Title: METHOD FOR PURIFYING 1,2-PROPANEDIOL FROM A FERMENTATION BROTH

Abstract: Methods for purification of 1,2-propanediol from a fermentation broth comprising precipitation of salts by addition of a solvent and evaporation of the alcohol on a falling film evaporator, a wiped film evaporator, a thin film evaporator or a short path evaporator.
Method for purifying 1,2-propanediol from a fermentation broth

The present invention relates to the purification of 1,2-propanediol (MPG) from a fermentation broth.

1,2-propanediol (MPG) is a widely-used chemical. It is a component of unsaturated polyester resins, liquid detergents, coolants, anti-freeze and de-icing fluids for aircrafts. Propylene glycol has been increasingly used since 1993-1994 as a replacement for ethylene derivatives, which are recognised as being more toxic than propylene derivatives.

1,2-propanediol is currently produced by chemical processes using a propylene oxide hydration process that consumes large amounts of water. Propylene oxide can be produced by either of two processes, one using epichlorhydrin, and the other hydroperoxide. Both routes use highly toxic substances. In addition, the hydroperoxide route generates by-products such as tert-butanol and 1-phenyl ethanol. For the production of propylene to be profitable, a use must be found for these by-products. The chemical route generally produces racemic 1,2-propanediol, whereas each of the two stereoisomers (R)1,2-propanediol and (S)1,2-propanediol are of interest for certain applications (e.g. chiral starting materials for specialty chemicals and pharmaceutical products).

The disadvantages of the chemical processes for the production of 1,2-propanediol make biological synthesis an attractive alternative. 1,2-propanediol may be produced by fermentation of microorganisms using sugars such as glucose or sucrose.

However, production of 1,2-propanediol by biological synthesis requires purification of the 1,2-propanediol from the fermentation broth. Further, synthesis of 1,2-propanediol by fermentation may lead to the production of by-products or impurities.

One major problem encountered during the purification of 1,2-propanediol from fermentation broths is the elimination of mineral salts. These salts are typically sodium chloride and calcium chloride but also ammonium and phosphate salts. These salts may precipitate during the purification of 1,2-propanediol fouling ion exchange resins, adsorbents and distillation columns.

Another major challenge is the elimination of heavy impurities including organic molecules such as organic acids which are less volatile or have a higher boiling point than 1,2-propanediol. These impurities tend to precipitate or to stick to the distillation columns used for purification of 1,2-propanediol.

The state of the art addresses mostly the purification of 1,3-propanediol from fermentation broths. However, 1,3-propanediol and 1,2-propanediol are not produced through the same metabolic pathway. Therefore the composition of the fermentation broth containing the product to be purified is not the same and in particular the impurity profile is different.
With respect to the removal of mineral salts, most notably it has been proposed to eliminate salts upstream from the purification steps by various techniques such as the use of ion–exchange resins (WO 2004/101479), electrodialysis (CN 101143301) and precipitation–filtration (US 6,361,983). CN 1460671 also describes purification of 1,3-propanediol from a fermentation broth comprising precipitation/separation steps with a solvent. However, these methods suffer from major drawbacks and they do not address the elimination of the heavy impurities after removal of the salts.

WO 2009/068110 describes a method for purifying an alcohol from a fermentation broth. In this method, the addition of glycerol to the concentrated fermentation broth prevents crystallization of salts at the bottom of the distillation columns. The addition of glycerol retains salts in the liquid phase until the end of the purification process. A major drawback of this process is that the amount of glycerol required to dissolve salts may be very high, leading to high purification costs.

WO 2004/101479 is related to the purification of biologically-produced 1,3-propanediol. The purification process comprises filtration, ion exchange purification and a distillation procedure comprising at least two distillation columns. Salts are removed at the start of the process using ion exchange resins. A major problem is the fouling of the ion exchange resins, which is due to the heavy impurities of the filtrated fermentation broth. Ion exchange is an efficient technique but it leads to very high operation costs due to the need for regeneration of the resin, when the technique is applied to solutions having a high salt content. Fouling of the ion exchange resin due to the heavy impurities and quick saturation due to high salts content both lead to elevated operation costs because regeneration and/or replacement of the resin are frequently required.

