

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
5 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
10 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
15 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).

20 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
25 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:

- 30 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

1a

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
5 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).

[006] In a further aspect the present invention relates to the use of a heating step d) to cleave
10 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
15 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
20 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
25 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
30 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
35 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 phosphorus to tungsten in the range of from 1:2 to 10:1, preferably from 4:1 to 8:1. The heteropolytungstate reacts with hydrogen peroxide in the liquid reaction mixture to form peroxotungstates and peroxotungstophosphates, for example $\text{PO}_4[\text{WO}(\text{O}_2)_2]_4^{3-}$ and $\text{HPO}_4[\text{WO}(\text{O}_2)_2]_2^{2-}$ as well as partially protonated forms thereof, which are presumably the catalytically active species for oxidizing propene.

[011] The catalyst mixture used in step a) also comprises a phase transfer catalyst. The phase transfer catalyst comprises a cation or a compound which forms a cation in the aqueous phase, whereby the cation can form a salt with a peroxotungstate or heteropolyperoxotungstate, which salt is soluble in the organic phase of the liquid reaction mixture. The phase transfer catalyst preferably comprises a singly-charged cation or a compound which forms a singly-charged cation in the aqueous phase. Suitable as phase transfer catalyst are tertiary amines, tertiary and quaternary ammonium salts, and quaternary phosphonium salts. Suitable counterions for tertiary and quaternary ammonium salts are the anions chloride, bromide, nitrate, sulphate, hydrogen phosphate, dihydrogen phosphate, methyl sulfonate, methyl sulphate and ethyl sulphate. The phase transfer catalyst is preferably used in an amount which results in a molar ratio in the liquid mixture of phase transfer catalyst to tungsten in the range of from 0.2:1 to 3:1 and particularly preferably of from 0.4:1 to 1:1, where the molar ratio refers to the cations or compounds forming cations in the employed phase transfer catalyst and to the employed amount of tungsten.

[012] In a preferred embodiment, the phase transfer catalyst is a tertiary amine or a tertiary or a quaternary ammonium salt which comprises in total at least 12 carbon atoms, preferably from 12 to 60 carbon atoms. Preferred are tetraalkylammonium salts. Suitable tertiary amines are for example dodecyldimethylamine, hexadecyldimethylamine, octadecyldimethylamine, tributylamine and trioctylamine. Suitable tertiary ammonium salts are the protonation products of these tertiary amines. Suitable quaternary ammonium salts are for example dodecyltrimethylammonium salts, hexadecyltrimethylammonium salts, octadecyltrimethylammonium salts, methyltributylammonium salts and methyltrioctylammonium salts. More preferably, the phase transfer catalyst comprises a tertiary or quaternary ammonium ion having the structure $\text{R}^1\text{R}^2\text{R}^3\text{NR}^4+$, 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. Most preferably, the phase transfer catalyst comprises methyltri(octyl/decyl)ammonium methylsulfate (CAS No. 2387913-24-6).

[013] In another preferred embodiment, the phase transfer catalyst comprises at least one salt having a tertiary or quaternary ammonium ion of the structure $\text{R}^1\text{R}^2\text{R}^3\text{R}^4\text{N}^+$, where R^1 is a $\text{Y-O}(\text{C}=\text{O})\text{R}^5$ group with Y being CH_2CH_2 , $\text{CH}(\text{CH}_3)\text{CH}_2$ or $\text{CH}_2\text{CH}(\text{CH}_3)$ and R^5 being an alkyl

group or alkenyl group having 11 to 21 carbon atoms,

R^2 is hydrogen or an alkyl group having 1 to 4 carbon atoms, and

R^3 and R^4 are each independently R^1 , an alkyl group having 1 to 4 carbon atoms or Y-OH.

