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Comprehensive Utilization of Hemicellulose and Cellulose To Release Fermentable Sugars from Corncobs via Acid Hydrolysis and Fast Pyrolysis

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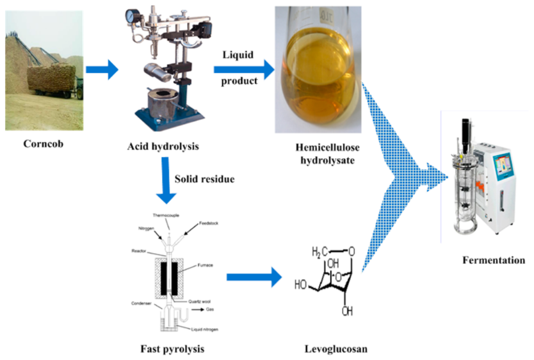
Supporting Information

ABSTRACT: Conversion of lignocellulose to sugars suitable for microbial fermentation is an outstanding obstacle in developing biorefinery. Both hemicellulose and cellulose fractions are polymers of sugars and thereby primary candidates for fermentable sugars production. In this study, the flexibility of an integrated biomass conversion process was offered. The hemicellulose of corncobs was utilized to release fermentable sugars by sulfuric acid hydrolysis first. The remaining solid residue from acid hydrolysis, containing a lot of cellulose, was further used to produce levoglucosan by fast pyrolysis. This process appeared to present several advantages: (i) Almost all of hemicellulose (99.7%) was hydrolyzed, and the yield of xylan was achieved 86.1%. (ii) The alkali and alkaline earth metals, which had negative catalytic influence on levoglucosan formation, were nearly and completely (93.7%) removed by acid pretreatment. (iii) A preferential degradation of hemicellulose and amorphous cellulose during acid hydrolysis resulted in accumulation of crystalline cellulose of acid-pretreated biomass, which was favorable for levoglucosan production. (iv) The yield of levoglucosan increased by 450.0% for acid-pretreated corncobs (37.4%) compared with that of raw material (6.8%). The effectiveness to enhance levoglucosan yields ranged as high as 63.4%. Further increase in sulfuric acid concentration (0−10%) and temperature (30−120 °C) in acid pretreatment prior to fast pyrolysis could enhance levoglucosan formation. Consequently, this strategy, which utilized simple chemical regents to overcome biomass recalcitrance and liberate fermentable sugars while also remaining cost-effective, has the potential to underlie a biorefinery.



KEYWORDS: *Hemicellulose, Cellulose, Acid hydrolysis, Fast pyrolysis, Levoglucosan*

■ INTRODUCTION

Biomass fast pyrolysis is a thermal decomposition process, which is a promising alternative for biomass transformation to derived products.[1,2] Compared with enzymatic saccharification and acid hydrolysis, the information on fast pyrolysis for fermentable sugars production from lignocellulose is limited. During cellulose pyrolysis, 1,6-anhydro-β-D-glucopyranose, known as levoglucosan, is one vital primary product, either as a product or as a intermediate for the formation of other products.[2−4] Previous researches have proven that after being phosphorylated to glucose 6-phosphate by levoglucosan kinase, levoglucosan can be metabolized via the pathway of glycolysis.[5] Levoglucosan can be offered as feedstock for microorganism fermentation. *Aspergillus niger* CBX-209 and *Aspergillus terreus* K26 were good candidates to produce citric acid and itaconic acid from levoglucosan at the same rate and with the same yield as produced from glucose.[6,7] Oleaginous yeasts *Rhodosporidium toruloides*, *Rhodotorula glutinis*, and *Rhodococcus jostii* RHA1 could convert levoglucosan to lipid production with high yield.[8,9] *Escherichia coli* KO11 was modified genetically and could ferment levoglucosan to ethanol.[10] Previous studies have indicated that levoglucosan present in bio-oil could be separated, hydrolyzed, detoxified, and used as substrate for fermentation to lipids or ethanol.[11,12] Furthermore, bio-oil contains a high concentration of levoglucosan (upward 33%), which is beneficial for subsequent fermentation. From the

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economical perspective, the technology of fast pyrolysis to release a large number of fermentable sugars without catalysts and enzymes in a short time shows a significant advantage. The economic analysis was performed for three biomass-to-ethanol conversion technologies: dilute sulfuric acid hydrolysis integrated with a fermentation process, simultaneous enzymatic hydrolysis and fermentation, and fast pyrolysis and fermentation.[13] Fast pyrolysis coupled with a fermentation process was comparable with the other two technologies.[13] Hence, biomass fast pyrolysis to obtain fermentable sugars should be considered for further development.

