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

Zhen-Hong Fang [a,1], Jian Zhang [a,b,1], Qi-Ming Lu [c], Jie Bao [a,*]

[a] State Key Laboratory of Bioreactor Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China
[b] Key Laboratory for Solid Waste Management and Environment Safety, Ministry of Education of China, Tsinghua University, Beijing 10084, China
[c] Caixin Sugar Industry Co., 43 Xinhua Road, Dancheng, Henan 477150, China

ARTICLE INFO

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,

---

* Corresponding author. Tel.: +86 21 64251799; fax: +86 21 64251799.
E-mail address: jbao@ecust.edu.cn (J. Bao).
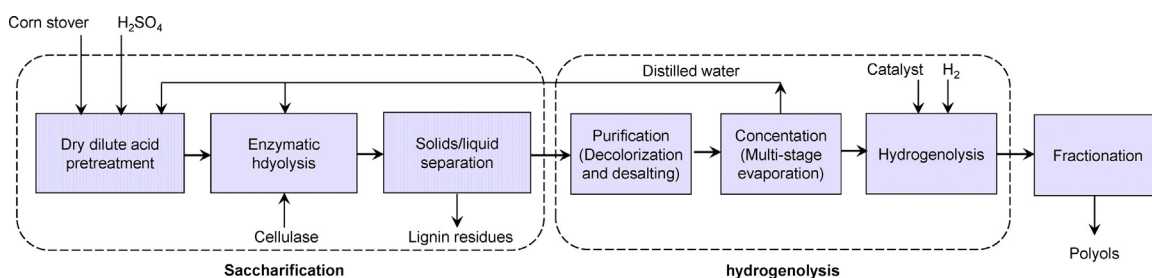[1] These authors contributed equally to this work.

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
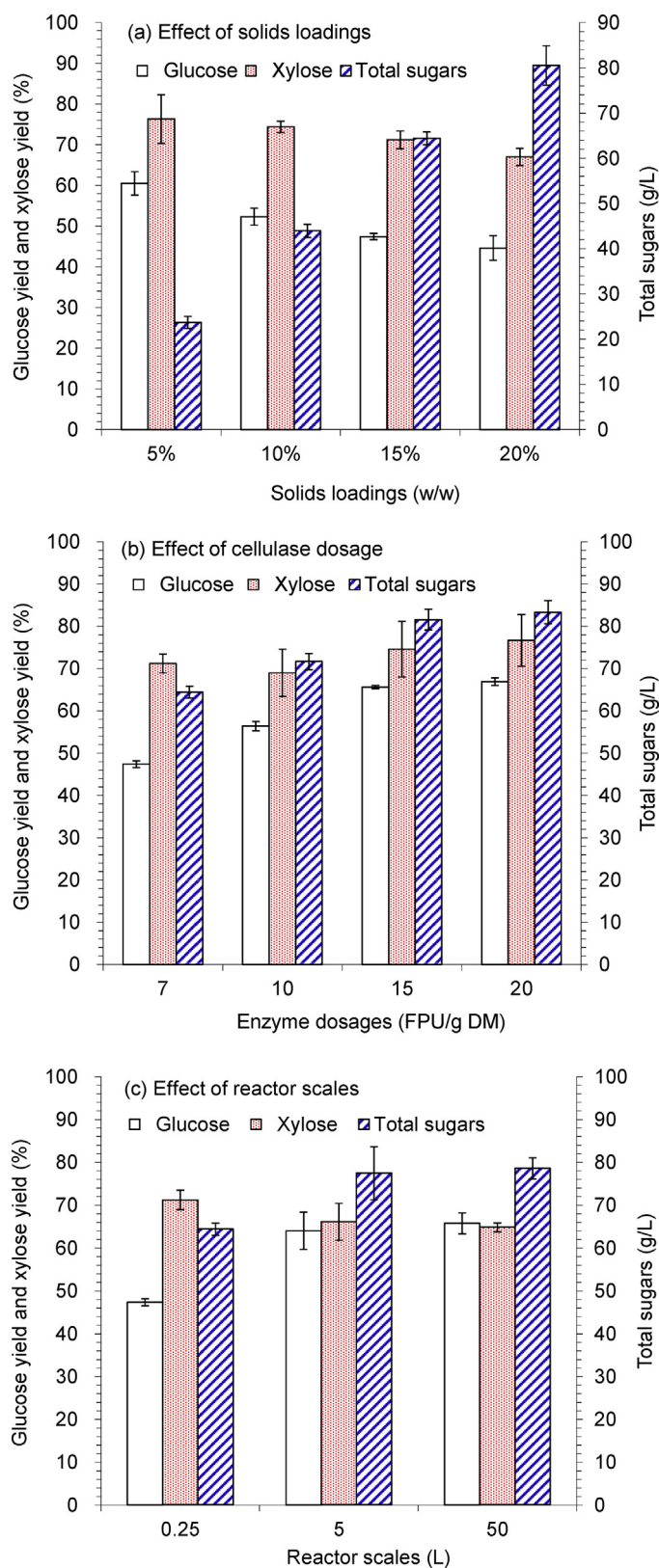
Fig. 2. Enzymatic hydrolysis of corn stover under various operation conditions. (a) Solids loadings; (b) cellulase dosages; (c) reactor scales. Conditions: solids loadings assays were performed at the conditions of 15 FPU/g DM, pH 4.8 with 0.1 M citric acid buffer, 150 rpm for 48 h while 20% (w/w) solids loading was performed in a 5 L helical stirring bioreactor. And the hydrolysis at 20% solids loading lasted for 72 h; the cellulase dosages assays were performed at 15% solids loading, pH 4.8 with 0.1 M citric acid buffer, 50 °C in flasks and 150 rpm for 48 h; the reactor scale assays were performed at 15% solids loading, 7 FPU/g DM, pH 4.8, 50 °C, 150 rpm in the 250 mL

