

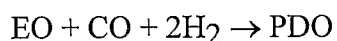
REMOVAL OF IMPURITIES FORMED DURING THE PRODUCTION OF 1,3-PROPANEDIOL

Field of the Invention

This invention relates to a process for the production of 1,3-propanediol (PDO) wherein an aqueous solution of 3-hydroxypropanal (HPA) is formed, and the neutralized HPA is hydrogenated to produce a PDO mixture that is distilled to produce purified PDO.

Background of the Invention

Several companies have developed technology for the manufacture of PDO starting with ethylene oxide as the main raw material. The ethylene oxide is reacted with synthesis gas (syngas), a mixture of carbon monoxide and hydrogen, which may be obtained by steam reforming of natural gas or partial oxidation of hydrocarbons. The idealized reaction of ethylene oxide (EO) with syngas to yield PDO is shown below:



U.S. Patents 4,873,378, 4,873,379, and 5,053,562 from Hoechst Celanese describe a single step reaction using 2:1 (molar) syngas at 110 to 120°C and about 1000 psig (6900 kPa) to give 65 to 78 mole percent yield of PDO and precursors thereof. The catalyst system used consisted of rhodium, various phosphines, and various acids and water as promoters.

U.S. Patents 5,030,766 and 5,210,318 to Union Carbide describe the reaction of EO with syngas in the presence of rhodium-containing catalysts. At 110°C and 1000 psig (6900 kPa) of 2:1 molar syngas, a selectivity of up to 47 mole percent was achieved but the combined rate of formation of PDO and 3-hydroxy propanal was quite low at 0.05 to 0.07 moles per liter per hour. Better results were achieved by increasing the ratio of phosphoric acid promoter to rhodium catalyst.

U.S. Patents 5,256,827, 5,304,686, and 5,304,691 to Shell Oil described PDO production from EO and syngas utilizing tertiary phosphine-complexed cobalt carbonyl catalysts. Reaction conditions of 90 to 105°C and 1400 to 1500 psig (9650 to 10,340 kPa) of syngas (1:1 molar ratio) for three hours produced selectivities in the range of 85 to 90 mole percent and the EO conversion was in the range of 21 to 34 percent. Later work reported increased selectivity and EO conversion.

U.S. Patent 5,527,973 describes a method for the purification of PDO which contains carbonyl byproducts including acetals. An aqueous solution of a carbonyl-containing PDO is formed having a pH less than 7 and then a sufficient amount of base is added to this solution to raise the pH to above 7. The solution is then heated to distill most of the water from it and then the remaining basic solution is heated to distill most of the PDO from the basic solution providing a PDO composition having a lower carbonyl content than the starting composition. This process has several steps and it would be a commercial advantage to provide a method which would lower the carbonyl content in fewer process steps.

MW132 acetal of PDO forms as an undesired byproduct of the hydroformylation and hydrogenation reactions. MW132 is difficult to separate from PDO by simple distillation because it exhibits volatility similar to that of PDO. Its formation lowers the overall recovery of PDO as well as its purity. Therefore, it would be highly advantageous to have a process wherein the MW132 acetal could be chemically reacted to other materials which are more easily separated from PDO. The present invention provides such a chemical method.

Summary of the Invention

In one embodiment, the present invention is an improvement upon the process for the production of 1,3-propanediol (PDO) wherein an aqueous solution of 3-hydroxypropanal (HPA) is formed, and the HPA is subjected to hydrogenation to produce a crude PDO mixture comprising PDO, water, MW176 acetal (so called because it is an acetal and has a molecular weight of about 176), and high and low volatility materials, wherein the crude PDO mixture is dried, usually by distillation, to produce a first overhead stream comprising water and some high volatility materials, such as ethanol and/or process solvents, and a dried crude PDO mixture as a first distillate bottoms stream comprising PDO, MW176 acetal, and low volatility materials, and wherein the dried crude PDO mixture is distilled to produce a second overhead stream comprising some high volatility materials, a middle stream comprising PDO and MW176 acetal, and a second distillate bottoms stream comprising PDO and low volatility materials. The major part of the recoverable PDO is in the middle stream which is as much as 99.9 %wt PDO. The second distillate bottoms stream may contain up to 50 %wt of PDO but this PDO is difficult to

TH1778-PCT

separate from the low volatility materials. There may be trace amounts of MW176 acetal in the bottoms stream.

In this embodiment, the improvement comprises contacting 1) the crude PDO mixture prior to drying and/or 2) the dried crude PDO mixture prior to distillation and/or 3) the middle stream (with this third embodiment, another distillation would be required to remove the more volatile MW176 acetal reaction products from the PDO) with an acidic zeolite (for example a mordenite clay) at 40 to 150°C to convert the MW176 cyclic acetal to alternate chemical species which can be more easily separated from PDO by distillation, in a process where the production of other color producing impurities and oligomers of PDO is minimized. In another embodiment of this invention, 1) and/or 2) and/or 3) are contacted with an acid form cation exchange resin, typically of the sulfonic acid type, at temperatures between ambient and 150°C. In another embodiment, soluble acids, such as H₂SO₄, are used to treat the streams, preferably in a column which is resistant to corrosion, at a temperature of 20 to 100°C.

The contacting of the crude PDO mixture with the solid acid purifier is done as a continuous process, or batchwise, using standard methods and practice for contacting a liquid stream with a solid catalyst or adsorbent. In this manner, difficult to separate impurities such as the MW176 acetal are largely eliminated, such that PDO may be distilled to high purity with high recovery efficiencies.

In another embodiment, this invention provides a process for producing 1,3-propanediol comprising the steps of:

- a) forming an aqueous solution of 3-hydroxypropanal,
- b) hydrogenating the 3-hydroxypropanal to form a first crude 1,3-propanediol mixture comprising 1,3-propanediol, water, and MW132 cyclic acetal,
- c) distilling the first crude 1,3-propanediol mixture to remove water and low boiling impurities and form a second crude 1,3-propanediol mixture,
- d) contacting the second crude 1,3-propanediol mixture with an acid form cationic exchange resin at a temperature of from 50 to 150°C to convert the MW132 cyclic acetal to more volatile cyclic acetals and/or other degradation products, and
- e) separating the more volatile cyclic acetals and/or other degradation products from the 1,3-propanediol by distillation or gas stripping.

