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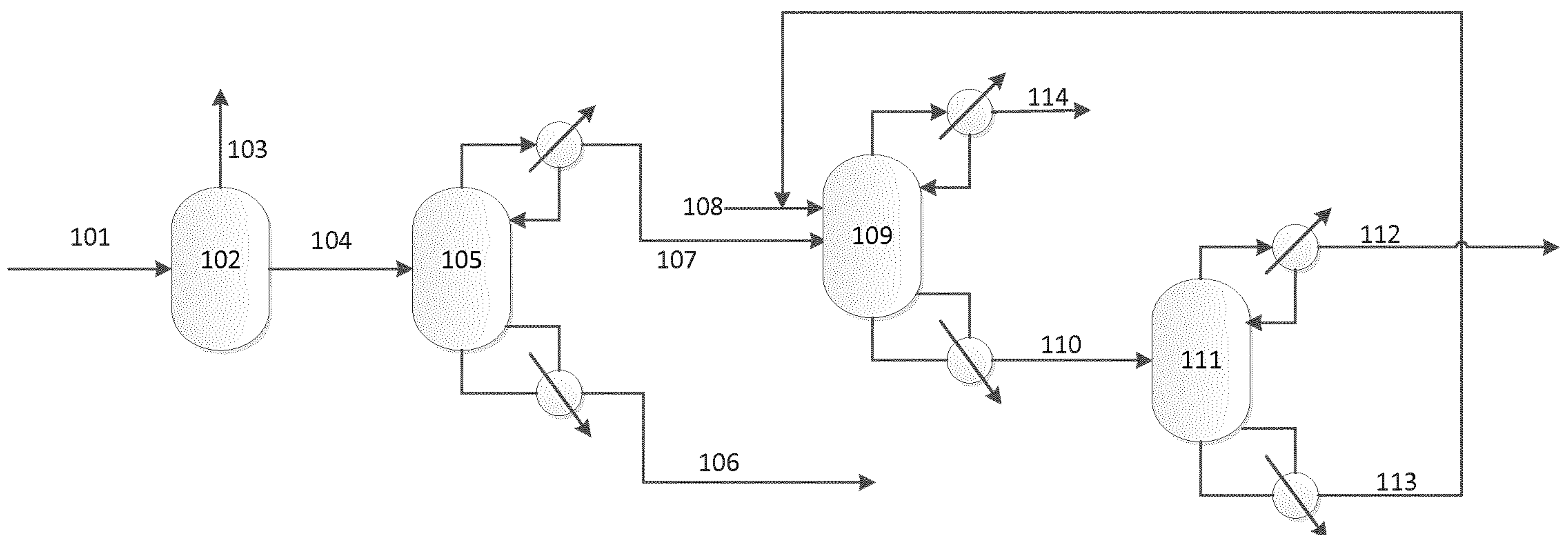
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(54) Titre : PROCÉDE DE SEPARATION DE GLYCOLS
(54) Title: PROCESS FOR THE SEPARATION OF GLYCOLS

Figure 1



(57) **Abrégé/Abstract:**

The invention provides a process for the production of a high purity first diol, selected from the group consisting of C2 to C7 diols from a product stream comprising two or more C2 to C7 diols, said process comprising the steps of: (i) subjecting the product stream to distillation in a first distillation column to provide a bottoms stream comprising high boiling by-products and a top stream comprising a mixture comprising the two or more C2 to C7 diols; (ii) providing said mixture comprising the two or more C2 to C7 diols as a feed to a second distillation column; (iii) providing a feed comprising an extractant to the second distillation column above the mixture comprising the two or more C2 to C7 diols; (iv) operating the second distillation column at a temperature in the range of from 50 to 250°C and a pressure in the range of from 0.1 to 400 kPa; (v) removing a stream comprising the first diol and the extractant as a bottoms stream from the second distillation column; and (vi) subjecting the stream comprising the first diol and the extractant to distillation in a third distillation column to provide a top stream comprising the first diol in high purity, wherein the extractant is selected from the group of C3 to C6 sugar alcohols and mixtures thereof.

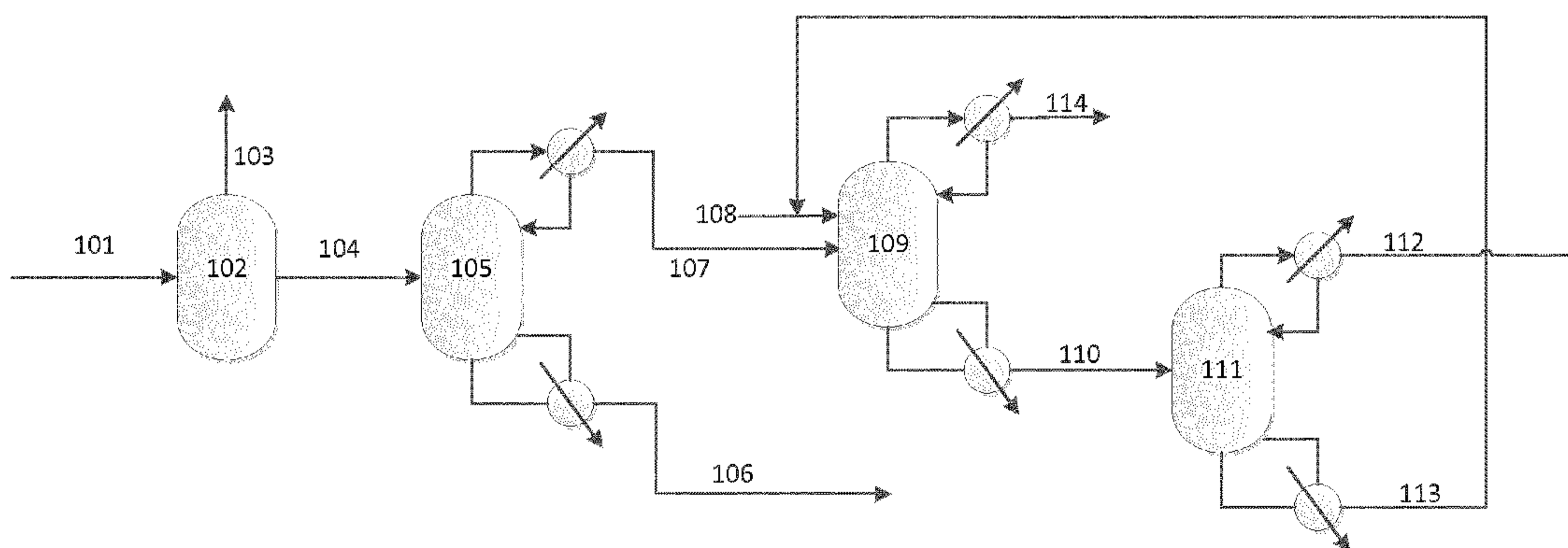
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(54) **Title:** PROCESS FOR THE SEPARATION OF GLYCOLS

