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(54) Title: IMPROVED PROCESS FOR MANUFACTURING BUTANEDIOL INCLUDING SELECTIVE REMOVAL OF Cu^{++} IONS FROM BUTYNEDIOL FEEDSTOCK

(57) Abstract: The present invention provides an improved process for manufacturing high quality butanediol. The invention relates to an improved process for manufacturing high quality butanediol from feedstock comprising butynediol having been manufactured by reacting feedstock comprising formalin to produce liquid phase product comprising butynediol and Cu^{++} ions in a reaction zone containing ethynylation catalyst comprising Cu and maintained at ethynylation reaction conditions. The improvement of the present invention is achieved by cost effectively selectively reducing Cu^{++} ions in the butynediol feedstock.

IMPROVED PROCESS FOR MANUFACTURING BUTANEDIOL INCLUDING SELECTIVE REMOVAL OF Cu^{++} IONS FROM BUTYNEDIOL FEEDSTOCK

FIELD OF THE INVENTION

[0001] This invention relates to an improved process for manufacturing refined butanediol. More particularly, the invention relates to an improved process for manufacturing high quality butanediol from butynediol feedstock having been manufactured by ethynylation of feedstock comprising formalin in the presence of catalyst comprising Cu leading to the presence of Cu^{++} ions in the butynediol feedstock. The improvement of the present invention is achieved by cost effectively selectively reducing Cu^{++} ions in the butynediol feedstock.

BACKGROUND OF THE INVENTION

[0002] Significant amounts of 1,4-butanediol ("BDO") are produced by the Reppe process. This involves major process steps including ethynylation of feedstock comprising formalin to form 1,4-butynediol ("BYD"), hydrogenation of the BYD to crude BDO (typically with 2 to 3 stages of high pressure hydrogenation), and refining of the crude BDO to refined BDO through multi-stage distillation. Ethynylation of feedstock comprising formalin to form BYD is disclosed in United States Patent Nos. 3,560,576; and 3,650,985. Hydrogenation of BYD to form BDO is disclosed in Great Britain Patent No. 1,242,358; and United States Patent No. 4,371,723. Distillation and purification of crude BDO to form refined BDO is disclosed in United States Patent Nos. 4,383,895; 4,371,723; Re. 32,072; and 5,209,825. United States Patent No. 4,383,895 discloses a distillative purification process for obtaining BDO with lower color formers. United States Patent No. 5,209,825 discloses using a combination of 4 distillation columns for purifying crude BDO.

[0003] Other methods for refining BDO contain various process steps. For example, United States Patent No. 5,209,825 discloses a process for refining BDO by removing high boiling materials including color forming materials and their

precursors, and precursors of tar, organic and inorganic salts present in the crude BDO. The process comprises fractionating a crude BDO feed stream at a temperature of no more than 210 °C into a purified concentrated BDO fraction and a bottom fraction, separating as bottoms a fraction having a weight of not greater than 6 % of the weight of the feed stream, the bottoms fraction containing high boiling organic compounds, inorganic and organic salts and not more than 60 % by weight of BDO, and separating as overhead a purified concentrated BDO fraction which contains about the same amount of water as, and less high boiling organic compounds and inorganic and organic salts than, were in the crude BDO feed stream.

[0004] BDO products of commercial processes often contain certain impurities which are close boiling to BDO. Some of these impurities make it through the distillation train mentioned above to the BDO product and produce a high BDO product color. When this BDO is processed further into certain downstream products, results are high BDO adipate polyester color and high Hardy color (where BDO is reacted with HCl). The crude BDO refining normally requires capital intensive multi-stage distillation equipment and energy intensive operation thereof to produce the higher quality refined BDO products. Even with the very elaborate refining scheme used by various producers/processes, the quality of the refined BDO could still vary significantly.

[0005] Further, United States Patent No. 2,629,686 describes a process to clean the technical grade BDO by first treating it with solid adsorbents, e.g. activated charcoal, then by filtration, and then vacuum distillations. United States Patent No. 2,768,214 discloses a process for reducing the color forming bodies of crude BDO by a 2nd stage hydrogenation of the BDO aqueous solution from 35% to 60%, presumably by way of re-diluting distilled BDO with water, at elevated temperature of 150 to 170 °C, and a pressure of 50 to 500 atmospheres, for a reaction time of 1 to 10 hours. Also, United States Patent No. 3,891,511 and United States Patent

Application No. 2010/0101931A1 disclose distillative refining of crude BDO using the combination of 5 distillation columns.

