THE METHOD OF PROPYLENE GLYCOL PRODUCTION FROM WASTE BIOMASS GENERATED IN THE SUGAR FACTORY

METOD PROIZVODNJE PROPILENOGLIOLA IZ OTPADNE BIOMASE SAKUPLJENE U FABRIKAMA ŠEĆERA

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Key words: propylene glycol, lactic acid, sugar beet pulp, hydrogenation.

ABSTRACT

Propylene glycol (PG), one of the most important raw chemical materials, has many properties of interest to the industry like: low viscosity, negligible toxicity, odorlessness and low freezing point. Because of this, it is often used in food, pharmaceutical and cosmetic industries. A new way of PG obtaining was developed in Lodz University of Technology in cooperation with the Polish National Sugar Company Ltd. This method involves catalytic reduction of lactic acid (LA) obtained on the route of microbiological transformation of hydrolysates of sugar beet pulp. Sugar beet pulp, firstly in the enzymatic form hydrolyzed into hexose and pentose feedstocks, was used in the fermentation process. The obtained medium enriched with nutrients was fermented by selected lactic acid bacteria. After the removal of the biomass, broth was purified on active carbon and silica, and finally used as a substrate in catalytic hydrogenation to propylene glycol. Hydrogenation of LA was performed in a 50 ml autoclave at the temperature of 130 °C, under 3.5 MPa of H2 pressure. 5% Ru/C catalyst was used with equal amounts (mcat = 0.5 g) in all reaction runs.

INTRODUCTION

The development and utilization of renewable and clean biomass resource have been of interest because of energy shortages and environmental pollution caused by overconsumption of non-renewable fossil fuel (Bond, 2010). What is more, renewable biomass is low-cost and emits less pollution in comparison with fossil fuels. Application of biomass as the raw material for the production of chemical stocks is likely to replace the petroleum-derived materials (Huber, 2007).

Propylene glycol, an important multi-purpose chemical, has many properties of interest to the industry, like: low viscosity, negligible toxicity, odorlessness and a low freezing point. For these reasons, it is often used in food, pharmaceutical and cosmetic industries (Cameron, 1998) (Saxena, 2010).

The commercial production of 1,2-propylene glycol is currently petroleum-based and involves the high-pressure and high-temperature hydrolysis of propylene oxide, manufactured by either the chlorohydrin process or the per-oxidation process (Reutov, 2004). Due to its industrial value, the interest in the synthesis of 1,2-propylene glycol has been increasing in recent years. Propylene glycol can be effectively obtained from cellulose and chitin derived sugars (Yan, 2013).

Researchers from Lodz University of Technology in cooperation with the Polish National Sugar Company Ltd. have developed a new method of propylene glycol synthesis via catalytic hydrogenation of lactic acid obtained by the fermentation of sugar beet pulp hydrolysates (Berlowska, 2015).

In this paper, the new results of catalytic reduction of postfermentation broths are presented.

MATERIAL AND METHOD

Beet pulp is waste from sugar production. It is obtained after the extraction of sucrose from sugar beet. For our investigation, sugar beet pulp was acquired from a sugar factory in Dobrzelin (Polish National Sugar Company), located in the central part of Poland.

The scheme of a new method of propylene glycol synthesis via catalytic hydrogenation of lactic acid obtained by the fermentation of sugar beet pulp hydrolysates is presented in Fig. 1. The first step of this process is the enzymatic hydrolysis of the sugar beet pulp. Enzymatic saccharification of this material requires the concerted action of cellulases, hemicellulases (including arabinosidases) and pectinases (Leijdekkers, 2013). In our research, a mixture of two commercial multienzyme preparations, Viscozyme and UltrafloMax from Novozymes, was
found to efficiently saccharify polysaccharides contained in the sugar beet pulp. After 24 hours of hydrolysis, conducted at 50 °C, pH = 5 and for the water solution in which a dry matter concentration was around 10 % (w/v), glucose yields in the hydrolyzates were over 30 % of the initial sugar beet pulp dry matter. The dominant reducing sugars released during the process were glucose (around 30 % of the total reducing sugars), arabinose and galacturonic acid (both around 25 %), while xylose accounted for around 2 % of all monosaccharides.