Figure 1



(57) **Abstract:** The invention provides a process for the production of a high purity first diol, selected from the group consisting of C2 to C7 diols from a product stream comprising two or more C2 to C7 diols, said process comprising the steps of: (i) subjecting the product stream to distillation in a first distillation column to provide a bottoms stream comprising high boiling by-products and a top stream comprising a mixture comprising the two or more C2 to C7 diols; (ii) providing said mixture comprising the two or more C2 to C7 diols as a feed to a second distillation column; (iii) providing a feed comprising an extractant to the second distillation column above the mixture comprising the two or more C2 to C7 diols; (iv) operating the second distillation column at a temperature in the range of from 50 to 250°C and a pressure in the range of from 0.1 to 400 kPa; (v) removing a stream comprising the first diol and the extractant as a bottoms stream from the second distillation column; and (vi) subjecting the stream comprising the first diol and the extractant to distillation in a third distillation column to provide a top stream comprising the first diol in high purity, wherein the extractant is selected from the group of C3 to C6 sugar alcohols and mixtures thereof.

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- 1 -

PROCESS FOR THE SEPARATION OF GLYCOLS

Field of the Invention

The present invention relates to a process for the selective separation of glycols.

Background of the Invention

Glycols and in particular ethylene glycol and propylene glycol are valuable materials with a multitude of commercial applications, e.g. as heat transfer media, antifreeze, and precursors to polymers, such as PET. Most glycols are prepared by industrial routes from petrochemicals derived from crude oil. For example, ethylene and propylene glycols are typically made on an industrial scale by hydrolysis of the corresponding alkylene oxides, which are the oxidation products of ethylene and propylene, produced from fossil fuels.

In recent years, increased efforts have focused on producing chemicals, including glycols, from renewable feedstocks, such as sugar-based materials. For example, US20110312050 describes a continuous process for the catalytic generation of polyols from cellulose, in which the cellulose is contacted with hydrogen, water and a catalyst to generate an effluent stream comprising at least one polyol.

CN102643165 is directed to a catalytic process for reacting saccharides in an aqueous solution with hydrogen in the presence of a catalyst in order to generate polyols.

As with many chemical processes, the reaction product stream in these reactions comprises a number of desired materials, diluents, by-products and other undesirable materials. In order to provide a high value

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process, the desirable product or products must be obtainable from the reaction product stream in high purity with a high percentage recovery of each product and with as low as possible use of energy and complex equipment.

In known processes to make glycols, the glycols are usually present at high dilution in a solvent, typically water. The water is usually removed from the glycols by distillation. Subsequent purification of the glycols is then carried out by fractional distillation. This process can have high costs both in terms of capital and operational expenditure. Further, repeated heating or maintenance at raised temperatures in the fractional distillation steps may also lead to decomposition of the desired glycol products.

When glycols are produced by hydrogenolysis of saccharides, a mixture of diols, including glycols and other by-products is produced. The main glycol constituents in the reaction product stream are monoethylene glycol (MEG), monopropylene glycol (MPG) and 1,2-butanediol (1,2-BDO). Other diols, such as 2,3-butanediol (2,3-BDO), pentanediols, hexanediols and heptanediols may also be present. The separation of these diols by fractional distillation is complicated due to the similarity in boiling points. For example, MEG and 1,2-BDO have normal boiling points of 198 and 196.8°C, respectively. Further, the isolation of a pure MEG overheads stream by fractional distillation from a mixture comprising MEG and 1,2-BDO is made impossible by the formation of a homogeneous minimum boiling azeotrope between MEG and 1,2-BDO at atmospheric pressure. A similar close-boiling, azeotrope-forming glycol pair is MPG and 2,3-pentanediol. Other close boiling and/or

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azeotropic mixtures may also be formed between other diols present, further complicating the purification process.

5 Degradation of the products at high temperatures makes the use of higher than atmospheric pressure for distillation undesirable.

Methods to separate diols and, in particular, 1,2-BDO and MEG have been described in the art.

10 US4966658 is directed to the separation of a mixture of 1,2-BDO and MEG using a process known as azeotropic distillation in which an azeotrope-forming agent is added to the mixture before distillation in order to facilitate separation. Suitable azeotrope-forming agents are stated to include 3-heptanone, o-xylene, cumene and heptane. A
15 similar process is described in US5423955 for the separation of 1,2-BDO and MPG, in this case using (among others) toluene, o-xylene, cumene and heptane as azeotrope-forming agents. Azeotropic distillation can lead to an increase in relative volatility between the
20 components but also leads to further process steps in order to remove the azeotrope forming agents.

CN102372600 describes an extractive distillation process for the separation of glycols. In this process, a mixture of MEG, MPG and 1,2-BDO are fed to a
25 distillation column and contacted therein with an extractant. The top product, comprising the light extractant and 1,2-BDO, is then separated in a further distillation column. The bottom product, comprising MEG, MPG and extractant is subjected to further distillation
30 to provide MEG as the bottoms product. Suitable extractants are stated to include C6-C9 aromatics, alkanes, alkenes, C6-C11 ketones or ethers with toluene, o-xylene, cumener, n-heptane, n-octane, 3-heptanone and

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diethylene glycol dimethyl ether mentioned as preferred extractant. This teaching appears to be somewhat inconsistent with the above cited cases, which name the materials as azeotrope-forming agents.

5 WO2015150520 discloses a process for separating monoethylene glycol from a mixture comprising monoethylene glycol and 1,2-butanediol, using a two column, pressure-swing distillation set-up.

10 It would be advantageous to provide a simple and efficient method suitable for the recovery of desired diol products, such as MEG or MPG, from a mixture of diols from a product stream derived from a saccharide hydrolysis process or other bio-based processes.