Xiu et al. (2008) is related to downstream processing of biologically produced 1,3-propanediol and 2,3-butandiol. However, biological production of 1,3-propandiol and 1,2-propanediol leads to different impurities requiring different purification methods.

Gao et al. (2007) is related to separation of 1,3-propanediol from glycerol-based fermentations by alcohol precipitation and dilution crystallization. This document does not describe purification of 1,2-propanediol and the purification methods do not combine alcohol precipitation and an evaporation step on a falling film evaporator, wiped film evaporator, a thin film evaporator or a short path evaporator.

US 2004/0222753 describes a process for producing 1,3-propanediol from an aqueous feed stream using a solvent extractant. Precipitation of impurities and purification of 1,2-propanediol are not described.

US 5,254,467 describes a process for the transformation of glycerol into 1,3-propanediol by microorganisms.

Thus, none of these techniques produce satisfactory results.
The present invention proposes a novel method for purifying 1,2-propanediol from a fermentation broth. The methods of the present invention provide both efficient desalination of the fermentation broth prior to further purification and efficient elimination of organic impurities and in particular of heavy impurities such as organic acids.

Advantageously, the methods of the present invention prevent degradation of 1,2-propanediol during the purification steps.

Advantageously, the methods according to the present invention make it possible to efficiently eliminate salts and impurities during the purification of 1,2-propanediol from a fermentation broth using a simple, cheap and easily scalable process.

SUMMARY OF THE INVENTION

The present invention is related to a method for purifying 1,2-propanediol from a fermentation broth comprising the following steps:

a) clarifying the fermentation broth in order to obtain an aqueous solution containing the 1,2-propanediol,

b) removing water from the aqueous solution containing the 1,2-propanediol obtained in step a),

c) adding a solvent to the solution obtained in the previous step to reach a proportion of solvent comprised between 0.1% and 99% per weight, wherein the solvent is selected from ethanol, methanol and acetone; and wherein addition of the solvent leads to precipitation of solids;

d) removing the solids which precipitated in the previous step,

e) evaporating solvent and water from the solution obtained in the previous step d),

f) evaporating the 1,2-propanediol from the solution obtained in step e) on a falling film evaporator, a wiped film evaporator, a thin film evaporator or a short path evaporator,

g) recovering the 1,2-propanediol.

Preferably, the clarification of the fermentation broth in step a) is carried out by filtration.

In preferred embodiments, filtration consists in successive microfiltration, ultrafiltration and/or nanofiltration steps.

Preferably, in step b) removing water from the aqueous solution containing the 1,2-propanediol is performed by evaporation.

Preferably, in step c) the solvent is ethanol.
Preferably, in step c) the solvent is added to reach a proportion of solvent comprised between 30% and 60% per weight.

Preferably, in step d) the solids are removed by filtration.

In the methods of the present invention it is preferred that before performing step f), steps c), d) and e) are repeated. Preferably, steps c), d) and e) are repeated two times before performing step f).

Preferably, the 1,2-propanediol is evaporated from the solution obtained in step e) in a whipped thin film evaporator with an internal condenser.

Optionally, the methods of the present invention comprise further purification of the 1,2-propanediol recovered in step g).

Further purification of the 1,2-propanediol may comprise removing by distillation products and/or azeotropes which have a boiling point lower than that of 1,2-propanediol by distillation; and removing products and/or azeotropes having a boiling point higher than that of 1,2-propanediol by distillation.

Further, purification of the 1,2-propanediol may also comprise removing water by evaporation.

Further purification of the 1,2-propanediol may comprises ion exchange and/or adsorption.

**DETAILED DESCRIPTION OF THE INVENTION**

The invention thus relates to the purification of 1,2-propanediol from a fermentation broth. 1,2-propanediol may, for example, be produced by the fermentation of various carbon sources e.g. glucose, sucrose or glycerol. The fermentation broth obtained after fermentation contains typically water, 1,2–propanediol, residual carbon source, mineral and organic salts of the carboxylate type.

