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Process development of short-chain polyols synthesis from corn stover by combination of enzymatic hydrolysis and catalytic hydrogenolysis

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ABSTRACT

Currently short-chain polyols such as ethanediol, propanediol, and butanediol are produced either from the petroleum feedstock or from the starch-based food crop feedstock. In this study, a combinational process of enzymatic hydrolysis with catalytic hydrogenolysis for short-chain polyols production using corn stover as feedstock was developed. The enzymatic hydrolysis of the pretreated corn stover was optimized to produce stover sugars at the minimum cost. Then the stover sugars were purified and hydrogenolyzed into polyols products catalyzed by Raney nickel catalyst. The results show that the yield of short-chain polyols from the stover sugars was comparable to that of the corn-based glucose. The present study provided an important prototype for polyols production from lignocellulose to replace the petroleum- or corn-based polyols for future industrial applications.

1. Introduction

Short-chain polyols such as ethanediol, propanediol, and butanediol are important commodity chemicals used as solvents, drugs, cosmetics, antifreezes, or as precursors for synthesizing unsaturated polyester resins [1,2]. Conventionally, short-chain polyols are produced from petroleum-based feedstocks, in which ethanediol is produced by epoxidation of ethylene; 1,2-propanediol is by chlorohydrination of propylene or epoxidation of ethylbenzene hydroperoxide; 1,3-propanediol is by hydration of acrolein known as "Degussa–DuPont route" or by hydroformylation of ethylene oxide to produce 3-hydroxypropionaldehyde and then hydrogenated known as "Shell route" [3,4]; and 1,4-butanediol is by synthesis of 1,4-butynediol with acetylene and formaldehyde and then hydrogenated known as "Reppe chemistry" [5].

In light of the fluctuating price of petroleum and limited reserves, microbial production of some specific polyols such as 1,3-propanediol and 1,4-butanediol from corn-based glucose has attracted more attentions and gone into commercialization [6,7]. Recently, a hydrogenolysis process using corn-based glucose for the production of few short-chain polyol compounds was developed and commercialized [8]; (http://www.globalbiochem.com; http://ty.mycaixin.cn). Lignocellulose-derived sugars from the cheap and abundant agricultural residues are an important option to replace the corn-based glucose for polyols production. However, great technical challenges exist on the short-chain polyols production from lignocellulose materials, including how to produce cheap sugars from lignocellulose through pretreatment and hydrolysis, how to purify the lignocellulose-derived sugars to meet the hydrogenolysis requirements, and how to find proper catalysts for hydrogenolysis of the mixed sugars from lignocellulose.

In this study, a combinational process for short-chain polyols production from corn stover was developed as shown in Fig. 1. Corn stover was pretreated using "dry dilute acid pretreatment" [9,10], then enzymatically hydrolyzed into monomer sugars (mainly glucose and xylose); the liquid hydrolysate was purified by decolorization and desalting, and then chemically transformed into short-chain polyols via hydrogenolysis. Finally, the short-chain polyols mixture was fractionated into different components, including ethanediol, 1,2-propanediol, and butanediol etc. To our knowledge, this is the first report on the hydrogenolysis of lignocellulose-derived sugars for short-chain polyols production.

2. Materials and methods

2.1. Materials

Corn stover was harvested in fall, 2011 from Dancheng County, Henan province, China. After collection, corn stover was unpacked,

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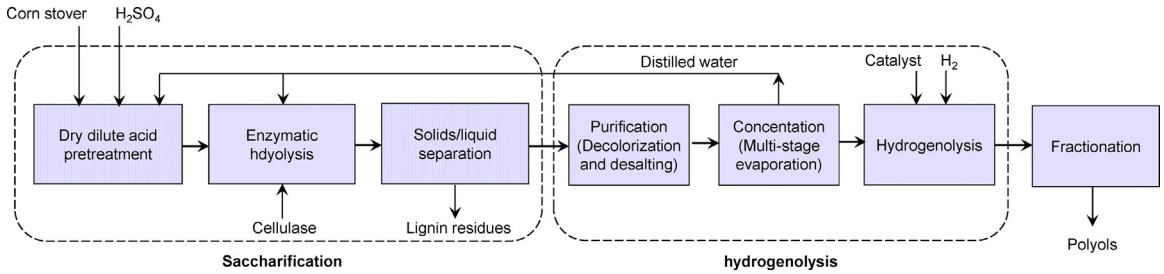

Fig. 1. Schematic diagram of short-chain polyols production by combination of enzymatic hydrolysis and catalytic hydrogenolysis of lignocellulosic materials.

water-washed to remove the impurities and air-dried, then milled coarsely using a beater pulverizer (SF-300, Ketai Milling Equipment, Shanghai, China) to a diameter less than 5 mm. The milled materials were stored in air-tight plastic bags before pretreatment.

Cellulase enzyme Youtell #6 used in this study was provided by the Hunan Youtell Biochemical Co., Yueyang, Hunan, China (http://www.youtellbio.com). The activity of Youtell #6 was 145.0 FPU/g in the filter paper unit (FPU) and 344.0 IU/g in the cellobiase unit (IU) analyzed according to the protocol of NREL LAP-006 [11]. Youtell #6 is a commercial cellulase enzyme with comparable performance to the other commercial cellulases [12–14].