Summary of the Invention

15 Accordingly, the present invention provides a process for the production of a high purity first diol, selected from the group consisting of C2 to C7 diols from a product stream comprising two or more C2 to C7 diols, said process comprising the steps of:

20 (i) subjecting the product stream to distillation in a first distillation column to provide a bottoms stream comprising high boiling by-products and a top stream comprising a mixture comprising the two or more C2 to C7 diols;

25 (ii) providing said mixture comprising the two or more C2 to C7 diols as a feed to a second distillation column;

(iii) providing a feed comprising an extractant to the second distillation column above the mixture comprising the two or more C2 to C7 diols;

30 (iv) operating the second distillation column at a temperature in the range of from 50 to 250°C and a pressure in the range of from 0.1 to 400 kPa;

(v) removing a stream comprising the first diol and the

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extractant as a bottoms stream from the second distillation column; and

(vi) subjecting the stream comprising the first diol and the extractant to distillation in a third distillation to provide a top stream comprising the first diol in high purity,

wherein the extractant is selected from the group of C3 to C6 sugar alcohols and mixtures thereof.

Brief Description of the Drawing

Figures 1 and 2 are schematic diagrams of exemplary, but non-limiting, embodiments of the process for the separation of glycols as described herein.

Detailed Description of the Invention

The present inventors have determined a new method for the production of a high purity diol from a product stream. Preferably, said product stream is derived from a saccharide hydrogenolysis process. Such a product stream from a process for the hydrogenolysis of a saccharide-containing feedstock comprises certain desirable diols as well as by-products comprising diols and other materials.

The product stream comprises two or more C2 to C7 diols. Preferably, said two or more C2 to C7 diols, including said first diol, are selected from the group consisting of C2 to C7 glycols. The term glycol as used herein is given its usual meaning, i.e. a diol in which the two hydroxyl groups are present on vicinal carbon atoms. Preferably, the first diol is monoethylene glycol (MEG) and the product stream comprises MEG and 1,2-butanediol (1,2-BDO), or the first diol is monopropylene glycol (MPG) and the product stream comprises MPG and 2,3-pentanediol. Most preferably, the first diol is monoethylene glycol (MEG) and the product stream comprises MEG and 1,2-butanediol (1,2-BDO)

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In this particularly preferred embodiment, the process for the production of a high purity first diol is a process for the production of high purity MEG from a product stream comprising a mixture of MEG and 1,2-BDO, said process comprising the steps of:

5

(i) subjecting the product stream to distillation in a first distillation column to provide a bottoms stream comprising high boiling by-products and a top stream comprising a mixture of MEG and 1,2-BDO;

10

(ii) providing said mixture comprising MEG and 1,2-BDO as a feed to a second distillation column;

(iii) providing a feed comprising an extractant to the second distillation column above the mixture comprising MEG and 1,2-BDO;

15

(iv) operating the second distillation column at a temperature in the range of from 50 to 250°C and a pressure in the range of from 0.1 to 400 kPa;

(v) removing a stream comprising MEG and the extractant as a bottoms stream from the second distillation column;

20

and

(vi) subjecting the stream comprising MEG and the extractant to distillation in a third distillation column to provide a top stream comprising MEG in high purity, wherein the extractant is selected from the group of C3 to C6 sugar alcohols and mixtures thereof.

25

In a preferred embodiment the product stream is, or is derived from, a reaction product stream from a process for the hydrogenolysis of a saccharide-containing feedstock, which as well as diols will also contain a solvent. In this embodiment, it is preferred that prior to subjecting the product stream to distillation in the first distillation column, the product stream is subjected to solvent removal, e.g. by distillation, in

30

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order to provide a solvent-lean product stream.

Typically, the reaction product stream from a process for the hydrogenolysis of a saccharide-containing feedstock comprises, as diols, at least MEG, MPG and 1,2-BDO. Other diols, such as 2,3-BDO, pentanediols, hexanediols and heptanediols may also be present. These diols are typically present at a concentration in the range of from 0.1 to 30 wt% of the overall reaction product stream.

In such a reaction product stream, MEG is suitably present as at least 10wt%, preferably as at least 30wt% of the non-solvent fraction of the stream. MEG is suitably present as at most 95wt%, preferably as at most 90wt%, most preferably as at most 80wt% of the non-solvent fraction of the stream.

In such a reaction product stream, MPG is suitably present as at least 2wt%, preferably as at least 4wt% of the non-solvent fraction of the stream. MPG is suitably present as at most 45wt%, preferably as at most 20wt% of the non-solvent fraction of the stream.

In such a reaction product stream, 1,2-BDO is typically present as at least 1wt%, generally as at least 4wt% of the non-solvent fraction of the stream. 1,2-BDO is suitably present as at most 20wt%, preferably as at most 8wt% of the non-solvent fraction of the stream.

The hydrogenolysis reaction is carried out in the presence of a solvent. Therefore, the reaction product stream will also contain said solvent. The solvent may be water or a C₁ to C₆ alcohol or polyalcohol (including sugar alcohols) or mixtures thereof. Preferred C₁ to C₆ alcohols include methanol, ethanol, 1-propanol and isopropanol. Polyalcohols of use include glycols, particularly products of the hydrogenation/

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hydrogenolysis reaction, glycerol, erythritol, threitol, sorbitol and mixtures thereof. Preferably, the solvent comprises water.

As well as the C2 to C7 diols and the solvent, the
5 reaction product streams from hydrogenolysis reactions of
saccharides may comprise oxygenates, hydrocarbons,
catalyst, degradation products, and gases in any
composition. The variety of compounds and their
concentration depend on the saccharide-containing
10 feedstock and the various hydrogenation and
hydrogenolysis conversion conditions, including
catalysts, reaction conditions such as temperature,
pressure and saccharide concentration. However, suitably
the hydrogenolysis reactions have gone to completion and
15 the aqueous stream contains less than 5wt%, preferably
less than 2wt%, more preferably less than 1wt%, even more
preferably less than 0.5wt%, most preferably
substantially no saccharides when considered as a weight
percentage of the overall stream. If the solvent used
20 comprises water or a C₁ to C₆ alcohol typically, the
reaction product stream also contains less than 5wt%,
preferably less than 2wt%, more preferably less than
1wt%, even more preferably less than 0.5wt%, most
preferably substantially no glycerol, when considered as
25 a weight percentage of the overall stream.