In the most preferred mode of this embodiment, steps d) and e) are carried out together (such as in the same vessel or column) such that the volatile cyclic acetals and/or other degradation products are separated from the 1,3-propanediol as they are formed. In another mode of this embodiment, an acidic zeolite can be used in place of the cationic acid exchange resin. In such case, the temperature preferably is from 80 to 200°C.

Brief Description of the Drawing

Figure 1 is very simple schematic representation of an example of a simplified distillation scheme.

Detailed Description of the Invention

The 3-hydroxypropanal (HPA) aqueous solution which is the starting material of the present invention, can be produced by a number of different processes. The aforementioned U.S. patents 4,873,378, 4,873,379, 5,053,562, 5,030,766, 5,210,318, 5,256,827, 5,304,686, and 5,304,691, all of which are herein incorporated by reference, describe different methods for producing aqueous solutions of HPA. HPA can also be produced by hydration of acrolein in the presence of acidic catalysts. Processes for accomplishing this result are described in U.S. Patents 5,426,249, 5,015,789, 5,171,898, 5,276,201, 5,334,778, and 5,364,987, all of which are herein incorporated by reference.

A preferred method for carrying out the entire process of the present invention is described in U.S. Patent No. 5,786,524, which is herein incorporated by reference, and is generally as follows. Ethylene oxide (EO) is hydroformylated in a reactor such as a bubble column or agitated tank at 200 to 5000 psi (1380 to 34,500 kPa) of syngas having a ratio of hydrogen to carbon monoxide of 1:5 to 25:1 at 50 to 110°C in the presence of a hydroformylation catalyst at a concentration of 0.05 to 15 weight percent, more preferably 0.05 to 1 percent.

The hydroformylation reaction effluent is preferably extracted with a small amount of water at water-solvent ratios ranging from 2:1 to 1:20 at 5 to 55°C under an atmosphere of greater than 50 psi (350 kPa) carbon monoxide. The solvent layer containing more than 90 percent of the catalyst in active form is recycled back to the hydroformylation reactor. The HPA is extracted in the water layer at a concentration of 10 to 45 weight percent.

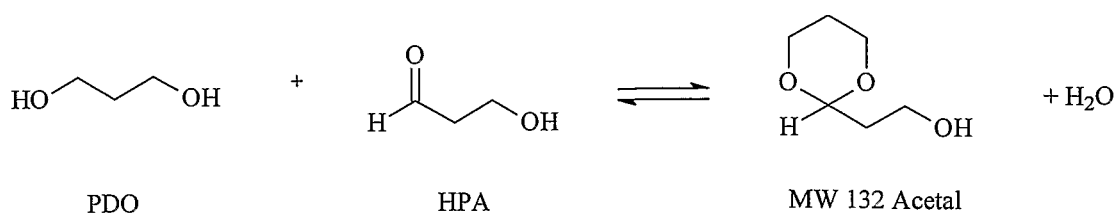
The catalyst may be removed from this aqueous solution of HPA by any known means including first oxidizing the catalyst and then removing it utilizing an acid ion exchange resin. The ion exchange resin may be a weak or strong acid ion exchange resin. Examples include AMBERLYST 15, 35, and XN-1010,
5 AMBERLITE IR-118, IRC76, A1200, DOWEX 50 x 2-100 and 5 x 8-100, XL-383 and -386, plus BIO RAD AG50W-X2 and AMBERSEP 252H resins, or other strong (sulfonic) acid or weak (carboxylic) acid resins (AMBERLYST, AMBERLITE, DOWEX, BIO RAD and AMBERSEP are trademarks).

After neutralization of the aqueous solution of 3-hydroxypropanal, the aqueous
10 solution is hydrogenated. This may be carried out by hydrogenation over a fixed bed of hydrogenation catalyst at typically 100 to 2000 psi (690 to 13,800 kPa) of hydrogen. The hydrogenation catalyst can be any of those described in U.S. 5,786,524, which is herein incorporated by reference, including catalysts of a group VIII metal such as nickel, cobalt, ruthenium, platinum, or palladium. Initial
15 hydrogenation is preferably conducted at 40 to 80°C and the temperature is preferably increased to 120 to 175°C to encourage the reaction of reactive components such as cyclic acetals to revert back to PDO. Finally, water and entrained light (low boiling) solvent and highly volatile (low boiling) impurities are
20 distilled (overhead stream) from the crude PDO and the lower volatility components are also separated during distillation as the bottoms stream.

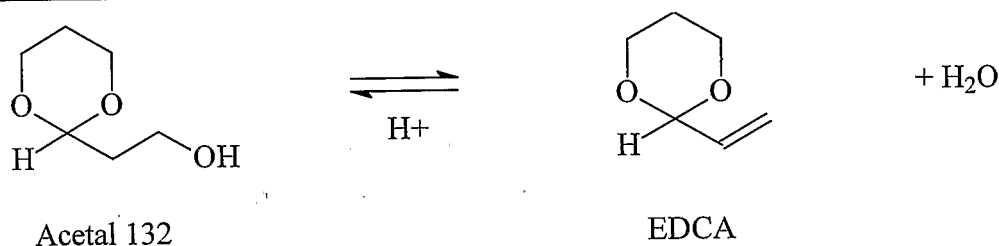
MW132 Acetal

To carry out the second embodiment of this invention, the dried crude product stream (of the distillation), containing MW132 acetal and PDO, is treated as described below to recover PDO in high yield and high purity. Crude PDO as
25 described above can exhibit high levels of MW132 cyclic acetal impurity. This impurity is undesirable and limits PDO recovery efficiencies during subsequent distillation. It can form by reaction of PDO with HPA.