[0006] United States Patent No. 5,981,810 discloses a crude BDO purification process that subjects the BDO to melt crystallization in addition to multi-step distillations. United States Patent Application No. 2014/0275465 A1 discloses a process of purifying BDO produced from fermentation by a two-column distillation scheme. The purification process includes two filtration steps, i.e. microfiltration or ultrafiltration followed by nanofiltration; the 2 column distillations; a hydrogenation step; additional one or two column vacuum distillations following the hydrogenation where BDO is collected from a side draw.

[0007] When ethynylation of feedstock comprising formalin to produce BYD product is conducted in the presence of catalyst comprising Cu, the BYD product will comprise Cu^{++} ions. When that BYD product is then hydrogenated to produce BDO in the presence of hydrogenation catalyst, copper will deposit on the surface of the catalyst. Copper depositions on the surface of the hydrogenation catalyst promotes formation of undesired by-products, such as n-BuOH *via* hydrogenolysis of BDO. Metal salts in BYD streams could be thoroughly removed by a combination of cation exchange resins in multiple beds, e.g. weak anion exchange and strong anion exchange resins, as illustrated in the US 4,371,723 and US Re. 32,072, where a supported copper catalyst is used in the ethynylation reaction and multiple metal salts are present, e.g. sodium, magnesium, copper, and silicic acid salts.

[0008] A simple economical process for manufacturing high quality butanediol from butynediol feedstock having been manufactured by ethynylation of feedstock comprising formalin in the presence of catalyst comprising Cu is needed. The present invention provides that by cost effectively selectively reducing Cu^{++} ions in the butynediol feedstock.

SUMMARY OF THE INVENTION

[0009] The present invention provides an economical improved process for manufacturing refined butanediol from feedstock comprising butynediol having been manufactured by reacting feedstock comprising formalin to produce liquid phase product comprising butynediol and Cu^{++} ions in a reaction zone containing ethynylation catalyst comprising Cu and maintained at ethynylation reaction conditions. The process of this invention involves a step for cost effectively reducing Cu^{++} ions in the butynediol feedstock. An embodiment of the invention process comprises the steps of: **a)** reacting feedstock comprising formalin to produce liquid phase product comprising butynediol and Cu^{++} ions in a reaction zone containing ethynylation catalyst comprising Cu and maintained at ethynylation reaction, hereinafter more particularly described, **b)** recovering liquid phase product from the reaction zone of step a) comprising butynediol and Cu^{++} ions, **c)** contacting the recovered product of step b), optionally with the butynediol at least partially concentrated, with specific chelating resin having certain properties, hereinafter more particularly described, in a vessel maintained at specified conditions, hereinafter more particularly described, and **d)** recovering liquid phase product from the vessel of step c) having Cu^{++} ion content reduced by 10 to 100 % from that of the liquid phase product from the reaction zone of step a).

[00010] Another embodiment of the invention comprises further steps of: **e)** passing the recovered liquid phase product of step d) and hydrogen to a reaction zone containing hydrogenation catalyst, hereinafter more particularly described, and maintained at reaction conditions, hereinafter more particularly described, to produce hydrogenated product comprising butanediol and by-products boiling below 250 °C, and **f)** recovering butanediol from the hydrogenated product comprising butanediol from step e).

[00011] In other embodiments of the invention, the ethynylation catalyst of step a) comprising Cu is modified with Bi; and/or the chelating resin of step c) comprises

aminophosphonic functional groups, iminodiacetic functional groups, bis-2-picolylamine groups, 2-hydroxypeoply picolylamine groups, or combinations thereof.

[00012] In another embodiment of the invention, the reaction zones of steps a) and e) comprise a fixed bed reactor.

[00013] In another embodiment of the invention, the reaction zone of step e) comprises a primary hydrogenation reaction vessel, an external circulation cooler wherein the cooled reaction product is partially recycled to the primary reaction vessel, an optional secondary hydrogenation reaction vessel, and a hydrogen circulation system for both reaction vessels.