Potential drawbacks of this conversion technology include sugar yields remaining for fast pyrolysis implementation. Levoglucosan yields from pure cellulose by fast pyrolysis have been reported as high as 60%.[14,15] However, the yield of levoglucosan from lignocellulose is low, approximately 5%.[16] High levoglucosan yields are desirable from lignocellulose.[17] Through combination of pretreatment and pyrolysis, the yield of levoglucosan from lignocellulose is comparable to that from pure cellulose. Dilute acid hydrolysis, hot water washing, and glycerol pretreatments prior to lignocellulose fast pyrolysis have been investigated to increase levoglucosan yields.[18,19] Due to demineralization, dilute acid pretreatment is an effective route to improve levoglucosan yield. Although the advantages of acid pretreatment have been demonstrated for increasing levoglucosan yields, operating parameters such as acid concentration, temperature, and time of pretreatment have yet to be investigated. Herein, this work describes the integration of acid pretreatment with fast pyrolysis for the production of fermentable sugars from corncobs.

■ EXPERIMENTAL SECTION

Materials. Corncobs were collected from Tianjin province (China) and the ground. Particle size was measured as 80 mesh. Feedstock was air-dried at 105 °C for 12 h. Sulfuric acid was obtained from Chuandong Chemical Co., Ltd., Chongqing. Standard reagents, including acetic acid, levoglucosan, 5-hydroxymethylfurfural (5-HMF), furfural, glucose, xylose, arabinose, galactose, and mannose, were bought from Sigma-Aldrich (Shanghai).

Elemental Analysis. The contents of organic elements, including C, H, N, and S, were determined by a Vario EL (Hanau, Germany). The contents of alkali and alkaline earth metals (AAEMs), including K, Na, Ca, and Mg, were measured by inductively coupled plasma-optical emission spectrometry (ICP-OES) (Optima 8000, PerkinElmer, USA).

Compositional Analysis. The components of corncobs were measured according to the analytical procedure of the National Renewable Energy Laboratory (NREL).[20] Briefly, via a two-step acid hydrolysis, the lignocellulose was hydrolyzed by concentrated sulfuric acid (72%) at 30 °C for 1 h and subsequently by dilute sulfuric acid (4%) for 1 h. The liquid and solid samples of the acid hydrolysate were separated by filtration. The filtrated was neutralized to pH 7 by $Ca(OH)_2$. High performance liquid chromatography (HPLC, Waters 2695) equipped with an Aminex HPX-87P column (Bio-Rad, USA) and a refractive index (RI) detector were utilized to analysis monosaccharides (xylose, galactose, arabinose, mannose, and glucose). The temperatures of oven and detector were 80 and 50 °C, respectively. Deionized water was used as the mobile phase with a flow rate of 0.4 mL/min. The content of glucan was calculated as a cellulose fraction. The sum content of galactan, arabinan, mannan, and xylan was calculated as a hemicellulose fraction. The acid-soluble lignin of corncobs was tested by an ultraviolet−visible (UV−vis) spectrometer at 320 nm (Lambda 750, USA). Acid insoluble lignin was calculated by the difference in weight loss. The content of the ash was obtained by oxidation of solid residue in a muffle furnace (575 °C).

Thermogravimetric Measurement. The thermal properties of biomass samples were examined by a thermogravimetric analyzer (TGAQ50, TA, USA). In the thermogravimetric analysis, the biomass was heated from 50 to 750 °C at a constant heating rate of 20 °C/min, then held at 750 °C for 40 min. A nitrogen atmosphere (20 mL/min) was utilized to study the pyrolytic decomposition of biomass.

