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(54) Title: PURIFICATION OF 1,3-PROPANEDIOL

(57) Abstract

A process is described for purifying a carbonyl-containing 1,3-propanediol composition, the process comprising: (a) forming a solution of said 1,3-propanediol composition in an acidic aqueous medium; (b) adding a sufficient amount of a base to the aqueous medium to form a basic solution having a pH greater than 7; (c) heating the basic solution under conditions effective to distil a major portion of the water therefrom; and (d) heating the remaining basic solution under conditions effective to distil a major portion of the PDO therefrom, to provide a 1,3-propanediol composition having a lower carbonyl content than the starting carbonyl-containing 1,3-propanediol composition. The process of the invention provides a purified 1,3-propanediol which can be used as a starting material for a low-colour polyester.

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PURIFICATION OF 1,3-PROPANEDIOL

This invention relates to the preparation of 1,3-propanediol. In a specific aspect, the invention relates to the recovery of 1,3-propanediol from a reaction product mixture containing carbonyl impurities.

1,3-Propanediol (PDO) is an important industrial chemical useful in the preparation of poly(propylene terephthalate) (PPT), a polyester from which films and fibres can be made. PDO can be prepared from ethylene oxide in a process involving cobalt-catalysed hydroformylation followed by hydrogenation, and it can alternatively be prepared by hydrolysis of acrolein in the presence of an acid catalyst followed by hydrogenation. In the preparation of PDO, it is common for the crude product to include 400 ppm or more carbonyl by-products including acetals. High levels of carbonyl impurities in PDO are associated with the production of acrolein during preparation of PPT and with poor colour in fibres spun from the PPT. Unfortunately, PDO purification by fractional distillation is inadequate. For instance, in US-A-5,334,778 is shown that distillates may still contain 3,000 to 10,000 ppm carbonyl impurities. Other methods have been developed to reduce the carbonyl content, such as steam stripping, solvent extraction, chemical treatment and treatment with solid polyvinyl alcohol (US-A-4,105,701), but a purification process based on distillation would be the simplest and hence preferred method.

It is therefore an object of the invention to provide a process for purifying PDO. In one aspect, it

is an object of the invention to provide a process which reduces the carbonyl content of PDO and reduces the amount of acrolein by-product in the condensation polymerisation to PPT.

According to the invention, a process is provided for purifying a carbonyl-containing 1,3-propanediol composition, the process comprising:

(a) forming a solution of the 1,3-propanediol composition in an aqueous medium having a pH less than 7;

(b) adding a sufficient amount of a base to said acidic solution to form a basic solution having a pH greater than 7;

(c) heating the basic solution under conditions effective to distil a major portion of the water therefrom; and

(d) heating the remaining basic solution under conditions effective to distil a major portion of the 1,3-propanediol therefrom, to provide a 1,3-propanediol composition having a lower carbonyl content than the starting carbonyl-containing 1,3-propanediol composition.

The process of the invention provides a purified PDO which can be used as a starting material for a low-colour polyester.

The process of the invention involves forming an acidic aqueous solution of a carbonyl-containing PDO composition. The source of the contaminating carbonyl species can be acetals, aldehydes or ketones. Water is generally present or added in an amount that is sufficient to provide an aqueous solution of 5 to 95 weight percent water, preferably 10 to 80, and most preferably 20 to 70 weight percent water. Less dilute PDO solutions have the advantage of requiring less subsequent purification and smaller equipment, with the

disadvantage of requiring longer times for removal of impurities. More dilute solutions can be purified in less time but require larger equipment and may not be as efficient because of the need to remove large amounts of water. The water is preferably distilled or deionised water.