DETAILED DESCRIPTION OF THE INVENTION

[00014] As a result of intense research in view of the above, we have found that we can economically and effectively manufacture high quality BDO from feedstock comprising BYD having been manufactured by reacting feedstock comprising formalin to produce liquid phase product comprising BYD and Cu^{++} ions in a reaction zone containing ethynylation catalyst comprising Cu and maintained at ethynylation reaction conditions. The process comprises steps of: **a)** reacting feedstock comprising formalin to produce liquid phase product comprising butynediol and Cu^{++} ions in a reaction zone containing ethynylation catalyst comprising Cu and maintained at ethynylation reaction conditions including pressure from 1 to 3 bar, temperature from 50 to 150 °C, and pH from 3.5 to 9, **b)** recovering liquid phase product from the reaction zone of step a) comprising butynediol and Cu^{++} ions, **c)** contacting the recovered product of step b), optionally with the butynediol at least partially concentrated, with chelating resin having total exchange capacity of 1 to 3 equivalents per liter as wet resin delivered in the sodium form in a vessel maintained at conditions including pressure from 1 to 20 bar, bed pressure drop less than 2 bar, and temperature from ambient to 100 °C, and **d)** recovering liquid phase product from the vessel of step c) having Cu^{++} ion content reduced by 10 to 100 % from that of the liquid phase product from the reaction zone of step a). Furthermore, the

process comprises the above steps and steps of: **e)** passing the recovered liquid phase product of step d) and hydrogen to a reaction zone containing hydrogenation catalyst and maintained at reaction conditions including pressure from 40 to 340 bar, and temperature of from 60 to 180 °C to produce hydrogenated product comprising butanediol and by-products boiling below 250 °C, and **f)** recovering butanediol from the hydrogenated product comprising butanediol from step e).

[00015] The term butynediol ("BYD") represents the compound structure $HOCH_2C{\equiv}CCH_2OH$. The term butanediol ("BDO") represents one or a combination of the compound structures $HOCH_2CH_2CH(OH)CH_3$, $HOCH_2CHOHCH_2CH_3$, $HOCH_2CH_2CH_2CH_2$ OH, and $CH_3CHOHCHOHCH_3$. The term "formalin" represents an aqueous solution of formaldehyde, for example, from 37 to 50 % formaldehyde, that may contain other components such as, for example, methyl alcohol, for example, 15 % methyl alcohol. Percentages are in volume % unless otherwise indicated. Pressures are in psig or bar, wherein 1 bar = 0.987 atmosphere = 14.5 psig = 98.7kPa, unless otherwise indicated. Flow rates of gaseous streams are presented in kg/hour. Flow rates of liquid streams are presented in kg/hour.

[00016] The feedstock reacted in the reaction zone of step a) of the present process comprises formalin, and compounds selected from the group consisting of acetylene, water, caustic, salts, nitrogen, and combinations thereof.

[00017] The product of step a) is manufactured by ethynylating the feedstock comprising formalin to produce liquid phase product comprising butynediol and Cu^{++} ions in a reaction zone containing ethynylation catalyst comprising Cu and maintained at ethynylation reaction conditions including pressure from 1 to 3 bar, for example, from 1.5 to 2 bar, temperature from 50 to 150 °C, for example, from 65 to 95 °C, and pH from 3.5 to 9, for example, from 5.9 to 6.3. The reaction for producing liquid phase product comprising butynediol and Cu^{++} ions may utilize an aqueous solution containing formalin, acetylene and suspended catalyst comprising Cu in a reaction vessel. For example, U. S. Patent No. 4,584,418A describes a means of

making a copper acetylide catalyst for synthesis of BYD in a single vessel wherein acetylene is bubbled through the reactor at 90 °C and atmospheric pressure. In a further example, U. S. Patent No. 5,444,169A discloses a process for synthesizing BYD from an aqueous solution containing formaldehyde by reaction with acetylene in the presence of a suspended catalyst, wherein the solution is conveyed in a cascade by several reactors, the solution drawn off from the first through the penultimate reactor of the cascade being fed to the next reactor in the cascade, acetylene being introduced into each of the reactors, and a BYD-rich solution being drawn off only from the last reactor in the cascade.

[00018] The BYD synthesis in step a) may be facilitated by bismuth modified copper catalyst, which may be either unsupported or supported. Depending on the reaction conditions in the reaction zone of step a), primarily the pH of the reaction mixture, trace amount of Cu^{++} salts are dissolved in the crude BYD product. The solubility of the Cu^{++} salts increases with decreasing pH of the reaction mixture solution.