Crystallinity Measurement. The X-ray diffraction (XRD) patterns were obtained by an X-ray diffractmeter (PANalytical B.V., The Netherlands) through scanning from 5° to 40° with a step of 0.02° with Cu Kα radiation (λ = 0.15406). The crystallinity index (CrI) was determined by taking a ratio between the intensity of crystalline cellulose and total intensity, which was shown as the empirical equation:

$$\mathrm{CrI}(\%) = \frac{I_{\mathrm{Cr}} - I_{\mathrm{Am}}}{I_{\mathrm{Cr}}} \times 100\% \tag{1}$$

where I_{Cr} is the peak area of crystlline and amorphous cellulose, and I_{Am} represents the peak area of amorphous cellulose.[21]

Acid Hydrolysis. For a typical procedure, corncobs (3 g) and 30 mL of 1−10 wt % sulfuric acid solution were loaded in 100 mL flasks. The flasks were placed in a rotary shaker-agitated water bath and high pressure autoclave (HKY-3, Haian Petroleum Research Co., Ltd., Jiangsu, China) to react at 30, 75, and 120 °C for 1 h, respectively. Then, the liquid hydrolysate and solid residue from acid hydrolysis were filtered for separation. The solid residue was washed repeatedly by deionized water until neutrality, then dried for 24 h in a freeze-dryer (Boyikang Co., Ltd., Beijing). All supernatants were collected and analyzed for sugars released from acid hydrolysis. HPLC was utilized to determine the concentration of monomeric sugars, acetic acid, furfural, and 5-HMF in acid hydrolysate. A Bio-Rad column (Aminex HPX-87H, USA) and 5 mM sulfuric acid as the mobile phase were used to separate furfural, 5-HMF, and acetic acid. The column temperature was maintained at 60 °C, and the flow rate of the mobile phase was set at 0.6 mL/min. Furfural and 5-HMF were measured by a UV detector (280 nm), while acetic acid was determined by an RI detector. All samples were carried out in triplicate. The recovery rate, xylose yield, and glucose yield were calculated using the following equations:

$$\text{Recovery rate(wt\%)} = \frac{\text{mass of pretreated lignocellulose(g)}}{\text{mass of initial lignocellulose(g)}} \times 100\% \tag{2}$$

$$\text{Xylose yield(wt\%)} = \frac{\text{mass of xylose in acid hydrolysate(g)}}{\text{mass of hemicellulose(g)}} \times 0.88 \times 100\% \tag{3}$$

$$\text{Glucose yield(wt\%)} = \frac{\text{mass of glucose in acid hydrolysate(g)}}{\text{mass of cellulose(g)}} \times 0.90 \times 100\% \tag{4}$$

Fast Pyrolysis. Fast pyrolysis of untreated and acid-pretreated corncobs were performed in a CDS Pyroprobe 5200 pyrolyser (CDS Analytical, USA). A microbalance (XP6152, Mettler Toledo, Germany) with an accuracy of 1 μg was utilized for biomass weighing. Some quartz wool and 200−400 μg of biomass were filled in a pyrolysis tube, and quartz wool was placed at both sides of the biomass. The pyrolysis temperature was performed at 500 °C with a heating rate of 10 K ms^{-1} and residence of 20 s. The compounds of biomass fast pyrolysis were measured by gas chromatography (Agilent 7890A) and mass spectrometry (Agilent 5975C). The injector temperature was maintained at 240 °C. Helium was utilized as the mobile phase at a flow rate of 1 mL/min. The split ration was set at 1:50. An HP-INNO wax capillary column (30 m × 0.25 mm × 0.25 μm) was used for the separation of pyrolysis products. The oven temperature was programmed from 50 °C (2 min) to 90 °C with a heating rate of 10 °C/min, and then to 230 °C (29 min) with a heating rate of 8 °C/min. The mass spectrometer was obtained from *m*/*z* 12 to 500 and under a total ion current (TIC) mode. The chromatographic peaks were identified based on the NIST mass spectral data library and comparing the retention times to pure standards of different compounds. The compounds were quantified by authentic standards. The compound yield and effectiveness were calculated as:

$$\text{Yield of compound(wt\%)} = \frac{\text{mass of compound(g)}}{\text{mass of lignocellulose(g)}} \times 100\% \tag{5}$$

$$\text{Effectiveness(\%)} = \frac{\text{actual levoglucosan yield}}{\text{potential yield}} \times 100\% \tag{6}$$