An acid is added to the aqueous PDO solution. The pKa (25 °C) of the acid in aqueous solution is less than 6, preferably less than 4. The acid may be an organic or inorganic acid. It preferably has a high boiling point, e.g., greater than 100 °C, so as not to be easily removed if sparging or vacuum is applied to the solution. Examples of suitable acids include carboxylic acids, preferably C_2 or greater, such as succinic, propionic, hexanoic, chloroacetic or benzoic acid; sulphonic acids, particularly arylsulphonic acids such as p-toluenesulphonic acid; hydrohalogenic acids; phosphoric acids including orthophosphoric acid and metaphosphoric acid; and compounds which can generate acids in the presence of water or hydroxyl groups, such as sulphur trioxide, phosphorus pentoxide, carboxylic anhydrides and Lewis acids such as aluminium chloride. Sulphonic and phosphoric acids are preferred. The acid may also be in insoluble form as, for example, an acidic polymeric ion exchange resin, acidic alumina or acidic clay, in which case it is desirable to remove the solid acid by filtration or other suitable means before distillation of the aqueous solution. Mixtures of suitable acids may be used. In general, oxidising acids such as sulphuric acid and nitric acid can be used but may cause unwanted side reactions. Acids containing heavy metals or halogens would not be preferred because of possible adverse effects on PDO quality from contamination by metal or halide ions.

The acid is added to the aqueous solution in an amount that is sufficient to achieve a pH of less than 7, preferably less than 5, most preferably less than 4. Typical pH levels will fall within the range of 2 to 6. Low levels of acid generally require longer reaction times than higher levels of acid (lower pH). However, very large amounts of acid are unnecessary. They will increase the cost of the reaction and may cause unwanted side reactions. In the case of insoluble acids, the pH of the solution may remain relatively high, i.e. close to 7. If the starting PDO composition is acidic, it is nonetheless generally advisable to form the aqueous solution with added acid.

In an optional but preferred embodiment of the process of the invention, the aqueous acidified PDO solution is sparged with a gas to aid in the removal of volatile impurities. The gas is preferably an inert gas such as nitrogen, argon or helium, with nitrogen preferred. The rate of sparging will affect the efficiency of removal of volatiles and is typically in the range of 0.01 to 10 litres/minute per litre of aqueous PDO solution. Reduced pressure can be applied instead of or along with sparging, to facilitate the removal of volatile impurities. In the latter embodiment, preferred operating pressures will roughly fall within the range of 10 to 90 kPa (100 to 900 mbar).

The acid treatment is preferably accompanied by stirring of the aqueous medium.

As the volatile impurities are removed from the PDO solution, they are recovered by suitable means, such as appropriate scrubbers or by passage into a caustic solution.

The temperature during the acid treatment can affect the rate of removal of the impurities and will

generally fall within the range of 0 to 100 °C, preferably within the range of 5 to 60 °C. Temperatures above 50 °C, i.e., near or above the boiling point of acrolein, can promote removal of volatile impurities, such as acrolein, formed in this step. Although higher temperatures can be used, particularly for short periods, high temperatures can promote undesired side reactions, especially acid-catalysed reactions.

The treatment time will vary depending upon the other reaction conditions such as level of impurities, the desired PDO purity, the amount of water and acid, the sparging (or vacuum) efficiency and the reaction temperature. Under preferred reactions conditions, the time of the acid treatment will usually be at least 30 minutes, generally within the range of 1 to 24 hours, preferably less than 6 hours.

Following the acid treatment, the aqueous solution is adjusted to a pH greater than 7, preferably to a pH of 8 or more, by the addition of a base. The amount of base is nominally the amount needed to neutralise the acid present in the first step, although additional base may be desirable, particularly if the starting PDO composition contained acidic species. The preferred bases are alkali and alkaline earth hydroxides, carbonates and bicarbonates, particularly sodium and potassium hydroxides. The addition of base may cause yellowing of the PDO. For PDO solutions acidified with an insoluble acid such as an acidic resin, the base is preferably added after the acid has been physically removed, e.g., by filtration or other suitable means.

The basic aqueous solution is then distilled to remove water. The distillation can be carried out at atmospheric pressure but is most efficiently carried out under reduced pressure within the range of 10 to

60 kPa (100 to 600 mbar). Distillation equipment such as distillation and fractionation columns may be used.