albumin (BSA) for making standard protein curve [17]. All the assays were performed in triplicates and the average data were presented.

2.7. Analysis of the compositions of virgin corn stover

The compositions of virgin corn stover were analyzed using ANKOM 200 Cellulose Analyzer (ANKOM Technology, Macedon, NY, USA) [14]. The original corn stover contained $45.09 \pm 0.08\%$ glucan, $31.74 \pm 0.18\%$ xylan, $5.15 \pm 0.34\%$ acid-insoluble lignin, and $4.98 \pm 0.28\%$ ash. All the above data were calculated on the dry solid matter.

2.8. Yield and selectivity calculations

The glucose and xylose yields were calculated using the following equations [18]:

$$\text{Glucose yield}(\%) = \frac{[Glu] \times V}{f \times [\text{Biomass}] \times m \times 1.111} \times 100\%$$

$$\text{Xylose yield}(\%) = \frac{[Xyl] \times V}{h \times [\text{Biomass}] \times m \times 1.136} \times 100\%$$

where $[Glu]$ and $[Xyl]$ were the glucose and xylose concentration at the end of the hydrolysis (g/L), respectively; V was the final liquid volume of the hydrolysis system (L); f was the cellulose content in corn stover (g/g); h was the hemicellulose content in corn stover (g/g); [Biomass] was the solids loading of corn stover in the enzymatic hydrolysis system (%, w/w); m was the total weight of the hydrolysis system (g).

The polyols yield based on sugars was calculated used the following equation:

$$\text{Polyols yield} = \frac{[\text{polyols}]}{[Glu]_1 + [Xyl]_1} \times 100\%$$

where [Polyols] was the sum of short-chain polyols concentration (g/L), including ethanediol, 1,2-propanediol and butanediol in the reaction broth; $[Glu]_1$ and $[Xyl]_1$ were the glucose and xylose concentration in the original reaction broth (g/L), respectively.

The product selectivity was calculated as follows:

$$\text{Product selectivity} = \frac{[\text{Product}]}{[\text{Hydrogenolysis products}]} \times 100\%$$

where [Product] was the concentration of a certain product (g/L), e.g., ethanediol, or 1,2-propanediol in the reaction broth; the [Hydrogenolysis products] was the total products concentration in the reaction broth (g/L).