RESULTS AND DISCUSSION

Components Analysis of Acid Hydrolysate. Various temperatures, ranging from 30 to 120 °C, and acid concentrations, varying from 1% to 10%, were tested for corncob pretreatment. After acid pretreatment, the recovery rate of the pretreated biomass was determined as presented in Table 1. The recovery rate was affected by reaction temperature and acid concentration. With an increase in temperature (120 °C) and acid concentration (10%), the recovery rate was reduced from 92.6% to 48.6%. The chemical components of untreated and dilute acid-pretreated corncobs are presented in Table 1. The untreated material contained 30.2% hemicellulose, 35.3% cellulose, and 15.3% lignin. The pretreated material (30−1%) contained 32.7% hemicellulose, 38.2% cellulose, and 15.8% lignin. With the removal of the water-soluble fraction, the contents of hemicellulose, cellulose, and lignin in corncobs were increased. However, the decrease in hemicellulose content was noticed when using 10% acid at 75 °C. The concentration of glucose, xylose, arabinose, acetic acid, furfural, and 5-HMF were analyzed as presented in Table 2. Xylose was the main product of hemicellulose acid hydrolysate. An increase in the acid concentration or temperature of pretreatment could increase xylose concentration. The hemicellulose content was diminished to 4.9% after pretreatment at 120 °C by 1% acid. The xylose hydrolysis yield was increased from 0.3% to 86.1%. However, the xylose concentration and the xylose hydrolysis yield were 21.2 g/L and 70.2% after 10% acid pretreatment at 120 °C. In acid hydrolysis, hemicellulose was hydrolyzed to monosaccharides, and the sugars were further degraded to form other products, which were not suitable for fermentation.[22] The most common degradation products are 5-HMF for hexose sugars and furfural for pentose sugars. The concentrations of acetic acid, furfural, and 5-HMF increased as a function of acid concentration, and reaction temperature increased. When compared to xylose, the glucose concentrations and yields increased. This could be attributed to the fact that hemicellulose and amorphous cellulose were more readily hydrolyzed than crystalline cellulose. The fermentability of hemicellulose acid hydrolysate was evaluated in previous studies, where it was shown as an attractive stream for biofuel and biochemistry production by microorganisms. In this study, corncobs hydrolyzed by 10% acid at 120 °C resulted in the production of a stream that was devoid of 99.7% of the hemicellulose content. Therefore, acid hydrolysis was an effective approach in removing hemicellulose and accumulating the fraction of crystalline cellulose.

Table 1. Components Analysis of Untreated and Acid-Pretreated Corncobs

samples	recovery rate (wt %)	hemicellulose (wt %)	cellulose (wt %)	lignin (wt %)	ash (wt %)
raw material	–	30.2	35.3	15.3	10.5
30−1%	92.6	32.7	38.2	15.8	6.6
30−10%	91.7	32.3	38.5	16.3	6.5
75−1%	83.2	30.5	41.1	17.9	5.7
75−10%	69.6	19.6	50.3	18.6	5.5
120−1%	54.6	4.9	60.8	23.8	3.8
120−10%	48.6	0.1	67.2	24.4	3.3

Elemental Analysis of Untreated and Acid-Pretreated Corncobs. The results of organic elemental and AAEMs analysis of raw and acid-pretreated corncobs are shown in Table 3. The content of C, H, and N changed before and after pretreatments (C: 45.2−47.7%; H: 6.1−6.4%; N: 0.2−0.3%). Biomass contained inorganic impurities, such as AAEMs, that could act as natural catalysts and affect the product distribution. AAEMs consisting of K, Na, Ca, and Mg in pretreated corncobs displayed a lower content than that of the original material. Acid (1%) pretreatment at 30 °C could remove 80.5% of AAEMs. Further removal of AAEMs from corncobs occurred when higher acid concentrations and temperature of pretreatments were used. After 1% and 10% acid pretreatment at 120 °C, the total concentration of AAEMs was reduced by 91.7% and 93.5%, respectively. Previous research indicated that the ash content had a negative influence on bio-oil yield.[23] The presence of AAEMs also resulted in an increase in light oxygenates yield via ring-fragmentation reactions, increasing the char and water yield via dehydration reactions of carbohydrates.[24,25] It had been reported that the presence of NaCl and KCl could be related to a decrease in the production of levoglucosan.[26] Previous research also investigated the catalytic influence of $MgCl_2$ and $CaCl_2$, which promoted char formation while suppressing the levoglucosan formation.[27] Cations, such as Ca^{2+} and Mg^{2+}, promoted the primary production of char from cellulose and the transformation of levoglucosan into light oxygenates and furans.[28] Depolymerization/fragmentation reactions were promoted to produce lower molecular weight oxygenates at the expense of levoglucosan by the catalytic