The modified Raney nickel catalyst #12-2 was provided by the Caixin Sugar Industry Co., Dancheng, Henan, China and commercially available in the company. The catalyst #12-2 is currently used for industrial hydrogenolysis of corn based glucose into short-chain polyols. The major ingredients of the catalyst include nickel, aluminium, tin and other necessary ingredients at different ratios. The particle size is ranged from 80 to 300 meshes per square inch.

2.2. Dry dilute acid pretreatment and enzymatic hydrolysis

Corn stover was pretreated using the dry dilute sulfuric acid pretreatment in a helical stirring reactor as described by [9] and [10]. Briefly, the corn stover was presoaked with dilute sulfuric acid (5.0%, w/w) at a solid/liquid ratio of 2:1 for 12 h (the moisture content of the impregnated corn stover was about 33.33%). Then the materials were put into the pretreatment reactor and the hot steam was jetted into the reactor heating the corn stover to 185 °C for 3 min (heating time from 0 to 185 °C was kept within 3–6 min). After that, the pressure was released within 10–30 s and the pretreated corn stover was discharged from the reactor. The reactor was operated at 50 rpm during the pretreatment process. The harvested pretreated corn stover contained about 50% solids materials and was stored at 4 °C before enzymatic hydrolysis.

The enzymatic hydrolysis cost highly depends on the enzyme dosage used, the substrate used, and the pretreatment method used [15,16]. Therefore, the enzymatic hydrolysis of corn stover using dry pretreatment and Youtell #6 enzyme was optimized to give the minimum cost of stover sugars. The solids loadings, cellulase dosages, and the reactor scales were considered in the hydrolysis study. The sugar yield obtained at different conditions was incorporated into the Eq. (10) as described in Supplementary Materials to calculate the stover sugar hydrolysate production costs. The conditions which could obtain a relative lower sugar production cost was chosen for the following experiments. The pretreated corn stover was used directly for enzymatic hydrolysis without any other detoxification process. All the enzymatic hydrolysis trials were performed in duplicates and the average data were reported.

2.3. Purification of stover sugar hydrolysate

The corn stover slurry after enzymatic hydrolysis was solid/liquid separated in a frame press (Shanghai Dazhang Filter Equipment Co., Shanghai, China). The obtained hydrolysate was decolorized by 3% (w/w) of activated charcoal (powder-like products, purchased from Sinopharm Chemical Reagent Co., Shanghai, China) at 80 °C for 30 min. Again the solid charcoal was separated using the frame press to obtain the decolorized stover sugar hydrolysate.

The decolorized hydrolysate was desalted using ion exchange resins. The strong acidic cation resins 732 and the weak base anion resins D315 (Sino Polymer Co., Shanghai, China) were used to remove the positive and negative ions (mainly Na^+ and SO_4^{2-} ions), respectively. The resins were activated according to the producer's specifications and the decolorized hydrolysate was flowed through a column (20 mm in diameter and 600 mm in length) filled with 180 mL wet activated 732 resins at a flowrate of 70 mL/min until the resins were saturated. Then the effluent hydrolysate was sent to flow through the column filled with 180 mL wet activated D315 resins at a flowrate of 25 mL/min until the resins were saturated. The samples were taken regularly for conductivity analysis using a DDS-307A conductivity meter (Shanghai INESA and Scientific Instrument Co., Shanghai, China), and sugars and inhibitors analysis on HPLC.

2.4. Hydrogenolysis of stover sugars into polyols

The stover sugar hydrolysate was concentrated to a 300–350 g/L sugar concentration by steam evaporation before hydrogenolysis. Then the concentrated stover sugar hydrolysate was sent to the hydrogenolysis reactor supplemented with 4% (w/w) sodium hydroxide and 15% modified Raney nickel catalyst #12-2 (w/w, based on the total sugar weight in system). The purified hydrogen was ventilated into the reactor to remove the inert air in the reactor and heated to 230 °C and 11.0 MPa slowly in an oil bath, then maintained for 120 min until glucose and xylose were completely converted. After each batch reaction, the Raney nickel catalyst was recycled by washing with deionized water then sent to the next round of catalytic operation.

2.5. Analysis of sugars, inhibitors, and hydrogenolysis products on HPLC

Glucose, xylose, inhibitory compounds, such as formic acid, furfural, 5-hydroxymethylfurfural (HMF), acetic acid and levulinic acid, and hydrogenolysis products, including ethanediol, 1,2-propanediol, butanediol, glycerol, sorbitol, lactic acid were determined using high-performance liquid chromatography (LC-20AD, refractive index detector RID-10A, Shimadzu, Japan) with a Bio-Rad Aminex HPX-87H column at the column temperature of 65 °C. The mobile phase was 0.005 M H_2SO_4 at the rate of 0.6 mL/min. All the samples were diluted properly and filtered through a 0.22 μm filter before analysis.

2.6. Determination of proteins in the hydrolysate

The protein content in the hydrolysate at different purification stages was determined according to Bradford using bovine serum