obtain a higher proportion of dipropylene glycol than possible for adiabatic hydrolysis of propene oxide.

[006] Subject of the invention is therefore a method for the preparation of 1,2-propanediol and dipropylene glycol comprising:

a) continuously reacting propene with hydrogen peroxide in the presence of a catalyst mixture comprising a phase transfer catalyst and a heteropolytungstate in a liquid reaction mixture comprising an aqueous phase with a maximum apparent pH of 6 and an organic phase to obtain 1,2-propanediol and dipropylene glycol;

b) separating the reaction mixture into an aqueous phase (P_a) comprising 1,2-propanediol and dipropylene glycol and an organic phase (P_o);

c) recycling at least a part of the separated organic phase (P_o) to the reaction step a); and

d) recovering 1,2-propanediol and dipropylene glycol from the separated aqueous phase (P_a);

wherein the reaction heat generated in step a) is at least partially removed and the ratio of 1,2-propanediol to dipropylene glycol is controlled by adjusting the weight ratio of hydrogen peroxide to water fed to step a), wherein the weight ratio of hydrogen peroxide to water is varied within the range of from 0.05 to 1.5.

Detailed description of the invention

[007] In the method of the present invention, propene is reacted in a step a) with hydrogen peroxide in the presence of a catalyst mixture comprising a phase transfer catalyst and a heteropolytungstate. This reaction is carried out in a liquid reaction mixture which comprises an aqueous phase with a maximum apparent pH of 6 and an organic phase.

[008] Propene can be used in pure form or in a mixture with propane, wherein the proportion of propane may be up to 20 mol%. The proportion of propane in the propene used is preferably less than 5 mol%. Propene is preferably employed in a molar excess to hydrogen peroxide, preferably in a molar ratio of propene to hydrogen peroxide of from 1.1:1 to 10:1.

[009] Hydrogen peroxide is preferably used in the form of an aqueous solution, preferably with a hydrogen peroxide content of 10 to 80 % by weight, particularly preferably 30 to 70 % by weight. Any commercially available grade of aqueous hydrogen peroxide solutions can be used. A crude hydrogen peroxide product obtained in the extraction stage of the anthraquinone process for producing hydrogen peroxide may also be used.

[010] The catalyst mixture used in step a) comprises a heteropolytungstate. The heteroatom is preferably phosphorus or arsenic and is particularly preferably phosphorus, i.e. the heteropolytungstate is particularly preferably a polytungstophosphate. Heteropolytungstates are well known to a person skilled in the art. Preferred polytungstophosphates have a molar ratio of phosphorus to tungsten in the range of from 1:2 to 1:12. The polytungstophosphate is preferably generated *in situ* by combining phosphoric acid and sodium tungstate, which can be carried out in the liquid reaction mixture itself or prior to adding the polytungstophosphate to the liquid reaction mixture. Phosphoric acid and sodium tungstate are preferably employed at a molar ratio of

$(CH_3)_2N^+(CH_2CH_2O(C=O)R^5)_2$ $CH_3OSO_3^-$, $CH_3N^+(CH_2CH_2OH)_2(CH_2CH_2O(C=O)R^5)$ $CH_3OSO_3^-$, $CH_3N^+(CH_2CH_2OH)(CH_2CH_2O(C=O)R^5)_2$ $CH_3OSO_3^-$, $CH_3N^+(CH_2CH_2O(C=O)R^5)_3$ $CH_3OSO_3^-$, $(CH_3)_3N^+CH_2CH(CH_3)O(C=O)R^5$ $CH_3OSO_3^-$, $(CH_3)_2N^+(CH_2CH(CH_3)OH)(CH_2CH(CH_3)O(C=O)R^5)$ $CH_3OSO_3^-$ and $(CH_3)_2N^+(CH_2CH(CH_3)O(C=O)R^5)_2$ $CH_3OSO_3^-$, in which R^5 is in each case a linear alkyl group or alkenyl group having 11 to 21 carbon atoms. Most preferred is the salt $(CH_3)_2N^+(CH_2CH(CH_3)O(C=O)R^5)_2$ $CH_3OSO_3^-$ in which R^5 is an alkyl group or alkenyl group having 11 to 17 carbon atoms. The phase transfer catalysts of this embodiment may be prepared by esterifying ethanolamine, isopropanolamine, diethanolamine, diisopropanolamine, triethanolamine or triisopropanolamine with a fatty acid and subsequent quaternization with dimethyl sulphate. These phase transfer catalysts have the advantage that they are readily biodegradable, unlike tetraalkylammonium salts, and can be introduced into a biological treatment plant without further pretreatment. The salts with methylsulphate as anion are also less corrosive than tetraalkylammonium halides.