Table 2. Components Analysis of Acid Hydrolysate

samples	concentration (g/L)						yield (%)	
	xylose	glucose	arabinose	acetic acid	furfural	5-HMF	xylose	glucose
30−1%	ND	ND	ND	0.1	ND	ND	ND	ND
30−10%	0.1	0.1	0.1	0.3	ND	ND	0.3	0.3
75−1%	0.1	0.1	0.4	0.4	ND	ND	0.3	0.3
75−10%	2.7	0.4	1.8	1.3	ND	ND	8.9	1.1
120−1%	26.0	2.2	2.5	2.7	0.2	ND	86.1	6.2
120−10%	21.2	4.0	2.5	4.2	2.2	0.1	70.2	11.3

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Table 3. Elements of Untreated and Acid-Pretreated Corncobs

samples	C (%)	H (%)	N (%)	S (%)	Na (mg/kg)	Ca (mg/kg)	Mg (mg/kg)	total AAEMs (mg/kg)
raw material	45.4	6.3	0.3	0.01	257.8	1479.0	581.4	8959.7
30−1%	45.2	6.3	0.3	ND	102.9	1065.4	411.0	1748.4
30−10%	46.0	6.4	0.3	ND	78.0	900.6	325.0	1438.7
75−1%	46.3	6.3	0.2	ND	130.6	838.4	241.3	1372.2
75−10%	45.7	6.3	0.2	ND	106.3	421.9	185.9	836.9
120−1%	46.1	6.2	0.2	ND	59.3	449.4	110.5	745.7
120−10%	47.7	6.1	0.2	ND	55.6	395.9	63.7	584.6

influence of K.[29] Various concentrations of cations were examined, and the following trends were found in terms of levoglucosan yield in the order of mildest to strongest effect: $Mg^{2+} < Ca^{2+} < Na^+ < K^+$.[30,31] In current research, more than 99.0% K was removed from corncobs by acid pretreatment. Using 10% acid pretreatment at 120 °C, about 78.4% Na, 73.2% Ca, and 89.0% Mg were removed from corncobs. The yield of levoglucosan was impacted by the ash content. It is more than likely that higher levoglucosan yields could be obtained by reducing AAEMs content of feedstock. In this study, most of AAEMs could be removed from corncobs by acid pretreatment.

Crystalline Structure and Thermal Behavior of Acid-Pretreated Corncobs. Figure S1 presents the XRD spectra obtained for untreated and acid-pretreated corncobs. The untreated corncobs had a CrI value of 42.9% (Table 4). Acid pretreatment resulted in an increase in CrI of biomass. The crystallinity of samples increased as a function of acid pretreatment progressed, achieving the highest CrI value of 70.5% in corncobs pretreated by 10% acid at 120 °C. A preferential degradation of hemicellulose, amorphous cellulose, and less ordered crystalline forms were noted during acid hydrolysis, which resulted in accumulation of crystalline cellulose, increasing the CrI of acid-pretreated biomass. The effect of cellulose crystallinity on levoglucosan yield has not been studied extensively. Previous research showed that levoglucosan formation was attributed to crystalline cellulose while amorphous cellulose led to gas and char. Higher crystallinity cellulose tended to obtain higher yield of levoglucosan.[32] In this study, the pretreated samples, which contained more crystalline cellulose with higher crystallinity than raw material, may be favorable for the formation of levoglucosan in fast pyrolysis subsequently. The thermogravimetry (TG) curve and differential TG (DTG) curve are shown in Figure 1. Due to the degradation of hemicelluloses, followed by cellulose, thermal decomposition of lignocellulosic biomass samples showed two distinct peaks in the DTG. After pretreatment by 10% dilute sulfuric acid at 120 °C, the first shoulder at lower temperature disappeared in acid-pretreated corncobs, suggesting that most of the hemicellulose was removed by the pretreatment. Furthermore, the removal of minerals by acid pretreatment could enhance the thermal stability of corncobs. Previous research investigated the catalytic influence of NaCl and KCl, indicating that these elements lowered the initial temperature of lignocellulose degradation.[26] It also had been concluded that $MgCl_2$ promoted dehydration at low temperatures.[33] The catalytic role of K^+ had been researched extensively, and the main influences of K^+ could be summarized as (1) lowering the initial temperature decomposition, (2) decreasing the temperature for maximum degradation, (3) reducing the maximum degradation rate, and (4) increasing the char yield.[34] In this study, the onset of degradation of the acid-pretreated samples was initiated at higher temperatures. The maximum degradation rate of acid-pretreated samples was noted at higher temperatures when compared to that of raw material. The crystalline structure was changed by acid pretreatment, which also had an influence on the thermal decomposition behavior of the biomass. Compared with amorphous cellulose, degradation of crystalline cellulose occurred at higher temperature.