The next step of this process is lactic fermentation of hydrolyzate used as a substrate. Three collection strains (Polish Collection of Microorganisms): *Lactococcus lactis* 2379, *Lactobacillus acidophilus* 2510 and *Lactobacillus delbrueckii* 490, as well as the environmental isolate (from sugar beet pulp) *Lactobacillus plantarum* II, were used in the study. In order to optimize the lactic fermentation process over selected bacteria strains we used MRS fermentation medium (composition of the MRS: yeast extract 4.0 g·L\(^{-1}\), meat extract 8.0 g·L\(^{-1}\), peptone K 10.0 g·L\(^{-1}\), Glucose 20.0 g·L\(^{-1}\), tri-ammonium citrate 2.0 g·L\(^{-1}\), dipotassium hydrogen phosphate 2.0 g·L\(^{-1}\), sodium acetate 5.0 g·L\(^{-1}\), magnesium sulfate 7 hydrate 0.20 g·L\(^{-1}\), pH = 6.3) produced by BTL LLC (Lodz, Poland).

For all fermentation media aerobic cultivation of lactic acid bacteria was conducted at 37 °C for 48 hours. The growth of bacteria was measured via spectrophotometric (optical density measurements) and plate count methods. After the lactic fermentation process over selected bacteria strains we used MRS fermentation medium (composition of the MRS: yeast extract 4.0 g·L\(^{-1}\), meat extract 8.0 g·L\(^{-1}\), peptone K 10.0 g·L\(^{-1}\), Glucose 20.0 g·L\(^{-1}\), tri-ammonium citrate 2.0 g·L\(^{-1}\), dipotassium hydrogen phosphate 2.0 g·L\(^{-1}\), sodium acetate 5.0 g·L\(^{-1}\), magnesium sulfate 7 hydrate 0.20 g·L\(^{-1}\), pH = 6.3) produced by BTL LLC (Lodz, Poland).

Hydrogenation of lactic acid in an aqueous solution (0.5 M·L\(^{-1}\), 25 mL) was performed in a 50 mL autoclave (Parr Instrument Company; USA) at a temperature of 130 °C and under 35 bar of H\(_2\) pressure. The reactions were conducted with equal amounts of catalyst (m\(_{\text{cat}}\)=0.5 g) in each experiment. The mixture was stirred at 500 rpm. The autoclave was flushed with argon (Ar, Linde 5.0, at a rate of 20 mL min\(^{-1}\), at 20 °C, for 15 min) to remove the air. It was then flushed again with hydrogen (H\(_2\), Air Products, Premium Plus, 99.99 %, at 20 °C, for 15 min). The autoclave was pressurized with hydrogen to 35 bar, and the temperature gradually increased to 130 °C with a heating rate of 20 °C min\(^{-1}\). The reaction was sustained for 4 h.

The reaction conditions were optimized for 5 % Ru/C\(_{\text{act}}\) commercial catalyst (Sigma-Aldrich, CAS 206180) and also a commercial solution of lactic acid (CHEMPUR; Poland). Optimal conditions for the catalytic reduction of lactic acid to propylene glycol using 5 %Ru/C\(_{\text{act}}\) are: t=4h, T=130 °C, m\(_{\text{cat}}\)=0.5 g, V\(_{\text{LA}}\)=0.25 mL, C\(_{\text{LA}}\)=0.5 M, pH\(_{2}\)=3.5 MPa.