3. Results and discussion

3.1. Stover sugars preparation by dry dilute acid pretreatment and enzymatic hydrolysis

The three key parameters, solids loadings, enzyme dosages, and the reactor scales, were selected for optimization to obtain the minimum cost of stover sugar preparation as shown in Fig. 2. The data in Fig. 2(a) shows that the production of total sugars (glucose and xylose) increased substantially with increasing solids loading from 5% to 20% (w/w), while the glucose yield and xylose yield decreased slightly. Fig. 2(b) shows that the more cellulase used, the higher sugar concentration and sugar yields were obtained, but only a minor increment of both sugar yield and concentration was obtained when the enzyme dosage was

flasks in a rotary water bath (lasted for 48 h), 5 L and 50 L helical stirring bioreactors (lasted for 72 h), respectively [19].

further increased from 15 FPU/g DM to 20 FPU/g DM. Fig. 2(c) shows that glucose yield and the total sugars in 5 L and 50 L reactors were similar, and both were higher comparing to that in 250 mL flasks, indicating that the scale-up effect could be reasonably ignored at least to the 50 L scale. Although the enzymatic hydrolysis conditions were kept the same while conducted at 0.25 L flasks, 5 L and 50 L bioreactors, the mixing and mass transfer demonstrated a better performance in the helical stirring bioreactor than in the flasks [19]. This might be the major reason for the difference in sugars yield between flasks and helical stirring bioreactors. And in the helical agitated bioreactors at different scales, 5 L and 50 L, the different hydrolysis yield should come from the difference of mass transfer in the forms of mixing efficiency, shear stress on enzymes, and fluid velocity distributions originated form the different helical ribbon sizes.

The preliminary cost estimation of stover sugars was calculated by considering the costs of feedstock (corn stover), sulfuric acid, cellulase enzyme, steam used in the pretreatment and in the sugar concentrating, the conditioning cost in terms of the sodium hydroxide used, as well as the purification costs. The method and the results are shown in Supplementary Materials. The target concentration of the stover sugars was 400 g/L to meet the requirement of hydrogenolysis by Raney nickel catalyst #12-2. The results show that the minimum cost of producing 1 t of stover sugar hydrolysate at 400 g/L was approximately $255.5 at 7.0 FPU/g DM and 15% solids loading for 72 h hydrolysis. The cost of stover sugars was close to that of the corn-based glucose with the same concentration (400 g/L) around $180–240 per ton [20]. In addition, there is still a large space for decreasing the production cost of stover sugars by the means of on-site cellulase production, supplementation of accessory enzymes etc. [21,22].

3.2. Purification of stover sugar hydrolysate used for hydrogenolysis

The stover sugar hydrolysate contained various impurities, including fine solid particles, degradation compounds (acetic acid, furfural, 5-hydromethylfurfural, phenol derivatives etc.), sodium sulfate salt from neutralization of sulfuric acid, and cellulase enzyme residues. These impurities would significantly reduce the activity and life time of nickel catalyst in the consequent hydrogenolysis of sugars into polyols [23,24], unless an extensive purification step was processed. Similar purification procedures used for the corn-based glucose preparation were applied to the stover sugar hydrolysate, including the two major steps: decolorization and desalting.

In the first purification step, the hydrolysate was adsorbed by activated charcoal to remove the pigmented impurities which gave the hydrolysate dark black color. Addition of activated charcoal at 3% (w/w) dosage was found to be sufficient to remove the pigmented impurities. Table 1 shows that all furfural and most 5-hydroxymethylfurfural were removed from the hydrolysate, while the sugars and organic acids maintained the same or even increased slightly due to the water loss. The results were in agreement with the previous studies [25,26]. It is worth noting that the protein content in the hydrolysate was not detected after

decolorization, indicating that the cellulase enzyme protein in the hydrolysate was completely removed by the activated charcoal.