In the process of the present invention, solvent,
for example water, may be removed from the product
stream, e.g. by distillation, prior to subjecting the
product stream to distillation in the first distillation
30 column. In this embodiment, the solvent removal may be
carried out in a single distillation column. Preferably,
it is carried out over a number of distillation steps,
for example by multi-effect evaporation or a combination

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of multi-effect evaporation and solvent removal (e.g. dehydration) by distillation.

In this embodiment, the solvent present in the reactor is removed to provide a solvent-lean product stream. The term 'solvent-lean' used herein refers to the fact that the product stream is essentially solvent free. In practice, a small amount of solvent may be present in the solvent-lean product stream within the scope of the invention. If the solvent comprises water or a C₁ to C₆ alcohol, then preferably no more than 1000ppmw, more preferably no more than 400ppmw, even more preferably no more than 200ppmw, most preferably no more than 100ppmw of solvent is present in the solvent-free product stream. If a polyalcohol, such as a sugar alcohol is used as the solvent, a higher amount of the solvent may be tolerated in the 'solvent-lean' product stream.

Other steps, such as removal of light ends or filtration off of a heterogeneous catalyst, may also be applied to the product stream upstream or downstream of the step of removing the solvent. The use of such steps will depend on the conditions and/or reaction mixture in the saccharide hydrogenolysis process.

The product stream, preferably the solvent-lean product stream, is then subjected to distillation in a first distillation column to provide a bottoms stream comprising high boiling by-products, referred to herein as 'heavies', and a top stream comprising a mixture comprising the two or more C₂ to C₇ diols.

In one embodiment, preferably, said top stream comprises at least a mixture comprising MEG and 1,2-BDO. Other materials, such as MPG and other light glycols may be present in the mixture comprising MEG and 1,2-BDO. In

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this embodiment, the mixture comprising MEG and 1,2-BDO preferably has a weight ratio of MEG:1,2-BDO of at least 5:1. More preferably the weight ratio of MEG:1,2-BDO is at least 25:1. Most preferably the weight ratio of
5 MEG:1,2-BDO is at least 150:1.

In another embodiment, preferably, said top stream comprises at least a mixture comprising MPG and 2,3-pentanediol. Other materials, such as light glycols may be present in the mixture comprising MPG and 2,3-
10 pentanediol. In this embodiment, the mixture comprising MPG and 2,3-pentanediol preferably has a weight ratio of MPG:2,3-pentanediol of at least 5:1. More preferably the weight ratio of MPG:2,3-pentanediol is at least 25:1. Most preferably the weight ratio of MPG:2,3-pentanediol
15 is at least 150:1.

The mixture comprising the two or more C2 to C7 diols is provided as a feed to a second distillation column. The second distillation column may be any suitable sort of column known in the art and may be
20 equipped with trays or structured or unstructured packing. The number of theoretical stages may vary in the range of from 3 to 140 and may easily be determined by the skilled person on the basis of simple economic optimization experiments.

A feed comprising an extractant is provided to the
25 second distillation column above the point at which the feed of the mixture comprising the two or more C2 to C7 diols is provided. Preferably, the feed comprising an extractant is provided at the top of or a few stages
30 below the top of the second distillation column.

The extractant is selected from the group of C3 to C6 sugar alcohols and mixtures thereof. Sugar alcohols have the general formula $\text{HOCH}_2(\text{CHOH})_n\text{CH}_2\text{OH}$. Suitable

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sugar alcohols include glycerol, erythritol, threitol, arabitol, xylitol, ribitol, mannitol, sorbitol, galacticol and iditol. Although some of these sugar alcohols may be solid at room temperature, pressures and compositions for suitable extractant mixtures, they can be used as liquids at suitable temperatures and pressures in the process of the invention. In a preferred embodiment of the present invention, the extractant comprises glycerol.

As well as the extractant, this stream may also comprise certain heavies, such as other poly-alcohols, especially other sugar alcohols, from a recycle stream in the process. One example of a suitable recycle stream is the bottoms stream comprising high boiling by-products provided in step (ii) of the instant process. Such high boiling by-products will include C3-C6 sugar alcohols. Preferably, at least a portion of said bottoms stream may be used as at least a portion of the extractant, more preferably after distillation to remove the heaviest portion of said bottoms stream.

Preferably, the extractant is added in an amount such that the weight ratio of the feed comprising extractant to the mixture comprising the two or more C2 to C7 diols is at least 0.05:1, more preferably at least 0.1:1, even more preferably at least 0.25:1, based on the overall weight of the feed/mixture. Preferably, the weight ratio of the feed comprising the extractant to the first mixture comprising the two or more C2 - C7 diols is at most 10:1, more preferably at most 5:1, even more preferably 2:1, more preferably at most 1.5:1, based on the overall weight of the feed/mixture.

The distillation in the second distillation column is carried out at a temperature in the range of from 50

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to 250°C, preferably of from 100 to 200°C and at a pressure of at least 0.1 kPa. Generally, a pressure of at least 1kPa is preferred for economic reasons, with a pressure of at least 5kPa more preferred for the same reasons. The pressure is at most 400kPa, preferably at most 200kPa, more preferably at most 120kPa. It will be clear to the skilled person to vary the temperature and pressure in relation to each other in order to achieve suitable conditions.

A secondary stream comprising one or more C2 to C7 diols is removed from the second distillation column above the point at which the feed comprising an extractant is provided to the second distillation column. In the separation of MEG and 1,2-BDO, this stream would comprise 1,2-BDO; and in the separation of MPG and 2,3-pentanediol, this stream would comprise 2,3-pentanediol. Preferably, the secondary stream is removed from the second distillation column as a condensed overheads stream.

This stream may contain other diols, such as MPG, 2,3-BDO, pentanediols, hexanediols and heptanediols. Preferably, this stream is subjected to one or more fractional distillation steps in order to produce desired products as pure product streams.

A stream comprising the first diol, preferably MEG or MPG, and the extractant is removed from the second distillation column as a bottoms stream.

In the preferred embodiment in which the first diol is MEG, suitably, the diols content of this bottoms stream, comprises at least 95wt% MEG, preferably at least 98wt% MEG, more preferably at least 99wt% MEG, even more preferably at least 99.5wt% MEG, , most preferably at least 99.9wt% MEG.

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This stream is then subjected to a further distillation step in a third distillation column in which the first diol, preferably MEG, is distilled off to provide a high purity first diol stream. This
5 distillation is carried out at the same or lower pressure than in the extractive distillation step (in the second distillation column) in order to restrict the temperature in the reboiler and avoid or minimize potential product degradation.