Reaction #1



The 2-ethylene-1,3-dioxane cyclic acetal (EDCA) formed upon acid catalyzed decomposition of MW132 acetal is known to be much more volatile than PDO. The following formula explains the dehydration of MW132 acetal to form the 2-ethylene-1,3-dioxane cyclic acetal (EDCA) that can be readily separated from the PDO by distillation. Acidic zeolites and acid form cationic exchange resins (such as used for cobalt removal) can be used to purify PDO via reaction of MW132 acetal to form EDCA:

Reaction #2

Thus, the dried crude PDO stream containing the undesirable MW132 cyclic acetal is contacted with an acid form cationic exchange resin or an acidic zeolite under conditions which favor the reaction scheme shown above for the conversion of MW132 acetal to EDCA. This step is combined with removal of the EDCA via concerted distillation or via use of a stripping gas such as nitrogen or steam.

Concerted distillation and reaction, where distillation and reaction are combined in the same processing unit to separate reactants from products as they are formed, may employ any of the well known methods for conducting a "reactive distillation." Alternatively, an inert gas such as nitrogen may be used to strip the reaction mixtures (concerted stripping and reaction) of the more volatile degradation product of MW132 acetal (EDCA), and thus prevent reformation of MW132 via chemical equilibrium. Use of water vapor (steam) is a common commercial practice for providing process heat and an inert stripping gas. In this case, the stripping is again conducted in the same processing unit as the reaction of MW132 acetal. The reaction products are removed as formed in order to drive the chemical equilibrium to eliminate or reduce the presence of MW132 acetal. In this manner, the combination of acid-catalyzed reaction plus stripping in the same processing step effects reactant-product separation in the same manner as the "reactive distillation" combination of acid-catalyzed reaction and distillation.

In general, water was found to suppress the reversion of and removal of MW132 acetal. However, small amounts of water are generally present due to incomplete removal, sorption in the solid catalyst, or due to the dehydration reaction itself (#1 above) and may allow a portion of the MW132 removal to proceed via the reversal of reaction #1. HPA, if formed in this manner, may then be further dehydrated to highly volatile acrolein, which is readily stripped or distilled from the reaction mixture. Regardless of which mechanism dominates, the concerted acid-catalyzed reaction with separation (distillation or stripping) of volatile reaction products results in a reduction in the MW132 impurity of the product PDO. Concerted distillation or inert gas stripping is required to drive the chemical equilibrium away from the thermodynamically favored MW132 cyclic acetal. An acid formed zeolite can also be used during the procedure described above to catalyze the degradation of the MW132 acetal.

Use of the acid form cationic exchange resin with concerted separation produces virtually complete conversion of the MW132 acetal. The reaction is preferably carried out at a temperature of from 50 to 150°C, more preferably at from 80 to 120°C. Contacting with the resin catalyst is either conducted batchwise, or in a continuous column, using well known reactor design methods to insure virtually complete conversion of the MW132 acetal. Batchwise contacting at 80 to 120°C may be conducted for 1 to 5 hours with 10 weight percent of acid resin, for example, to effect complete conversion. Alternately, the contacting may be effected in a continuous reaction vessel, preferably a column, with a "weight hourly space velocity" (weight of impure PDO feed per weight of acid resin per hour—"WHSV") of 0.1 to 1 per hour.

With zeolites, the activity for acetal reversion is lower, such that a higher temperature or increased contact time with the zeolite is required. The reaction with acidic zeolite is preferably carried out at a temperature of from 70 to 250°C, more preferably at from 90 to 170°C, via batch or continuous contacting. Similar contacting times or weight hourly space velocities could be used. For either system, the combination of temperature and contact time with the solid acidic purifier (acid form cationic exchange resin or acidic zeolite) must be optimized to limit the production of undesirable color-imparting impurities and to minimize the production of dimer and higher oligomers of PDO.

The preferred catalysts are ion exchange resins with strongly acidic cation exchange (acid form cationic exchange resins). These include the gel type or macroreticular (macroporous) ion exchange resins with sulfonic acid functional groups wherein the sulfonic acid function is bonded directly or indirectly to an organic polymer backbone. Examples include Rohm and Haas AMBERLITE or AMBERLYST A200, A252, IR-118, IR120, A15, A35, XN-1010, or uniform particle size A1200 resins; Dow MSC-1, M-31, or DOWEX 50-series resins, SYBRON C-249, C-267, CFP-110 resins; PUROLITE C-100 or C-150 resins; RESINTECH CG8; IWT C-211, SACMP; IWT C-381; or other comparable commercial strong acid cation exchange resins. Another example of cation exchange resins is NAFION acidified perfluorinated polymer of sulphonic acid (SYBRON, PUROLITE, RESINTECH and NAFION are trademarks).

The suitable zeolite catalysts contain one or more modified zeolites preferably in the acidic form. These zeolites should contain pore dimensions large enough to admit the entry of the acyclic or aliphatic compounds. The preferred zeolites include, for example, zeolites of the structural types MFI (e.g., ZSM-5), MEL (e.g., ZSM-11), FER (e.g., ferrierite and ZSM-35), FAU (e.g., zeolite Y), BEA (e.g., beta), MFS (e.g., ZSM-57), NES (e.g. NU-87), MOR (e.g. mordenite), CHA (e.g., chabazite), MTT (e.g., ZSM-23), MWW (e.g., MCM-22 and SSZ-25), EUO (e.g. EU-1, ZSM-50, and TPZ-3), OFF (e.g., offretite), MTW (e.g., ZSM-12) and zeolites ITQ-1, ITQ-2, MCM-56, MCM-49, ZSM-48, SSZ-35, SSZ-39 and zeolites of the mixed crystalline phases such as, for example, zeolite PSH-3. The structural types and references to the synthesis of the various zeolites can be found in the "Atlas of Zeolite Structure Types" (published on behalf of the Structure Commission of the International Zeolite Association), by W.M. Meier, D.H. Olson and Ch. Baerlocher, published by Butterworth-Heinemann, fourth revised edition, 1996. Structural types and references to the zeolites mentioned above are available on the World Wide Web at www.iza-structure.org Such zeolites are commercially available from Zeolyst International, Inc. and ExxonMobil Corporation. Additional examples of suitable zeolite catalysts can be found in U.S. Patent Nos. 5,762,777; 5,808,167; 5,110,995; 5,874,646; 4,826,667; 4,439,409; 4,954,325; 5,236,575; 5,362,697; 5,827,491; 5,958,370; 4,016,245; 4,251,499; 4,795,623; 4,942,027 and WO99/35087, which are hereby incorporated by reference.