In the second purification step, the Na_2SO_4 and other salts in the decolorized stover sugar hydrolysate were removed by ion exchange absorption in two steps: the positive ions such as Na^+ were removed by the cation resins 732, and then the negative ions such as SO_4^{2-} were removed by anion resins D315, respectively. Fig. 3(a) shows that the conductivity of the hydrolysate elute increased quickly in the first 2 min of cation ions exchange, indicating the exchanging of positive ions in the hydrolysate with hydrogen ions on resins started. The hydrolysate conductivity was maintained at a higher value (44,000 μS/cm) until the resins were saturated by the ions such as Na^+. Then the hydrolysate was sent for anion ion exchange using the resin D315 to remove negative ions such as SO_4^{2-}. Fig. 3(b) shows that the conductivity of the stover sugar hydrolysate decreased sharply from 44,000 μS/cm to 4000 μS/cm, indicating the negative ions such as SO_4^{2-} were sufficiently absorbed by D315 resins.

No apparent change of the sugar concentrations (glucose and xylose) between the purified and the original hydrolysates, implying that the sugar loss was negligible during the purification steps.

3.3. Short-chain polyols synthesis by catalytic hydrogenolysis of stover sugars

The catalytic hydrogenolysis of stover sugars for short-chain polyols synthesis was conducted as shown in Table 2. The polyols product here refers to ethanediol, 1,2-propanediol, and butanediol. The byproducts in the hydrogenolysis included formate, acetate, lactate, and glycerol etc. The results show that the polyols yield using the untreated original stover sugars was only 34.42%. The polyols yield increased to 58.54% after the stover suagar hydrolysate was decolorized, and to 67.22% after the hydrolysate was decolorized and desalted, which was close to that using corn-based glucose (71.42%). The results indicate that the two purification steps were important for keeping a high polyols yield when the stover sugars were used as the feedstock.

Fig. 4 shows the recycling of the Raney nickel catalyst #12-2 using different sugar feedstocks. The activity of the catalyst maintained stable with respect to polyols yield in the four successive runs when the corn-based glucose was used. When the original stover sugars were used, the polyols yield decreased sharply with only twice recycling of the catalyst, indicating the purification of stover sugar hydrolysate was absolutely necessary to keep the expensive catalyst to maintain a high catalytic activity. When the stover sugars were purified by decolorization, the activity of the nickel catalyst maintained stable in the three successive runs of hydrogenolysis, but the polyols yield was pretty lower. When the stover sugars were purified by both delocorization and desalting, the polyols yield was maintained at high level in the four successive runs.

The mixtures of the short-chain polyols could be obtained by vacuum distillation and then directly used as precursors for synthesizing the unsaturated polyester resins with a relative low value added. Alternatively, the hydrogenolysis products could be

Table 1
Effect of decolorization with activated charcoal powders on the stover sugar hydrolysate compostion.

Stover sugars hydrolysate	Glucose (g/L)	Xylose (g/L)	Acetate (g/L)	Levulic acid (g/L)	HMF (g/L)	Furfural (g/L)	Proteins (μg/mL)
Original	53.87	18.18	3.10	0.54	0.33	1.50	83.05
Control	57.12 ± 1.29	20.91 ± 0.76	3.21 ± 0.12	0.68 ± 0.06	0.30 ± 0.03	1.27 ± 0.15	84.80 ± 0.12
Decolorized	56.78 ± 1.46	21.04 ± 0.52	2.68 ± 0.21	1.03 ± 0.14	0.07 ± 0.01	0	0