[00019] If the Cu^{++} ions dissolved in the liquid phase product recovered from the reaction zone of step a) are not significantly reduced or removed, the liquid phase BYD product passed to the reaction zone of step e) for hydrogenation will cause problems, for example, poisoning of the hydrogenation catalyst, with that important step in manufacture of BDO. For example, commonly used catalysts for BYD hydrogenation comprise nickel metal, e.g. the Raney® nickel catalyst. Over time, the catalyst comprising nickel produces more n-BuOH as it ages and it needs to be replaced when the n-BuOH reaches certain levels. It is evident that the surface of discharged nickel catalyst is coated with metallic copper from either physical appearance, i.e. reddish color, or by surface metal analysis, e.g. SEM/Edex.

[00020] It is believed that copper depositions on the surface of the hydrogenation catalyst present in step e) promote formation of n-BuOH *via* hydrogenolysis of BDO. The present invention selectively removes dissolved Cu^{++} ions from the refined BYD

aqueous solution in step c) using a specific chelating ion exchange resin to minimize the copper metal poisoning of the hydrogenation catalyst. This extends its service time for converting BYD to BDO more selectively.

[00021] The abundant benefits of this invention compared to current methods for manufacturing butanediol from feedstock comprising butynediol having been manufactured by reacting feedstock comprising formalin to produce product comprising butynediol and Cu^{++} ions in the presence of ethynylation catalyst comprising Cu include selective removal the trace amount of Cu^{++} ions, e.g. below or above 1 ppm level of Cu^{++}, in the presence of up to about 1,000 ppm sodium ions, while current methods remove all ions, cation and anion. Because of the very high concentration of the total ions, complete removal thereof requires multiple unit operations, e.g. 3 beds, and very frequent ion exchange resin regenerations that are very capital intensive and incur high cost. On the other hand, the selective removal of the very low levels of Cu^{++} ions, e.g. 1 ppm or so, using the specific chelating resin required herein only needs a single resin bed and very infrequent resin regeneration with much less waste that will be very cost effective.

[00022] The chelating resin required in step c) will have properties including total exchange capacity of 1 to 3 equivalents per liter as wet resin delivered in the sodium form, such as, for example, 1.3 to 2 equivalents per liter. These resins contain functional groups that can effectively chelate with metal ions, especially, with multi-valent metal ions, so their affinity for the multi-valent metal ions such as Cu^{++} is much higher than that with the mono-valent alkali metal ions such as the Na^{+}. Non-limiting examples of such chelating resins include, but are not limited to, resins with aminophosphonic functional groups, e.g. Amberlite™ IRC 747; resins with iminodiacetic functional groups, e.g. Amberlite™ IRC 748; and resins with bis-2-picolylamine and/or 2-hydroxypeopyl picolylamine groups, e.g. Dowex™ M4195 and Dowex™ XUS-43605. Since the liquid phase product of step a) contains far higher concentration of Na^{+} ions than the Cu^{++} ions, for example up to 1000 times more, it is desirable to use the chelating resin in the sodium form if applicable where the Na^{+}

ions in the liquid phase product will not be changed by the process step, i.e. the pH of the liquid phase product will remain the same.

[00023] The reaction zone of step e) in the present invention may, for example, comprise unit operations exemplified by a primary hydrogenation reaction vessel, an external circulation cooler wherein the cooled reaction product is partially recycled to the primary reaction vessel, a secondary hydrogenation reaction vessel, and a hydrogen circulation system for both reaction vessels. The reaction vessel for use as the reaction zone of step e) in the present invention may comprise one of current use in such a process. Particularly useful as a reaction vessel for use in this process is a fixed bed reactor or a mixed slurry bed reactor. These reaction vessels may be cooled or heated by heat exchanger either internal to the reactor or externally by circulation. A fixed bed reactor may be operated using any of the following types of contact: (i) co-current downflow trickle bed contact, (ii) countercurrent gas-liquid contact, or (iii) co-current upflow gas-liquid contact.

[00024] The hydrogen supplied to the reaction zone of step e) may be, at least in part, recovered from process or facility waste gas. For example, U. S. Patent No. 8,552,234 B2 describes use of a hydrogen permeable membrane to recover and recycle hydrogen from a carboxylic acid hydrogenation process. In a further example, U. S. Patent No. 8,168,685 B2 describes recovering hydrogen from a process waste gas.

[00025] Reaction conditions in the reaction zone of step e) include a pressure of from 40 to 340 bar and temperature from 60 to 180 °C, for example, a pressure from 250 to 310 bar and temperature from 100 to 160 °C. If a fixed bed reactor is used, contents of the reaction zone may be agitated by either or both of mechanical means, for example a stirrer, or gaseous injection.