MW176 Acetal

As shown in the exemplary simplified distillation scheme of Figure 1 which is helpful in describing the first embodiment of this invention, the aqueous PDO containing MW176 acetal flows into drying distillation column 2. Water and some high volatility materials are removed in the overhead stream 3 and the dried PDO with MW176 acetal from the distillate bottoms stream flows into distillation column 5. More high volatility materials are separated and leave through overhead stream 6 and the distillate bottoms stream 8 contains low volatility materials and some PDO as well as trace amounts of MW176 acetal. The recoverable PDO exits in the middle stream. Vessels 1, 4, and 7 are optional (although at least one is required in the system shown in the figure) acid treatment vessels. The acid catalyst treatment may take place before drying in vessel 1 or it may take place after drying in vessel 4 but before distillation or it may take place after distillation in vessel 7. When the last embodiment is carried out, an additional distillation is required to separate the more

volatile MW176 acetal reaction products from the PDO.

Crude PDO as described above sometimes exhibits high levels of MW176 cyclic acetal impurity. This impurity was found to be only marginally less volatile than PDO, which limits PDO recovery efficiencies. Given difficulty in separation from PDO, laboratory batch distillation was conducted to assess the relative volatilities of MW176 impurity and PDO. Approximately 85 grams of PDO tainted with this impurity and also a C₅ diol were refluxed at a nominal 10 mm Hg (1.3 kPa) pressure and 143°C bottoms temperature. Ethylene glycol (EG) and butanediol markers were added at about 1 wt% to assist in assignment of relative volatilities. The results (Table 1) show both the MW176 acetal and C₅ diol to be heavier than PDO. Good agreement was obtained between measured vs. reported relative volatility of EG vs. PDO which indicates that equilibrium was indeed approached for these measurements.

Table 1: Relative Volatility¹

BATCH DISTILLATION DATA:			
Species	Distillation bottoms wt%	Distillation tops wt%	Volatility ratio: t/b ²
PDO	97.88	98.09	1.00
Ethylene glycol	0.369	0.824	2.233
C ₅ diol	0.326	0.280	0.859
MW176 acetal	0.055	0.047	0.855
Butanediol	1.375	0.762	0.554

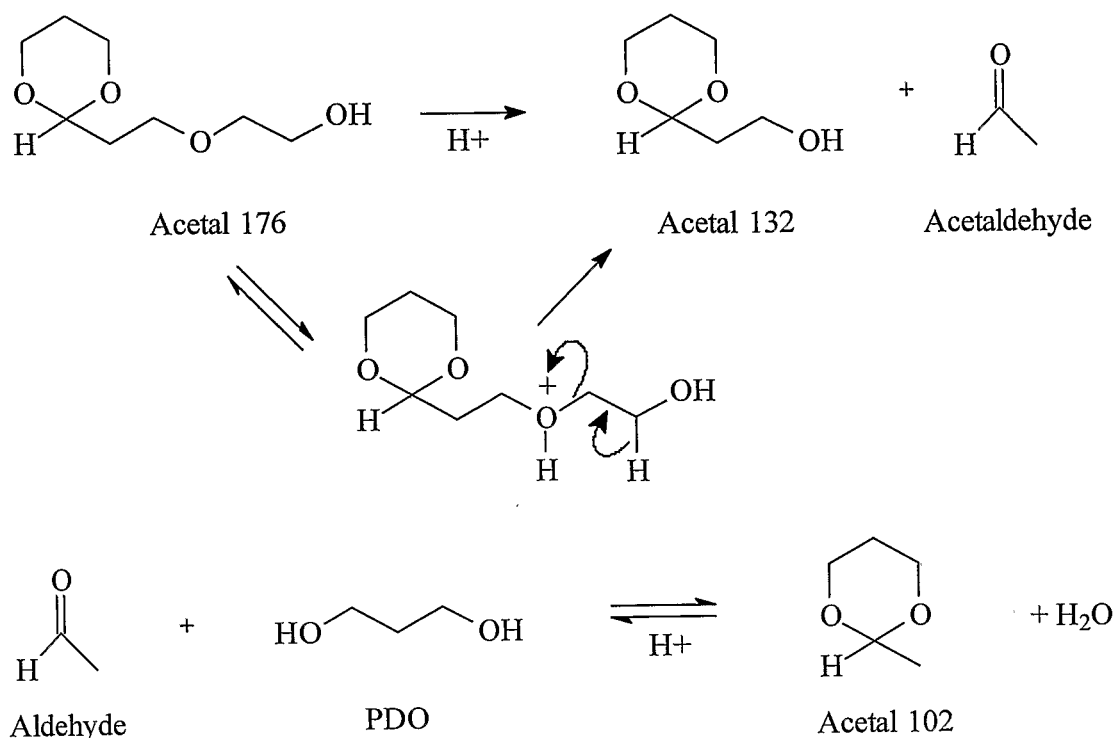
¹ Reported relative volatility EG/PDO at 230°F (110°C) = 2.16

² t = distillation "tops" or "overhead product"

b = distillation "bottoms"