Conditions: The stover sugar hydrolysate was mixed vigorously with 3% (w/w) dosage of activated charcoal powders at 80 °C for 30 min in the water bath, then the charcoal was separated by plate press and the decolorized hydrolysate was obtained. The control was conducted without activated charcoal supplementation but undergone the same procedure.
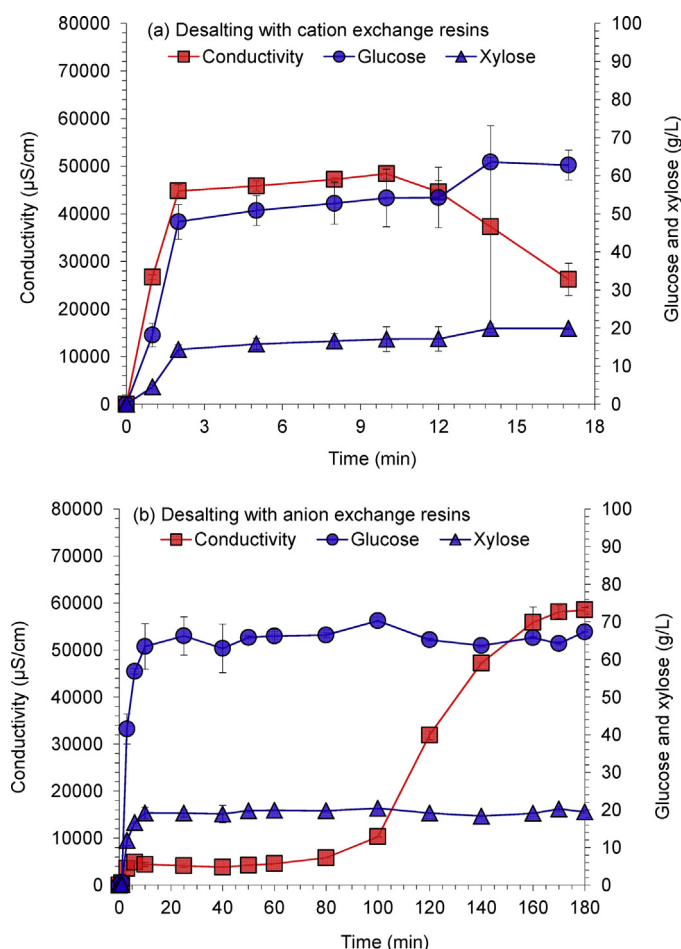
Fig. 3. Desalting of the stover sugar hydrolysate with cation and anion exchange resins. (a) Desalting with cation exchange resins to remove Na$^+$; (b) desalting with anion exchange resins to remove SO$_4^{2-}$.

Fig. 4. Catalytic stability of Raney nickel catalysts #12-2 during recycling in the hydrogenolysis reactions. The hydrogenolysis condition of the stover sugars was the same as that described detailedly in Table 1 except the nickel catalysts were reused by centrifugation after each batch operation. There was no fresh catalysts supplementation in the next round hydrogenolysis operation.

fractionated into different pure ingredients with high value added applications.

The pigmented compounds (mostly in the form of lignin sulfonate salts) and the enzyme proteins in the stover sugar hydrolysate tend to deposit on the surface of the catalyst particles and inhibit its activity [24,27]. The results in Tables 1 and 2 show that the decolorization step by activated charcoal adsorbed most of the pigmented substances and proteins, and led to the significant increase of polyols yield.

The ionic strength of the reaction system significantly affects the catalyst structure and activity [23,24,28]. The ions in the
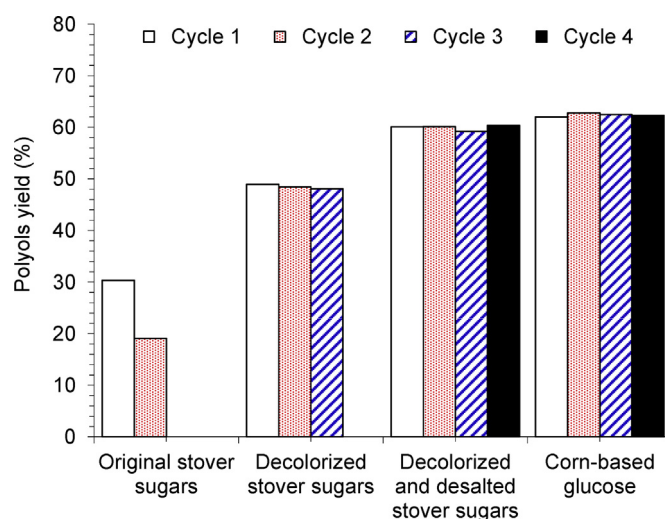
hydrolysate included the cation metal ions such as Fe^{2+}, Na$^+$, Ca^{2+}, Mg^{2+} etc., and the anion ions such as SO$_4^{2-}$, Cl$^-$ etc. The sulfate salts from the pretreatment tend to absorb to the metal surface and then poison the catalyst irreversibly [28]. Desalting step by exchange resins removed most cation and anion ions effectively, thus the ionic strength of the hydrolysate was significantly decreased. The catalytic efficiency of the nickel catalysts was greatly improved accordingly.