A major challenge is the separation of the 1,2-propanediol produced by fermentation from the salts and impurities contained in the fermentation broth. Contrary to 1,2-propanediol produced by chemical processes, 1,2-propanediol produced by fermentation contains a high concentration of organic and mineral salts.

The term “salt” means any mineral or organic salt present in the fermentation broth, mineral salts include ions such as Na⁺, K⁺, Cl⁻, SO₄²⁻ and PO₄³⁻, Mg²⁺, Ca²⁺, NH₄⁺. Organic impurities and by-products may include citrates, glucose, sucrose, succinates, acetates, pyruvates glycerol, hydroxyacetone and methylglyoxal.

The present invention relates to a method for removing salts from a fermentation broth after fermentative production of 1,2-propanediol. The methods of the present
invention also relate to further purification of the 1,2-propanediol after removal of mineral and organic salts.

Another object of the present invention is the efficient purification of 1,2-propanediol from an aqueous solution containing mineral and/or organic salts. Purification of an alcohol from a fermentation broth by techniques such as distillation and evaporation leads to the crystallization of the mineral and organic salts which can prevent the further purification of the alcohol. Various attempts have been made to remove mineral and organic salts from the fermentation broth prior to further purification of the alcohol. In distillation methods, crystallization of salts at the bottom of the distillation column is a common problem, other methods such as ion exchange lead to quick fouling of the ion exchange resin due to the high amount of mineral salts and organic salts present in the fermentation broth.

Typically, an object of the present invention is the separation of the 1,2-propanediol from sodium chlorides, calcium chlorides, potassium chlorides, ammonium, sulfates and phosphate salts.

Another object of the present invention is the separation of 1,2-propanediol from heavy impurities present in the fermentation broth including organic molecules such as organic acids which are less volatile or have a higher boiling point than 1,2-propanediol.

A first embodiment of the present invention is a method for purifying 1,2-propanediol from a fermentation broth comprising the following steps:

a) clarifying the fermentation broth in order to obtain an aqueous solution containing the 1,2-propanediol,

b) removing water from the aqueous solution containing the 1,2-propanediol obtained in step a),

c) adding a solvent to the solution obtained in the previous step to reach a proportion of solvent comprised between 0.1% and 99 per weight, wherein the solvent is selected from ethanol, methanol and acetone; and wherein addition of the solvent leads to precipitation of solids;

d) removing the solids which precipitated in the previous step,

e) evaporating solvent and water from the solution obtained in the previous step d),

f) evaporating the 1,2-propanediol from the solution obtained in step e) on a falling film evaporator, a wiped film evaporator, a thin film evaporator or a short path evaporator,

g) recovering the 1,2-propanediol.
Fermentation may optionally be stopped by addition of a base to the fermentation broth. A base is added, for example, in the form of soda, potash or ammonia with the purpose of stopping bacterial activity. The pH achieved is between 7.5 and 14.

The first step of the 1,2-propanediol purification method consists in clarification of the fermentation broth to eliminate insoluble elements, most notably large molecules, biomass, proteins and all suspended particles. Preferably, all molecules having a size over 0.1μm are eliminated by filtration. In other embodiments, all molecules having a molecular weight over 200 Da are eliminated by clarification. Any convenient method may be used for clarification of the fermentation broth.

In preferred embodiments, clarification of the fermentation broth is carried out by filtration. “Filtration” refers to a membrane separation method. Advantageously, filtration consists successively of microfiltration, ultrafiltration and nanofiltration steps. Preferably, the clarification step consists of microfiltration and ultrafiltration. More preferably, the clarification step consists of microfiltration. Most preferably, microfiltration is a 0.1μm cutoff microfiltration. Filtration may be carried out on a filter press or a rotary filter.

In other embodiments, clarification of the fermentation broth is carried out by centrifugation.