[014] The reaction of step a) is carried out in a liquid reaction mixture which comprises two liquid phases, an aqueous phase with a maximum apparent pH of 6 and an organic phase. The term “apparent pH” here refers to a value determined by measurement with a glass electrode employing a commercial pH meter calibrated with aqueous buffer solutions of known pH for measuring dilute aqueous solutions. This apparent pH differs from the notional pH, i.e. the negative logarithm of the hydrogen ion activity, by a constant value because the normal potential of the glass electrode in the aqueous phase of the reaction mixture, which comprises hydrogen peroxide and glycols, is different than the normal potential in pure water. The apparent pH of the aqueous phase is preferably maintained in the range from 1.0 to 3.5, particularly preferably in the range from 2.0 to 3.0. The apparent pH can be maintained in this range by addition of acid, preferably sulphuric acid or phosphoric acid, or by addition of base, preferably aqueous sodium hydroxide solution. Adjusting the apparent pH in the preferred range provides high selectivity for 1,2-propanediol and prevents enriching propene oxide in the aqueous phase, which simplifies the subsequent separation of propylene glycols from the aqueous phase.

[015] In the reaction of step a), the weight ratio of hydrogen peroxide to water fed to step a) is preferably adjusted while maintaining a molar excess of propene to hydrogen peroxide fed to step a). The weight ratio of hydrogen peroxide to water is varied within the range of from 0.05 to 1.5, preferably from 0.10 to 0.7 and more preferably from 0.15 to 0.45. The molar ratio of propene to hydrogen peroxide fed to step a) is preferably from 1.1:1 to 10:1, more preferably from 1.2:1 to 4:1.

[016] The concentration of hydrogen peroxide in the aqueous phase of step a) is preferably kept within a range of from 0.1 to 5 % by weight, preferably from 0.12 to 1.0 % by weight.

[017] The reaction is preferably conducted at a temperature in the range of from 50 to 110 °C, more preferably 60 to 100 °C and particularly preferably 70 to 90 °C. The reaction pressure is preferably higher than the vapor pressure of propene at the reaction temperature to ensure that most of the propene is present in the liquid organic phase of the liquid mixture.

[027] In step c) of the method of the present invention, at least a part of the separated organic phase (P_o) is recycled to the reaction step a). Thereby, propene oxide present in the organic phase (P_o) is recycled to step a) in order to achieve a complete conversion of propene to 1,2-propanediol, dipropylene glycol and tripropylene glycol. Preferably, the heteropolytungstate present in the organic phase (P_o) is recycled into step a), and it is particularly preferred to recycle substantially all of the catalyst mixture that is present in the organic phase into step a).

[028] The organic phase (P_o) separated from the liquid reaction mixture provided by step a) may be recycled to step a) without further treatment. If the propene fed to step a) contains propane, it is preferred to separate a stream of unreacted propene from the organic phase in step c) before the organic phase is recycled to step a), with the separated stream of unreacted propene containing as much propane as the impure propene fed to step a). This way, an accumulation of propane in the organic phase of the reaction mixture of step a) can be avoided for a continuous reaction. The separated stream of unreacted propene may be passed to a C3 splitter for separating propene and propane and the recovered propene may be recycled to step a).

[029] The aqueous phase (P_a) obtained in step b) is preferably further processed without recycling any part of it directly or indirectly to step a).

