

METHOD FOR SEPARATING ORGANIC ACID
FROM A HYDROPEROXIDE STREAM

The invention relates to a method for separating organic acid from an organic hydroperoxide stream by bringing the hydroperoxide stream into contact with an extraction fluid.

Known methods for separating organic acids from organic hydroperoxides are currently used to prevent corrosion problems in process equipment and deactivation of catalysts. Such known methods comprise liquid-liquid extraction of acids from a hydroperoxide stream. For instance, in US 5,883,268 a method for obtaining a purified ethyl benzene hydroperoxide stream, useful for the solid heterogeneous catalyst catalyzed reaction with propylene to form propylene oxide includes contacting a crude ethyl benzene hydroperoxide stream obtained by peroxidation of ethyl benzene with an aqueous solution of an alkali metal base, and separating the resulting mixture into an aqueous stream and a deacidified organic stream; contacting said organic stream with water, and separating the resulting mixture into an organic-contaminated water phase and an organic phase having a reduced alkali metal content; and contacting the organic-contaminated water phase with an extractive hydrocarbon, selected from ethyl benzene, benzene, cyclohexane, and alkanes, and separating the resulting mixture into a purified water phase having a reduced level of organic contaminants as compared to the organic-contaminated water phase and an organic phase consisting of

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hydrocarbon extractant and organic impurities from the organic-contaminated water phase.

However, such known methods make use of caustic extraction steps, usually leading to severe caustic hydroperoxide emulsion formation, which is the cause of many problems such as equipment corrosion, operational instability, and increased catalyst consumption in subsequent steps. Furthermore, a relatively expensive settling step is necessary using additional equipment to settle the caustic emulsion.

As indicated by GB-A-1251042, once mixed, mixtures of organic peroxides and water are difficult to separate. GB-A-1251042 describes a laborious method for drying liquid organic peroxides containing suspended aqueous liquid, comprising passing the liquid peroxide through a body of microporous material, allowing the resulting coalesced aqueous droplets to separate into an aqueous layer.

Therefore, there is a need for a method for obtaining a purified organic hydroperoxide stream by removing organic acid from an organic hydroperoxide stream, which is devoid of the hereinbefore-mentioned disadvantages. It has now been found that an advantageous method of removing organic acid comprises bringing the hydroperoxide stream into contact with an extraction fluid, whereby the extraction fluid and the hydroperoxide stream are separated from each other by a membrane. By keeping the hydroperoxide stream separate from the extraction fluid by means of the membrane, whilst extracting the organic acid from the hydroperoxide stream into the extraction fluid, mixing of the hydroperoxide stream with the extraction fluid can be avoided. In such process, organic acid can be removed preferably by being converted

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into a salt either in the pores of the membrane or at its surface. Salts will subsequently transfer into the extraction fluid. Hence, laborious coalescence methods such as the one described in GB-A-1251042 are no longer necessary.

Methods for transferring compounds through membranes are known under the acronym "pertraction" which stands for permeation enhanced extraction, which is also known under the term "membrane facilitated extraction."

Pertraction, in general, is a known method. For instance, GB 2,355,455 describes the removal and recovery of phenolic compounds from an aqueous effluent using a non-porous selectively permeable membrane and the mathematical theory behind this process has been described by R. Basu et al., AIChEJ., vol. 36 (3), p. 450-460 (1990). Separation of olefins from a hydrocarbon feed by contacting the mixture with a preferably hydrophobic polymeric, sintered glass, metal, or ceramic ultrafiltration membrane has been disclosed in US 5,107,058. In US 5,095,171 aromatic compounds are separated from non-aromatic compounds by a permeation process through a selective membrane. The pertraction method, however, has never been used or suggested for separating organic acids from an organic hydroperoxide stream.

According to the invention the hydroperoxide stream contains the organic acid. The hydroperoxide stream is preferably non-aqueous. The term "non-aqueous" in this respect means that the hydroperoxide stream contains less than 10 %wt of water, preferably less than 5 %wt, most preferably less than 2 %wt.

According to the invention membrane extraction or pertraction are extraction processes in which the

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exchanging phases are separated with use of a barrier or membrane. In this case, the hydroperoxide stream is separated from the extraction fluid by a membrane and organic acid can be exchanged from the hydroperoxide stream into the extraction fluid. In this way, mixing feed mixture of organic acid and hydroperoxide with the extraction fluid is prevented. Mass-transfer of organic acid can take place through the pores of the membrane barrier from the feed-side towards the extraction fluid.

The membrane can comprise hydrophilic or, preferably hydrophobic material (e.g., porous polypropylene available as Celgard or Membrana, both ex Polypore trademarks). For hydrophobic membranes it is preferred to apply a slight pressure on the extraction fluid side in order to facilitate this phase into the pore structure of the membrane. However, this pressure is restricted in order to prevent break-through of the membrane barrier from the extraction fluid side into the organic hydroperoxide side. Preferably, the extraction fluid has a pressure that is 1 to 10 bar, more preferably 1.5 to 3 bar, higher than the pressure of the hydroperoxide stream. When a hydrophilic membrane is used, such as a membrane of the cellulose type, it is preferred to apply a slight pressure on the hydroperoxide stream. In that case the hydroperoxide stream preferably has a pressure that is 1 to 10 bar, more preferably 1.5 to 3 bar, higher than the pressure of the extraction fluid.

