**A method for the preparation of 1,2-propanediol**

Field of the invention

[001] The present invention relates to a method for the preparation of 1,2-propanediol by reacting propene with hydrogen peroxide wherein the amount of phosphoric ester of 1,2-propanediol can be reduced.

Background of the invention

[002] In a well-established process used in the industry, 1,2-propanediol is prepared by reacting propene oxide with water. Propene oxide can be made on an industrial basis using the HPPO process comprising the reaction of propene with hydrogen peroxide in the presence of a titanium zeolite catalyst and an organic solvent. Propene oxide is then isolated and purified prior to the step of reacting it with water to make 1,2-propanediol.

[003] WO 2017/089075 discloses a method for producing 1,2-propanediol from propene and hydrogen peroxide comprising: a) reacting propene with hydrogen peroxide in the presence of a catalyst mixture comprising a phase transfer catalyst and a heteropolytungstate, wherein the reaction is carried out in a liquid mixture comprising an aqueous phase with a maximum pH of 6 and an organic phase, b) dividing the two-phase mixture from step a) into an aqueous phase and an organic phase containing propylene oxide, c) returning the propylene oxide contained in the separated organic phase into the reaction from step a) and d) separating 1,2-propanediol from the aqueous phase separated in step b).

Summary of the invention

[004] The inventor of the present invention has now found that in the method described in WO 2017/089075, phosphoric acid esters of 1,2-propanediol are formed in reaction step a) in a side reaction by reaction of propene oxide with phosphoric acid present in the reaction mixture. The inventor has also found that the selectivity for 1,2-propanediol can be improved by heating all or a part of the aqueous phase separated from the oxidation reaction mixture to a temperature of more than 140 °C at a pressure sufficient to maintain a substantial part of the water as a liquid phase, which hydrolyzes the phosphoric acid esters of 1,2-propanediol to give 1,2-propanediol.

[005] Subject of the invention is therefore a method for the preparation of 1,2-propanediol comprising:

a) reacting propene with hydrogen peroxide in the presence of a catalyst mixture comprising a phase transfer catalyst, phosphoric acid and a heteropolytungstate in a liquid reaction mixture comprising an aqueous phase with a maximum apparent pH of 6, wherein 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, and an organic phase;

b) separating the reaction mixture into an aqueous phase ($P_a$) comprising 1,2-propanediol and phosphoric acid esters of 1,2-propanediol and an organic phase ($P_o$);

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

d) heating at least a part of the aqueous phase ($P_a$) separated in step b) to a temperature of more than 140 °C at a pressure sufficient to maintain at least 20 % by weight of the water of said aqueous phase (Pa) in a liquid phase, wherein heating step d) is performed without adding hydrogen; and

e) recovering 1,2-propanediol from the aqueous phase heated in step d).

[006] In a further aspect the present invention relates to the use of a heating step d) to cleave phosphoric acid esters of 1,2-propanediol into 1,2-propanediol and phosphoric acid in a method for the preparation of 1,2-propanediol comprising:

a) reacting propene with hydrogen peroxide in the presence of a catalyst mixture comprising a phase transfer catalyst, phosphoric acid and a heteropolytungstate in a liquid reaction mixture comprising an aqueous phase with a maximum apparent pH of 6 and an organic phase;

b) separating the reaction mixture into an aqueous phase ($P_a$) comprising 1,2-propanediol and phosphoric acid esters of 1,2-propanediol and an organic phase ($P_o$);

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

d) heating at least a part of the aqueous phase ($P_a$) separated in step b) to a temperature of more than 140 °C at a pressure sufficient to maintain at least 20 % by weight of the water of said aqueous phase ($P_a$) in a liquid phase; and

e) recovering 1,2-propanediol from the aqueous phase heated in step d).

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

2-hydroperoxy-1-propanol formed by reaction of propene oxide with hydrogen peroxide, and formic acid, acetic acid and hydroxyacetone formed by further oxidation of 1,2-propanediol. The aqueous phase also comprises phosphoric acid and phosphoric acid esters of 1,2-propanediol and may further contain sodium salts of phosphoric acid if a polytungstophosphate generated *in situ* by combining phosphoric acid and sodium tungstate is used in step a). The organic phase ($P_o$) comprises unreacted propene and propene oxide that is formed as intermediate when propene is reacted with hydrogen peroxide and has not been hydrolyzed to 1,2-propanediol. The organic phase ($P_o$) typically also comprises one or more salts formed of the heteropolytungstate and the cation of the phase transfer catalyst. The organic phase $P_o$ will also comprise propane, if the propene starting material contains propane, and organic solvent, if an organic solvent having a low solubility in water is used as described further above.

