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(54) Title: PROCESS FOR PRODUCING GLYCOL FROM RENEWABLE FEEDSTOCK

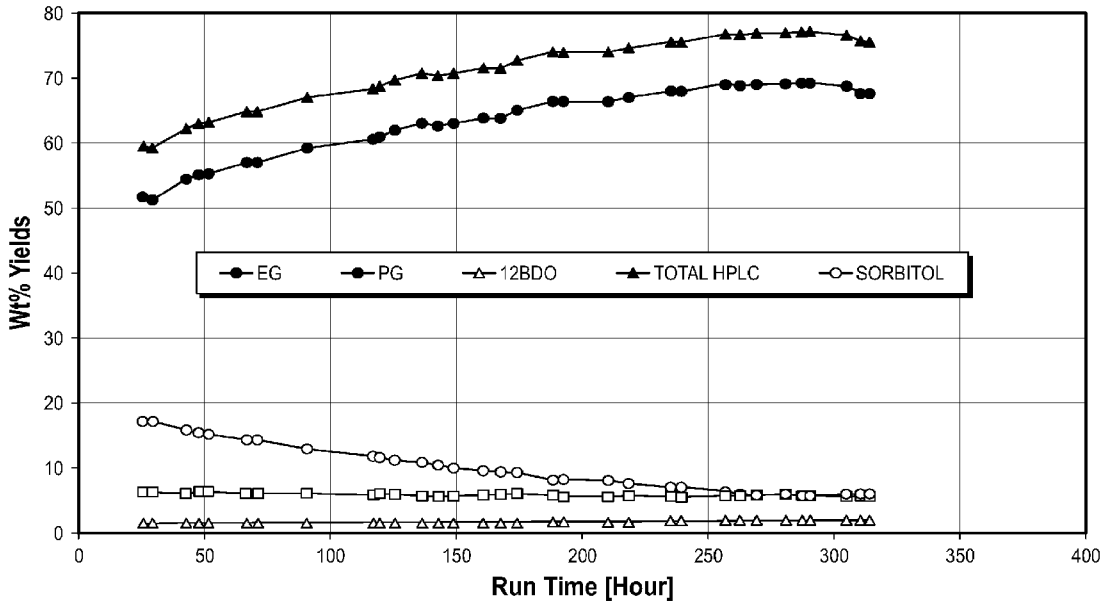


FIG. 2

(57) Abstract: A process for the production of glycol from a saccharide-containing feedstock in the presence a catalyst system having a retro-aldol catalyst and a hydrogenation catalyst has a conditioning step for the hydrogenation catalyst. The hydrogenation catalyst is conditioned with a treatment solution comprising a conditioning retro-aldol catalyst in the absence of the saccharide-containing feedstock. Thereafter, the saccharide-containing feedstock and a catalytic retro-aldol catalyst are introduced to the reactor containing the conditioned hydrogenation catalyst, and glycol is produced by hydrogenolysis of the saccharide-containing feedstock.

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PROCESS FOR PRODUCING GLYCOL FROM RENEWABLE FEEDSTOCK

FIELD OF THE INVENTION

[0001] This invention relates to a process for producing glycol from renewable feedstock through catalytic hydrogenolysis.

BACKGROUND OF THE INVENTION

[0002] Certain glycols, such as monoethylene glycol (MEG) and monopropylene glycol (MPG), are useful as heat transfer media, antifreeze and precursors to polymers, such as polyester and polyethylene terephthalate.

[0003] In a typical industrial process, MEG is prepared in a two-step process. In the first step, ethylene is converted to ethylene oxide by reaction with oxygen over a silver oxide catalyst. The ethylene oxide can then be converted into MEG. This may be carried out directly by catalytic or non-catalytic hydrolysis. Alternatively, in one well-known process, ethylene oxide is catalytically reacted with carbon dioxide to produce ethylene carbonate. The ethylene carbonate is subsequently hydrolyzed to provide ethylene glycol.

[0004] These routes rely for their starting material on ethylene, which is produced in the petrochemical industry by steam cracking of hydrocarbons derived from fossil fuels.

[0005] In recent years, increased efforts have been focused on reducing the reliance on fossil fuels as a primary resource for the provision of fuels and commodity chemicals. Carbohydrates and related biomass are seen as key renewable resources in the efforts to provide new fuels and alternative routes to desirable chemicals.

[0006] Production of glycols, from non-petrochemical renewable feedstocks, such as biomass, is highly desirable with the conversion of sugars such as glucose to glycols representing an efficient use of the starting materials since the oxygen atoms remain intact in the desired end product.

[0007] In particular, certain carbohydrates can be reacted with hydrogen in the presence of a catalyst system to generate polyols and sugar alcohols. Current methods for the conversion of saccharides to glycols revolve around a nickel-promoted tungsten carbide catalytic hydrogenation/retro-aldol process, for example, as described in Ji et al. ("Direct Catalytic Conversion of Cellulose into Ethylene Glycol using Nickel-Promoted Tungsten Carbide Catalysts" Angew. Chem. Int. Ed. 47:8510-8513; 2008). Typically, the hydrogenation catalyst

compositions tend to be heterogeneous. However, the retro-aldol catalysts are generally homogeneous in the reaction mixture. Such catalysts are inherently limited due to solubility constraints.

[0008] Muthusamy (EP3356314B1, 21 Oct 2020) describes processes for the preparation of glycols such as MEG and MPG using a catalyst system consisting of a catalyst component with retro-aldol catalytic capabilities and a first hydrogenation catalyst comprising an element selected from Groups 8, 9 and 10 of the periodic table.