After the water and other low-boiling components are removed, the PDO can be distilled overhead. Preferably, it is distilled at a temperature within the range of 100 to 160 °C and at reduced pressure (typically at less than 20 kPa) to avoid excessive heating of the PDO. Distillation removes the yellow colour generated in the neutralisation step, i.e., the distillate is water-white whereas the residue may be highly coloured.

Each of the process steps can be carried out independently as batch, semi-batch, semi-continuous or continuous processes.

The purified PDO can be used, for example, to prepare condensation polymers and copolymers. The purified PDO is particularly useful for preparing poly(propylene terephthalate) by the condensation polymerisation of PDO with terephthalic acid.

Example 1

In this and the following examples, carbonyl analyses were made using a test based on ASTM E411-70. In this test total carbonyls (from both acetals and free carbonyl) are determined by conversion to 2,4-nitrophenylhydrazone derivatives which are measured colorimetrically. The carbonyls are reported in ppm based on C=O.

A flask with a magnetic stir bar was charged with 250 g of PDO (carbonyl content 665 ppm) and 250 ml deionised water. The pH of the resulting solution was about 4.5-5. Phosphoric acid (0.23 g, 85 wt%) was added to the solution to adjust the pH to about 3-3.5. The solution was stirred at room temperature (circa 23 °C) for 5 hours. A sample of the solution had a carbonyl content of 217 ppm. The acidic aqueous solution was

then neutralised and adjusted to a pH of about 10-10.5 by addition of 8.5 ml of 1 N sodium hydroxide solution. The basic reaction solution was distilled using a 20-cm Vigreux column to remove the water and a small forecut of PDO (combined total 262 g), and the major portion of purified, water-white PDO was distilled over at about 124 °C (oil bath temperature 153 to 157 °C) and about 3 kPa (30 mbar). The purified PDO (203 g) had a carbonyl content of 245 ppm. The distillation residue (about 29 g) was tannish orange and had a carbonyl content of 685 ppm.

Example 2

A flask with magnetic stir bar was charged with 750 ml commercial PDO (carbonyl content 365 ppm, average of two analyses), 750 ml purified water (EM Omnisolve HPLC grade) and, 0.6 g p-toluenesulphonic acid monohydrate. The solution was stirred at room temperature and sparged with a fine stream of nitrogen bubbles at about 0.4 litres per minute through a glass sparge tube with a sintered glass tip immersed to the bottom of the flask. After 5 hours, 0.16 g phosphoric acid (85 wt%) was added to the mixture. After a total of 88 hours, the solution (carbonyl analysis 137 ppm) was made basic by addition of about 14 ml 1N solution of sodium hydroxide, which caused the reaction mixture to turn slightly yellow. The basic solution was transferred to a distillation flask and heated at an oil bath temperature of about 125 to 130 °C under a reduced pressure of about 40 kPa (400 mbar) to remove the water. After 4 hours, about 701 g aqueous distillate had been collected. Over a period of 3 hours, the pressure was reduced gradually from about 40 kPa (400 mbar) to about 11 kPa (110 mbar) and held for a time at this pressure to collect an additional 28 g aqueous distillate. The temperature or the oil

bath was then raised to about 150-155 °C at 11 kPa (110 mbar), and the pressure was reduced until steady distillation of the PDO occurred at about 8 to 9 kPa (80 to 90 mbar). The first 100 ml of this distillate was discarded and the middle cut of purified, water-white PDO was collected. A yellow residue (about 80 g) was left in the distillation flask. The purified PDO showed hardly any acrolein by GC, and colorimetric analysis showed 128 ppm carbonyls.

Table 1 shows the amount of acrolein and allyl alcohol collected based on the distillate weight and analysis. The colour of the PDO after this reaction was measured according to ASTM method D-1209 (using 35-ml samples) and is shown in Table 1. In Table 1 also grades of commercially available PDO have been included, which differ (substantially) in composition. Sample C 1, however, was very impure, and has been distilled only.