10 High purity diol as used herein refers to a diol of at least 99wt% purity, preferably at least 99.5wt%, more preferably at least 99.6wt% purity, most preferably at least 99.9wt% purity.

15 Preferably, in the embodiment wherein the first diol is MEG, the high purity MEG is suitable for use as fibre grade MEG.

The bottoms stream from this distillation comprises a used extractant stream.

20 At least a portion of the used extractant stream may then be recycled to the second distillation column as at least a portion of the feed comprising an extractant. Any heavies left that had been present in the first mixture comprising MEG and 1,2-BDO may also be present in the extractant stream to be recycled. If the mixture
25 comprising two or more C2 to C7 diols and a solvent is derived from the reaction product stream from a process for the hydrogenolysis of a saccharide-containing feedstock, such heavies are likely to be sugar alcohol like in their structure, boiling point and other physical
30 properties and may be recycled with the rest of the extractant stream.

A portion of this used extractant stream may be removed as a bleed in order to prevent a build-up of

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5 heavies. In this embodiment, fresh extractant will need to be provided to the second distillation column to make up the required amount of extractant. This fresh extractant should be provided to the second distillation column at the same height or above the used extractant stream.

10 Optionally, at least a portion of this recycle stream may be subjected to further processing steps to further increase its purity. Optionally, the first diol, preferably MEG, stream may be subjected to further processing steps to further increase its purity or remove trace compounds that could affect the quality of the final product.

15 The present invention has a number of advantages over prior art processes, wherein problems are encountered with close-boiling and azeotrope-forming by-products. After reaction-solvent removal, the separation of diols is based on a two-step process. Firstly, heavy (high-boiling) by-products are removed by distillation in a first distillation column. Then, in a second distillation column, one or more sugar alcohols is used as extractant for the selective extractive distillation of the first diol. The strong interaction between the sugar alcohols and the first diol breaks any azeotrope and affects the volatility of the diols present, allowing them to be separated. A simple distillation of the first diol as overhead product from the extractant in a third distillation column results in a high purity first diol stream, for example high purity MEG suitable for use as fibre grade MEG either immediately or after removal of trace compounds.

30 Optionally, a finishing section may be added to the top of this third distillation column in order to remove

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any type of light impurities/ light degradation products formed at the separation process. This section would be above the point at which the high purity first diol stream is removed.

5 The combination of a heavies removal (first distillation) column followed by extractive distillation (in the second distillation column) has been termed 'orthogonal separation'. This robust process allows diols to be separated from the by-products of a
10 saccharide hydrogenolysis reaction in high purity and with high recovery of said diols. Suitably at least 90wt%, preferably at least 95wt%, more preferably at least 98wt% and most preferably at least 99.9wt% of the first diol formed in the hydrogenolysis reaction is
15 recovered.

Detailed Description of the Drawings

 The invention will now be further illustrated with reference to the non-limiting embodiments shown in the drawings. In the drawings, the first numeral of each
20 reference number refers to the Figure number, e.g. 1XX for Figure 1 and 2XX for Figure 2. The remaining figures relate to the individual features within the Figures. The same number is used to refer to the same feature in each Figure. Therefore, 107 refers to the same feature
25 in Figure 1 as 207 refers to in Figure 2.

 In this description, the separation of high purity MEG from a mixture comprising MEG and 1,2-BDO from a saccharide hydrogenolysis process is described. The same system could be used to separate other mixtures such as
30 MPG and 2,3-pentanediol.

 In Figure 1, a product stream 101 from a saccharide hydrogenolysis process, is subjected to one or more distillation processes 102 to remove solvent 103,

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suitably water. Suitable steps to remove light compounds may also have been applied to this stream. The solvent-free stream 104 is then supplied to a first distillation column 105 where it undergoes distillation to remove high boiling products 106. The resulting stream 107 comprising a mixture comprising MEG and 1,2-BDO is then supplied as a feed to a second distillation column 109. A feed comprising an extractant 108 is provided to the second distillation column 109 above the mixture comprising MEG and 1,2-BDO. A stream comprising MEG and the extractant 110 is removed from the bottom of the second distillation column 109 and supplied to a third distillation column 111, wherein a top stream comprising high purity MEG 112 is obtained. The bottoms stream 113 from this distillation can be recycled to form at least a portion of the feed comprising an extractant 108. An overheads stream 114 from the third distillation column 109 will comprise 1,2-BDO and typically, other diols.

Fresh extractant may be added to the feed comprising an extractant 108, as required.

The 'orthogonal separation' concept of this application is illustrated by the combination of the three columns 105, 109 and 111.

A further illustration of the invention is shown in Figure 2. In this embodiment, the overheads stream 214 is further purified in a first fractional distillation column 217, to provide an overheads stream 218 of 2,3-BDO. The bottoms stream 219 from the first fractional distillation column 217 may then be provided to a second fractional distillation column 220 to provide a high purity MPG stream 221 and a stream comprising residual glycols, such as 1,2-BDO, 1,2-pentanediol, etc.

An extractant bleed stream 216 is also illustrated

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in Figure 2. The remainder of the bottoms stream 213 is recycled to provide at least a portion 215 of the feed comprising an extractant 208. Potential heat integrations may be used to increase the energy efficiency of the system, for example recovering the heat from the extractant recycle 215 to use it on a side reboiler for the extractive distillation column 209.

Examples

The invention will be further illustrated by the following, non-limiting examples.

Example 1

Experimental basic data measurements were taken for the vapour-liquid-equilibrium for the ternary system comprising MEG, 1,2-BDO and Glycerol. Data points were measured at low/vacuum pressures and different compositions.

Aspen Plus software was used to model the process as shown in Figure 1. A thermodynamic package was used. Said package resulted from fitting of the experimental basic data (VLE) measured for the mixtures considered.

Examples were then generated from Aspen Plus using glycerol as the extractant (entrainer) and feed mixtures with different MEG/1,2-BDO weight ratios and glycerol/MEG mixture weight ratios.

In each example, the MEG mixture is fed to the second (extractive) distillation column 109 at about the middle of its height. The glycerol feed 108 location is at the upper part of the column (first stages). The results for the second (extractive) distillation column 109 are shown in Tables 1 to 4, below.