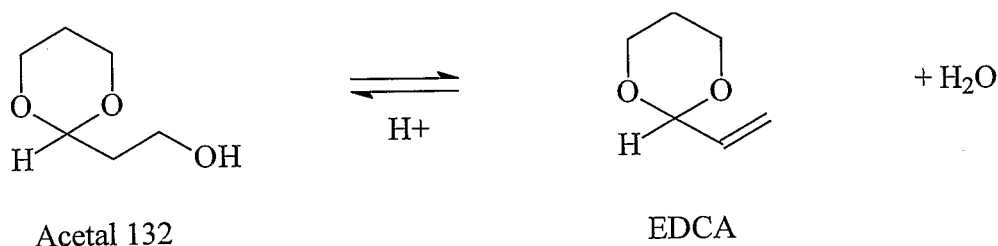
The MW102 acetal formed upon acid catalyzed decomposition of MW176 acetal is known to be much more volatile than PDO and hence can be readily separated from PDO with high efficiency. This result was expected basis the absence of hydroxyl groups in MW102 due to condensation elimination. While we do not wish to be bound by a specific mechanism, the following reactions may explain the degradation of MW176 acetal and formation of MW102 acetal (that can be readily separated from the PDO by distillation) and also the formation of MW132 acetal as observed in the experiments.

TH1778-PCT



"De-ethoxylation" is known to occur under acidic conditions. Aldehydes readily condense with PDO under acidic conditions to form thermodynamically favored cyclic acetals, in this case, MW102 acetal.

An acid form cation exchange resin or an acidic zeolite also facilitates the removal of MW132 acetal via conversion to 2-ethylene-1,3-dioxane cyclic acetal (EDCA) which is a substantially higher volatility material.



The crude PDO stream containing the undesirable MW176 acetal is treated with an acid form cation exchange resin or an acidic zeolite or soluble acid under conditions which favor the reaction schemes shown above. Batch or continuous flow processes may be used in any manner providing intimate contacting of the liquid stream with the solid acid purifier or the soluble acid. Typically, continuous contacting in a fixed, fluidized, or expanded bed will be preferred commercially, in either downflow or upflow operation or via a horizontal contactor. While the optimal

size of the bed will depend upon the particle size and nature of the solid acid purifier employed, a typical design will entail a "weight hourly space velocity" (WHSV) from 0.1 to 10, with WHSV expressed as the mass flowrate of crude PDO per mass of solid acid purifier per hour. The optimal bed size and operating temperature are selected to effect a high level of conversion of MW176 acetal, while minimizing the oligomerization of PDO to other heavy ends components.

When acidic zeolites are employed as the solid acid purifier, a temperature in the range of 40 to 150°C, preferably 60 to 120°C, is typically desired. Temperatures of ambient to 150°C or lower temperatures (as low as ambient temperature to 100°C) may be employed with acid form cation exchange resins, which are indicated to be more active in removal of the MW176 impurity. When soluble acids are used, the temperature may be from 20 to 100°C.

The preferred zeolite catalysts contain one or more modified zeolites preferably in the acidic form. These zeolites should contain pore dimensions large enough to admit the entry of the acyclic or aliphatic compounds. The preferred zeolites include, for example, zeolites of the structural types MFI (e.g., ZSM-5), MEL (e.g., ZSM-11), FER (e.g., ferrierite and ZSM-35), FAU (e.g., zeolite Y), BEA (e.g., beta), MFS (e.g., ZSM-57), NES (e.g. NU-87), MOR (e.g. mordenite), CHA (e.g., chabazite), MTT (e.g., ZSM-23), MWW (e.g., MCM-22 and SSZ-25), EUO (e.g. EU-1; ZSM-50, and TPZ-3), OFF (e.g., offretite), MTW (e.g., ZSM-12) and zeolites ITQ-1, ITQ-2, MCM-56, MCM-49, ZSM-48, SSZ-35, SSZ-39 and zeolites of the mixed crystalline phases such as, for example, zeolite PSH-3. The structural types and references to the synthesis of the various zeolites can be found in the "Atlas of Zeolite Structure Types" (published on behalf of the Structure Commission of the International Zeolite Association), by W.M. Meier, D.H. Olson and Ch. Baerlocher, published by Butterworth-Heinemann, fourth revised edition, 1996. Structural types and references to the zeolites mentioned above are available on the World Wide Web at www.iza-structure.org Such zeolites are commercially available from Zeolyst International, Inc. and ExxonMobil Corporation. Additional examples of suitable zeolite catalysts can be found in U.S. Patent Nos. 5,762,777; 5,808,167; 5,110,995; 5,874,646; 4,826,667; 4,439,409; 4,954,325; 5,236,575; 5,362,697; 5,827,491; 5,958,370; 4,016,245; 4,251,499; 4,795,623; 4,942,027 and WO99/35087, which are hereby incorporated by reference.

Other suitable catalysts include acid form cation exchange resins. These include the gel type or macroreticular (macroporous) ion exchange resins with sulfonic acid functional groups in acid form, wherein the sulfonic acid function is bonded directly or indirectly to an organic polymer backbone. Examples include: Rohm and Haas AMBERLITE or AMBERLYST A200, A252, IR-118, IR120, A15, A35, XN-1010, or uniform particle size A1200 resins; Dow MSC-1 or DOWEX 50-series resins; SYBRON C-249, C-267, CFP-110 resins; PUROLITE C-100 or C-150 resins; RESINTECH CG8; IWT C-211; SACMP; IWT C-381; and other comparable commercial resins. Another example of these cation exchange resins is NAFION acidified perfluorinated polymer of sulphonic acid.

Soluble acids which can be used include H_2SO_4 , H_3PO_4 , HCl, and soluble sulfonic acids such as para-toluene sulfonic acid, benzene sulfonic acid, and methane sulfonic acid, etc. H_2SO_4 and soluble sulfonic acids are preferred. If these soluble acids are used, corrosion-resistant columns are highly preferred. The acid is removed with the heaviest components (heavy ends). The concentration of the acid is preferably 0.1 to 1.0 wt%.