Preferred are quaternary ammonium salts with methylsulphate as the counterion, where R^2 is a

5 methyl group and R^5 is a linear alkyl group or alkenyl group. Particularly preferred are the salts

$(CH_3)_3N^+CH_2CH_2O(C=O)R^5 CH_3OSO_3^-$, $(CH_3)_2N^+(CH_2CH_2OH)(CH_2CH_2O(C=O)R^5) CH_3OSO_3^-$,

$(CH_3)_2N^+(CH_2CH_2O(C=O)R^5)_2 CH_3OSO_3^-$, $CH_3N^+(CH_2CH_2OH)_2(CH_2CH_2O(C=O)R^5) CH_3OSO_3^-$,

$CH_3N^+(CH_2CH_2OH)(CH_2CH_2O(C=O)R^5)_2 CH_3OSO_3^-$, $CH_3N^+(CH_2CH_2O(C=O)R^5)_3 CH_3OSO_3^-$,

$(CH_3)_3N^+CH_2CH(CH_3)O(C=O)R^5 CH_3OSO_3^-$, $(CH_3)_2N^+(CH_2CH(CH_3)OH)(CH_2CH(CH_3)O(C=O)R^5)$

10 $CH_3OSO_3^-$ 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

15 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.

20 [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

25 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

30 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 step a) the weight ratio of hydrogen peroxide to water fed to step a) is

35 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 preferably varied within the range of from 0.05 to 1.5, more preferably from 0.10 to 0.7 and most 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 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.

5 [017] The reaction of step a) can be carried out with or without addition of an organic solvent. The reaction is preferably conducted in the presence of at least one organic solvent having a boiling point of more than 100 °C, preferably more than 120 °C, which has a solubility in water of less than 250 mg/kg at 20 °C. Suitable as solvents are alcohols having one or more hydroxyl groups, ethers, esters, ketones and alkylated aromatic hydrocarbons. Adding a solvent can
10 improve extraction of a salt formed of the heteropolytungstate and the phase transfer catalyst into the organic phase. Preferably the amount of organic solvent is selected to provide a proportion of organic solvent in the organic phase during the reaction in the range of from 10 to 90 % by weight.

[018] In a preferred embodiment, the organic solvent comprises an epoxidized fatty acid methyl ester. The epoxidized fatty acid methyl ester can be formed *in situ* in the reaction mixture of step a)
15 by employing a fatty acid methyl ester with unsaturated fatty acid groups which reacts with hydrogen peroxide to the epoxidized fatty acid methyl ester. Particularly preferred are epoxidized fatty acid methyl esters which comprise fatty acid groups originating from vegetable oils, in particular soybean oil. The epoxidized fatty acid methyl esters have the advantage that they have low solubility in the aqueous phase.

20 [019] In another preferred embodiment, the solvent comprises an alkylated aromatic hydrocarbon having 8 to 12 carbon atoms. Suitable alkylated aromatic hydrocarbons are, for example, 1,2-dimethylbenzene (o-xylene), 1,3-dimethylbenzene (m-xylene), 1,4-dimethylbenzene (p-xylene), ethylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene (mesitylene), 1-ethyl-2-methylbenzene, 1-ethyl-3-methylbenzene and 1-ethyl-4-methylbenzene and
25 n-propylbenzene. Preferably, hydrocarbon mixtures comprising more than 50% by weight, particularly preferably more than 80% by weight, of alkylated aromatic hydrocarbons having 8 to 12 carbon atoms are used as solvent. The use of these solvents enables extracting most of the peroxotungstates into the organic phase of the reaction mixture and recycling them, which allows for operating the process without a need for recovering heteropolytungstate from the aqueous
30 phase of the reaction mixture of step a). The phase transfer catalyst, the molar ratio of phase transfer catalyst to heteropolytungstate, the molar ratio of heteroatom of the heteropolytungstate to tungsten, the molar ratio of propene to hydrogen peroxide and the amount of solvent are then preferably selected to transfer as much as possible of the tungsten present in the liquid reaction mixture into the organic phase.

35 [020] The phase transfer catalyst, the heteropolytungstate and the optionally used solvent can be added in step a) of the method of the present invention separately or in the form of mixtures containing two or all three of these components. Preferably, a solvent is used in step a) and the phase transfer catalyst and the heteropolytungstate are added dissolved in an organic phase comprising the solvent.