The results for the third distillation (solvent recovery) column 111 that provides final MEG 99.9% wt. purity are shown in Table 7. This last MEG

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purification step comprises the distillation of MEG from the solvent in a rectification column with low number of stages and low reflux ratio, thanks to the high relative volatility of MEG compared to the extractive solvents

5 used.

Table 1 - MEG/1,2-BDO Ratio of 31; Glycerol/MEG Mixture Weight Ratio of 6.5; 99.5% MEG Recovery and 99.9% 12-BDO Recovery

	Feed MEG mixture	Feed Glycerol	Top	Bottom
Temperature	130°C	170°C	126°C	190°C
Pressure	1.2 Bar	1.2 Bar	0.1 Bar	0.13 bar
Component	Wt. %	Wt. %	Wt. %	Wt. %
Glycerol	0	≈ 100	≈ 0	88.2
MEG	87.4	≈ 0	3.4	11.8
MPG	9	0	69.2	≈ 0
1,2-BDO	2.8	0	21.6	≈ 0
2,3-BDO	0.45	0	3.5	≈ 0
1,2-PDO	0.11	0	0.7	0.0025
2,3-PDO	0.23	0	1.73	≈ 0
1,2-HDO	0.01	0	≈ 0	0.0015

PDO and HDO make reference to pentanediol and hexanediol glycols, respectively.

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Table 2 - MEG/1,2-BDO Ratio of 16; Glycerol/MEG Mixture
Weight Ratio of 6.5; 99.5% MEG Recovery and 99.9% 1,2-BDO
Recovery

	Feed MEG mixture	Feed Glycerol	Top	Bottom
Temperature	130°C	170°C	127°C	191°C
Pressure	1.2 Bar	1.2 Bar	0.1 Bar	0.13 bar
Component	Wt. %	Wt. %	Wt. %	Wt. %
Glycerol	0	≈ 100	≈ 0	88.5
MEG	85.0	≈ 0	2.8	11.5
MPG	8.8	0	56.9	≈ 0
1,2-BDO	5.5	0	35.5	≈ 0
2,3-BDO	4.4	0	2.8	≈ 0
1,2-PDO	0.11	0	0.6	0.0029
2,3-PDO	0.23	0	1.4	≈ 0
1,2-HDO	0.01	0	≈ 0	0.0015

Table 3 - MEG/1,2-BDO Ratio of 31; Glycerol/MEG Mixture
Weight Ratio of 5; 95% MEG Recovery and 99.9% 1,2-BDO
Recovery

	Feed MEG mixture	Feed Glycerol	Top	Bottom
Temperature	130°C	170°C	128°C	188°C
Pressure	1.2 Bar	1.2 Bar	0.1 Bar	0.13 bar
Component	Wt. %	Wt. %	Wt. %	Wt. %
Glycerol	0	≈ 100	≈ 0	85.6
MEG	87.4	≈ 0	25.6	14.25
MPG	9	0	53.1	≈ 0
1,2-BDO	2.8	0	16.6	≈ 0
2,3-BDO	0.45	0	2.7	≈ 0
1,2-PDO	0.11	0	0.6	0.0029
2,3-PDO	0.23	0	1.3	≈ 0
1,2-HDO	0.01	0	≈ 0	0.002

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Table 4 - MEG/1,2-BDO Ratio of 52; Glycerol/MEG Mixture
 Weight Ratio of 2; 95% MEG Recovery and 99.5% 12-BDO
 Recovery

	Feed MEG mixture	Feed Glycerol	Top	Bottom
Temperature	130°C	170°C	127°C	166°C
Pressure	1.2 Bar	1.2 Bar	0.1 Bar	0.13 bar
Component	Wt.%	Wt.%	Wt.%	Wt.%
Glycerol	0	≈ 100	≈ 0	61.4
MEG	88.4	≈ 0	27.8	38.6
MPG	9.1	0	57.2	≈ 0
1,2-BDO	1.7	0	10.7	≈ 0
2,3-BDO	0.45	0	2.9	≈ 0
1,2-PDO	0.06	0	0.0005	0.026
2,3-PDO	0.23	0	1.4	≈ 0
1,2-HDO	0.01	0	≈ 0	0.0052

5 These examples show the separation performance for
 mixtures of MEG, MPG, 12-BDO, 1,2-BDO, 1,2-PDO, 2,3-PDO
 and 1,2-HDO. MEG/12-BDO ratios of 16, 31 and 52 have been
 used. Simulations for Glycerol/MEG weight ratios of 6.5,
 5 and 2 have been conducted, rendering MEG (bottom
 stream) and 1,2-BDO (top stream) recoveries ranging from
 10 95% to 99.9%,.

The examples demonstrate the production of a bottoms
 stream containing extractant (glycerol), MEG and minor
 glycol impurities, which after distillation of MEG off
 the extractant would result in an MEG stream of at least
 15 99.9wt% purity.

Example 2

Aspen Plus software was used to model the process as
 shown in Figure 1. A thermodynamic package was used. Said
 package resulted from fitting of experimental basic data
 20 of the vapour pressure curves for the individual
 components and the vapour-liquid equilibrium (VLE)
 measured for mixtures of those components.

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5 Examples were then generated from Aspen Plus using glycerol as the extractant (entrainer) and feed mixtures with different MPG/other glycols weight ratios and glycerol/MPG mixture weight ratios, to exemplify the separation and purification of a glycol with 3 carbon atoms, in this case MPG. For this application, the separation of MPG from close boilers as 2,3-Pentenediol species is a challenge since those glycols form close-boiling point azeotropes when compared to the pure components.

10 In each case, the MPG mixture is fed first to a first distillation column 105 in which the heavy components are removed. The results of this distillation are exemplified in Table 5. Then, the resulting top product is fed to the extractive distillation (second distillation column). In each example, the MPG mixture is fed to the second (extractive) distillation column 109 at about the middle of its height. The glycerol feed 108 location is at the upper part of the column (first stages). The results for the second (extractive) distillation column 109 are shown in Table 6.

25 The results for the third distillation (solvent recovery) column 111 that provides final MPG high-purity product are shown in Table 7. This MPG last purification step comprises the distillation of MPG from the solvent in a rectification (third distillation) column with low number of stages and low reflux ratio, making use of the high relative volatility of the glycol (MPG) compared to the extractive solvents used.