After clarification of the fermentation broth, water is removed prior to further purification of the 1,2-propanediol. Any appropriate method may be applied to remove water from the aqueous solution, e.g; but not limited to evaporation, cristalization or reverse osmosis. Preferably, water is removed by evaporation. Evaporation may be carried out in a thermosyphon-type evaporator or in any suitable evaporator. During this first step, consisting in the concentration of the clarified fermentation broth, between 10% and 95% of the aqueous solution is evaporated; preferably at least 60%, 70% or at least 80% of the aqueous solution is evaporated. A concentrated aqueous solution enriched in 1,2-propanediol is recovered after this first evaporation step. Preferably, this concentrated solution comprises at least 15%, 20% or 25% of 1,2-propanediol.

The next steps provide for precipitation of salts contained in the aqueous solution by addition of an appropriate solvent, precipitation and removal of the salts and evaporation of solvent and water as an azeotropic composition. These steps may be repeated 2-3 times to remove most of the mineral and organic salts.

Precipitation of solids from the aqueous solution containing the 1,2-propanediol is obtained by adding a solvent to reach a proportion of solvent comprised between 0.1% and 99% per weight, preferably comprised between 30% and 60% per weight. The amount of solvent added is sufficient to promote the precipitation of solids from the aqueous solution. The solvent is selected from ethanol, methanol and acetone. In preferred embodiments, the solvent is ethanol.
After precipitation of the solids caused by the addition of solvent, the solids are removed by any appropriate method. Preferably, the solid-liquid mixture is filtered to separate the wet cake consisting of the precipitated solids and the solution containing the 1,2-propanediol.

After precipitation and filtration, solvent and water are removed from the solution containing the 1,2-propanediol. Typically, solvent and water are removed by evaporation of an azeotropic composition. When the solvent is ethanol, solvent and water are preferably evaporated at atmospheric pressure and the evaporation rate is at least 50%, 60% or 65%.

These steps, including solvent addition, precipitation and removal of solvent/water may be performed several times in order to remove most of the salts. In preferred embodiments, these steps are performed three times. At this stage, mineral salts and organic salts are removed from the solution containing the 1,2-propanediol. The final evaporation of solvent and water is performed under conditions allowing removal of 100% of the solvent.

After precipitation the aqueous solution containing the 1,2-propanediol is fed to a falling film evaporator, a wiped film evaporator, a thin film evaporator or a short path evaporator. In preferred embodiments, the aqueous solution containing the 1,2-propanediol is fed to a wiped thin film evaporator with an internal condenser.

Operating conditions are set to maximize the evaporation of 1,2-propanediol. Advantageously, vacuum i.e. low pressure evaporation is used. A substantial decrease of the boiling temperature of the 1,2-propanediol is obtained by reducing the operating pressure. Thus, degradation of the 1,2-propanediol is prevented. The operating pressure is set typically between 0.1 and 200 mbar, preferably between 1 and 50 mbar and the temperature is set between 50 and 150 °C.

Preferably, the conditions are set to evaporate most but not the total amount of 1,2-propanediol in order to avoid the evaporation of impurities at this step. At this step, the evaporate to fed mass ratio is comprised between 5 and 95 %, most preferably, the evaporate to fed mass ratio is 70%.

The evaporated product typically comprises mostly 1,2-propanediol and water.

The bottom product contains heavy impurities, for example sugar, biomass, proteins and some remaining salts. Use of a falling film evaporator, a wiped film evaporator, a thin film evaporator or of a short path evaporator, wherein impurities drawn out mechanically at the bottom of the evaporator by scraping are eliminated, reduces fouling compared to a classical distillation, wherein impurities stay over the walls of the reboiler. The bottom product may also comprise some residual 1,2-propanediol, which has not been evaporated. The residual 1,2-propanediol amounts are preferably less than 10%
and preferably less than 5% of the 1,2-propanediol fed to the evaporator. This 1,2-
propanediol may also be recovered later in the process.

A successful evaporation step will provide both a high yield of 1,2-propanediol in
the evaporated product, and sufficient liquid bottom product to draw out the heavy
impurities and remaining salts. Although the evaporated product contains most of the 1,2-
propanediol, it is preferred that some residual 1,2-propanediol is recovered in the bottom
product to avoid contamination of the evaporated 1,2-propanediol with impurities. The
residual 1,2-propanediol in the bottom product of the evaporator may amount to at least
1%, 2%, 5% or 10% of the 1,2-propanediol of the aqueous solution fed to the evaporator.