After the reaction, the autoclave was cooled to room temperature in a controlled manner using a water bath. The reaction mixture was filtered and analyzed using HPLC to determine the concentration of lactic acid (La Chrome, Merck-Hitachi, column; Kromasil 100 C18, mobile phase: acetonitrile/phosphate buffer= 5:95 (v/v), pH = 4.5, C\(_{\text{phosphate}}\)= 0.01, UV: λ = 210 nm). Products of lactic acid hydrogenation were also screened using GC-FID analysis (Hewlett Packard 5890A; packed column 8 % Carbowax 1540 on Chromosorb W; injection port temperature: 170 °C, injection volume: 5 µl; FID detector temperature: 250 °C; column oven temperature: 190 °C; He (Linde, 99.999 %): 30 mL min\(^{-1}\)).
RESULTS AND DISCUSSION

As lactic acid is formed in fermentation processes in an industrial scale, it must be neutralized with base to maintain pH in the range that the microorganism will function. The raw product of fermentation is, therefore, an aqueous solution consisting of sodium, ammonium, or calcium lactate. To recover free lactic acid, the lactate salt has to be acidulated. This is typically done by addition of H₂SO₄, particularly when calcium hydroxide is used as the neutralizing agent in fermentation, so that the CaSO₄ formed immediately precipitates from solution (Zhang, 2001). That is the reason, in our investigations we conducted fermentation process without pH correction and purified fermentation broths on the mixture of active carbon and silica.

Postfermentation broths without and after purification on active carbon and silica were used as a substrate in catalytic reduction processes over 5 %Ru/C act. For each medium, three reaction runs were conducted. Hydrogenation of lactic acid was performed in an autoclave at a temperature of 130 °C and under 35 bar of H₂ pressure. The concentrations of lactic acid and propylene glycol after 4 h of reaction are summarized in Table 1.

Catalytic results are expressed as conversion of lactic acid (X, %) and selectivity towards propylene glycol (S, %). Those parameters were defined as:

\[ X = \left( 1 - \frac{C_{\text{av. LA}}}{C_{\text{LA}}^0} \right) \times 100\% \]

\[ S = \frac{C_{\text{PG}}}{C_{\text{av. PG}} - C_{\text{LA}}^0} \times 100\% \]

where \( C_{\text{LA}}^0 \) is a molar concentration of lactic acid at the beginning of the hydrogenation process, \( C_{\text{PG}} \) is amolarconcentration of lactic acid at the end of reaction, \( C_{\text{PG}} \) is a molar concentrationof propylene glycol at the end of the reaction. The tests of catalytic activity were performed for each postfermentation broths three times. The results of LA conversion and selectivity to PG are calculated for the average values of lactic acid and propylene glycol concentrations in the reaction mixture. This is the first study of catalytic hydrogenation of lactic acid present in fermentation broths to propylene glycol. The reaction take place at mild temperature 130 °C and at moderate hydrogen pressure 3.5 MPa, especially when compared to prior work reported using 20-30 MPa H₂ (Zhang, 2001; Chen, 2007; Zhang, 2002). The conversion degree of LA and selectivity to PG stated for fermentation broths purified on the mixture of active carbon and silica are comparable to this catalytic parameters obtained for water solution of commercial LA. On the basis of these results, it was concluded that the purification of the broths on the mixture of active carbon and silica was sufficient for the effective conversion of lactic acid into propylene glycol.

Table 1. Concentrations of lactic acid and propylene glycol in reaction mixture. Hydrogenation of lactic acid was performed for 4 h in an autoclave at a temperature of 130 °C and under 35 bar of H₂ pressure.