30 The examples in the following tables use: MPG initial concentration of 71.8%wt; Glycerol/MPG mixture weight ratio of 8.6 (mass) towards second (extractive) distillation column; Overall MPG recovery of 98%. MPG

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recovery on the extractive distillation of 99% (bottom) with 98% 2,3-PDO recovery (top). Final MPG product purity of 99.96%wt is then achieved in column 111.

Table 5: Results for the first distillation column 105

	Feed MPG mixture	Top	Bottom
Temperature	130.0°C	141.1°C	160.8°C
Pressure	1.2 Bar	0.2 Bar	0.13 bar
Component	Wt.%	Wt.%	Wt.%
Glycerol	2.7	0.0	8.9
Sorbitol	2.7	0.0	8.9
Isosorbitol	2.7	0.0	8.9
MEG	3.6	0.0	12.0
MPG	71.8	97.5	12.0
1,2-BDO	13.5	0.0	44.7
2,3-BDO	0.9	1.3	0.0
1,2-PDO	0.4	0.0	1.5
2,3-PDO	0.9	1.2	0.1
1,2-HDO	0.4	0.0	1.5
1,2-HHDO	0.4	0.0	1.5

5 PDO, HDO and HHDO make reference to pentanediol, hexanediol and heptanediols glycols, respectively.

Table 6: Results for the second distillation column 109

	Feed MPG mixture	Feed Glycerol	Top	Bottom
Temperature	141°C	170°C	107.6°C	170.5°C
Pressure	1.2 Bar	1.2 Bar	0.05 Bar	0.10 bar
Component	Wt.%	Wt.%	Wt.%	Wt.%
Glycerol	0.00	≈ 100	2.2	89.9
Sorbitol	0.00	0	0.0	0.0
Isosorbitol	0.00	0	0.0	0.0
MEG	0.00	0	0.0	0.0
MPG	97.50	0	28.1	10.1
1,2-BDO	0.00	0	0.0	0.0
2,3-BDO	1.30	0	35.4	0.0
1,2-PDO	0.00	0	0.0	0.0
2,3-PDO	1.20	0	34.3	0.0
1,2-HDO	0.00	0	0.0	0.0
1,2-HHDO	0.00	0	0.0	0.0

Table 7: Results for the third distillation column 111

	Feed MPG mixture	Top	Bottom
Temperature	170°C	110°C	200°C
Pressure	1.2 Bar	0.2 Bar	0.13 bar
Component	Wt. %	Wt. %	Wt. %
Glycerol	89.90	≈ 0	100.0
Sorbitol	0.00	0.0	0.0
Isosorbitol	0.00	0.0	0.0
MEG	0.00	0.0	0.0
MPG	10.10	99.96	0.0
1,2-BDO	0.00	0.01	0.0
2,3-BDO	0.00	0.03	0.0
1,2-PDO	0.00	0.0	0.0
2,3-PDO	0.00	0.0	0.0
1,2-HDO	0.00	0.0	0.0
1,2-HHDO	0.00	0.0	0.0

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1. A process for the production of a high purity first diol, selected from the group consisting of C2 to C7 diols from a product stream comprising two or more C2 to C7 diols, said process comprising the steps of:

5 (i) subjecting the product stream to distillation in a first distillation column to provide a bottoms stream comprising high boiling by-products and a top stream comprising a mixture comprising the two or more C2 to C7 diols;

10 (ii) providing said mixture comprising the two or more C2 to C7 diols as a feed to a second distillation column;

(iii) providing a feed comprising an extractant to the second distillation column above the mixture comprising the two or more C2 to C7 diols;

15 (iv) operating the second distillation column at a temperature in the range of from 50 to 250°C and a pressure in the range of from 0.1 to 400 kPa;

(v) removing a stream comprising the first diol and the extractant as a bottoms stream from the second

20 distillation column; and

(vi) subjecting the stream comprising the first diol and the extractant to distillation in a third distillation column to provide a top stream comprising the first diol in high purity,

25 wherein the extractant is selected from the group of C3 to C6 sugar alcohols and mixtures thereof.

2. A process according to claim 1, wherein the first diol is MEG and the product stream comprises at least MEG and 1,2-BDO.

30 3. A process according to claim 2, wherein the first diol

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is MPG and the product stream comprises at least MPG and 2,3-pentanediol.

4. A process according to any one of claims 1 to 3, wherein the product stream is, or is derived from, a product stream of a saccharide hydrogenolysis process.

5. A process according to claim 4, wherein said product stream comprises at least MEG and 1,2-BDO and a solvent and prior to step (i) the solvent is removed from the product stream to provide a solvent-lean product stream.

6. A process according to any one of claims 1 to 5, wherein a bottoms stream comprising a used extractant stream is also obtained in step (vi).

7. A process according to claim 6, wherein at least a portion of the bottoms stream comprising the extractant is then recycled to the second distillation column as at least a portion of the feed comprising an extractant.

8. A process according to any one of claims 1 to 7, wherein the feed comprising the extractant is provided at the top of or a few trays below the top of the first distillation column.

9. A process according to any one of claims 6 to 9, wherein a portion of the used extractant stream is removed as a bleed stream.

10. A process according to claim 9, wherein fresh extractant is provided to the first distillation column, at the same height or above the used extractant stream, to make up the required amount of extractant.

11. A process according to any one of claims 2 to 10, wherein the first mixture comprising MEG and 1,2-BDO has a weight ratio of MEG:1,2-BDO of at least 5:1.

12. A process according to any one of claims 1 to 11, wherein the extractant is added in an amount such that the weight ratio of the feed comprising an extractant to