EXAMPLES

MW176 Examples

Example 176-1

The results in Table 2 show that ambient temperature treatment of a PDO sample contaminated with MW176 acetal with acid-form USY-type zeolite was ineffective in reverting MW176 acetal. Room temperature reversion using strong acid resin A15 (Rohm and Haas AMBERLYST 15) was demonstrated. High temperature treatment with the zeolite at 150°C overnight resulted in elimination of MW176 with formation of 2-methyl -1,3-dioxane. However, formation of poly PDO (di-1,3-propylene glycol) and higher oligomers occurred at higher concentrations than the original MW176 acetal. Overall purity and yield was thus reduced, though the more difficult to separate MW176 acetal was eliminated.

Additional timed studies were conducted at 100°C using the USY H⁺ form zeolite. The results show reactive conversion of the MW176 acetal, especially the first gc (gas chromatograph) peak MW176-1 which reacted to virtual completion within 5 hours (MW176 acetal shows up as three peaks in gc/mass spec analysis; the dominant MW176-1 peak described in Table 2 readily vanished during acid

treatment experiments, while a second "isomer" appeared to be unreactive). Unlike the earlier test at 150°C, at 100°C the reversion was selective with no measurable formation of di- or tri-1,3-propylene glycol via condensation of PDO.

5 A mordenite sample was inadvertently first tested in sodium form overnight at 150°C, giving copious amounts of new heavy ends byproducts, presumably via degradation of PDO. A sample of the acid-form mordenite heated with the same PDO overnight at 60°C showed, however, essentially complete elimination of the MW176 acetal, with formation of the same 2-methyl-1,3-dioxane (MW102 acetal) and MW132 acetal impurities as observed with the USY type zeolite. The reversion
10 was selective as no additional byproducts were observed. The performance of the acid-form mordenite was thus comparable with that of the USY acid-form zeolite. These results indicate an optimal temperature for complete or partial removal of the MW176 acetal, with minimal degradation of PDO to other byproducts.

Table 2: Solid Acid Purification of MW176 Contaminated PDO

Time Hours	Catalyst	Temp °C	Catalyst wt%	MW176 wt%	MW132 wt%	MW102 wt%	RT26.8 MW176- 1 wt%	di-PDO wt%	tri-PDO wt%	other new H.E. wt%
0	none (feed)	25	0.0	0.240	0.050	0.000	0.168	0.000	0.000	0.0
24	Acid resin A35	25	4.0	0.010	0.290	0.100	0	0.000	0.000	0.0
24	USY H+ zeolite	25	4.0	0.240	0.050	0.000	na	0.000	0.000	0.0
24	USY H+ zeolite	150	4.0	0.010	0.041	0.124	0.002	0.545	0.514	0.0
0	none (feed)	25	0.0	0.237	0.093	0.000	0.161	0.000	0.000	0.0
18	Acid resin A15	25	10.0	0.005	0.402	0.161	0.002	0.000	0.000	0.0
18	Acid A15+15% H ₂ O	25	10.0	0.01	0.111	0.048	0.005	0.000	0.000	0.0
27	Na-mordenite	150	10.0	0.016	0.084	0.018	0.013	0.000	0.000	20.5
22	H+ mordenite	60	3.6	0.017	0.431	0.143	0.005	0.000	0.000	0.0
0	none (feed)	100	0.0	0.237	0.093	0.000	0.161	0.000	0.000	0.0
1	USY H+ zeolite	100	10.0	0.136	0.209	0.075	0.082	0.000	0.000	0.0
3	USY H+ zeolite	100	10.0	0.048	0.330	0.127	0.018	0.000	0.000	0.0
5	USY H+ zeolite	100	10.0	0.033	0.371	0.142	0.004	0.000	0.000	0.0
27	USY H+ zeolite	100	10.0	0.030	0.351	0.147	0.003	0.000	0.000	0.0

USY H+ zeolite = CBV-500-X16 LR22765 (4/2/2000)

H-mordenite = LR23768-128 (1/28/2000)

Example 176-2

MW176 acetal impurity with a strong cation acid ion exchange resin (Rohm and Haas AMBERLYST A35) at room temperature. The results shown in Table 3 indicate degradation of MW176 acetal, with formation of MW102 acetal, MW18 (H₂O), and MW132 acetal.

5

Table 3: Preliminary PDO Treatment Over A35 Resin at Room Temperature

Name	MW	%wt	
		Start	End
2-methyl cyclic acetal	102	0.00	0.10
cyclic acetal	132	0.05	0.29
cyclic acetal diol	176	0.24	0.01
Water	18	0.02	1.02
PDO	76	99.47	98.39
Other	162	0.02	0.00
Other	176	0.02	0.01
		99.81	99.83
mole balance		1.31	1.35

Solid acid treatment of PDO tainted with MW176 acetal can degrade this impurity into lighter components (MW102 nonhydroxylated acetal) which are readily separable via distillation. Strong cation acid ion exchange resins can revert the MW176 acetal at room temperature. Acidic zeolites can also revert the MW176 acetal at a higher temperature. At still higher temperatures (as demonstrated for 150°C), PDO is condensed by the acidic zeolites to poly 1,3-propylene glycols, leading to yield loss and lower purity.

10

MW 132 Examples

Example 132-1 (comparative)

Acid Resin Treatment Prior to Distillation

This experiment entailed treatment of 1500 grams of crude PDO following water removal, via distillation, with 43.5 grams dry A15 (Amberlyst A15 resin) strong acid form cationic exchange resin under a nitrogen atmosphere for 3 hours at 100°C with minimal separation (stripping). The treated material was bright yellow. MW 132 acetal was reduced only from 3.2 wt% to 2.6 wt%. The treated material was distilled and successive distillation cuts showed reduction in MW 132 acetal from 11% to 2 wt% but formation of up to 2700 ppm acrylate by the final cut. Excessive formation of acrylate can be expected because of the strong acid treatment which freed 3-hydroxypropionic acid, thus giving maximal ester and ultimately acrylate formation. This example illustrates that no significant MW132 acetal removal was observed for the resin treatment in the absence of concerted separation (stripping or distillation) of the volatile impurities.