[00026] Catalyst for use in the reaction zone of step e) of the present process is a hydrogenation catalyst, such as but not limited to, for example, one or more metals from Group VIII of the Periodic Table of the Elements, e.g. Ni, Pd, Pt, Ru and Rh,

with Ni most commonly used. The catalyst composition may include an inorganic oxide material matrix or binder upon which the metal resides. Such matrix materials include synthetic or naturally occurring substances as well as inorganic materials such as clay, silica and/or metal oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Naturally occurring clays which can be used for this include those of the montmorillonite and kaolin families, which families include the subbentonites and the kaolins commonly known as Dixie, McNamee, Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite. Specific useful catalyst matrix or binder materials which may be employed herein include silica, alumina, zirconia, titania, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. A mixture of these components could also be used. The relative proportions of hydrogenation catalyst metal and binder or matrix, if present, may vary widely with the catalyst metal content ranging from about 1 to about 90 percent by weight, and more usually in the range of about 40 to about 75 percent by weight of the total composition.

[00027] The liquid phase product recovered from the reaction zone of step a) comprises butynediol, Cu^{++} ions, and components selected from the group consisting of formalin, salts, organic by-products, and combinations thereof. The liquid phase product recovered from the reaction zone of step c) comprises butynediol, Cu++ ions, and components selected from the group consisting of formalin, salts, organic by-products, and combinations thereof, with the Cu^{++} ions significantly reduced from that of the product recovered from the reaction zone of step a). The reduction of Cu^{++} ions is from 10 to 100 %, such as from 50 to 99 %. The hydrogenated product comprising butanediol recovered from the reaction zone of step e) comprises butanediol, salts, water, organic by-products, and combinations thereof. Reaction by-products recovered from step e) may include compounds

boiling below 250 °C, methanol, propanol, butanol, tetrahydrofural, butanediol acetal, other glycols, and combinations thereof. The butynediol in the product recovered from the reaction zone of step a) may, if desired, be partially concentrated prior to step c) by, for example, distillation at pressure from 3 to 7 bar, e.g. 5 bar, and temperature from 140 to 220 °C, e.g. 160 °C.

[00028] The following Examples demonstrate the present invention and its capability for use. The invention is capable of other and different embodiments, and its several details are capable of modifications in various apparent respects, without departing from the scope and spirit of the present invention. Accordingly, the Examples are to be regarded as illustrative in nature and non-limiting.

EXAMPLE 1

[00029] A 250 gram quantity of liquid phase product having a pH of 4.35 comprising butynediol and 0.75 ppm Cu^{++} ions prepared commercially from feedstock comprising formalin in a reaction zone containing ethynylation catalyst comprising Cu at a pressure of 1.8 bar, temperature of 90 °C, and pH of 6.0, then partially concentrated by distillation at 5 bar and 160 °C, was stirred in a covered beaker with various quantities of Dowex™ M4195 resin from Dow Chemical for 18 hours each at ambient temperature and then measured for pH and Cu^{++} ions. Measurements of the Cu^{++} ion content of the solutions was carried out with a HACH Pocket Colorimeter™ II unit. Results are shown in the table below.

Resin (g)	0.000	0.084	0.202	0.334	0.666	1.290
pH	4.35	4.30	4.26	4.28	4.23	4.15
Cu^{++} (ppm)	0.75	0.19	0.03	0.05	0.04	0.00

EXAMPLE 2

[00030] A 50 gram quantity of liquid phase product having a pH of 4.09 comprising butynediol and 0.45 ppm Cu^{++} ions prepared commercially from feedstock

comprising formalin in a reaction zone containing ethynylation catalyst comprising Cu at a pressure of 1.8 bar, temperature of 90 °C, and pH of 6.0, then partially concentrated by distillation at 5 bar and 160 °C, was stirred in a covered beaker with various quantities of Dowex™ XUS-43605 resin from Dow Chemical for 18 hours each at ambient temperature and then measured for pH and Cu^{++} ions. Measurements of the Cu^{++} ion content of the solutions was carried out with a HACH Pocket Colorimeter™ II unit. Results are shown in the table below.