TABLE 1

PDO	Carbonyls[a] (ppm)	Acrolein (mg)	Allyl Alcohol (mg)	Colour[c]
C 1[b]	1100	11.6	27	250-300
C 2	365	4.2	20	100
C 3	365	3.1	22	ND[d]
Example 2	128	2.9	26	5-10
C 4	112	0.3	10	50

[a]Average, as C=O.
[b]Distilled only.
[c]Pt-Co scale.
[d]ND = not determined.

Note from Table 1 that the PDO purified in Example 2 produced less acrolein than the unpurified,

commercial PDO compositions with higher carbonyl contents. Note also that mere distillation (as in C 1) does not automatically produce a PDO of sufficient purity. The colour of the PDO after heating with acid was the lowest with the purified PDO of Example 2, which was even lower in colour than the untreated PDO having somewhat lower carbonyl content.

Example 3

A flask with magnetic stir bar was charged with 800 g commercial PDO (average carbonyl analysis 365 ppm), 200 g water and 0.5 g p-toluenesulphonic acid monohydrate. The stirred mixture was sparged as in Example 2 at room temperature for 17 hours, heated gently with sparging on a hot plate to 41 to 66 °C for 3 hours, and cooled to room temperature. After a total of 25 hours, about 7 ml 1N sodium hydroxide solution was added to bring the pH to between 7 and 8. The PDO solution turned slightly yellow. The reaction solution was distilled as in Example 2 at a bath temperature of about 140 °C at atmospheric pressure, then at about 150 to 160 °C, then at about 125 °C at about 40 kPa (400 mbar) and decreasing to about 11 kPa (110 mbar), then at 150 °C at about 6 to 7 kPa (60 tot 70 mbar). Analyses showed 216 ppm carbonyls in the PDO in the distillation flask after removal of most of the water and 178 ppm carbonyls in the final, distilled (455 g), water-white PDO.

Example 4

In this experiment, PDO was polymerised with terephthalic acid to produce a polyester. A 600-ml stainless steel pressure reactor fitted with a distillation column, condenser and collection vessel was charged with 133.2 g of the indicated PDO (Table 2; 1.75 mole) and 207.7 g terephthalic acid (1.25 mole). The reactor was pressurised to 345-552 kPa (50-80 psi)

with nitrogen, degassed by release of pressure five times, and re-pressurised to 138 kPa (20 psi) and heated to 150 °C. For the first two hours, the pressure was maintained near 345 kPa (50 psi) and was lowered in 69 kPa (10 psi) increments each hour thereafter. After a total of 6 hours, any pressure was released and the aqueous distillate was collected, weighed and analysed by GC. The molten oligomer was poured into a pan and cooled. The yellowness index of the oligomer was measured by reflectance with a Gardner Colorgard System 105 according to ASTM D-1925. Results are shown in Table 2.

TABLE 2

	Aqueous Distillate			
PDO	Distillate (g)	Acrolein (ppm)	Allyl Alcohol (%)	PPT Colour
C 1[b]	47.3	4390	1.2	13
C 2	45.2	2120	0.8	6.6
Example 3	48.9	1320	0.7	-0.5
Example 2	45.9	1460	0.8	-0.6
C 3	44.7	1170	0.8	4.7

[a]Average, as C=0.
[b]Distilled only.
[c]Yellowness Index

As can be seen from Table 2, the purified PDOs from Examples 2 and 3 gave less acrolein by-product in the aqueous distillate than the PDOs having higher total carbonyl analyses. The purified PDOs also gave an oligomeric PPT product with yellowness index lower than that of the commercial grade having a lower carbonyl content.

Example 5

A larger-scale preparation of PDO by the invention process was carried out as follows:

A 379 l (100-gallon) reactor was charged with 178.9 kg (394.3 lbs) of PDO containing about 212 ppm (average) carbonyl impurities and 125 kg (275 lbs) deionised water. A mixture of 38.6 g 85 wt% phosphoric acid and 143.7 g p-toluenesulphonic acid monohydrate was added to the reactor. The pH of the reactor mixture dropped to 2.6 following addition of the acid. Sodium hydroxide solution (1N, 131.5 ml) was added at ambient temperature and pressure to adjust the pH to about 3.1. Nitrogen sparging was carried out by introducing nitrogen gas at 653 kPa (80 psig) through a dip tube extending to the bottom portion of the reactor. Nitrogen flow rate was 1.93 to 2.68 m^3/h (72 to 100 scfh.) The surface of the liquid was covered with an even spread of nitrogen bubbles. The solution was vigorously agitated with a stirrer.