[030] In a preferred embodiment, the aqueous phase (P_a) separated in step b) is subjected to a hydrogenation treatment before it is passed to step d). The hydrogenation is preferably carried out using a supported hydrogenation catalyst comprising one or more metals from the group of Ru, Rh, Pd, Pt, Ag, Ir, Fe, Cu, Ni and Co on a support, wherein activated carbon, SiO_2, TiO_2, ZrO_2, Al_2O_3 and aluminium silicates are preferred as support materials. Preference is given to hydrogenation catalysts comprising ruthenium as active metal. The catalytic hydrogenation is preferably carried out at a partial hydrogen pressure of 500 000 Pa to 5 000 000 Pa (5 to 50 bar), preferably 500 000 Pa to 3 500 000 Pa (5 to 35 bar), more preferred 700 000 Pa to 3 000 000 Pa (7 to 30 bar), even more preferred 800 000 Pa to 2 500 000 Pa (8 to 25 bar), and a temperature of 80 °C to 140 °C, preferably 90 °C to 120 °C. The hydrogenation catalyst may be used as a suspension or as a fixed bed, a trickle bed hydrogenation with a fixed bed catalyst being preferred. The hydrogenation can prevent problems caused by decomposition of hydrogen peroxide, which has not reacted in step a), in step d) of recovering 1,2-propanediol and dipropylene glycol. The hydrogenation also converts the by-products 1-hydroperoxy-2-propanol, 2-hydroperoxy-1-propanol and hydroxyacetone formed in step a) to 1,2-propanediol and thereby improves the yield of 1,2-propanediol.

[031] In step d) of the method of the present invention, 1,2-propanediol and dipropylene glycol are recovered from the optionally hydrogenated aqueous phase of step b). 1,2-Propanediol and dipropylene glycol are preferably recovered by a sequence of distillation steps. Preferably, a sequence of distillation steps as described in Ullmann's Encyclopedia of Industrial Chemistry, online edition, entry "Propanediols", page 4, DOI 10.1002/14356007.a22_163.pub2 is used where an overhead product comprising water is separated from a bottoms product comprising 1,2-propanediol and dipropylene glycol in a series two to four heat integrated distillation steps, followed by successive vacuum distillation steps which provide 1,2-propanediol and dipropylene glycol as overhead products and a bottoms product containing higher boiling organic compounds

and salts. From this bottoms product, tripropylene glycol may be recovered as an overhead product in a further vacuum distillation step.

[032] The present invention will now be explained in more detail with reference to examples.

Examples

Preparation of initial epoxidation catalyst solution

[033] A mixture of 100 g 70 % by weight hydrogen peroxide, 155 g demineralized water, 160 g 85 % by weight phosphoric acid and 100 g sodium tungstate dihydrate was stirred for 2 h at room temperature. Then, a solution of 150 g of methyltri(octyl/decyl)ammonium methylsulfate (CAS No. 2387913-24-6) in 1020 g Hydrosol A 200 ND (a mixture of C10 alkyl benzenes) was added and the mixture was stirred for another 2 h at room temperature. The aqueous and organic phases were then separated to provide 1230 g of organic phase as initial epoxidation catalyst solution.

Reaction of propene with hydrogen peroxide

[034] The reaction of propene with hydrogen peroxide was carried out at a temperature of 80 °C and a pressure of 3 000 000 Pa (30 bar) in a loop reactor with a loop volume of 0.45 l, a circulation pump and a heat exchanger for adjusting the reaction temperature, which was operated at a circulation rate of 130 kg h^{-1}. The reactor was equipped with a catalyst feed reservoir, an organic phase collection vessel equipped with a stirrer, and feed pumps for feeding liquid propene, liquid propane, an aqueous hydrogen peroxide solution and liquid from the catalyst feed reservoir. The initial epoxidation catalyst solution was charged to the catalyst feed reservoir and a mixture of 100 g 70 % by weight hydrogen peroxide, 155 g demineralized water, 160 g 85 % by weight phosphoric acid and 20 g sodium tungstate dihydrate was charged to the organic phase collection vessel. The loop initially contained reaction mixture from a previous experiment. Circulation was started and maintained at 130 kg h^{-1} and the circulating mixture was heated to 80 °C. Then 80 g h^{-1} of propene, 50 g h^{-1} of propane, an aqueous hydrogen peroxide solution containing 0.1 % by weight phosphoric acid, and 320 g h^{-1} of organic catalyst solution from the catalyst feed reservoir were introduced into the loop reactor, cooling the circulating mixture to maintain a reaction temperature of 80 °C. The concentration and feed rate of the hydrogen peroxide solution was varied in the three examples to the values given in table 1. A two-phase oxidation reaction mixture was removed from the loop reactor in an amount corresponding to the amounts added and 18 g h^{-1} of a 9 % by weight aqueous disodium sulfate solution was added to this mixture at the reactor outlet to speed up phase separation. The organic phase and the aqueous phase of the resulting mixture were separated, and the organic phase was passed to the organic phase collection vessel after depressurizing and cooling to 25 °C. When 500 g of the organic phase had accumulated in the organic phase collection vessel, the content of the vessel was thoroughly mixed by stirring for 5 min, phases were separated by settling and the organic phase was passed to the catalyst feed reservoir with the aqueous phase remaining in the organic phase collection vessel. After about 11 h of operation, the feeding of reactants and the circulation in the loop reactor were stopped and 0.33 g of sodium