[0009] van der Bijl et al. (US2018/0273452A1, 27 Sep 2018) describes a process for producing glycols from saccharide-containing feedstocks under conditions that convert a catalyst precursor into an unsupported hydrogenation catalyst.

[0010] Continuous flow processes for the production of glycols from saccharide feedstock have been described in Kalnes et al. (US2011/0313212A1, 22 Dec 2011), (Tao Zhang et al. (CN102675045A, 19 Sep 2012, and CN102643165A, 22 Aug 2012), and Chen et al. (WO2013/015955A2, 31 Jan 2013). Schreck et al. (WO2017/210614A1, 7 Dec 2017) also describes a continuous process from making ethylene glycol wherein the carbohydrate feed is rapidly heated to reduce the production of hexitol and other side products such as propylene glycol. A process for the co-production of bio-fuels and glycols is described in Powell (WO2012/174087A1, 20 Dec 2012).

[0011] Singh et al. (US2020/0406237A1, 31 Dec 2020) relates to a process for producing ethylene glycol with a homogeneous catalyst and a heterogeneous catalyst. Spent heterogeneous catalyst is regenerated by removing deposited tungsten and then recycled to the reaction step.

[0012] Whilst there are various processes for production of glycols from biomass that are well established there still remains a need to further improve the performance of the bifunctional catalysts used in these processes. In particular, it may take several days for catalyst performance to reach steady state once a catalytic hydrogenation/retro-aldol reaction has commenced. In this reactor start-up phase of the process there can be a consequent loss of yield and efficiency until steady state. Hence, it would be desirable to improve the performance of retro-aldol/hydrogenation catalysts, especially in the start-up phase of a reaction.

[0013] One approach to address this problem is described in de Vlieger et al. (WO2020055831A1, 19 Mar 2020), which discloses introducing the retro-aldol catalyst component, suitably comprising tungsten, into the reactor whilst also in the presence of one or more agents that suppress catalyst precipitation. These homogeneous tungsten-based catalysts are known to be susceptible to conversion to undesirable products, for example by reduction

and precipitation of the metal that reduces process efficiency and can clause clogging of the reactor.

[0014] Nevertheless, it would be even more desirable to reduce the actual time taken for the start-up process as a whole to reach steady state conditions, thereby reducing the opportunity for undesirable side reactions to occur.

[0015] These and other uses, features and advantages of the invention should be apparent to those skilled in the art from the teachings provided herein.

SUMMARY OF THE INVENTION

[0016] According to one aspect of the present invention, there is provided a process for the production of glycol from a saccharide-containing feedstock in the presence a catalyst system having a retro-aldol catalyst and a hydrogenation catalyst, the process comprising the steps of: loading the hydrogenation catalyst in a reactor; feeding hydrogen to the reactor; conditioning the hydrogenation catalyst with a treatment solution comprising a conditioning retro-aldol catalyst in the absence of the saccharide-containing feedstock; introducing the saccharide-containing feedstock and a catalytic retro-aldol catalyst to the reactor containing the conditioned hydrogenation catalyst; and producing glycol by hydrogenolysis of the saccharide-containing feedstock.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] The process of the present invention will be better understood by referring to the following detailed description of preferred embodiments and the drawings referenced therein, in which:

[0018] Fig. 1 is a graph showing the results of Comparative Example 1; and

[0019] Fig. 2 is a graph showing the results of Example 2.

DETAILED DESCRIPTION OF THE INVENTION

[0020] The present invention provides a process for the production of glycol from a saccharide-containing feedstock in the presence of a catalyst system having a retro-aldo catalyst and a hydrogenation catalyst. Reactions include hydrolysis, retro-aldol condensation, and hydrogenation. For example, when the saccharide-containing feedstock comprises cellulose, reactions include hydrolysis of cellulose to glucose, C-C cleavage of glucose by retro-aldol condensation to form glycolaldehyde, and hydrogenation of glycolaldehyde to ethylene glycol. In addition, glucose may be isomerized to fructose, and fructose is converted to propylene glycol. The hydrogenation catalyst also tends to produce sorbitol and/or mannitol,

as undesirable by-products. Accordingly, in conventional processes, there is an initial ramping up of glycol production while sorbitol production decreases. This ramp-up period can last several days, for example, 300 hours.

[0021] In conventional processes, acidic conditions destabilize the hydrogenation catalyst, and a more stable catalyst is needed. A highly active retro-aldol catalyst is needed for the reaction to work well under the conditions of high-concentration glucose in the reaction mixture, but that activity cannot be provided by simply raising the concentration of the homogeneous tungstate because of its tendency to destabilize by precipitation, leading to clogging of the reactor and/or deleterious deposits on process equipment.

[0022] The present inventor has surprisingly discovered that, by conditioning the hydrogenation catalyst with a conditioning retro-aldol catalyst before introducing the saccharide-containing feedstock to the reactor, the ramp-up period can be significantly reduced. By conditioning the hydrogenation catalyst, high activity sites are inhibited at the surface, resulting in a net reduction in the specific activity of the hydrogenation catalyst but with a higher stability.

[0023] In accordance with the present invention, an equilibrium amount of metal from the conditioning retro-aldol catalyst is deposited on the surface of the hydrogenation catalyst. This deposit provides a portion of the conditioning retro-aldol activity, supplemental to the normally available activity of the catalytic retro-aldol catalyst. To compensate for the lower specific activity of the hydrogenation catalyst thus treated, the volumetric concentration of the catalyst may be increased. The total retro-aldol activity available for the reaction is thus higher than possible without the conditioning of the hydrogenation catalyst.