Example 132-2

Acid Resin Treatment with Concerted Stripping to Remove Acetal:

The results of this experiment are shown in Table 4. 1 gram of vacuum dried A15 strong acid resin was added to 10 grams of the PDO distillate containing 1.38 wt% MW 132 cyclic acetal from which a majority of the water had been removed by distillation. The sample was heated via a metal block heater to 100°C with vigorous nitrogen stripping (concerted stripping) as evidenced by an expansion of the liquid by about 10 volume percent. MW 132 acetal was readily eliminated with formation of significant quantities of di- and tri-PDO via direct PDO self condensation.

Table 4

Sample	Time Hours	MW 132 Acetal wt%	di-PDO wt%	tri-PDO wt%
167-9	0	1.38	0	0
194-1	1	0.345	0.548	1.356
194-2	3	0.017	3.009	1.934
194-3	5	0.012	6.667	1.997

This study was repeated with a different distillate. 1 gram of dry A15 resin was used to treat 12 grams of PDO distillate. The MW 176 (a higher boiling cyclic acetal) and MW 132 acetals were eliminated. Di- and tri-PDO formed in significant quantities. The results are shown in Table 5.

TH1778-PCT

Table 5: Resin Dry Stripping

Sample	Time Hours	EG wt%	rt ¹ =21.69 Acrylate ² wt%	MW 132 Acetal wt%	MW 176 rt=26.18 wt%	rt ¹ =24.6 di-PDO wt%	rt ¹ =29.4 tri-PDO wt%
High acetal feed							
197-3	0	0.142	0.416	2.409	0.421	0	0
20b	1	0.126	0.175	1.032	0	0.615	2.559
20d	2	0.122	0.078	0.282	0	3.004	3.938
20f	5	0.084	0.031	0.067	0	5.929	3.535
Low acetal feed							
192-5	0	0	0.023	0.3	0.051	0	0
20a	1	0	0	0.077	0	0.557	0.138
20c	2	0	0	0.044	0	2.027	0.156
20e	5	0	0	0.028	0	4.486	0.206

¹ rt is chromatographic retention time.² 2 3-hydroxypropylacrylate

Another similar experiment was carried out using 5 wt% of M31 strong acid form cationic exchange resin (macroreticular resin). As in the previous experiments, the amount of the MW 132 acetal was decreased and PDO dimer was produced with contacting with acid catalyst and with concerted nitrogen stripping. The results are shown in Table 6.

Table 6: Acid Resin + N2 Strip

5% resin 100°C Catalyst	Time Hours	MW 132 Acetal wt%	di-PDO wt%
none	12	2.865	0
A15	12	1.509	10.427
M31	12	1.024	10.316

Example 132-3

Acid Resin Dry Stripping with Subsequent Redistillation

A twice distilled PDO product sample exhibiting a visible light yellow color upon testing for color body precursors was contacted with 5 wt% dry A15 strong acid form cationic exchange resin with nitrogen stripping for 4 hours at 105°C. MW 132 acetal was virtually eliminated while 1.7 wt% di-PDO was formed (Table 7), giving a gc (gas chromatographic) purity of 97.9 wt%. The treated sample was redistilled at 9 mm Hg (1.3 kPa) in a small 2-ft (0.6 meter) concentric tube column with a bottoms temperature of 121 to 123°C. Distillation showed ready separation of di-PDO from the PDO distillate. Distillate cuts were substantially reduced in MW 132 acetal with the gc purity approaching 99.9%. The color test now gave only slightly yellow tint, indicating a reduction in the amount of color body precursors.

Table 7: Acid Stripping With Redistillation

		grams	MW 132 ppm	PDO wt%	di-PDO wt%
Feed		160.44	n.d.	97.933	1.713
Dist cut#	1	17.34	500	99.766	0
	2	43.15	200	99.910	0
	3	51.19	0	99.894	0
	4	43.41	0	99.846	0
Total		155.09			

A less pure sample containing 3 wt% MW 132 acetal, which exhibited significant color when analyzed for color body precursors, was similarly treated with 5 wt% strong acid resin (A15) while nitrogen stripping. The resulting PDO contained no MW 132 acetal after 4 hours, but it did contain 2.9 wt% di-PDO. Redistillation at 8 mm Hg (1.3 kPa) and 122 to 129°C bottoms temperature in a 2-foot (0.6 meter) concentric tube column gave the distillation cuts shown in Table 8. Again, the acid resin stripping eliminated a significant portion of the MW 132 acetal such that distillation overhead products free of this impurity could then be produced. Di-PDO formed during the resin treatment was readily separated by distillation. The purities of the final distillate cuts would have been quite high if not for progressive formation of MW 102 acetal (2-methyl-1,3-dioxane), which is known to be more volatile than PDO, during the distillation. Yet another distillation would have rid the product of this impurity.

Table 8: Acid Stripping With Redistillation

		grams	MW 132 ppm	PDO wt%	di-PDO wt%	2-me- dioxan MW 102 Acetal wt%
Feed		192.66	n.d.	95.204	2.974	0
Dist cut#	1	15.96	460	99.756	0	0.304
	2	50.45	0	98.292	0	0.308
	3	45.87	0	99.106	0	0.505
	4	52.60	0	99.329	0	0.606
	5	10.57	0	98.579	0	1.186
	Total	175.45				

Example 132-4

Inorganic solid acids such as silica-aluminas or zeolites are more amenable to commercial use in a nitrogen or steam stripper. However, their activity in dehydrating beta-hydroxy cyclic acetals such as MW 132 is poorer than the activity strong acid ion exchange resins under comparable conditions (Table 9). The highly active resins, on the other hand, make more di- and tri-PDO as byproducts. These oligomers are not believed to be color precursors, however, and are more readily separated by distillation than the original MW132 acetal. Temperatures and reaction (contacting) times preferably are optimally adjusted for the acid form cationic exchange resin vs. the acidic zeolite to maximize MW132 acetal reversion to PDO while minimizing the formation of other heavy impurities.