The membrane can be any hydrophilic or hydrophobic membrane. Hydrophobic membranes are preferred, such as porous polypropylene, polyimide, polysulfone, PVDF (polyvinylidenedifluoride), or PTFE (polytetrafluoroethylene). For reasons of efficiency hollow fiber membranes are particularly preferred. The hydroperoxide stream and the

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extraction fluid can be operated in counter-current, co-current, or cross-current mode. For obtaining maximum concentration differences between the hydroperoxide stream and the extraction fluid and obtaining maximum mass transfer the counter-current method is preferred.

The relative pore diameters of the membranes are in the range of 0.1-6 μm , preferably 0.5-2 μm , whereby the pore configurations can have any form, for instance round or slit shaped. The membrane porosity is normally between 70 and 90%. A very high membrane surface area per module volume can be obtained due to specific membrane module configurations such as hollow fibers, which accordingly enhances the mass transfer.

An example of a commercially available configuration is for instance a membrane surface of 2000 m^2 , which provides a separation of an organic acid from an ethyl benzene hydroperoxide stream at a flow of 300 ton/h and an extraction stream of 25 ton/h, wherein the incoming stream contains $4 \cdot 10^{-3}$ weight fraction of acids.

Preferably, the ratio of the flow of the extraction fluid and the flow of the hydroperoxide stream is 1:100 to 1:10, more preferably 1:25 to 3:50.

The membrane facilitates the contact between the extraction fluid and the feed phase without mixing. Additionally, the overall mass-transfer is enhanced due to large contact area of the membrane, and the chosen extraction fluid determines the eventual selectivity and velocity of the process.

The extraction fluid can be chosen from a wide range of fluids of which someone skilled in the art will understand that these can be used. The polarity of the extraction fluid will generally be substantially different from the polarity of the organic hydroperoxide

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stream in order to efficiently remove the acids. In a more preferred embodiment, the extraction fluid is an aqueous solution or water. The aqueous solution preferably comprises base. If a base is present, the organic acid can be converted to a salt by an acid-base reaction. The conversion will generally take place in the pores of the membrane and optionally on its surface. When the acid has been converted to its salt it can be transferred into the aqueous extraction fluid. This conversion makes that a high concentration gradient is maintained for organic acids across the membrane.

The solution preferably contains of from 0.01 to 10 %wt of base, based on total amount of extraction fluid, more specifically of from 0.05 to 5 %wt, preferably of from 0.05 to 1 %wt. The base is preferably selected from sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium hydrogen carbonate, potassium hydrogen carbonate, and mixtures thereof. Most preferably, the extraction fluid comprises an anion of which the pK_b is smaller than the pK_a of the organic acid. Furthermore, the pH of the extraction fluid is preferably greater than 7, preferably of from 7.5 to 10, more specifically of from 8 to 10.

The method can be used for the separation of any organic acid from any organic hydroperoxide stream. Preferably, the organic hydroperoxide stream is obtained by oxidation of an organic compound such as ethylbenzene and/or cumene. The oxidation can be carried out in the liquid phase in the presence of a diluent. This diluent is preferably a compound which is liquid under the reaction conditions and does not react with the starting materials and product obtained. However, the diluent can also be a compound necessarily present during the

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reaction. For example, if the alkylaryl is ethylbenzene the diluent can be ethylbenzene as well and if the alkylaryl is cumene the diluent can be cumene as well. Besides the desired organic hydroperoxide, a range of
5 contaminants are created during the oxidation of organic compounds.

The method of the present invention is particularly useful for separating organic acids such as formic acid, acetic acid, propionic acid, and benzoic acid from an
10 ethyl benzene hydroperoxide or cumene hydroperoxide stream.

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C L A I M S

1. A method for separating organic acid from an organic hydroperoxide stream by bringing the hydroperoxide stream into contact with an extraction fluid, characterized in that the extraction fluid and the hydroperoxide stream are separated from each other by a membrane.
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2. The method according to claim 1 wherein the extraction fluid is an aqueous fluid comprising base.
3. The method according to claim 2 wherein the base is selected from sodium hydroxide, potassium hydroxide,
10 sodium carbonate, potassium carbonate, sodium hydrogen carbonate, potassium hydrogen carbonate, and mixtures thereof.
4. The method according to any one of claims 1 to 3 wherein the extraction fluid has a pH of more than 7.
- 15 5. The method according to any one of claims 1 to 4 wherein the hydroperoxide stream and the extraction fluid are in counter-current.
6. The method according to any one of claims 1 to 5 wherein the ratio of the flow of the extraction fluid and the flow of the hydroperoxide stream is 1:100 to 1:10,
20 preferably 1:25 to 3:50.
7. The method according to any one of claims 1 to 6 wherein organic acid is separated from an ethyl benzene hydroperoxide stream or a cumene hydroperoxide stream.
- 25 8. The method according to any one of claims 1 to 7 wherein the membrane is a hollow fiber membrane.
9. The method according to any one of claims 1 to 8 wherein a hydrophobic membrane is used and the extraction fluid has a pressure that is 1 to 10 bar, preferably 1.5

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to 3 bar, higher than the pressure of the hydroperoxide stream.

10. The method according to any one of claims 1 to 8 wherein a hydrophilic membrane is used and the hydroperoxide stream has a pressure that is 1 to 10 bar, preferably 1.5 to 3 bar, higher than the pressure of the extraction fluid.