[0024] In conventional processes for producing glycol from renewable feedstock, there is a ramp-up period before glycol production reaches a steady state. In contrast to conventional processes, the process of the present invention significantly reduces the length of the ramp-up period by at least 50%, preferably at least 60%, to reach a steady-state in the reactor. In the example presented herein, the ramp-up period was reduced by 70%. Accordingly, the yield of glycol is significantly improved by the process of the present invention. Consequently, the economics of the glycol production process are improved by reducing waste due to inefficiency, improving catalyst life, and improving overall product yield.

[0025] Preferably, the glycol is selected from the group consisting of ethylene and propylene glycols. More preferably, the glycol is selected from monoethylene glycol (MEG), monopropylene glycol (MPG), and combinations thereof. The saccharide-containing feedstock for the process of the present invention is selected from the group consisting of

monosaccharides, disaccharides, oligosaccharides and polysaccharides. Preferably, the saccharide-containing feedstock comprises saccharides selected from glucose, sucrose, starch, maltose, cellobiose, corn syrup, cellulose, hemicellulose, glycogen, chitin, and combinations thereof. More preferably, the saccharide-containing feedstock comprises saccharides selected from glucose, sucrose, starch, and combinations thereof. Most preferably, the saccharide-containing feedstock comprises glucose.

[0026] If the saccharide-containing feedstock includes, or is derived from, oligosaccharides or polysaccharides, the oligosaccharides and polysaccharides are preferably subjected to pre-treatment before being used in the process of the present invention. Suitable pre-treatment methods are known in the art and one or more may be selected from the group including, but not limited to, sizing, drying, milling, hot water treatment, steam treatment, hydrolysis, pyrolysis, thermal treatment, chemical treatment, biological treatment, saccharification, fermentation, and solid removal. However, after pre-treatment, the starting material still comprises mainly monomeric and/or oligomeric saccharides. The saccharides are, preferably, soluble in the reaction solvent.

[0027] Preferably, the saccharide-containing feedstock, after any pre-treatment, comprises saccharides selected from glucose, starch and/or hydrolysed starch. Hydrolysed starch comprises glucose, sucrose, maltose, and oligomeric forms of glucose. The saccharides are suitably present as a solution, a suspension, or a slurry in a solvent.

[0028] After pre-treatment, the treated feedstock stream is suitably converted into a solution, a suspension, or a slurry in a solvent. The solvent may be water, or a C1 to C6 alcohol or polyalcohol, or mixtures thereof including 50:50 mixtures of water and C1 to C6 alcohol or polyalcohol. Suitable C1 to C6 alcohols include methanol, ethanol, 1-propanol, and isopropanol. Suitable polyalcohols include glycols, particularly products of the hydrogenation reaction, glycerol, erythritol, threitol, sorbitol, 1, 2-hexanediol, and mixtures thereof. More suitably, the polyalcohol may be glycerol or 1, 2-hexanediol. Further solvent may also be added to a reactor vessel or reactor vessels in a separate feed stream or may be added to the treated feedstock stream before it enters the reactor.

[0029] The concentration of the saccharide-containing feedstock as a solution in the solvent supplied to the reactor vessel is at most at 80 wt.%, preferably at most 60 wt.%, more preferably, at most 45 wt.%. The concentration of the saccharide-containing feedstock as a solution in the solvent supplied to the reactor vessel is at least 5 wt.%, preferably at least 20 wt.%, more preferably at least 35 wt.%.

[0030] The catalyst system used in the process of the present invention is comprised of a hydrogenation catalyst and a retro-aldol catalyst.

[0031] The hydrogenation catalyst comprises a transition metal having catalytic hydrogenation capabilities selected from Groups 8, 9 and 10 of the periodic table. Preferably, the hydrogenation catalyst comprises a metal selected from the group consisting of iron, cobalt, nickel, ruthenium, rhodium, palladium, iridium, platinum, and combinations thereof. The metal or metals may be present in elemental form or as compounds. It is also suitable that this component is present in chemical combination with one or more other ingredients in the hydrogenation catalytic composition.

[0032] In some embodiments, the hydrogenation catalytic composition comprises metals supported on a solid support. In some embodiments, the solid supports may be in the form of a powder or in the form of regular or irregular shapes such as spheres, extrudates, pills, pellets, tablets, monolithic structures. Alternatively, the solid supports may be present as surface coatings, for example on the surfaces of tubes or heat exchangers. Suitable supports for the hydrogenation catalyst are those known to the skilled person and include, without limitation, alumina, silica, zirconium oxide, magnesium oxide, zinc oxide, titanium oxide, carbon, activated carbon, zeolite, clay, silica alumina and combinations thereof.

[0033] In one embodiment, the hydrogenation catalyst is a Raney-metal type catalyst, suitably a Raney-nickel (Raney-Ni) catalyst. Preferably, Raney-Ni is provided in a pelletised form. In another embodiment, the first catalyst is a supported hydrogenation catalyst, such as ruthenium supported on activated carbon.