Claims:

1. A method for the preparation of 1,2-propanediol and dipropylene glycol comprising:
   a) continuously reacting propene with hydrogen peroxide in the presence of a catalyst mixture comprising a phase transfer catalyst and a heteropolytungstate in a liquid reaction mixture comprising an aqueous phase with a maximum apparent pH of 6 and an organic phase to obtain 1,2-propanediol and dipropylene glycol;
   b) separating the reaction mixture into an aqueous phase (P_a) comprising 1,2-propanediol and dipropylene glycol and an organic phase (P_o);
   c) recycling at least a part of the separated organic phase (P_o) to the reaction step a); and
   d) recovering 1,2-propanediol and dipropylene glycol from the separated aqueous phase (P_a);

   wherein the reaction heat generated in step a) is at least partially removed and the ratio of 1,2-propanediol to dipropylene glycol is controlled by adjusting the weight ratio of hydrogen peroxide to water fed to step a), wherein the weight ratio of hydrogen peroxide to water is varied within the range of from 0.05 to 1.5.

2. The method of claim 1, wherein the weight ratio of hydrogen peroxide to water fed to step a) is adjusted while maintaining a molar excess of propene to hydrogen peroxide fed to step a).

3. The method of claim 2, wherein the molar ratio of propene to hydrogen peroxide fed to step a) is from 1.1:1 to 10:1, preferably from 1.2:1 to 4:1.

4. The method of any one of claims 1 to 3, wherein the ratio of 1,2-propanediol to dipropylene glycol is reduced by increasing the weight ratio of hydrogen peroxide to water fed to step a) or the ratio of 1,2-propanediol to dipropylene glycol is increased by reducing the weight ratio of hydrogen peroxide to water fed to step a).

5. The method of any one of claims 1 to 4, wherein the weight ratio of hydrogen peroxide to water is varied within the range from 0.10 to 0.7 and preferably from 0.15 to 0.45.

6. The method of any one of claims 1 to 5, wherein the concentration of hydrogen peroxide in the aqueous phase of step a) is from 0.1 to 5 % by weight, preferably from 0.12 to 1.0 % by weight.

7. The method of any one of claims 1 to 6, wherein the residence time of the reaction mixture in step a) is adjusted to maintain a hydrogen peroxide conversion in the range of from 80 to 99 %.

8. The method of any one of claims 1 to 7, wherein step a) is conducted in a loop reactor and the reaction heat generated in step a) is at least partially removed by circulating the reaction mixture through a heat exchanger.

9. The method of any one of claims 1 to 8, wherein the aqueous phase (P_a) obtained in step b) is further processed without recycling any part of it directly or indirectly to step a).

10. The method of any one of claims 1 to 9, wherein in step d) the aqueous phase (P_a) is subjected to catalytic hydrogenation.

11. The method of any one of claims 1 to 10, wherein step a) is conducted in the presence of phosphoric acid and the heteropolytungstate is a polytungstophosphate.

12. The method of any one of claims 1 to 11, wherein the organic phase in step a) comprises an organic solvent having a boiling point of more than 100 °C at atmospheric pressure and a solubility in water at 20 °C of less than 250 mg/kg, the organic solvent being preferably selected from alkylated aromatic hydrocarbons having 8 to 12 carbon atoms.

13. The method of any one of claims 1 to 12, wherein the phase transfer catalyst is selected from tertiary amines and tertiary or quaternary ammonium salts and comprises in total at least 12 carbon atoms.

14. The method of claim 13, wherein the phase transfer catalyst comprises a tertiary or quaternary ammonium ion having the structure $R^1R^2R^3NR^{4+}$, wherein R^1, R^2 and R^3 are the same or different and are each selected from alkyl groups having from 8 to 10 carbon atoms and R^4 is hydrogen or methyl.

15. The method of any one of claims 1 to 14, wherein steps b), c) and d) are carried out continuously.