-products being less than a second quantity of said non-recoverable byproducts produced from said components by the same process at a cleavage reaction temperature of 75 °C or higher.

Fig. 1 is a schematic diagram of a preferred embodiment of the cleavage process.

The "low temperature cleavage" of the present application is run at cleavage temperatures that decrease the loss of DMBA and EMBA to non-recoverable by-products.

Low temperature cleavage will be described with reference to a preferred embodiment in which the cleavage zone comprises a first cleavage reactor and a second cleavage reactor. However, low temperature cleavage encompasses the use of one or more reactors, and is not limited to a system using two reactors.

The cleavage reaction feed comprises from about 0.5 wt.% to about 2 wt.% water, a ketone stream selected from an acetone stream, a MEK stream, or a mixed acetone/MEK stream, and hydroperoxides selected from s-butylbenzene hydroperoxide, cumene hydroperoxide, or combinations thereof. It has been found that a ketone feed, preferably from the ketone recovery zone(s) is an aid in reducing production of non-recoverable by-products from DMBA and/or EMBA. When the cleavage reaction occurs in a single reactor, the cleavage reaction mixture is first exposed to first reaction conditions (described below) comprising a relatively low temperature, and subsequently exposed to second reaction conditions (also described below) in the same reactor. In a preferred embodiment,

the initial cleavage reaction feed is a first cleavage reactor feed 26 (Fig. 1) to a first cleavage reactor 12.

The cleavage reactor(s) may be a variety of reactor types. Preferred reactors include, but are not necessarily limited to plug-flow reactors ("PFR's"); plug-flow reactors with recycle (PFRR's); and continuous stirred tank reactors (CSTR's).

The first cleavage reactor 12 can be a stirred tank reactor with associated internal or external heat exchange equipment effective to maintain the first cleavage reaction mixture at the first cleavage reaction temperature. In a preferred embodiment the first cleavage reactor 12 is a pipeline loop reactor comprising one or more heat exchangers 14, 16 at appropriate locations to provide cooling sufficient to maintain the first cleavage reaction mixture at the first cleavage reaction temperature. Generally, the first cleavage reaction temperature is from 45°C to 70°C. In a preferred embodiment, the first cleavage reaction temperature is from 45°C to 60°C, more preferably from 45°C to 55°C. The first cleavage reaction pressure is maintained sufficiently high to maintain the first cleavage reaction mixture in the liquid phase. Operating at 0.5 atmosphere (50kPa) or more generally is sufficient to maintain the first cleavage reaction mixture in the liquid phase.

A pump 18 is installed in the pipeline loop to provide for recirculation of a recycle flow of the first cleavage reaction mixture through the first cleavage reactor 12. A second portion of the first cleavage reaction mixture, the "first cleavage reaction product," is withdrawn from the pipeline loop reactor at a withdrawal point 20 located a short distance upstream of the feed point 22 for the first cleavage reactor feed 26. The recycle flow 24 through the pipeline loop of the first cleavage reactor 12 is much larger than the flow of the first cleavage reactor feed 26 (sometimes referred to as the "first cleavage reactor feed flow 26"). Preferably, the ratio of the recycle flow 24 to the first cleavage reactor feed flow 26 is from 10:1 to 100:1 on a weight basis, and more preferably from 20:1 to 40:1 on a weight basis.

The first cleavage reaction conditions comprise a first cleavage reaction residence time effective to cleave from 95% to 98% of hydroperoxides selected from the group consisting of s-butylbenzene hydroperoxide, cumene hydroperoxide, and combinations thereof. Depending upon the hydroperoxides

present in the first cleavage reaction mixture, the hydroperoxides are converted to phenol and a compound selected from the group consisting of methyl ethyl ketone (MEK), acetone, and combinations thereof. Generally, the first cleavage reaction residence time is from 1 minute to 10 minutes.

The first cleavage reaction conditions comprise an acid catalyst effective to catalyze the cleavage of s-butylbenzene hydroperoxide and (if present) cumene hydroperoxide. Suitable acid catalysts include but are not necessarily limited to sulfuric acid, sulfuric acid anhydride, perchloric acid, and phosphoric acid. A preferred acid catalyst is sulfuric acid. In a preferred embodiment, the acid catalyst 28 (preferably concentrated sulfuric acid), is added to a reaction mixture side stream 27 at one or more acid addition points 29. The reaction mixture side stream is located between the first cleavage reaction product withdrawal point 20 and the first cleavage reactor feed point 22.

The acid catalyst is used in an amount of from 0.005% to 0.1% by weight based on the first cleavage reactor feed flow 26. Concentrated sulfuric acid and other suitable acid catalysts are commercially available from a variety of sources.