[0034] The conditioning retro-aldol catalyst and the catalytic retro-aldol catalyst each independently preferably comprise a transition metal compound, complex or elemental material comprising tungsten, molybdenum, lanthanum, tin, vanadium, niobium, chromium, titanium, zirconium, and combinations thereof. More preferably, the retro-aldol catalyst composition comprises one or more material selected from the group consisting of tungstic acid, molybdic acid, ammonium tungstate, ammonium metatungstate, ammonium paratungstate, tungstate compounds comprising at least one Group I or II element, such as sodium tungstate; metatungstate compounds comprising at least one Group I or II element, such as sodium metatungstate, paratungstate compounds comprising at least one Group I or II element, such as sodium paratungstate, heteropoly compounds of tungsten, heteropoly compounds of molybdenum, tungsten oxides, molybdenum oxides, vanadium oxides, metavanadates, chromium oxides, chromium sulfate, titanium ethoxide, zirconium acetate, zirconium carbonate, zirconium hydroxide, niobium oxides, niobium ethoxide, and

combinations thereof. Preferably, the retro-aldol catalyst composition comprises one or more compound, complex or elemental material selected from those containing tungsten or alternatively those containing molybdenum. The conditioning retro-aldol catalyst and the catalytic retro-aldol catalyst may be the same or different.

[0035] In the process of the present invention, the hydrogenation catalyst is loaded in a reactor. Preferably, the hydrogenation catalyst is a heterogenous catalyst and is retained or supported within the reactor vessel.

[0036] The amount of hydrogenation catalyst loaded to the reactor is selected to provide the desired weight ratio of the hydrogenation catalyst composition (based on the amount of metal in said composition) to the potential saccharide-containing feedstock. Suitably, the amount of hydrogenation catalyst is provided to reach a catalyst:feed weight ratio in a range of from 10:1 to 1:100. Preferably, the hydrogenation catalyst is loaded to achieve an operating catalyst:feed weight ratio in the producing step of 1:1.8 to 10:1.8. Hydrogen is fed to the reactor to displace a majority of air and/or oxygen-containing gas. Hydrogen may be fed continuously during the conditioning step or halted until the feedstock is introduced and/or until the producing step.

[0037] In accordance with the present invention, the catalyst is then conditioned by adding a treatment solution comprising a conditioning retro-aldol catalyst in the absence of the saccharide-containing feedstock. The ratio of conditioning retro-aldol catalyst to hydrogenation catalyst is in a range from 100:1 to 1:100 (w/w). 1 wt.% conditioning retro-aldol catalyst (based on weight of hydrogenation catalyst) has a conditioning effect. An excess of conditioning retro-aldol catalyst beyond a threshold concentration required for a monolayer coverage on the hydrogenation catalyst surface is not expected to have additional benefit.

[0038] Optionally, the treatment solution may further comprise a glycol reaction product, suitably selected from the group consisting of ethylene glycol, propylene glycol, 1,2-butanediol, glycerol, erythritol, threitol, sorbitol, 1,2-hexanediol, and combinations thereof. Preferably, the treatment solution comprises sorbitol.

[0039] The pH of the conditioning step is preferably controlled by adding an acidic component, for example by adding glycolic acid, lactic acid, acetic acid, and/or phosphoric acid.

[0040] By conditioning the hydrogenation catalyst with the conditioning retro-aldol catalyst, high activity sites are preferentially inhibited at the surface of the hydrogenation catalyst, resulting in a net reduction in the specific activity but with a higher stability for the conditioned hydrogenation catalyst. To compensate for the lower specific activity of the

hydrogenation catalyst thus treated, the volumetric concentration of the catalyst is increased. The volumetric catalyst concentration may be increased, for example, by 50 – 100%.

[0041] Further, the deposited retro-aldo catalyst provides additional retro-aldol catalytic activity supplemental to the retro-aldol activity when the catalytic retro-aldol catalyst is later fed to the reactor with the saccharide-containing feedstock. Hence, the total retro-aldol activity available for the reaction is thus higher than is possible without first conditioning the hydrogenation catalyst.

[0042] In a preferred embodiment of the invention, the hydrogenation catalyst is a Raney-Ni catalyst that is treated with tungstic acid, as the retro-aldol catalyst. In this embodiment, an equilibrium amount of tungstate is deposited on the surface of the Raney-Ni.

[0043] The conditioning step is conducted in the reactor in the presence of hydrogen that was fed to the reactor with a treatment solution comprising a conditioning retro-aldol catalyst in the absence of the saccharide-containing feedstock to produce a conditioned hydrogenation catalyst. Preferably, the conditioning step is conducted at a temperature in a range of from 150°C to 280°C, preferably in a range of from 160°C to 270°C, more preferably in a range of from 180°C to 250°C. Optionally, the conditioning step is conducted at an acidic pH. Preferably, the pH is in a range from 2 to 8, more preferably from 3 to 6, as measured in the reactor effluent at room temperature. The conditioning step can be carried out over a time period of up to 48 hours, typically not less than 24 hours, suitably not less than 12 hours, more suitably not less than 6 hours.

[0044] After the conditioning step, an optional testing step may be conducted by introducing a first portion of the saccharide-containing feedstock to the reactor containing the conditioned hydrogenation catalyst. The first portion of the saccharide-containing feedstock is preferably diluted before introduction to the reactor. The testing step is used to determine the amount of feedstock converted to product glycol and/or by-products and intermediates.

[0045] When used, the testing step is preferably conducted at a temperature in a range of from 50°C to 120°C, depending, for example, on the feed rate.

[0046] After the conditioning step, and optional testing step, the saccharide-containing feedstock and the catalytic retro-aldol catalyst are introduced to the reactor. The feedstock and catalytic retro-aldol catalyst may be combined prior to introducing to the reactor. Alternatively, the saccharide-containing feedstock and the catalytic retro-aldol catalyst are fed separately to the reactor.

[0047] The weight ratio of the catalytic retro-aldol catalyst to saccharide is suitably in the range of from 1:1 to 1:1000, preferably 1:50 to 1:100, based on the metal content of the catalytic retro-aldol catalyst.