Resin (g)	0.000	0.017	0.066	0.131	0.259	0.519
pH	4.09	4.07	4.02	3.99	3.95	3.92
Cu^{++} (ppm)	0.45	0.05	0.04	0.03	0.03	0.02

[00031] All patents, patent applications, test procedures, priority documents, articles, publications, manuals, and other documents cited herein are fully incorporated by reference to the extent such disclosure is not inconsistent with this invention and for all jurisdictions in which such incorporation is permitted.

[00032] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated.

[00033] While the illustrative embodiments of the invention have been described with particularity, it will be understood that various other modifications will be apparent to and may be readily made by those skilled in the art without departing from the spirit and scope of the invention. Accordingly, it is not intended that the scope of the claims hereof be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present invention, including all features which would be treated as equivalents thereof by those skilled in the art to which the invention pertains.

What is claimed is:

1. An improved process for manufacturing product comprising butanediol comprising the steps of:

a) reacting feedstock comprising formalin to produce liquid phase product comprising butynediol and Cu^{++} ions in a reaction zone containing ethynylation catalyst comprising Cu and maintained at ethynylation reaction conditions including pressure from 1 to 3 bar, temperature from 50 to 150 °C, and pH from 3.5 to 9,

b) recovering liquid phase product from the reaction zone of step a) comprising butynediol and Cu^{++} ions,

c) contacting the recovered product of step b) with chelating resin having properties including total exchange capacity of 1 to 3 equivalents per liter in a vessel maintained at conditions including pressure from 1 to 20 bar, and temperature from ambient to 100 °C, and

d) recovering liquid phase product from the vessel of step c) having Cu^{++} ion content reduced by 10 to 100 % from that of the liquid phase product from the reaction zone of step a).

2. The process of claim 1 comprising a further step of concentrating the butynediol of the liquid phase product recovered in step b) prior to step c).

3. The process of claim 1 comprising further steps of:

e) passing the recovered liquid phase product of step d) and hydrogen to a reaction zone containing hydrogenation catalyst and maintained at reaction conditions including pressure from 40 to 340 bar, and temperature of from 60 to 180 °C to produce hydrogenated product comprising butanediol and by-products boiling below 250 °C, and

f) recovering butanediol from the hydrogenated product comprising butanediol from step e).

4. The process of claim 3 comprising a further step of concentrating the butynediol of the liquid phase product recovered in step b) prior to step c).

5. The process of claim 1 wherein the ethynylation catalyst of step a) comprising Cu is modified with Bi.

6. The process of claim 1 wherein the chelating resin of step c) comprises aminophosphonic functional groups, iminodiacetic functional groups, bis-2-picolylamine groups, 2-hydroxypeoply picolylamine groups, or combinations thereof.

7. The process of claim 3 wherein the hydrogenation catalyst of step e) comprises one or more metals from Group VIII of the Periodic Table of the Elements.

8. The process of claim 7 wherein the hydrogenation catalyst comprises a metal selected from the group consisting of Ni, Pd, Pt, Ru, Rh and combinations thereof.

9. The process of claim 8 wherein the hydrogenation catalyst comprises Ni.

10. The process of claim 3 wherein the reaction zone of steps a) and e) comprise a fixed bed reactor.

11. The process of claim 10 wherein the reaction zone of step e) comprises a primary hydrogenation reaction vessel, an external circulation cooler wherein the cooled reaction product is partially recycled to the primary reaction vessel, an optional secondary hydrogenation reaction vessel, and a hydrogen circulation system for both reaction vessels.

12. The process of claim 3 wherein by-products boiling below 250 °C resulting from step e) are flashed off the hydrogenated product comprising butanediol.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/013389

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C29/42 C07C29/17 C07C31/20 C07C33/046
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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 practicable, search terms used)
EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	US 2010/016643 A1 (PINKOS ROLF [DE] ET AL) 21 January 2010 (2010-01-21) the whole document	1-6, 10-12 7-9
Y	D. KOLODYNSKA ET AL: "DOWEX M 4195 and LEWATIT MonoPlus TP 220 in Heavy Metal Ions Removal from Acidic Streams", SEPARATION SCIENCE AND TECHNOLOGY, vol. 49, no. 13, 2 September 2014 (2014-09-02), pages 2003-2015, XP055466675, ISSN: 0149-6395, DOI: 10.1080/01496395.2014.908920 the whole document	1-6, 10-12
A	US 4 371 723 A (CHIDDIX MAX E) 1 February 1983 (1983-02-01) cited in the application the whole document	1-12

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

☒ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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