Once most of the salts and most of the heavy impurities have been removed, the
1,2-propanediol can be further purified according to any known alcohol-purification
technique, in particular by distillation.

Advantageously, both topping and stripping may be performed. Optionally, an ion
exchange step and/or adsorption step may also be included in the distillation sequence, as a
polishing step, to maximize final product quality. These methods are well known to the
skilled person and described in the literature.

Another optional step of the method of the present invention is adjusting the pH to
a pH>7 during purification. By raising the pH, acids can be separated and eliminated as
ions.

In preferred embodiments, the method according to the present invention also
comprises further removal of water leading to concentration of the evaporated product
containing the 1,2-propanediol. Water can be eliminated by various techniques known to
persons skilled in the art. Preferably, water is removed by evaporation.

Preferably, further purification of the 1,2-propanediol is performed by distillation
techniques. Elimination by distillation of products with a boiling point lower than that of
the 1,2-propanediol to be purified and products with a boiling point higher than that of the
1,2-propanediol to be purified is carried out according to conventional techniques known
to persons skilled in the art.

In some embodiments, an ion exchange step and/or adsorption may be performed in
between the different distillation steps or after the final distillation step. These techniques
are used as a final polishing step, in order to maximize product quality.

As discussed above, ion exchange is an efficient technique for the removal of salts from
various solutions. However, the removal of high salt concentration requires frequent
regeneration or renewal of ion exchange resins and is linked to high operation costs.

In the methods of the present invention, the majority of organic and mineral salts
are removed by precipitation of the salts and further evaporation of the 1,2-propanediol on
a falling film evaporator, a wiped film evaporator, a thin film evaporator or a short path evaporator.

Ion exchange may be used primarily to remove residual ionic impurities. Fouling of the resin is thus reduced, avoiding frequent regeneration and/or replacement of the ion exchange resins and preventing high operation costs. In the methods of the present invention, so-called ion exchange resins may further be used for the removal of other impurities. For example, ion exchange resins may be used for adsorption of various organic impurities. Ion exchange is a well-known technique and may be carried out with any suitable resin. In preferred embodiments, ion exchange resins are selected from strong anion exchange resins, weak anion exchange resins, strong cation exchange resins and weak cation exchange resins, or mixtures thereof, e.g. well known mixed-bed type ion exchange resins. The ion exchange step may consist in a treatment on any combination of the above-mentioned ion exchange resins.

Further purification of the 1,2-propanediol may further comprise adsorption of impurities on adsorbent solids. The term “adsorption” refers to the collection of impurities onto the surface of an adsorbent solid. This adsorption step allows removal of impurities, which are bound to the adsorbent solid by chemical or physical attraction.

In the methods of the present invention, activated charcoal or other solid adsorbents are used to remove impurities from the purified 1,2-propanediol. As discussed above, ion exchange resins may also be used for adsorption of such impurities. In preferred embodiments, adsorption and/or ion exchange are performed after distillation, thus reducing fouling of the solid adsorbent and minimizing costs.

In preferred embodiments, an ion exchange step and/or adsorption step is performed at the end of the distillation sequence, to produce pure 1,2-propanediol from distilled 1,2-propanediol. Depending on the resin or adsorbent used, addition of water to the distilled 1,2-propanediol may be needed to prevent degradation of the resin or adsorbent solid degradation and/or to decrease viscosity, thus increasing mass transfer coefficients and adsorption efficiency. At this stage, water may have to be added in proportions ranging from 1 and 100%, more preferably from 10 and 20%.