[0048] Glycol is produced by hydrogenolysis of the saccharide-containing feedstock. The temperature in the reactor is suitably at least 80°C, preferably at least 130°C, more preferably at least 160°C, most preferably at least 190°C. The temperature in the reactor is suitably at most 300°C, preferably at most 280°C, more preferably at most 250°C, most preferably at most 230°C. Operating at higher temperatures has the potential disadvantage of increased amounts of side-reactions, leading to lower yield, and operating at a low temperature might result in suppression or inactivation of the retro-aldol activity. Preferably, the production step is conducted at a temperature in a range of from 180°C to 250°C, more preferably in a range of from 210°C to 250°C.

[0049] The pressure in the reactor is suitably at least 1 MPa, preferably at least 2 MPa, more preferably at least 3 MPa. The pressure in the reactor is suitably at most 25 MPa, preferably at most 20 MPa, more preferably at most 18 MPa. Preferably, the production step is conducted at a pressure in a range of from 3 MPa to 14 MPa. Preferably, the reactor is pressurised to a pressure within these limits by addition of hydrogen before the introducing step and is maintained at such a pressure as the reaction proceeds through on-going addition of hydrogen.

[0050] The residence time in the reactor during the glycol production step is suitably at least 1 minute, preferably at least 2 minutes, more preferably at least 5 minutes. Suitably the residence time in the reactor is no more than 5 hours, preferably no more than 2 hours, more preferably no more than 1 hour.

[0051] It will be understood by those skilled in the art that reaction parameters may be adjusted as needed over time to achieve a steady state concentration of product in the reactor. For example, the parameters that may be adjusted include, without limitation, feed rate, residence time, saccharide concentration in the feed, temperature and/or pressure. A corresponding amount of reactor effluent is removed continuously from the reactor.

[0052] In accordance with one embodiment of the present invention, the spent conditioned hydrogenation catalyst is removed from the reactor and mixed with powdered aluminum metal. The mixture is melted to form a Ni-W-Al alloy catalyst that may be used for producing glycol from a further saccharide-containing feedstock.

[0053] In this embodiment, the Ni-W-Al alloy is preferably crushed and leached with a concentrated NaOH solution to produce an active hydrogenation catalyst. Alternatively, the

Ni-W-Al alloy is crushed and leached with an acid under high-pressure hydrogen conditions to produce an active hydrogenation catalyst.

[0054] In yet another embodiment of the present invention, the spent conditioned hydrogenation catalyst is removed from the reactor and treated with a solution of ammonium salt to form a fresh hydrogenation catalyst and a solution comprising oxidized soluble tungstate. The fresh hydrogenation catalyst may be recycled to the loading step of the present invention. The solution comprising oxidized soluble tungstate may be recycled to the conditioning step and/or the introducing step of the present invention.

[0055] The solution of ammonium salt is preferably a dilute solution containing ammonium nitrate and/or ammonium carbonate. By this treatment, the W-oxides are oxidized into soluble tungstates, and removed from the surfaces, providing a cleaner surface on the hydrogenation catalyst. The ammonium-salt wash solution is suitable for the recovery of the active form retro-aldol catalyst.

[0056] In a further embodiment of the present invention, an effluent is removed from the reactor after the producing step. Product glycol is separated from a heavy-end stream comprising conditioned hydrogenation catalyst and retro-aldol catalyst. The heavy-end stream is then passed to a treatment reactor for converting organic acids to alcohols and/or for converting polyols to glycols. A stream comprising the conditioned hydrogenation catalyst is separated from the effluent of the treatment reactor and can be recycled to the reactor.

[0057] The invention will now be further illustrated by reference to the following non-limiting examples.

EXAMPLES

Comparative Example 1

[0058] 15.0 g of WR Grace Raney®-Ni 2800 (supplied by Aldrich-Sigma chemical company) was water-washed until neutral pH was reached and loaded into a 1-liter Hastelloy-C autoclave together with 550 ml water. The reactor was closed, air present in the reactor was displaced by nitrogen, then by hydrogen and the pressure was raised to 103.4 bar. Water was introduced at a feed rate of 7 ml/min and the volume inside the reactor was kept constant by controlling the discharge rate. The temperature was increased to 230°C in a period of 3 hours. The temperature was reduced to 70°C over a period of 3 hours.

[0059] The feed composition was changed to 10 wt.% glucose in water and introduced at a feed rate of 5 ml/min over a period of 12 hours to test the yield/activity of the hydrogenation

catalyst. Partial conversion of glucose to sorbitol was observed at a sorbitol yield of 47.7 wt.%, which translates to a reaction rate of 2.94 x 10^{-4} mol sorbitol/min/ g Raney-Ni)/glucose concentration (mol/l).

[0060] The reactor temperature was increased to 230°C over a period of 4 hours, after which the feed composition was changed to 20 wt.% glucose, 0.043 wt.% glycolic acid and 0.527 wt.% $Na_2WO_4.2H_2O$. The pH was controlled at 3.75, as measured in the reactor effluent, by feeding additional trace amounts of glycolic acid. After reaching steady state, the conversion of glucose was virtually complete and after 26 hours a yield of 44.5 wt.% MEG, 7.8 wt.% MPG, 1.6 wt.% 1,2-butanediol and 20.6 wt.% sorbitol was observed. Glycol yield increases and sorbitol yield decreases over time.