Table 4. Characteristic Parameters of Untreated and Acid-Pretreated Corncobs

	characteristic parameters			
samples	CrI (%)	T_i (°C)	T_{max} (°C)	DTG_{max} (%/min)
raw material	42.9	220.1	307.6	0.9
30−1%	43.4	224.4	337.8	1.0
30−10%	45.1	238.9	336.9	1.0
75−1%	47.3	242.1	330.1	1.0
75−10%	56.8	230.2	343.0	1.2
120−1%	66.2	257.1	345.3	1.5
120−10%	70.5	265.6	348.1	1.6

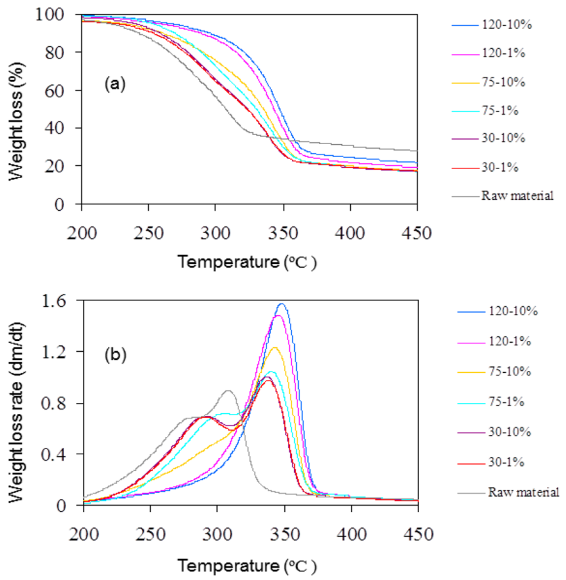

Figure 1. TG and DTG profiles of untreated and acid-pretreated corncobs: (a) TG profile and (b) DTG profile.

Levoglucosan Production from Acid-Pretreated Biomass. Raw material and acid-pretreated corncobs were used to produce levoglucosan. The yields of main products are presented in Table 5. Even under conditions that promoted the depolymerization of cellulose and anhydrosugar over the decomposition of pyranose rings into light oxygenates, levoglucosan reacted further to form char and light oxygenates.

Table 5. Yields of Main Compounds and Effectiveness of Acid-Pretreated Corncobs Fast Pyrolysis[a]

	yield (wt %)					
samples	acetic acid	furfural	5-HMF	levoglucosan	levoglucosan[a]	effectiveness (%)
raw material	7.8	0.8	0.3	2.4	6.8	11.5
30−1%	7.3	0.8	0.5	4.7	12.3	20.8
30−10%	6.9	0.7	0.5	6.0	15.6	26.4
75−1%	4.5	0.6	0.6	10.8	26.3	44.6
75−10%	3.2	0.5	0.7	16.4	32.6	55.3
120−1%	2.5	0.5	0.8	20.9	34.4	58.3
120−10%	1.7	0.4	0.7	25.1	37.4	63.4

[a] Data (%) were based on the cellulose mass of untreated and acid-pretreated corncobs.

Levoglucosan acted as an intermediate for the production of furfural, 5-HMF, hydroxyacetaldehyde, and hydroxyacetone in the cellulose pyrolysis system. The compound of 5-HMF was obtained by initial ring-opening, dehydrative cyclization, and dehydration. Previous research indicated that the main product of 5-HMF decomposition was furfural.[35] The levoglucosan yield was only 2.4% from untreated corncobs. The higher acid concentration (from 1% to 10%) and temperature (from 30 to 120 °C) of acid hydrolysis promoted levoglucosan formation in fast pyrolysis. The yields of levoglucosan and 5-HMF from the acid-pretreated corncobs were higher than those from raw material. However, the yields of acetic acid from the acid-pretreated samples (ranging from 1.7 to 7.3%) were lower than those from the untreated sample (7.8%). The yield of levoglucosan increased by 405.9% for the 1% acid-pretreated sample (34.4%) and increased by 450.0% for the 10% acid-pretreated sample at 120 °C (37.4%) compared with that of the raw material (6.8%). The effectiveness of acid pretreatment prior to fast pyrolysis to improve levoglucosan yields reached as high as 63.4% (Table 5). The yield of levoglucosan was affected by the source of the cellulose and the experimental conditions. This research indicated that acid pretreatment could effectively promote the generation of levoglucosan. The improvement was mainly contributed to the accumulation of crystalline cellulose and removal of AAEMs. Fast pyrolysis was a promising approach to achieve a suitable substrate for fermentation. Cellulose could be converted to levoglucosan through thermal route as currently envisioned for cellulosic biofuels production if the catalytic role of AAEMs could be decreased substantially or eliminated. Additionally, it cannot be ignored that the phenolic compounds derived from fast pyrolysis of lignin have an inhibition effect in subsequent bioconversion. Considerable additional investigation would be required to boost the wide implementation of this technology.