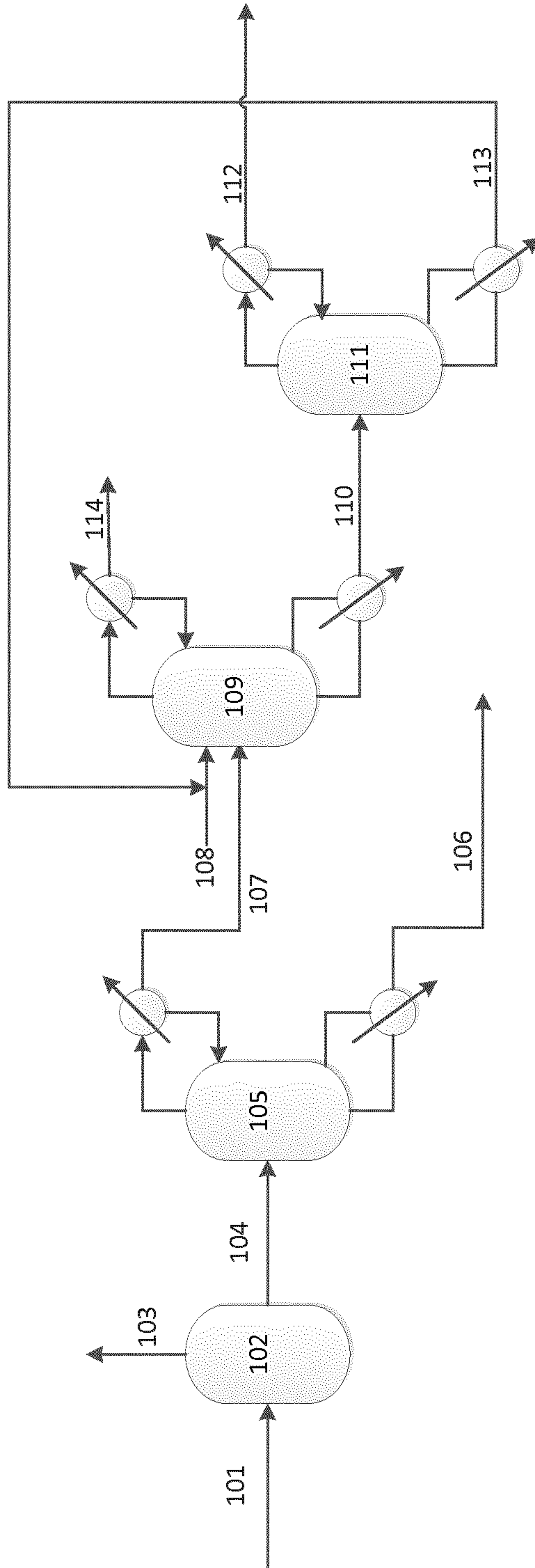
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the feed comprising the mixture comprising the two or more C2 to C7 diols is at least 0.25:1 and at most 10:1 based on the overall weight of the feed/mixture.

5 13. A process according to any one of claims 1 to 12, wherein glycols content of the stream comprising the first diol and the extractant, comprises at least 99.9wt% of the first diol.

10 14. A process according to any one of claims 1 to 13, wherein a finishing section is added to the top of the third distillation column above the point at which the high purity first diol stream is obtained, in order to remove any type of light impurities/ light degradation products formed in the separation process.

Figure 1



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Figure 2

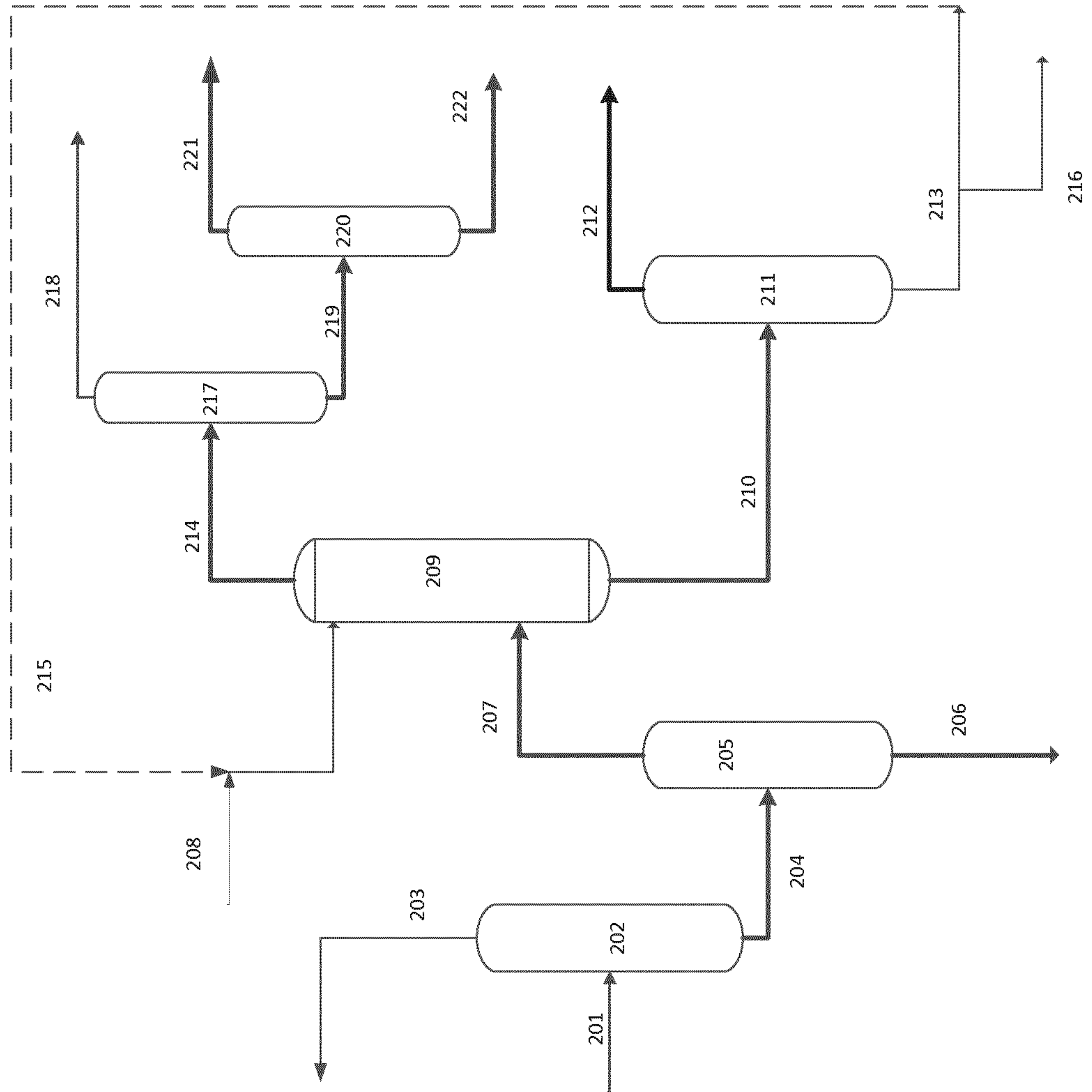


Figure 1