[0061] After 241 hours run time, a yield of 51.7 wt.% MEG, 6.5 wt.% MPG, 1.7 wt.% 1,2-butanediol and 17.1 wt.% sorbitol was observed. After 450 hours run time, a yield of 59.8 wt.% MEG, 6.0 wt.% MPG, 1.8 wt.% 1,2-butanediol and 12.3 wt.% sorbitol was observed. The results are shown in Fig. 1.

Example 2

[0062] 15.0 g of WR Grace Raney®-Ni 2800 (supplied by Aldrich-Sigma chemical company) was water-washed until neutral pH was reached and loaded into a 1-liter Hastelloy-C autoclave together with 550 ml water. The reactor was closed, air present in the reactor was displaced by nitrogen, then by hydrogen and the pressure was raised to 103.4 bar. Water was introduced at a feed rate of 7 ml/min and the volume inside the reactor was kept constant by controlling the discharge rate. The temperature was increased to 230°C in a period of 3 hours. A feed solution of 2.5 wt.% sorbitol, 0.56 wt.% $Na_2WO_4.2H_2O$ and 0.48 wt.% glycolic acid was introduced to the reactor at a feed rate of 3 ml/min and the temperature was kept constant at 230 °C over a period of 24 hours. The temperature was reduced to 70 °C over a period of 3 hours. As noted above, this step of reducing temperature was done for purposes of the optional testing step wherein a first portion of the saccharide-containing feedstock is introduced to the reactor for determining the amount of feedstock converted to product glycol and/or by-products and intermediates.

[0063] For this optional testing step, the feed composition was changed to 10 wt.% glucose in water and introduced at a feed rate of 5 ml/min over a period of 14 hours to test the yield/activity of the conditioned hydrogenation catalyst. Partial conversion of glucose to sorbitol was observed at a sorbitol yield of 35.6 wt.%, which translates to a reaction rate of 1.80 x 10^{-4} mol sorbitol/min/(g Raney-Ni)/glucose concentration (mol/l). The reaction rate for

hydrogenation has been reduced by 38.7%, due to treatment with the tungstate containing feed, relative to the reaction rate observed after catalyst treatment in the absence of tungstate (see Comparative Example 1).

[0064] The reactor temperature was increased to 230°C over a period of 4 hours, after which the feed composition was changed to 20 wt.% glucose, 0.043 wt.% glycolic acid and 0.527 wt.% $Na_2WO_4.2H_2O$. The pH was controlled at 3.75, as measured in the reactor effluent, by feeding additional trace amounts of glycolic acid. After reaching steady state, the conversion of glucose was virtually complete and, after 26 hours, a yield of 51.6wt.% MEG, 6.3 wt.% MPG, 1.5 wt.% 1,2-butanediol and 17.2 wt.% sorbitol was observed. Closely matching yields were observed in the absence of tungstate during catalyst treatment after 241 hours (Comparative Example 1). Glycol yields were significantly higher from the beginning of the reaction onwards, in comparison with glycol yields observed in the absence of tungstate during catalyst conditioning.

[0065] Glycol yield increases and sorbitol yield decreases over time. After 91 hours run time, a yield of 59.1 wt.% MEG, 6.1 wt.% MPG, 1.7 wt.% 1,2-butanediol and 13.0 wt.% sorbitol was observed. Closely matching yields were observed in the absence of tungstate during catalyst treatment only after 450 hours (Comparative Example 1).

[0066] Hence, it has been found that condition the hydrogenation catalyst in the presence of tungstate surprisingly results in comparable glycol yields but 341 hours earlier in the process.

[0067] Although particular embodiments of the invention have been disclosed herein in detail, this has been done by way of example and for the purposes of illustration only. The aforementioned embodiments are not intended to be limiting with respect to the scope of the appended claims, which follow. It is contemplated by the inventors that various substitutions, alterations, and modifications may be made to the invention without departing from the spirit and scope of the invention as defined by the claims.

CLAIMS

1. A process for the production of glycol from a saccharide-containing feedstock in the presence a catalyst system having a retro-aldol catalyst and a hydrogenation catalyst, the process comprising the steps of:

loading the hydrogenation catalyst in a reactor;

feeding hydrogen to the reactor;

conditioning the hydrogenation catalyst with a treatment solution comprising a conditioning retro-aldol catalyst in the absence of the saccharide-containing feedstock;

introducing the saccharide-containing feedstock and a catalytic retro-aldol catalyst to the reactor containing the conditioned hydrogenation catalyst; and

producing glycol by hydrogenolysis of the saccharide-containing feedstock.

2. The process according to claim 1, wherein the hydrogenation catalyst comprises a metal selected from the group consisting of iron, cobalt, nickel, ruthenium, rhodium, palladium, iridium, platinum, and combinations thereof.

3. The process according to claim 2, wherein the hydrogenation catalyst comprises nickel in the form of Raney-nickel.

4. The process according to claim 1, wherein the conditioning retro-aldol catalyst and the catalytic retro-aldol catalyst independently comprise a metal selected from the group consisting of tungsten, molybdenum, lanthanum, tin, vanadium, niobium, chromium, titanium, zirconium, and combinations thereof.

5. The process according to claim 1, wherein the conditioning retro-aldol catalyst is the same as the catalytic retro-aldol catalyst.

6. The process according to claim 1, wherein the conditioning retro-aldol catalyst is different than the catalytic retro-aldol catalyst.

7. The process according to claim 1, wherein the treatment solution further comprises a glycol selected from the group consisting of ethylene glycol, propylene glycol, 1,2-butanediol, glycerol, erythritol, threitol, sorbitol, 1,2-hexanediol, and combinations thereof.