Once most of the salts have been removed, further purification is performed using techniques well known to the skilled person. The different purification steps may be carried out in a different order and additional purification steps may be performed to improve the purity of the end product.
FIGURES

Figure 1: Method for purifying 1,2-propanediol from a fermentation broth with one pass of solvent. (1) Microfiltration (2) Ultrafiltration (3) Nanofiltration (4) Water evaporation (5) Addition of the solvent (6) Mixing of fermentation broth with precipitation solvent (7) Solid-Liquid separation unit (8) Solvent and water evaporation (9) Evaporation on a falling film or wiped film wherein 1,2-propanediol, light products and a fraction of the heavy products are recovered in the vapour phase whereas salts crystallize in the evaporator and are drawn out mechanically at the bottom of the evaporator by scraping (10) Topping: elimination of light impurities by distillation (11) Stripping: elimination of heavy impurities by distillation.

Figure 2: Method for purifying 1,2-propanediol from a fermentation broth with two passes of solvent. (1) Water evaporation (2) Addition of the solvent (3) Mixing of fermentation broth with precipitation solvent (4) Solid-Liquid separation unit (5) Solvent and water (in azeotropic composition) evaporation (6) Addition of the solvent (7) Mixing of MPG mixture from fermentation broth with precipitation solvent (8) Solid-Liquid separation unit (9) Solvent and water evaporation (10) Evaporation on a falling film or wiped film wherein 1,2-propanediol, light products and a fraction of the heavy products are recovered in the vapour phase whereas salts crystallize in the evaporator and are drawn out mechanically at the bottom of the evaporator by scraping (11) Topping: elimination of light impurities by distillation (12) Stripping: elimination of heavy impurities by distillation.

Figure 3: Method for purifying 1,2-propanediol from a fermentation broth with one pass of solvent and a final purification. (1) Water evaporation (2) Addition of the solvent (3) Mixing of fermentation broth with precipitation solvent (4) Solid-Liquid separation unit (5) Solvent and water evaporation (6) Evaporation on a falling film or wiped film wherein 1,2-propanediol, light products and a fraction of the heavy products are recovered in the vapour phase whereas salts crystallize in the evaporator and are drawn out mechanically at the bottom of the evaporator by scraping (7) Topping: elimination of light impurities by distillation (8) Stripping: elimination of heavy impurities by distillation (9) Optional ion exchange and/or adsorption step on ion exchange resin, activated charcoal or other adsorbent solids, for removal of residual ionic impurities and/or color-forming impurities.

These examples, while indicating preferred embodiments of the invention, are given by way of illustration only.
EXAMPLES

A filtered fermentation broth containing 1,2-propanediol (MPG) (A1) was used as a starting material for the following experiments.

Filtration of the fermentation broth consisted in a 0.10 μm cutoff microfiltration.

The (A1) filtered fermentation broth was first concentrated by evaporation. (A1) Filtered fermentation broth (55.6 kg) was loaded into a thermosyphon-type evaporator. Operating top pressure was 120 mbar. 84.6 wt% of the solution was evaporated. 8.3 kg of a MPG-rich mixture (B1) was recovered. This concentrate mixture was analyzed by HPLC and results are reported in Table 1.

Table 1: Composition of the concentrated solution (Mixture B1)

<table>
<thead>
<tr>
<th>Organic analysis</th>
<th>Ionic analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compound</strong></td>
<td><strong>Concentration %</strong></td>
</tr>
<tr>
<td>1,2 propanediol</td>
<td>29.39</td>
</tr>
<tr>
<td>Citrate</td>
<td>0.0</td>
</tr>
<tr>
<td>Glucose</td>
<td>0.0</td>
</tr>
<tr>
<td>Succinate</td>
<td>0.42</td>
</tr>
<tr>
<td>Glycerol</td>
<td>0.0</td>
</tr>
<tr>
<td>Acetate</td>
<td>6.54</td>
</tr>
<tr>
<td>Hydroxycetone</td>
<td>0.0</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.0</td>
</tr>
<tr>
<td>Pyruvate</td>
<td>0.0</td>
</tr>
<tr>
<td>Methylglyoxal</td>
<td>0.0</td>
</tr>
<tr>
<td>Phosphate</td>
<td>0.62</td>
</tr>
<tr>
<td><strong>Water</strong>: qs 1L</td>
<td></td>
</tr>
</tbody>
</table>

997 g of ethanol was then added to 988 g of (B1) concentrated mixture. Ethanol was purchased from Sigma-Aldrich (99.8% vol. purity – GC analysis), and used without further purification. The addition of ethanol caused precipitation of solid in (B1) concentrated mixture.