<table>
<thead>
<tr>
<th>Postfermentation broth sample</th>
<th>C₀ LA [mmol L⁻¹]</th>
<th>C₁ LA [mmol L⁻¹]</th>
<th>C av. LA [mmol L⁻¹]</th>
<th>Standard deviation</th>
<th>Range</th>
<th>Confidence Interval (Student’s t-distribution)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water solution lactic acid ⁵</td>
<td>500</td>
<td>145</td>
<td>7.94</td>
<td>15.0</td>
<td>128± 11.8</td>
<td></td>
</tr>
<tr>
<td>L. lactis PCM 2379</td>
<td>238</td>
<td>222.8</td>
<td>151.3</td>
<td>2.72</td>
<td>148.4± 4</td>
<td></td>
</tr>
<tr>
<td>L. acidophilus 2510</td>
<td>229</td>
<td>117.9</td>
<td>113.6</td>
<td>2.05</td>
<td>114.5± 4.5</td>
<td></td>
</tr>
<tr>
<td>L. delbrueckii PCM 490</td>
<td>94</td>
<td>91.7</td>
<td>119.1</td>
<td>0.12</td>
<td>91.8± 0.2</td>
<td></td>
</tr>
<tr>
<td>L. delbrueckii PCM 490</td>
<td>81</td>
<td>66.7</td>
<td>66.3</td>
<td>0.56</td>
<td>66.2± 0.8</td>
<td></td>
</tr>
<tr>
<td>L. delbrueckii PCM 490</td>
<td>85</td>
<td>10.9</td>
<td>9.2</td>
<td>1.65</td>
<td>9.2± 2.4</td>
<td></td>
</tr>
<tr>
<td>L. lactis PCM 2379</td>
<td>80</td>
<td>9.8</td>
<td>6.9</td>
<td>1.45</td>
<td>8.3±2.2</td>
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</tr>
<tr>
<td>L. acidophilus 2510</td>
<td>78</td>
<td>77.3</td>
<td>77.5</td>
<td>0.20</td>
<td>77.3± 0.3</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Postfermentation broth sample</th>
<th>PG [mmol L⁻¹]</th>
<th>C av. PG [mmol L⁻¹]</th>
<th>Standard deviation</th>
<th>Range</th>
<th>Confidence interval (Student’s t-distribution)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water solution lactic acid ⁵</td>
<td>313.6</td>
<td>303.97</td>
<td>11.73</td>
<td>22.70</td>
<td>304± 18</td>
</tr>
<tr>
<td>L. lactis PCM 2379</td>
<td>0.43</td>
<td>0.42</td>
<td>0.02</td>
<td>0.04</td>
<td>0.42± 0.03</td>
</tr>
<tr>
<td>L. acidophilus 2510</td>
<td>8.92</td>
<td>8.19</td>
<td>0.64</td>
<td>1.19</td>
<td>8.19± 0.95</td>
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<tr>
<td>L. acidophilus 2510</td>
<td>9.96</td>
<td>9.68</td>
<td>0.42</td>
<td>0.76</td>
<td>9.68± 0.62</td>
</tr>
<tr>
<td>L. delbrueckii PCM 490</td>
<td>10.05</td>
<td>10.05</td>
<td>0.59</td>
<td>1.18</td>
<td>10.05± 0.88</td>
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<tr>
<td>L. delbrueckii PCM 490</td>
<td>47.05</td>
<td>46.79</td>
<td>2.00</td>
<td>3.97</td>
<td>46.79± 3</td>
</tr>
<tr>
<td>L. lactis PCM 2379</td>
<td>58.15</td>
<td>58.15</td>
<td>3.40</td>
<td>6.65</td>
<td>58.15± 5.1</td>
</tr>
<tr>
<td>L. acidophilus 2510</td>
<td>0.46</td>
<td>0.46</td>
<td>0.02</td>
<td>0.04</td>
<td>0.46± 0.03</td>
</tr>
</tbody>
</table>
CONCLUSION

We developed a process for 1,2-propylene glycol catalytic production from waste biomass from the sugar industry. The combination of the lactic fermentation step of sugar pulp hydrolyzates obtained from waste biomass from sugar industry with catalytic transformation of lactic acid on 5 % Ru/C act leads to the 1,2-propylene glycol. This method may be competitive with the traditional chemical method for obtaining this compound from petroleum. What is more, the use of waste biomass as a substrate may result in the decrease in the cost of 1,2-propylene glycol production.

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REFERENCES


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