8. The process according to claim 7, wherein the treatment solution comprises sorbitol.

9. The process according to claim 1, wherein the saccharide-containing feedstock comprises a saccharide selected from the group consisting of glucose, sucrose, starch, and combinations thereof.

10. The process according to claim 9, wherein the saccharide-containing feedstock comprises an aqueous solution of glucose.

11. The process according to claim 1, further comprising the step of testing hydrogenation activity by feeding a first portion of the saccharide-containing feedstock to the reactor containing the conditioned hydrogenation catalyst and determining the amount of feedstock converted.

12. The process according to claim 1, wherein the conditioning step is conducted at a temperature in a range of from 150°C to 280°C, preferably in a range of from 160°C to 270°C, more preferably in a range of from 180°C to 250°C.

13. The process according to claim 1, wherein the producing step is conducted at a reaction temperature in a range of from 180°C to 250°C, preferably in a range of from 210°C to 250°C.

14. The process according to claim 11, wherein the testing step is conducted at a temperature in a range of from 50°C to 120°C.

15. The process according to claim 1, further comprising the steps of:

removing spent conditioned hydrogenation catalyst;

mixing the spent catalyst with powdered aluminum metal;

melting the mixture to form a Ni-W-Al alloy catalyst; and

using the Ni-W-Al alloy catalyst for producing glycol from a further saccharide-containing feedstock.

16. The process according to claim 1, further comprising the steps of:

removing spent conditioned hydrogenation catalyst;

treating the spent conditioned hydrogenation catalyst with a solution comprising an ammonium salt to form a fresh hydrogenation catalyst and a solution comprising oxidized soluble tungstate;

recycling the fresh hydrogenation catalyst to the loading step; and

recycling the solution comprising oxidized soluble tungstate to the conditioning step and/or the introducing step.

17. The process according to claim 1, further comprising the steps of:

removing an effluent from the reactor after the producing step;

separating the product glycol from a heavy-end stream comprising the conditioned hydrogenation catalyst and retro-aldol catalyst;

passing the heavy-end stream to a treatment reactor for a converting step selected from group consisting of converting organic acids to alcohols, converting polyols to glycols, and combinations thereof;

separating a stream comprising the conditioned hydrogenation catalyst from the effluent of the treatment reactor; and

recycling the conditioned hydrogenation catalyst to the reactor.

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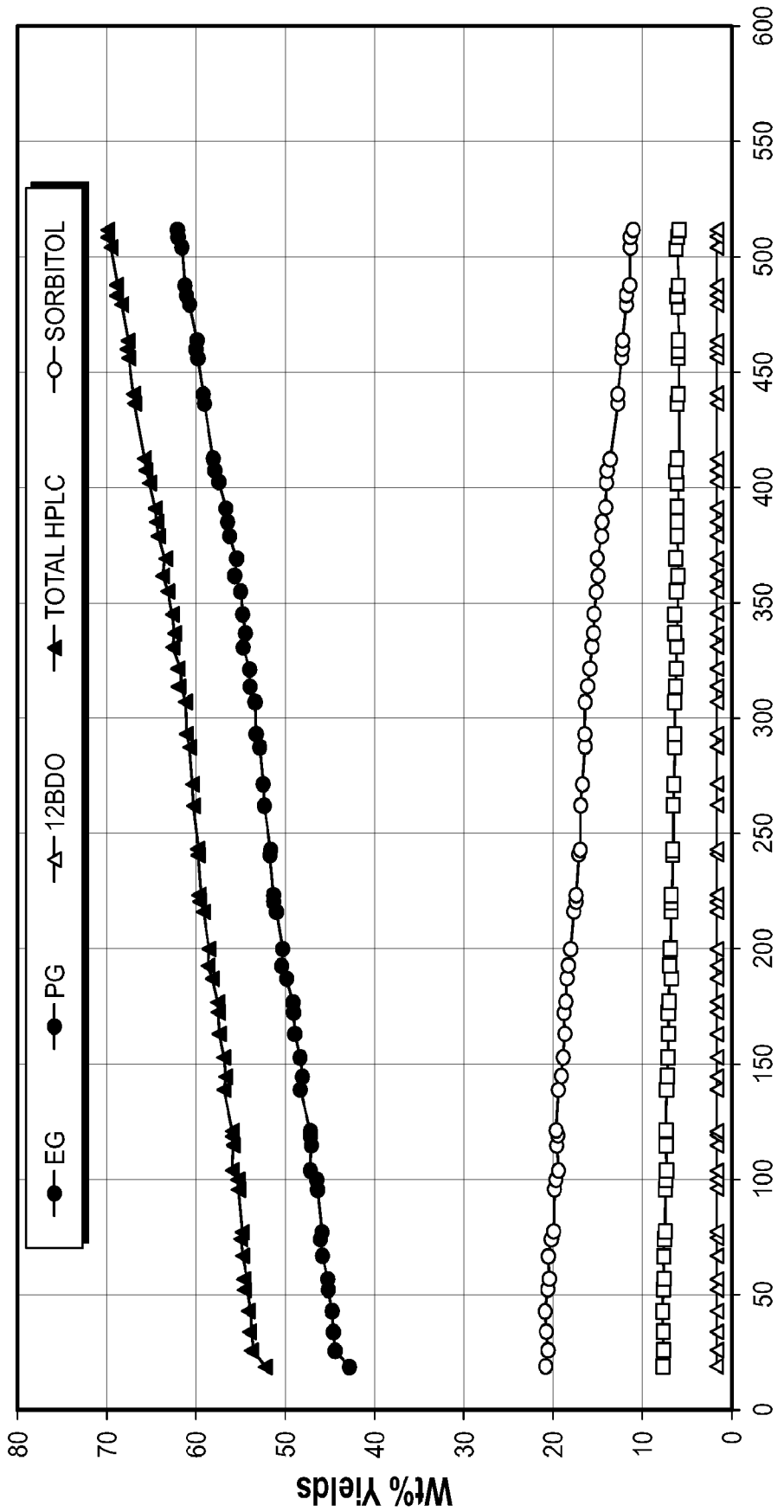