The solid-liquid mixture is filtered to separate 1770 g of (C1) solution and 55 of wet (D1) cake filtration. 160 g of (B1)-ethanol mixture were lost due to the filtration process hold-up.

(D1) cake filtration was partially dried at least two days in a desiccator. Samples of (C1) mixture and (D1) dried solid were analyzed by HPLC and results are reported in Table 2 and Table 3.
Table 2: Composition of the filtered solution (Mixture C1)

<table>
<thead>
<tr>
<th>Organic analysis</th>
<th>Ionic analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compound</strong></td>
<td><strong>Concentration</strong></td>
</tr>
<tr>
<td></td>
<td>%</td>
</tr>
<tr>
<td>1,2 propanediol</td>
<td>14.88</td>
</tr>
<tr>
<td>Citrate</td>
<td>0.0</td>
</tr>
<tr>
<td>Glucose</td>
<td>0.0</td>
</tr>
<tr>
<td>Succinate</td>
<td>0.0</td>
</tr>
<tr>
<td>Glycerol</td>
<td>0.0</td>
</tr>
<tr>
<td>Acetate</td>
<td>2.42</td>
</tr>
<tr>
<td>Hydroxyacétone</td>
<td>0.0</td>
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<tr>
<td>Ethanol</td>
<td>41.35</td>
</tr>
<tr>
<td>Pyruvate</td>
<td>0.0</td>
</tr>
<tr>
<td>Methylglyoxal</td>
<td>0.0</td>
</tr>
<tr>
<td><strong>Water : qg 1L</strong></td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Composition of the cake filtration (Solid D1)

<table>
<thead>
<tr>
<th>Organic analysis</th>
<th>Ionic analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compound</strong></td>
<td><strong>Concentration</strong></td>
</tr>
<tr>
<td></td>
<td>%</td>
</tr>
<tr>
<td>1,2 propanediol (MPG)</td>
<td>27.41</td>
</tr>
<tr>
<td>Citrate</td>
<td>1.04</td>
</tr>
<tr>
<td>Glucose</td>
<td>0.0</td>
</tr>
<tr>
<td>Succinate</td>
<td>0.06</td>
</tr>
<tr>
<td>Glycerol</td>
<td>0.16</td>
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<tr>
<td>Acetate</td>
<td>2.98</td>
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<tr>
<td>Hydroxyacétone</td>
<td>0.0</td>
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<td>Ethanol</td>
<td>0.0</td>
</tr>
<tr>
<td>Pyruvate</td>
<td>0.18</td>
</tr>
<tr>
<td>Methylglyoxal</td>
<td>0.05</td>
</tr>
<tr>
<td>Phosphate</td>
<td>6.51</td>
</tr>
<tr>
<td><strong>Water : qg 1L</strong></td>
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</table>

Precipitation removes a significant portion of salts.
Ethanol and water in azeotropic composition were evaporated at atmospheric pressure of (C1) filtered solution to form 607 g of (E1) concentrated mixture. Evaporation rate is about 66%.

The following steps were applied again two times to (E1) solution:
- Adding of ethanol: in the same quantity as MPG mixture,
- Filtration to recover MPG solution with less salts,
- Evaporation of ethanol and water (azeotropic composition). Evaporation rates were between 50 and 60%.

Finally, 473 g of (F1) final MPG-rich mixture were recovered.

The (F1) MPG-rich mixture obtained was fed to a laboratory wiped thin film evaporator with an internal condenser. The operating pressure was set to 25 mbar. The heating temperature was set to 140 °C up to 170°C. Valuable compounds, including most part of the MPG, were evaporated. Remaining salts and heavy compounds were collected in the bottom product. The recovered mass of (G1) distillate was 332 g, and the distillate to feed mass ratio was 70.2%.