Two hours into the nitrogen sparge, the reactor was heated briefly from 32 °C to 70 °C and then allowed to cool to 45 °C, where it remained during the remainder of the nitrogen sparge.

After six hours, a sample of the solution showed about 60 ppm carbonyls. Sparging was continued for a total of 51 hours. After the nitrogen flow was stopped, the pH of the solution was adjusted to 8.2 by addition of 1810 ml of 1N sodium hydroxide solution. Vacuum was applied to distil off the water. The initial boiling point of the mixture was 85 °C at 40.7 kPa (305 mm Hg). The pH of the water distillate averaged 4.5. After removal of 87 kg (191.9 lbs) of water, the PDO solution pH was about 7.8. The amount of PDO in the water cut was about 3 kg (6.6 lbs).

The PDO/water fraction was distilled by decreasing the pressure to about 11.3 kPa (85 mm Hg). The boiling temperature was about 153 °C. 15.4 kg (34 lbs) of PDO/water was removed. The pressure was then decreased to about 87 kPa (65 mm Hg) to distil the PDO. The distillate from the first half hour (29 kg = 64 lbs) was considered the PDO forecut. The concentration of this forecut was about 98 wt% PDO. The boiling point at 87 kPa (65 mm Hg) was about 146 °C. After 3 hours, the pressure was further decreased to 73 kPa (55 mm Hg) to distil the remaining PDO. Total PDO middle cut collected was 128.4 kg (283 lbs), which was shown to have about 48 ppm carbonyls (average). About 3 kg (6.5 lbs) of highly-coloured bottoms liquid remained in the reactor.

C L A I M S

1. A process for purifying a carbonyl-containing 1,3-propanediol composition, the process comprising:
(a) forming a solution of said 1,3-propanediol composition in an aqueous medium having a pH less than 7;
(b) adding a sufficient amount of a base to the aqueous medium to form a basic solution having a pH greater than 7;
(c) heating the basic solution under conditions effective to distil a major portion of the water therefrom; and
(d) heating the remaining basic solution under conditions effective to distil a major portion of the 1,3-propanediol therefrom, to provide a distilled 1,3-propanediol composition having a lower carbonyl content than the starting carbonyl-containing 1,3-propanediol composition.

2. The process of claim 1 in which step (a) comprises adding an acid selected from the group consisting of C_2 or greater carboxylic acids, sulphonic acids, hydrohalogenic acids, phosphoric acids, Lewis acids, acidic polymeric ion exchange resins, acidic aluminas and acidic clays to an aqueous solution of said 1,3-propanediol composition.

3. The process of claim 1 in which the solution of step (a) comprises at least one of p-toluenesulphonic acid and phosphoric acid.

4. The process of claim 1 in which the solution of step (a) has a pH less than 4.

5. The process of claim 1 in which step (a) is carried out under a gas sparge with a gas selected from the group consisting of nitrogen, argon and helium.

6. The process of claim 1 in which step (a) is carried out over a time within the range of 1 to 6 hours.

7. The process of claim 6 in which the solution of step (a) is maintained at a temperature within the range of 5 to 60 °C.

8. The process of claim 1 in which the solution of step (a) comprises 20 to 70 weight percent water.

9. The process of claim 1 in which the base added in step (b) is selected from sodium hydroxide and potassium hydroxide.

10. The process of claim 1 in which step (a) is carried out under a pressure less than 90 kPa.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C29/88 C07C31/20

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 261 554 (RUHRCHEMIE AG) 30 March 1988 ---	1-10
P,X	US,A,5 459 229 (KELSEY DONALD R ET AL) 17 October 1995 see the whole document -----	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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.mation on patent family members

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