[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 step d) of the method of the present invention, at least a part and preferably all of the aqueous phase ($P_a$) separated in step b) is heated to a temperature of more than 140 °C at a pressure sufficient to maintain at least 20 % by weight of the water of said aqueous phase ($P_a$) in a liquid phase. Preferably, the aqueous phase (Pa) is heated to a temperature in the range of 142 °C to 200 °C. The pressure in heating step d) may be from 4 to 200 bar and is preferably the autogenous pressure resulting from the vapor pressure of water at the temperature used in step d). Heating step d) is performed without adding hydrogen. The aqueous phase ($P_a$) is preferably heated in step d) for a time sufficient to hydrolyze more than 30 mol-% of the phosphoric acid esters of 1,2-propanediol, preferably from 50 to 90 mol-%, which will typically require from 5 to 60 min. The heating of step d) can be carried out in any type of pressure reactor and is preferably carried out in a plug flow reactor, such as a pipe reactor.

Claims

1. A method for the preparation of 1,2-propanediol comprising:

   a) reacting propene with hydrogen peroxide in the presence of a catalyst mixture comprising a phase transfer catalyst, phosphoric acid and a heteropolytungstate in a liquid reaction mixture comprising an aqueous phase with a maximum apparent pH of 6 , wherein 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, and an organic phase;

   b) separating the reaction mixture into an aqueous phase ($P_a$) comprising 1,2-propanediol and phosphoric acid esters of 1,2-propanediol and an organic phase ($P_o$);

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

   d) heating at least a part of the aqueous phase ($P_a$) separated in step b) to a temperature of more than 140 °C at a pressure sufficient to maintain at least 20 % by weight of the water of said aqueous phase ($P_a$) in a liquid phase, wherein heating step d) is performed without adding hydrogen; and

   e) recovering 1,2-propanediol from the aqueous phase heated in step d).

2. The method of claim 1, wherein between steps b) and d) or between steps d) and e) at least a part of the aqueous phase is subjected to a step f) of catalytic hydrogenation at a temperature of from 80 ° to 140 °C, preferably from 90 °C to 120 °C.

3. The method of claim 1 or 2, wherein in step d) the aqueous phase ($P_a$) is heated to a temperature in the range of 142 °C to 200 °C.

4. The method of any one of claims 1 to 3, wherein the pressure in heating step d) is from 4 to 200 bar.

5. The method of any one of claims 1 to 4, wherein step e) comprises a multi-step distillation, with the first distillation step and optionally further distillation steps providing an overhead product comprising water and a bottoms product which is passed to the next distillation step, and a distillation step providing an overhead product comprising 1,2-propanediol and a residuals bottoms product.

6. The method of claim 5, wherein the residuals bottom product is subjected to at least one further distillation step.

7. The method of any one of claims 1 to 6, wherein the heteropolytungstate is a polytungstophosphate.

8. The method of any one of claims 1 to 7, 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.

9. The method of any one of claims 1 to 8, 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.

10. The method of claim 9, 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.

11. Use of a heating step d) to cleave phosphoric acid esters of 1,2-propanediol into 1,2-propanediol and phosphoric acid in a method for the preparation of 1,2-propanediol comprising:

a) reacting propene with hydrogen peroxide in the presence of a catalyst mixture comprising a phase transfer catalyst, phosphoric acid and a heteropolytungstate in a liquid reaction mixture comprising an aqueous phase with a maximum apparent pH of 6 and an organic phase;
b) separating the reaction mixture into an aqueous phase ($P_a$) comprising 1,2-propanediol and phosphoric acid esters of 1,2-propanediol and an organic phase ($P_o$);
c) recycling at least a part of the separated organic phase ($P_o$) to the reaction step a);
d) heating at least a part of the aqueous phase ($P_a$) separated in step b) to a temperature of more than 140 °C at a pressure sufficient to maintain at least part of said aqueous phase as a liquid; and
e) recovering 1,2-propanediol from the aqueous phase heated in step d).

12. The use of claim 11, wherein the method for the preparation of 1,2-propanediol is performed as defined in any one of claims 2 to 10.