EG
PG
12BDO
TOTAL HPLC
SORBITOL
Wt% Yields
Run Time [Hour]
0
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20
30
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80
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50
100
150
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550
600

FIG. 1

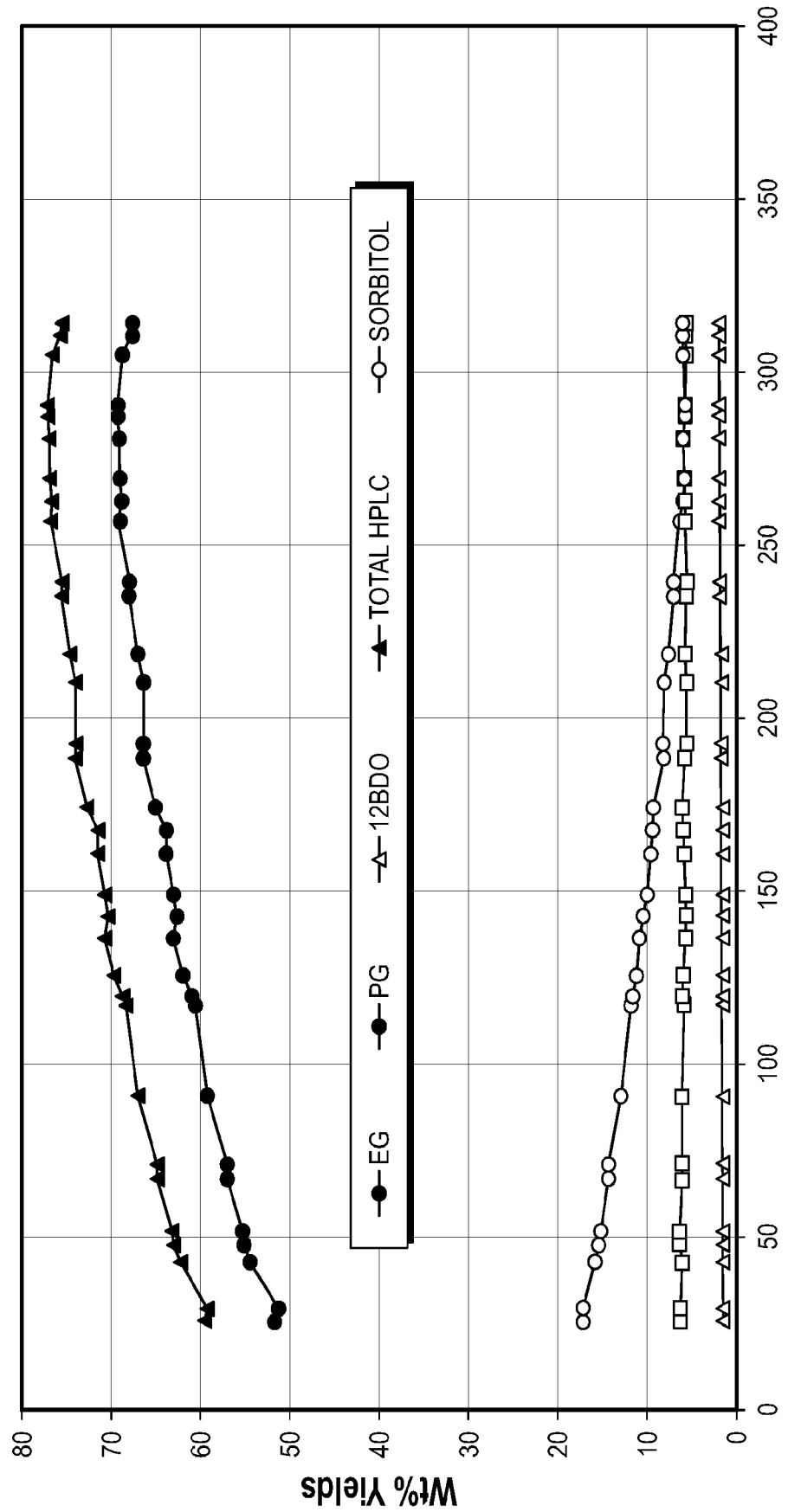

Wt% Yields
0
10
20
30
40
50
60
70
80
Run Time [Hour]
0
50
100
150
200
250
300
350
400
EG
PG
12BDO
TOTAL HPLC
SORBITOL

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2023/061899

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C29/132 C07C29/60 C07C31/20 B01J23/888 B01J25/02
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 B01J

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	claims; examples; tables paragraphs [0079], [0080]	7,8,16
X	US 2018/273452 A1 (VAN DER BIJL JOHANNES LEO MARIE [NL] ET AL) 27 September 2018 (2018-09-27) cited in the application	1-14,17
Y	claims; examples	16

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[x] Further documents are listed in the continuation of Box C.

[x] See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 June 2023	07/07/2023

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Kardinal, Siegmar

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2023/061899

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	WO 2020/055831 A1 (SHELL OIL CO [US]; SHELL INT RESEARCH [NL]) 19 March 2020 (2020-03-19) cited in the application claims; examples paragraphs [0021], [0029] -----	7,8

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