The Raney nickel catalyst belongs to a commonly used catalyst for hydrogenation of glucose, xylose, furfural etc., with the similar ingredients but different preparations as reviewed in details by [29]. Some kinds of Raney nickel catalysts are commercially available and can be bought from Merk KGaA (Darmstadt, Germany) or other related companies [30,31]. Some modifications, such as impregnating the Raney nickel with heteropolyacid salts, particularly Cu$_{3/2}$PMo$_{12}$O$_{40}$ could greatly enhance its catalytic activity [29,30]. The other catalysts, such as the copper catalysts or the ruthenium and rhodium catalysts or others, with high selectivity and catalytic performance should be tested for hydrogenolysis of the lignocellulose-derived sugars in the following research [4].

Currently, cellulosic ethanol is considered a model product of lignocellulose biorefinery [32]. However, two major barriers still exist for commercialization of cellulosic ethanol [33,34]. One is the

Table 2
Short-chain polyols production using different sugars.

Sugars	Hydrogenolysis selectivity (%, w/w)								Polyols yield (%)
	Polyols			Byproducts					
	Ethanediol	1,2-Propanediol	Butanediol	Glycerol	Sorbitol	Formate	Acetate	Lactate	
Corn-based glucose	18.15 ± 0.06	38.33 ± 0.00	11.06 ± 0.01	9.56 ± 0.01	0.18 ± 0.00	18.85 ± 0.03	2.45 ± 0.03	1.55 ± 0.04	71.42 ± 0.12
Original stover sugars	9.19 ± 1.22	26.52 ± 3.95	7.80 ± 0.88	15.08 ± 0.99	2.38 ± 0.37	23.57 ± 1.88	10.75 ± 2.17	4.75 ± 0.65	34.42 ± 5.79
Decolorized stover sugars	14.99 ± 0.05	34.93 ± 0.30	10.60 ± 0.01	12.28 ± 0.08	0.55 ± 0.02	18.20 ± 0.17	5.54 ± 0.10	3.96 ± 0.01	58.54 ± 0.17
Decolorized and desalted stover sugars	16.70 ± 0.10	35.84 ± 0.12	11.02 ± 0.05	7.53 ± 0.17	0.24 ± 0.00	24.12 ± 0.29	2.66 ± 0.01	1.81 ± 0.05	67.22 ± 0.04

Conditions: Glucose concentration in the corn-based glucose solution was 350 g/L. The glucose and xylose concentration in the original stover sugars, the decolorized stover sugars, and the decolorized and desalted stover sugars were approximately the same, about 229 g/L and 86 g/L, respectively. But the loss of the sugars in the residues retained in the activated charcoals in the desalting fibers and the resins in the desalting column were not considered. Chemical hydrogenolysis of the stover sugar hydrolysate was operated at 230 °C, 11.0 MPa, 10,000 rpm for 120 min in the reactor with a reaction volume of 500 mL.

inhibition to ethanol fermenting strains by toxic compounds derived from the harsh pretreatment, such as the acetic acid, furfural and 5-hydroxymethylfurfural [35]. The other is low efficiency of xylose conversion to ethanol [34]. In contrast, these two barriers were simply avoided in the present cellulosic polyols production process: the inhibitors were efficiently removed by the two-step purification of decolorization and desalting, and the xylose was easily hydrogenolyzed into short-chain polyols simultaneously with glucose by Raney nickel catalyst [36].