The first cleavage reaction product 32 is fed to a second cleavage reactor 30, preferably a once through plug flow reactor, to produce a second cleavage reaction mixture. The second cleavage reactor 30 is operated at second cleavage reaction conditions effective to produce a second cleavage reaction product 44 (SCRP). The first cleavage reaction product preferably is heated to a second cleavage reaction temperature and maintained in the second cleavage reactor 30 for a second cleavage reaction residence time effective to perform one or more, preferably all of the following functions: cleave greater than 95 wt.% of remaining hydroperoxides present in the first cleavage reaction product; convert 60 wt.% or more, preferably 75 wt.% or more, preferably 85 wt.% or more of DMBA (if present) in the first cleavage reaction product to AMS; and, convert 60 wt.% or more, preferably 75 wt.% or more, preferably 85 wt.% or more of EMBA (if present) in the first cleavage reaction product to AES and 2P2B. In this preferred embodiment, selectivity of conversion of DMBA to AMS and/or of EMBA to AES and 2P2B is maximized. Generally the second cleavage reaction residence time is from 5 seconds to 1 minute.

Suitably, the second cleavage reaction conditions comprise a second cleavage reaction temperature of from 60 °C to 130 °C, preferably from 70 °C to 120 °C. The second cleavage reaction conditions also comprise a second cleavage reaction

pressure which, when combined with the second cleavage reaction temperature, is sufficient to maintain the second cleavage reaction mixture in the liquid phase. At the foregoing temperatures, a pressure of 30 psig or more is sufficient. The second cleavage reaction product 44 is withdrawn from the second cleavage reactor 30 and passed to additional stages for recovering the cleavage products.

By increasing the yield of AMS, AES, and 2P2B, the low temperature initial cleavage effectively reduces the amount of cumene and s-butylbenzene required to co-produce a given amount of phenol and MEK and/or acetone. Conversion efficiency is improved and the formation of non-recoverable by-products during cleavage is reduced.

Depending on the ratio of s-butylbenzene hydroperoxide to cumene hydroperoxide, the cleavage produces a second cleavage reaction product 44 with molar acetone:phenol ratios from 0.8:1 to 0.23:1 Molar MEK:phenol ratios in the second cleavage reaction product 44 are from 0.2:1 to 0.77:1. In a most preferred embodiment, the acetone to phenol ratio in the second cleavage reaction product 44 varies from 0.44:1 to 0.25:1.

Reactions which occur at lower temperatures occur in the early cleavage stages, preferably in the first cleavage reaction, which occurs in the first cleavage reactor 12. 95% to 98% conversion of hydroperoxides to phenol and MEK and/or acetone is achieved in the first cleavage reactor 12. Reactions which require higher temperatures occur in the later cleavage stages, preferably in the second cleavage reactor 30. The conversion of DMBA to AMS and EMBA to AES and 2P2B require relatively high temperatures of from 70 °C to 130 °C and these reactions are postponed, preferably until the first cleavage reaction product 32 reaches the second cleavage reactor 30. At this point, little hydroperoxide remains to be cleaved. The second cleavage reaction conditions can be optimized to maximize the conversion of DMBA to AMS and EMBA to AES and 2P2B.

In a preferred embodiment, the safety of the cleavage reaction is enhanced compared to other embodiments. By using a pipeline loop reactor as the first cleavage reactor 12, it is possible to make multiple exotherm measurements to verify that the reaction is being carried properly and to control the amount of acid catalyst added to the first cleavage reaction mixture side stream 27. In typical boiling pot cleavage reactors, acid addition typically is controlled by the single exotherm measurement taken at the sulfuric acid addition point. The single exotherm

measurement is made by pumping a small amount of the cleavage reactor mixture out of the reactor at the acid addition point and mixing that small amount of the cleavage reaction mixture with acid. The exotherm generated upon acid addition is measured for process control and to determine if a shutdown is required for safety purposes. If the reaction is running well, then the exotherm measured is moderate (typically 15 °C). If the reaction is running too fast, then no exotherm is measured. If the exotherm is large (25 °C or more), then the reaction is running too slowly. The risk of the reaction running too slowly is that a runaway reaction can occur when additional acid is added.