To remove all remaining impurities, (G1) distillate was feed to the bottom of a discontinue distillation column. The operating pressure was set to 80 mbar. The top operating temperature was 114°C. One sample of MPG was produced with a purity higher than 99.5% (surface value measured by GC/MS), without any trace of the impurities reported in Table 1.

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1. A method for purifying 1,2-propanediol from a fermentation broth comprising the following steps:
   a) clarifying the fermentation broth in order to obtain an aqueous solution containing the 1,2-propanediol,
   b) removing water from the aqueous solution containing the 1,2-propanediol obtained in step a),
   c) adding a solvent to the solution obtained in the previous step to reach a proportion of solvent comprised between 0.1% and 99% per weight, wherein the solvent is selected from ethanol, methanol and acetone; and wherein addition of the solvent leads to precipitation of solids;
   d) removing the solids which precipitated in the previous step,
   e) evaporating solvent and water from the solution obtained in the previous step d),
   f) evaporating the 1,2-propanediol from the solution obtained in step e) on a falling film evaporator, a wiped film evaporator, a thin film evaporator or a short path evaporator,
   g) recovering the 1,2-propanediol.

2. A method for purifying 1,2-propanediol from a fermentation broth according to claim 1, wherein clarification of the fermentation broth in step a) is carried out by filtration.

3. A method for purifying 1,2-propanediol from a fermentation broth according to claim 2, wherein filtration comprises a 0.1 μm cut off microfiltration step.

4. A method for purifying 1,2-propanediol from a fermentation broth according to anyone of claims 1-3, wherein in step b) removing water from the aqueous solution containing the 1,2-propanediol is performed by evaporation.

5. A method for purifying 1,2-propanediol from a fermentation broth according to anyone of claims 1-4, wherein in step c) the solvent is ethanol.

6. A method for purifying 1,2-propanediol from a fermentation broth according to anyone of claims 1-5, wherein in step c) the solvent is added to reach a proportion of solvent comprised between 30% and 60% per weight.
7. A method for purifying 1,2-propanediol from a fermentation broth according to anyone of claims 1-6, wherein in step d) the solids are removed by filtration.

8. A method for purifying 1,2-propanediol from a fermentation broth according to anyone of claims 1-7, wherein, before performing step f), steps c), d) and e) are repeated.

9. A method for purifying 1,2-propanediol from a fermentation broth according to claim 8, wherein steps c), d) and e) are repeated two times before performing step f).

10. A method for purifying 1,2-propanediol from a fermentation broth according to anyone of claims 1-9, wherein the 1,2-propanediol is evaporated from the solution obtained in step e) in a wiped thin film evaporator with an internal condenser.

11. A method for purifying 1,2-propanediol from a fermentation broth according to anyone of claims 1-10, comprising further purification of the 1,2-propanediol recovered in step g).

12. A method for purifying 1,2-propanediol from a fermentation broth according to claim 11 wherein further purification of the 1,2-propanediol comprises removing by distillation products and/or azeotropes which have a boiling point lower than that of 1,2-propanediol by distillation; and removing products and/or azeotropes having a boiling point higher than that of 1,2-propanediol by distillation.

13. A method for purifying 1,2-propanediol from a fermentation broth according to anyone of claims 11-12 wherein further purification of the 1,2-propanediol comprises removing water by evaporation.

14. A method for purifying 1,2-propanediol from a fermentation broth according to anyone of claims 11-13 wherein further purification of the 1,2-propanediol comprises ion exchange and/or adsorption.
### A. CLASSIFICATION OF SUBJECT MATTER

**INV.** C07C29/76  C12P7/18

**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  C12P

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

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

EPO-Internal, WPI Data, BEILSTEIN Data, CHEM ABS Data

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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**Further documents are listed in the continuation of Box C.**

**See patent family annex.**

* Special categories of cited documents:
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**Date of the actual completion of the international search**

18 January 2011

**Date of mailing of the international search report**

28/01/2011

**Name and mailing address of the ISA/**

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**Authorized officer**

Butkowskyj-Walkiw, T
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