4. Conclusion

A combinational process of enzymatic hydrolysis and catalytic hydrogenolysis for short-chain polyols production from corn stover was developed in this study. The results show that the production cost of stover sugars via enzymatic hydrolysis was competitive to the corn based glucose. The purification processes used for corn-based glucose worked well with stover sugars and the short-chain polyols yield from hydrogenolysis of 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.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.btre.2014.05.010.

References

[1] T.Y. Deng, J.Y. Sun, H.C. Liu, Cellulose conversion to polyols on supported Ru catalysts in aqueous basic solution, Sci. China Ser. B 53 (2010) 1476–1480.
[2] G.W. Huber, S. Ibarra, A. Corma, Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering, Chem. Rev. 106 (2006) 4044–4098.
[3] S.U. Lee, K. Jung, G.W. Park, Bioprocess aspects of fuels and chemicals from biomass, Korean J. Chem. Eng. 29 (2012) 831–850.
[4] A.M. Ruppert, K. Weinberg, R. Palkovits, Hydrogenolysis goes bio: from carbohydratesand sugar alcohols to platform chemicals, Angew. Chem. Int. Ed. 51 (2012) 2564–2601.
[5] H. Yim, R. Haselbeck, W. Niu, Metabolic engineering of Escherichia coli for direct production of 1,4-butanediol, Nat. Chem. Biol. 7 (2011) 445–452.
[6] Emptage, M., Haynie, S.L., Laffend, L.A., Pucci, J.P., Whited, G., 2003. Process for the biological production of 1,3-propanediol with high titer. United States Patent, No. 6514733.
[7] Laffend, L.A., Nagarajan, V., Nakamura, C.E., 1997. Bioconversion of a fermentable carbon source to 1,3-propanediol by a single microorganism. United States Patent, No. 5686276.
[8] L. Ge, X.M. Wu, J.W. Chen, J.L. Wu, A new method for industrial production of 2,3-butanediol, J. Biomater. Nanobiotechnol. 2 (2011) 335–336.
[9] J. Zhang, X.S. Wang, D.Q. Chu, Y.Q. He, J. Bao, Dry pretreatment of lignocellulose with extremely low steam and water usage for bioethanol production, Bioresour. Technol. 102 (2011) 4480–4488.
[10] Y.Q. He, L.P. Zhang, J. Zhang, et al., Helically agitated mixing in dry dilute acid pretreatment enhances the bioconversion of corn stover into ethanol, Biotechnol. Biofuels 7 (1) (2014).
[11] B. Adney, J. Baker, Measurement of Cellulase Activities, National Renewable Energy Laboratory, Golden, CO, 1996 LAP-006.
[12] D.Q. Chu, H.B. Deng, X.X. Zhang, J. Zhang, J. Bao, A simplified filter paper assay method of cellulase enzymes based on HPLC analysis, Appl. Biochem. Biotechnol. 167 (2012) 190–196.
[13] J. Zhang, Z.H. Fang, H.B. Deng, X.X. Zhang, J. Bao, Cost analysis of cassava cellulose utilization scenarios for ethanol production on flowsheet simulation platform, Bioresour. Technol. 134 (2013) 298–306.
[14] K. Zhao, Q.A. Qiao, D.Q. Chu, H.Q. Gu, T.H. Dao, J. Zhang, J. Bao, Simultaneous saccharification and high titer lactic acid fermentation of corn stover using a newly isolated lactic acid bacterium Pediococcus acidilactici DQ2, Bioresour. Technol. 135 (2013) 481–489.
[15] S.Y. Leu, J.Y. Zhu, Substrate-related factors affecting enzymatic saccharification of lignocelluloses: our recent understanding, Bioenergy Res. 6 (2013) 405–415.
[16] D. Rana, V. Rana, B.K. Ahring, Producing high sugar concentrations from loblolly pine using wet explosion pretreatment, Bioresour. Technol. 121 (2012) 61–67.