[021] The reaction of step a) is carried out in the presence of phosphoric acid. Phosphoric acid is preferably used in an amount providing an apparent pH of the aqueous phase (P_a) of the reaction mixture of from 1.0 to 3.5, preferably of from 2.0 to 3.0. The concentration of phosphoric acid and phosphates in the aqueous phase (P_a) of the reaction mixture is preferably from 0.2 to 0.8 % by weight, calculated as PO_4^{3-} relative to the mass of the aqueous phase. Phosphoric acid may be present from *in situ* formation of a polytungstophosphate in the aqueous phase (P_a) of the reaction mixture as described above.

[022] The reaction of step a) may be carried out in batch or continuously, with a continuous reaction being preferred. The concentration of hydrogen peroxide in the aqueous phase is preferably maintained in the range of 0.1 to 5% by weight, particularly preferably 0.5 to 3% by weight. The concentration of hydrogen peroxide can be adjusted in this range by appropriate selection of the reaction temperature, the molar ratio of propene to hydrogen peroxide and the residence time of the liquid mixture in the reactor in which the reaction takes place. The residence time of the reaction mixture is preferably adjusted to maintain a hydrogen peroxide conversion in the range of from 80 to 99 %.

[023] During the reaction, the liquid mixture is preferably mixed in order to generate a large phase interface between the aqueous phase and the organic phase. For this purpose, the reaction is preferably carried out continuously in a loop reactor which has fixed internals in a tubular section and the liquid mixture is passed through the loop reactor at a flow rate which generates a turbulent flow at the internals. Baffles, static mixing elements, structured packings or random packings can be used as internals for this purpose. In combination to these internals or as an alternative, heat exchangers, such as plate heat exchangers or tube bundle heat exchangers, may be used, in which turbulent flow is generated, for example between the plates of a plate heat exchanger or in the tubes of a tube bundle heat exchanger.

[024] Preferably, all or a part of the reaction heat generated in step a) is removed while the reaction proceeds, preferably by cooling the reaction mixture in a heat exchanger. More preferably, the reaction is carried out continuously in a loop reactor which comprises a heat exchanger within the reactor loop for cooling the reaction mixture.

[025] In step b) of the method of the present invention, the liquid reaction mixture provided by step a) is separated into an aqueous phase (P_a) comprising 1,2-propanediol and phosphoric acid esters of 1,2-propanediol and an organic phase (P_o). The separation of the two-phase reaction mixture provided by step a) is preferably carried out in a settler vessel. The two-phase reaction mixture is preferably passed through a coalescer element comprising a structured packing or a random packing with a surface wetted by the dispersed phase of the two-phase mixture in order to achieve a more complete separation.

[026] The aqueous phase (P_a) typically comprises water, unreacted hydrogen peroxide and the reaction product 1,2-propanediol. The aqueous phase typically also contains dipropylene glycol and tripropylene glycol as well as reaction byproducts, such as 1-hydroperoxy-2-propanol and

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 (P_a) 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.

[031] In a preferred embodiment, at least a part and preferably all of the aqueous phase (P_a) obtained in step b) is subjected to a step f) of catalytic hydrogenation at a temperature of from 80 °C to 140 °C, preferably from 90 °C to 120 °C, between steps b) and d) or between steps d) and e). 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, SiO₂, TiO₂, ZrO₂, Al₂O₃ 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 5 to 50 bar, preferably 5 to 35 bar, more preferred 7 to 30 bar, even more preferred 8 to 25 bar. 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 e) 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. Preferably, step f) of catalytic hydrogenation is carried out between steps b) and d) to prevent decomposition of hydrogen peroxide or hydroperoxide by-products in heating step d).