One preferred embodiment of the process for cleaving one or more hydroperoxides selected from s-butylbenzene hydroperoxide, cumene hydroperoxide, and/or combinations thereof, such process comprising:

feeding to a first cleavage reactor at a first cleavage reaction feed flow a cleavage reaction feed comprising from about 0.5 wt.% to 2 wt.% water, a ketone stream selected from the group consisting of an acetone stream, a MEK stream, and a mixed acetone/MEK stream, and an acid catalyst effective to catalyze the cleavage of hydroperoxides selected from the group consisting of s-butylbenzene hydroperoxide, cumene hydroperoxide, and combinations thereof, producing a first cleavage reaction mixture comprising one or more hydroperoxides selected from the group consisting of said s-butylbenzene, said cumene hydroperoxide, and combinations thereof;

exposing said first cleavage reaction mixture to first cleavage reaction conditions effective to cleave s-butylbenzene hydroperoxide to phenol and MEK and to cleave cumene hydroperoxide to phenol and acetone,

wherein said first cleavage reaction conditions comprise:

a first cleavage reaction temperature of less than 75 °C which is sufficiently high to cleave a majority of the one or more hydroperoxides but sufficiently low to produce a first quantity of non-recoverable byproducts from components selected from the group consisting of dimethylbenzyl alcohol (DMBA), ethyl methyl benzyl carbinol (EMBA), and combinations thereof, the first quantity of said non-recoverable byproducts being less than a second quantity of said non-recoverable byproducts produced by the same process at a cleavage reaction temperature of 75 °C or higher;

a first cleavage reaction pressure sufficiently high to maintain the first cleavage reaction mixture in the liquid phase;

recirculating a recycle flow of the first cleavage reaction mixture through the first cleavage reactor, said recycle flow being greater than the first cleavage reactor feed flow; and

feeding the first cleavage reaction product to a second cleavage reactor to produce a second cleavage reaction mixture;

subjecting the second cleavage reaction mixture to second cleavage reaction conditions comprising a second cleavage reaction temperature effective to cleave a majority of the one or more hydroperoxides remaining in the second cleavage reaction mixture, to convert a majority of DMBA in the second cleavage reaction mixture to α-methyl styrene, and to convert a majority of EMBA in the second cleavage reaction mixture to one or more compound selected from the group consisting of α-ethyl styrene (AES), 2-phenyl-2-butene (2P2B), and combinations thereof, producing a second cleavage reaction product; and,

subjecting the second cleavage reaction product to final conditions effective to produce a final cleavage reaction product comprising phenol and one or more component selected from the group consisting of methyl ethyl ketone (MEK), acetone, and combinations thereof.

Another preferred embodiment of the process for cleaving one or more hydroperoxides selected from of s-butylbenzene hydroperoxide, cumene hydroperoxide, and/or combinations thereof, such process comprising:

feeding a cleavage reaction feed comprising from about 0.5 wt.% to 2 wt.% water, a ketone stream selected from the group consisting of an acetone stream, a MEK stream, and a mixed acetone/MEK stream, and an acid catalyst to a first cleavage reactor at a first cleavage reaction feed flow, producing a first cleavage reaction mixture, said acid catalyst being effective to catalyze the cleavage of hydroperoxides selected from the group consisting of s-butylbenzene hydroperoxide, cumene hydroperoxide, and combinations thereof;

exposing said first cleavage reaction mixture to first cleavage reaction conditions effective to produce a first cleavage reaction product comprising the one or more hydroperoxides, said first cleavage reaction conditions comprising a

first cleavage reaction temperature of less than 75 °C and a first cleavage reaction pressure sufficiently high to maintain the first cleavage reaction mixture in the liquid phase, said first cleavage reaction conditions further comprising recirculating a recycle flow of the first cleavage reaction mixture through the first cleavage reactor, wherein the ratio of said recycle flow to said first cleavage reactor feed flow is from 10:1 to 100:1 on a weight basis, said first cleavage reaction conditions being effective to cleave 95% or more of s-butylbenzene hydroperoxide in the first cleavage reaction mixture to phenol and MEK, to cleave 95% or more of cumene hydroperoxide in the first cleavage reaction mixture to phenol and acetone, and to produce a first quantity of non-recoverable byproducts from components selected from the group consisting of dimethylbenzyl alcohol (DMBA), ethyl methyl benzyl carbinol (EMBA), and combinations thereof, the first quantity of said non-recoverable byproducts being less than a second quantity of said non-recoverable byproducts produced by the same process at a cleavage reaction temperature of 75 °C or higher; and

feeding the first cleavage reaction product to a second cleavage reactor to produce a second cleavage reaction mixture;

subjecting the second cleavage reaction mixture to second cleavage reaction conditions comprising a second cleavage reaction temperature effective to cleave 95 wt.% or more of the hydroperoxides remaining in the second cleavage reaction mixture, to convert 70 wt% or more of DMBA in the second cleavage reaction mixture to α-methyl styrene, and to convert 70 wt.% or more of EMBA in the second cleavage reaction mixture to one or more compound selected from the group consisting of α-ethyl styrene (AES), 2-phenyl-2-butene (2P2B), and combinations thereof, producing a second cleavage reaction product; and,

subjecting the second cleavage reaction product to final conditions effective to produce a final cleavage reaction product comprising phenol and one or more component selected from the group consisting of methyl ethyl ketone (MEK), acetone, and combinations thereof.