[17] M.M. Bradford, A rapid and sensitive method for the quantification of microgram quantities of protein utilizing the principle of protein dye binding, Anal. Biochem. 72 (1976) 248–254.
[18] L. Brown, R. Torget, Enzymatic Saccharification of Lignocellulosic Biomass, National Renewable Energy Laboratory, Golden, CO, 1996 LAP-009.
[19] J. Zhang, D.Q. Chu, J. Huang, et al., Simultaneous saccharification and ethanol fermentation at high corn stover solids loading in a helical stirring bioreactor, Biotechnol. Bioeng. 105 (2010) 718–728.
[20] H. Kobayashi, A. Fukuoka, Synthesis and utilization of sugars compounds derived from lignocellulosic biomass, Green Chem. 15 (2013) 1740–1763.
[21] J. Larsen, M.O. Petersen, L. Thirup, et al., The IBUS process-lignocellulosic bioethanol close to a commercial reality, Chem. Eng. Technol. 31 (2008) 765–772.
[22] J.G. Hu, V. Arantes, A. Pribowo, et al., The synergistic action of accessory enzymes enhances the hydrolytic potential of a "cellulase mixture" but is highly substrate specific, Biotechnol. Biofuels 6 (112) (2013).
[23] Y.C. Lin, G.W. Huber, The critical role of heterogeneous catalysis in lignocellulosic biomass conversion, Energy Environ. Sci. 2 (2009) 68–80.
[24] M. Besson, P. Gallezot, Deactivation of metal catalysts in liquid phase organic reactions, Catal. Today 81 (2003) 547–559.
[25] G.B.M. Carvalho, S.I. Mussatto, E.J. Candido, J.B.A. e Silva, Comparison of different procedures for the detoxification of eucalyptus hemicellulosic hydrolysate for use in fermentative processes, J. Chem. Technol. Biotechnol. 81 (2006) 152–157.
[26] A.C. Schirmer-Michel, S.H. Flores, P.F. Hertz, et al., Production of ethanol from soybean hull hydrolysate by osmotolerant Candida guilliermondii NRRL Y-2075, Bioresour. Technol. 99 (2008) 2898–2904.
[27] T. Mallat, A. Baiker, L. Botz, Liquid-phase oxidation of 1-methoxy-2-propanol with air III: chemical deactivation and oxygen poisoning of platinum catalysts, Appl. Catal. A 86 (1992) 147–163.
[28] B.J. Arena, Deactivation of ruthenium catalysts in continuous glucose hydrogenation, Appl. Catal. A 87 (1992) 219–229.
[29] P. Gallezot, Conversion of biomass to selected chemical products, Chem. Soc. Rev. 41 (2012) 1538–1558.
[30] B.J. Liu, L.H. Lu, B.C. Wang, T.X. Cai, I. Katsuyoshi, Liquid phase selective hydrogenation of furfural on Raney nickel modified by impregnation of salts of heteropolyacids, Appl. Catal. A 171 (1998) 117–122.
[31] H.L. Hoggun, M. Yildiz, H.F. Gercel, Hydrogenolysis of aqueous glycerol over Raney nickel catalyst comparison of pure and biodiesel by-product, Ind. Eng. Chem. Res. 51 (2012) 3863–3869.
[32] C. Schubert, Can biofuels finally take center stage? Nat. Biotechnol. 24 (2006) 777–784.
[33] C.A. Cardona, O.J. Sanchez, Fuel ethanol production: process design trends and integration opportunities, Bioresour. Technol. 98 (2007) 2415–2457.
[34] T. Hasunuma, A. Kondo, Development of yeast cell factories for consolidated bioprocessing of lignocellulose to bioethanol through cell surface engineering, Biotechnol. Adv. 30 (2012) 1207–1218.
[35] Y. Kim, E. Ximenes, N.S. Mosier, et al., Soluble inhibitors/deactivators of cellulase enzymes from lignocellulosic biomass, Enzyme Microb. Technol. 48 (2011) 408–415.
[36] Werpy, T.A., Frye, J.G., Zacher, A.H. et al., 2005. Hydrogenolysis of 6-carbon sugars and other organic compounds. United States Patent, No. 6841085B2.