Part-Stream Distillation

The present invention relates to a continuous process for the preparation of propylene oxide wherein in a downstream acetonitrile solvent recovery stage, a stream S1 containing the solvent acetonitrile and at least one component which has a normal boiling point which is higher than the normal boiling point of acetonitrile, wherein the decadic logarithm of the octanol-water partition coefficient (log K_{OW}) of the at least one component B, measured at 25 °C, is greater than zero, is divided into two streams S2 and S3, wherein the total weight of S3 relative to the total weight of S1 is in the range of from 0.01 to 25 %. The stream S3 is subjected to a vapor-liquid fractionation comprising to serially coupled fractionation units, and a stream S4, obtained from the vapor-liquid fractionation and depleted of the at least one component B, optionally after further work-up, is recycled as solvent stream to the epoxidation reaction.

Especially in industrial-scale continuous processes for the epoxidation of propene in acetonitrile as solvent, one of the key features of the overall process is the recycling of the solvent back into the epoxidation step. An advantageous process which allows to effectively recycle acetonitrile is described in WO 2011/006990 A1. This document discloses a method for the separation of the acetonitrile from water, which method can be advantageously included in a continuous process for the preparation of propylene oxide in acetonitrile as solvent. Carrying out this epoxidation process, it was found that although the process allows to achieve excellent results, in particular with regard to the recycling of acetonitrile, certain impurities, contained in in at least one of the starting materials in the acetonitrile or in the hydrogen peroxide employed for the epoxidation reaction or obtained during the epoxidation reaction as by-products or side-products or formed during at least one of the work-up stages which are preferably carried out downstream the epoxidation reaction, may tend to a accumulate in the acetonitrile recycling stream. These impurities may further tend to have a negative influence on the performance of the heterogeneous catalyst which is preferably employed in the epoxidation process, in particular a zeolite-based catalyst having framework structure MWW and containing Ti. Such a decrease in performance may be observed either in a decrease in selectivity and/or in activity of the catalyst.

Therefore, it was an object of the embodiments disclosed herein to provide an economically advantageous continuous process for the preparation of propylene oxide in acetonitrile as solvent which allows to essentially avoid the accumulation of such impurities in the recycling acetonitrile solvent stream.

Usually, if such impurities accumulate in a certain stream, the stream is subjected to one or more suitable separation stages such as distillation stages which, if carried out under suitable distillation conditions, may result in a stream depleted of the impurities. However, in particular in

industrial-scale processes, subjecting a solvent recycling stream to such separation stages necessarily involves considerable investment and energy consumption, due to the usually high flow rates and the thus resulting large apparatuses.

Surprisingly, however, it was found that for the separation of impurities from an acetonitrile recycling stream in a continuous process for the preparation of propylene oxide, these disadvantage can be avoided by subjecting only a fraction of a specific recycling stream to impurity separation using a specifically designed fractionation unit, and leaving the major portion of this specific recycling stream untreated. For the impurities which were found to be critical, it was surprisingly found that the performance of the catalyst can be ensured over a very long period of time although only said minor fraction of a recycling stream is subjected to impurity separation.

Therefore, in an aspect, there is provided a continuous process for the preparation of propylene oxide, comprising

(a) reacting propene, optionally admixed with propane, with hydrogen peroxide in a reaction apparatus in the presence of acetonitrile as solvent, obtaining a stream S0 leaving the reaction apparatus, S0 containing propylene oxide, acetonitrile, water, at least one further component B, optionally propene and optionally propane, wherein the normal boiling point of the at least one component B is higher than the normal boiling point of acetonitrile and wherein the decadic logarithm of the octanol-water partition coefficient (log K_{OW}) of the at least one component B is greater than zero;

(b) separating propylene oxide from S0, optionally after having separated propene and optionally propane, obtaining a stream S1 containing acetonitrile, water and the at least one further component B;

(c) dividing S1 into two streams S2 and S3, wherein the total weight of S3 relative to the total weight of S1 is in the range of from 0.01 to 25 %;

(d) subjecting S3 to a vapor-liquid fractionation in a first fractionation unit, obtaining a vapor fraction stream S4a being depleted, relative to S3, of at least one of the at least one component B and obtaining a liquid bottoms stream S4b, and subjecting at least part of the vapor fraction stream S4a to a vapor-liquid fractionation in a second fractionation unit, obtaining a vapor fraction stream S4c and a liquid bottoms stream S4 being depleted, relative to S4a, of at least one of the at least one component B;

(e) recycling at least a portion of S4, optionally after work-up, to (a), and recycling at least a portion of S2, optionally after work-up, to (a).