Plug flow reactors (PFR's) and plug flow reactors with recycle (PFRR's) are especially adaptable to multiple exotherm measurements. Controlling acid addition based on multiple exotherm measurements lowers the risk of adding too little or too

much acid catalyst to the first cleavage reactor 12 due to an incorrect exotherm measurement by any one failed control system component, and essentially decouples safety components from control components.

In a preferred embodiment, the exotherm preferably is measured at multiple locations. The exotherm is measured across one or more reaction mixture exotherm measurement points, preferably a first reaction mixture side stream exotherm measurement point 51 (or a first RMSEM point 51) and a second RMSEM point 50 along the reaction mixture side stream 27. The exotherm also preferably is measured in the first cleavage reactor 12 across one or more first cleavage reactor (FCR) exotherm measurement points, preferably a first FCR exotherm measurement point 30 and a second FCR exotherm measurement point 31 along the first cleavage reactor 12. The exotherm also preferably is measured across the second cleavage reactor, preferably across a second cleavage reactor (SCR) entry exotherm measurement point 40 and a second SCR exit measurement point 41.

The second cleavage reaction product 44 generally is fed to a neutralization apparatus and may be treated using known procedures for producing phenol and other products, depending upon the oxidation feed.

Persons of ordinary skill in the art will recognize that many modifications may be made to the foregoing without departing from the spirit and scope thereof. The embodiment described herein is meant to be illustrative only and should not be taken as limiting the invention, which will be defined in the claims.

CLAIMS

1. A process for cleaving one or more hydroperoxides selected from s-butylbenzene hydroperoxide, cumene hydroperoxide, and/or combinations thereof, the process comprising the steps of:

feeding a cleavage reaction feed to a cleavage reactor to produce a cleavage reaction mixture comprising the one or more hydroperoxides wherein the first cleavage reactor is a pipeline loop reactor comprising one or more heat exchangers effective to maintain a first cleavage reaction mixture at a first cleavage reaction temperature; and

subjecting a cleavage reaction mixture to cleavage reaction conditions to produce a cleavage reaction product comprising phenol and one or more components selected from the group consisting of methyl ethyl ketone, acetone, and combinations thereof;

wherein the cleavage reaction conditions comprise a cleavage reaction temperature of less than 75 °C to produce cleavage product of the one or more hydroperoxides and a first quantity of non-recoverable byproducts from components selected from the group consisting of dimethylbenzyl alcohol, ethyl methyl benzyl carbinol, and combinations thereof.

2. A process according to claim 1, wherein at least one further cleavage reactor is used.

3. A process according to claims 1 or 2, wherein the cleavage reaction conditions is carried out in the presence of a homogeneous acid catalyst suitable to catalyze the cleavage of hydroperoxides selected from the group consisting of s-butylbenzene hydroperoxide, cumene hydroperoxide, and combinations thereof.

4. A process according to claim 3, wherein the acid catalyst is selected from sulphuric acid, sulphuric acid anhydride, perchloric acid, or phosphoric acid.

5. A process according to claim 2, wherein the further cleavage reactor is selected from the group consisting of plug-flow reactors, plug-flow reactors with recycle, and continuous stirred tank reactors.

6. A process according to any one of claims 2 or 5, wherein said cleavage reaction feed comprises from about 0.5 wt.% to 2 wt.% water and a ketone stream and the first cleavage reaction conditions comprise

a first cleavage reaction temperature of from 45°C to 70°C;

a first cleavage reaction pressure sufficiently high to maintain the first cleavage reaction mixture in the liquid phase; and,

a first cleavage reaction residence time effective to cleave 95% or more of s-butylbenzene hydroperoxide in the first cleavage reaction mixture to phenol and methyl ethyl ketone and to cleave 95% or more of cumene hydroperoxide in the first cleavage reaction mixture to phenol and acetone.

7. A process according to any one of claims 2, 5 or 6 wherein the first cleavage reaction conditions comprise a first cleavage reaction pressure of 50 kPa or more.

8. A process according to any one of claims 2 or 5-7, wherein the first cleavage reaction conditions comprise recirculating a recycle flow of the first cleavage reaction mixture through the first cleavage reactor.

9. A process according to claim 8, further comprising withdrawing the first cleavage reaction product from the first cleavage reactor at a first cleavage reaction product withdrawal point upstream of the first cleavage reactor feed.

10. A process according to claim 9, wherein the recycle flow is greater than the first cleavage reactor feed flow.

11. A process according to claim 10, wherein a ratio of the recycle flow to the first cleavage reactor feed flow is from 10:1 to 100:1 on a weight basis.

12. A process according to claim 10, wherein the first cleavage reaction residence time is from 1 minute to 10 minutes.

13. A process according to any one of claims 1-12, further comprising controlling the amount of acid catalyst added to the first cleavage reaction mixture based on the multiple exotherm measurements.