Table 9: Inorganic Solid Acids vs. Ion Exchange Resin for Acid Stripping

Solid Acid	Type	Temp °C	Solid Acid wt%	Time Hours	MW 132 Initial wt%	MW 132 Final wt%	di-PDO Final wt%
ASA	Amorphous silica-alumina	100	23	3	0.296	0.253	0
ASA	Amorphous silica-alumina	155	22	2	0.296	0.209	0
Y	H+ zeolite	100	5.7	1	0.296	0.323	0
ZSM5	H+ zeolite	100	4	3	2.4	1.5	0
ZSM5	H+ zeolite	100	4	3	0.3	0.07	0
A15	Strong acid ion exchange resin	105	5	4	0.058	0	1.73
A15	Strong acid ion exchange resin	105	5.2	4	3	0	2.97
A15	Strong acid ion exchange resin	105	5	12	2.9	1.5	10.3
A15	Strong acid ion exchange resin	100	10	3	1.38	0.017	3

CLAIMS

1. A process for producing 1,3-propanediol comprising the steps of:

a) forming an aqueous solution of 3-hydroxypropanal,

b) hydrogenating the 3-hydroxypropanal to form a crude 1,3-propanediol mixture comprising 1,3-propanediol, water, and MW 132 cyclic acetal and/or MW176 cyclic acetal,

c) distilling (drying) the said crude 1,3-propanediol mixture to remove water and form a second crude 1,3-propanediol mixture (first distillate bottoms stream) comprising 1,3-propanediol and MW 132 cyclic acetal and/or MW176 cyclic acetal,

d) contacting a stream containing MW 132 cyclic acetal and/or MW176 cyclic acetal with an acid form cationic exchange resin or with an acidic zeolite or with a soluble acid, and

e) removing the MW 132 cyclic acetal and/or MW176 cyclic acetal from the 1,3-propanediol.

2. The process of claim 1 for producing 1,3-propanediol where an aqueous solution of 3-hydroxypropanal is formed, the 3-hydroxypropanal is hydrogenated to form a crude 1,3-propanediol mixture comprising 1,3-propanediol, water, MW176 cyclic acetal, and high and low volatility materials, the crude 1,3-propanediol mixture is dried to produce a first overhead stream comprising water and a first distillate bottoms stream comprising 1,3-propanediol, MW176 cyclic acetal, and high and low volatility materials, and the first distillate bottoms stream is distilled to produce a second overhead stream comprising high volatility materials, a middle stream comprising 1,3-propanediol and MW176 acetal, and a second distillate bottoms stream comprising 1,3-propanediol and low volatility materials, wherein at least one of the crude 1,3-propanediol mixture or the first distillate bottoms stream or the middle stream is contacted, prior to drying thereof, with an acidic zeolite or with an acid form cationic exchange resin or with a soluble acid to convert the MW176 cyclic acetal to more volatile materials which can be easily separated from 1,3-propanediol by distillation.

3. The process of claim 2 wherein said crude 1,3-propanediol mixture is contacted, prior to drying thereof, with an acidic zeolite at 40 to 150°C, preferably from 60 to 120°C, whereby the production of color-producing impurities and dimer and higher oligomers of 1,3-propanediol is minimized, or with an acid form cationic exchange resin at ambient to 150°C, preferably 100°C, or with a soluble acid at a temperature of 20 to 100°C to convert the MW176 cyclic acetal to more volatile materials which can be easily separated from 1,3-propanediol by distillation.

4. The process of claim 2 wherein said first distillate bottoms stream, prior to distillation thereof, with an acidic zeolite at 40 to 150°C, preferably from 60 to 120°C, whereby the production of color-producing impurities and dimer and higher oligomers of 1,3-propanediol is minimized, or with an acid form cationic exchange resin at ambient to 150°C, preferably 100°C, or with a soluble acid at a temperature of 20 to 100°C to convert the MW176 cyclic acetal to more volatile materials which can be easily separated from 1,3-propanediol by distillation.

5. The process of claim 2 wherein said middle stream is contacted with an acidic zeolite at 40 to 150°C, preferably from 60 to 120°C, whereby the production of color-producing impurities and dimer and higher oligomers of 1,3-propanediol is minimized, or with an acid form cationic exchange resin at ambient to 150°C, preferably 100°C, or with a soluble acid at a temperature of 20 to 100°C to convert the MW176 cyclic acetal to more volatile materials which can be easily separated from 1,3-propanediol by distillation.

6. The process of claim 1 for producing 1,3-propanediol wherein the process comprises the steps of:

- a) forming an aqueous solution of 3-hydroxypropanal,
- b) hydrogenating the 3-hydroxypropanal to form a first crude 1,3-propanediol mixture comprising 1,3-propanediol, water, and MW 132 cyclic acetal,
- c) distilling the first crude 1,3-propanediol mixture to remove water and low boiling impurities and form a second crude 1,3-propanediol mixture,
- d) contacting the second crude 1,3-propanediol mixture with an acid form cationic exchange resin at a temperature of from 50 to 150°C, preferably from 80 to 120°C, or with an acidic zeolite at a temperature of from about 70 to 250°C, preferably 90 to

170°C, to convert the MW 132 cyclic acetal to more volatile cyclic acetals and/or other degradation products, and

e) separating the more volatile cyclic acetals and/or other degradation products from the 1,3-propanediol by distillation or gas stripping.

5 7. The process of claim 6 wherein steps d) and e) are carried out together such that the volatile cyclic acetals and/or other degradation products are separated from the 1,3-propanediol as they are formed.

8. The process of claim 6 wherein the second crude 1,3-propanediol mixture is contacted with the cationic exchange resin or the zeolite batchwise for from about 1
10 to about 5 hours.

9. The process of claim 6 wherein the second crude 1,3-propanediol mixture is contacted with the cationic exchange resin or the zeolite in a continuous reaction vessel at a weight hourly space velocity of about 0.1 to about 10.

10. The process of claim 6 comprising the further step of distilling the 1,3-
15 propanediol to separate 1,3-propanediol from high boiling impurities formed as a result of step d).