Claims

1. A continuous process for the preparation of propylene oxide, comprising
   (a) reacting propene, optionally admixed with propane, with hydrogen peroxide in a reaction apparatus in the presence of acetonitrile as solvent, obtaining a stream S0 leaving the reaction apparatus, S0 containing propylene oxide, acetonitrile, water, at least one further component B, optionally propene and optionally propane, wherein the normal boiling point of the at least one component B is higher than the normal boiling point of acetonitrile and wherein the decadic logarithm of the octanol-water partition coefficient (log K_{OW}) of the at least one component B is greater than zero;
   (b) separating propylene oxide from S0, optionally after having separated propene and optionally propane, obtaining a stream S1 containing acetonitrile, water and the at least one further component B;
   (c) dividing S1 into two streams S2 and S3, wherein the total weight of S3 relative to the total weight of S1 is in the range of from 0.01 to 25 %;
   (d) subjecting S3 to a vapor-liquid fractionation in a first fractionation unit, obtaining a vapor fraction stream S4a being depleted, relative to S3, of at least one of the at least one component B and obtaining a liquid bottoms stream S4b, and subjecting at least part of the vapor fraction stream S4a to a vapor-liquid fractionation in a second fractionation unit, obtaining a vapor fraction stream S4c and a liquid bottoms stream S4 being depleted, relative to S4a, of at least one of the at least one component B;
   (e) recycling at least a portion of S4, optionally after work-up, to (a), and recycling at least a portion of S2, optionally after work-up, to (a).

2. The process of claim 1, wherein in (c), the total weight of S3 relative to the total weight of S1 is in the range of from 0.05 to 20 %.

3. The process of claim 1, wherein from 90 to 99.9 weight-% of S1 consist of acetonitrile and water and wherein from 0.01 to 5 weight-% of S1 consist of the at least one component B.

4. The process of claim 1, wherein S3 is fed to the top of the first fractionation unit and the at least part of the vapor fraction stream S4a is fed to the bottom of the second fractionation unit, wherein in (d), the first fractionation unit is operated at an absolute pressure at the top of the first fractionation unit in the range of from 0.5 to 5 bar and wherein the second fractionation unit is operated at an absolute pressure in the bottom

of the second fractionation unit in the range of from 65 to 95 of the pressure at the top of the first fractionation unit.

5. The process of claim 1, wherein in (d), the number of theoretical trays of the first fractionation unit is in the range of from 1 to 100 and the number of theoretical trays of the second fractionation unit is in the range of from 1 to 100.

6. The process of claim 1, wherein in (d), the first fractionation unit is operated without reflux, the at least part of the vapor fraction stream S4a subjected to the vapor-liquid fractionation in the second fractionation unit not being condensed prior to subjecting to the vapor-liquid fractionation in the second fractionation unit, and the second fractionation unit is operated with reflux, wherein a fraction of the vapor fraction stream S4c is used, after condensation, as reflux and wherein the reflux ratio is in the range of from 0.5 : 1 to 1 : 1.

7. The process of claim 1, wherein from 10 to 30 weight-% of the liquid bottoms stream S4b consist of acetonitrile and from 0.1 to 10 weight-% of the liquid bottoms stream S4b consist of the at least one further component B.

8. The process of claim 1, wherein from 90 to 99.99 weight-% of S4 consist of acetonitrile and water, and wherein from 0.0001 to 0.2 weight-% of S4 consist of the at least one component B.

9. The process of claim 1, wherein (e) comprises working-up S4, said working-up comprising combining at least a portion of S4 with S2 obtaining a liquid stream.

10. The process of claim 9, wherein (e) comprises subjecting the liquid stream to acetonitrile-water separation obtaining a stream enriched in acetonitrile, and recycling said stream enriched in acetonitrile, optionally after further work-up, to (a).

11. The process of claim 10, wherein (e) comprises

(i) preparing a liquid stream S5 by adding a liquid stream P to S2, or to at least the portion of S4, or to the liquid stream obtained from combining S2 and at least the portion of S4,
wherein P comprises at least 95 weight-% of C3, based on the total weight of P,
wherein C3 is propene optionally admixed with propane with a minimum weight ratio of propene relative to propane of 7:3, and
wherein P is added in an amount so that in S5, the weight ratio of C3 relative to acetonitrile is in the range of from 0.2:1 to 5:1;

(ii) subjecting S5 to a temperature of 92 °C at most and a pressure of at least 10 bar, , obtaining a first liquid phase L1 and a second liquid phase L2,
wherein at least 95 weight-%of L1 consist of C3, acetonitrile, water and the at least one component B, the water content of L1 being less than 10 weight-% based on the total weight of L1, and
wherein at least 95 weight-% of L2 consist of C3, acetonitrile, water and the at least one component B, the C3 content of L2 being 5 weight-% at most, based on the total weight of L2, and the acetonitrile content of L2 being less than 45 weight-% based on the total weight of L2;

(iii) separating L1 from L2;

(iv) recycling L1 as the stream enriched in acetonitrile, optionally after further work-up, to (a).