[032] In step e) of the method of the present invention, 1,2-propanediol is recovered from the heat treated and optionally hydrogenated aqueous phase (P_a), preferably by distillation. Preferably, 1,2-propanediol and higher propylene glycols, like dipropylene glycol and tripropylene glycol, are recovered by a sequence of distillation steps, such as 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 which is preferably subjected to at least one further distillation step. Most 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 higher propylene glycols in a series of two to four heat integrated distillation steps, followed by a vacuum distillation step which provides 1,2-propanediol as the overhead product and a bottoms product containing higher boiling organic compounds and salts. From this bottoms product, dipropylene glycol and tripropylene glycol may be recovered as overhead products in further vacuum distillation steps. In a preferred embodiment, the heated aqueous phase obtained in step d) is directly fed to a distillation step where an overhead product comprising water is separated in order to use the heat supplied in step d) for recovering 1,2-propanediol in step e).

[033] Heating all or a part of the separated aqueous phase (P_a) prior to recovering 1,2-propanediol increases the yield of 1,2-propanediol by converting the phosphoric acid esters of 1,2-propanediol, which are unwanted by-products, to the desired product 1,2-propanediol.

[034] The present invention will now be explained in more detail with reference to an example.

Example

Preparation of initial epoxidation catalyst solution

[035] A mixture of 86 g 70 % by weight hydrogen peroxide, 98 g demineralized water, 207 g 85 % by weight phosphoric acid and 129 g sodium tungstate dihydrate was stirred for 2 h at room temperature. Then, a solution of 194 g of methyltri(octyl/decyl)ammonium methylsulfate (CAS No. 2387913-24-6) in 800 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 1067 g of organic phase as initial epoxidation catalyst solution.

Reaction of propene with hydrogen peroxide

10 [036] The reaction of propene with hydrogen peroxide was carried out at a temperature of 80 °C and a pressure of 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 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. 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, 210 g h⁻¹ of a 15 % by weight aqueous hydrogen peroxide solution containing 0.3 % 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. 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 4.8 % 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 catalyst feed reservoir after depressurizing and cooling to 25 °C. After about 11 h of operation, the feeding of reactants and the circulation in the loop reactor were stopped. The next day, circulation in the loop reactor was restarted, dosing of reactants was resumed after the reaction temperature had been established in the loop reactor and the reaction was continued for another 11 h. Aqueous phase for further hydrogenation and heat treatment was collected after a stationary operating state was reached.

Hydrogenation of the separated aqueous phase

[037] 504 g of the aqueous phase separated from the reaction mixture of reacting propene with hydrogen peroxide were charged to a 1 l spinning basket autoclave containing 75 g of a 2 % by weight ruthenium on activated carbon supported catalyst in the spinning basket. The autoclave was flushed with nitrogen followed by hydrogen and hydrogenation was carried out at 120 °C and 1.6 MPa hydrogen pressure for 5 h with the basket spinning.

Heat treatment of the hydrogenated aqueous phase

[038] 50 g of the hydrogenated aqueous phase having a pH of 7 were added to a 300 ml autoclave. After flushing with nitrogen the autoclave content was heated to 180 °C and held at this temperature for 15 min at a nitrogen pressure of 15 bar. The autoclave was then cooled to ambient temperature and depressurized.

[039] Prior to and after the heat treatment the aqueous phase was analyzed for 1,2-propanediol (MPG), dipropylene glycol (DPG) and tripropylene glycol (TPG) by capillary GC (25 m CP-WAX-52 CB column from Agilent, He carrier gas, temperature program starting at 50 °C with ramps of 20 K/min to 90 °C, 10 K/min to 220 °C and 5 K/min to 235 °C, FID detector). Table 1 shows the analysis data. Ion chromatography with a conductivity detector (Metrohm A Supp 5-250 column (polyvinyl alcohol with quaternary ammonium groups), 0.5 ml/min aqueous eluent with 1 mmol/l NaHCO₃ and 3.2 mmol/l Na₂CO₃, aqueous suppressor regenerant with 100 mmol/l sulfuric acid and 20 mmol/l oxalic acid) showed that the heat treatment decreased the area of the peak associated to propanediol mono phosphoric acid ester to 23% of the area prior to heat treatment.

15 Table 1

Propylene glycol contents in % by weight prior to and after the heat treatment

	prior to heat treatment	after heat treatment
MPG	22.7	23.7
DPG	3.2	3.4
TPG	0.3	0.3

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.