12. The process of claim 11, further comprising working up L1, said working-up comprising subjecting L1 to a distillation stage wherefrom a bottoms stream BL1 is obtained, wherein at least 95 weight-% of BL1 consist of C3, acetonitrile, water and the at least one component B, wherein the C3 content of BL1 is in the range of from 7 to 18 weight-%, and recycling BL1 as the stream enriched in acetonitrile, optionally without any further work-up, to (a).

13. The process of claim 12, wherein from 0.01 to 5 weight-% of BL1 consist of the at least one component B.

14. The process of any of claim 1, wherein (b) comprises

(I) separating propene, optionally together with propane, and oxygen which is optionally additionally contained in S0, from S0, obtaining a stream S01 enriched in propylene oxide, acetonitrile, water, and the at least one component B, wherein at least 99 weight-% of S01 consist of acetonitrile, water, the at least one component B and propylene oxide; wherein for separation, a fractionation unit is used, wherein at the top of the fractionation unit, liquid acetonitrile, optionally admixed with liquid water, is added as entraining agent;

(II) separating propylene oxide from S01, obtaining a stream S02 enriched in acetonitrile, water and the at least one component B, wherein at least 95 weight-% of S02 consist of acetonitrile, water and the at least one component B, and wherein the weight ratio of acetonitrile relative to water is greater than 1:1, wherein S02 is subjected to (c) as S1.

15. The process of claim 14, wherein (b) further comprises

(IIIa) subjecting S02 obtained from (II) to hydrogenation; and/or

(IIIb) subjecting the stream obtained from (II) or (IIIa) to distillation to obtain a bottoms stream,

wherein the hydrogenated stream obtained from (IIIa) or the bottoms stream obtained from (IIIb) is subjected to (c) as S1.

16. The process of claim 1, wherein in (a), propene is reacted with hydrogen peroxide in the presence of a heterogeneous catalyst, said heterogeneous catalyst comprising a zeolite.

17. The process of claim 1, wherein from 90 to 97 weight-% of S0 consist of acetonitrile, water, and propylene oxide, and wherein from 0.01 to 3 weight-% of S0 consist of the at least one component B.

18. The process of claim 1, wherein the at least one component B is propionitrile, 1-nitropropane, 2-nitropropane, 3-methylbutanenitrile, n-pentanenitrile, 1-pentanol, 2-pentanol, 2-butanone, 2-pentanone, 2-hexanone, 4-methyl-2-heptanone, 2,6-dimethyl-4-heptanol, 4,6-dimethyl-2-heptanol, 2,6-dimethyl-4-heptanone, 4,6-dimethyl-2-heptanone, 2,6-dimethyl-4,6-heptandiol, 2,4-dimethyloxazoline, 2,5-dimethyloxazoline, cis-2,4-dimethyl-1,3-dioxolane, trans-2,4-dimethyl-1,3-dioxolane, acetaldehyde, propionaldehyde, at least one impurity contained in the hydrogen peroxide employed in (a), or a combination of two or more of these compounds.

19. The process of claim 18, wherein the at least one component B comprises a combination of propionitrile, 1-nitropropane, 2-nitropropane, 2,6-dimethyl-4-heptanol, 4,6-dimethyl-2-heptanol, 2,6-dimethyl-4-heptanone, acetaldehyde, and propionaldehyde.

20. The process of claim 18, wherein in (d), the stream S3 is subjected to a vapor-liquid fractionation in a first fractionation unit, obtaining a vapor fraction stream S4a being depleted, relative to S3, of at least one of the at least one component B, the at least one of the at least one component B comprising propionitrile, or 1-nitropropane, or 2-nitropropane, or 2,6-dimethyl-4-heptanol, or 4,6-dimethyl-2-heptanol, or 2,6-dimethyl-4-hepta-none, or a combination of two or more thereof, and obtaining a liquid bottoms stream S4b, wherein at least part of the vapor fraction stream S4a is subjected to a vapor-liquid fractionation in a second fractionation unit, obtaining a vapor fraction stream S4c and a liquid bottoms stream S4 being depleted, relative to S4a, of at least one of the at least one component B, the at least one of the at least one component B comprising acetaldehyde, or propionaldehyde, or 2-butanone, or a combination of two or more thereof.

21. The process of claim 18, wherein the at least one impurity contained in the hydrogen peroxide employed in (a) is selected from the group of compounds consisting of an alkyl phosphate, a nonyl alcohol, an alkylcyclohexanol ester, an N,N-dialkyl carbonamide, an N-alkyl-N-aryl carbonamide

, an N,N-dialkyl carbamate, a tetraalkyl urea, a cycloalkyl urea, a phenylalkyl urea, an N-alkyl-2-pyrrolidone, an N-alkyl caprolactam, and a combination of two or more of these compounds.

22. The process of claim 1, wherein in (d), 90 to 100 weight-% of the vapor fraction stream S4a are subjected to the vapor-liquid fractionation in the second fractionation unit.