CONCLUSION

In this study, an integration of technology was evaluated for the transformation of hemicellulose and cellulose to fermentable sugars. Most of hemicellulose (99.7%) of corncobs was removed by sulfuric acid hydrolysis, and the xylose yield was reached as high as 86.1%. The solid residual from acid hydrolysis, which was rich in crystalline cellulose and poor in AAEMs, was collected for levoglucosan production by fast pyrolysis. The yield of levoglucosan increased by 405.9% for a 1% acid-pretreated sample (34.4%) and increased by 450.0% for a 10% acid-pretreated sample at 120 °C (37.4%) compared with that of raw material (6.8%). Further increase in sulfuric acid concentration (from 0% to 10%) and temperature (from 30 to 120 °C) in acid pretreatment could favor the formation of levoglucosan. This technology was very attractive to release fermentable sugars from biomass via acid hydrolysis and a fast pyrolysis process as a conversion strategy for biofuels production.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b00561.

XRD analyses of untreated and acid-pretreated corncobs. (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Bridgwater, A. V.; Meier, D.; Radlein, D. An overview of fast pyrolysis of biomass. *Org. Geochem.* **1999**, *30*, 1479−1493.

(2) Wang, Z.; Lu, Q.; Zhu, X. F.; Zhang, Y. Catalytic fast pyrolysis of cellulose to prepare levoglucosenone using sulfated zirconia. *ChemSusChem* **2011**, *4*, 79−84.

(3) Zhang, X. L.; Yang, W. H.; Dong, C. Q. Levoglucosan formation mechanisms during cellulose pyrolysis. *J. Anal. Appl. Pyrolysis* **2013**, *104*, 19−27.

(4) Cao, F.; Schwartz, T. J.; McClelland, D. J.; Krishna, S. H.; Dumesic, J. A.; Huber, G. W. Dehydration of cellulose to levoglucosenone using polar aprotic solvents. *Energy Environ. Sci.* **2015**, *8*, 1808−1815.

(5) Kitamura, Y.; Abe, Y.; Yasui, T. Metabolism of levoglucosan (1,6-anhydro -β-D-glucopyranose) in microorganisms. *Agric. Biol. Chem.* **1991**, *55*, 515−521.

(6) Nakagawa, M.; Sakai, Y.; Yasui, T. Itaconic acid fermentation of levoglucosan. *J. Ferment Technol.* **1984**, *62*, 201−203.

(7) Zhuang, X. L.; Zhang, H. X. Identification, characterization of levoglucosan kinase, and cloning and expression of levoglucosan kinase cDNA from *Aspergillus niger* CBX-209 in *Escherichia coli*. *Protein Expression Purif.* **2002**, *26*, 71−81.

(8) Lian, J. N.; Garcia-Perez, M.; Chen, S. L. Fermentation of levoglucosan with oleaginous yeasts for lipid production. *Bioresour. Technol.* **2013**, *133*, 183−189.

(9) Xiong, X. C.; Lian, J. N.; Yu, X. C.; Garcia-perez, M.; Chen, S. L. Engineering levoglucosan metabolic pathway in *Rhodococcus jostii* RHA1 for lipid production. *J. Ind. Microbiol. Biotechnol.* **2016**, *43*, 1551−1560.

(10) Layton, D. S.; Ajjarapu, A.; Choi, D. W.; Jarboe, L. R. Engineering ethanologenic *Escherichia coli* for levoglucosan utilization. *Bioresour. Technol.* **2011**, *102*, 8318−8322.

(11) Lian, J. N.; Chen, S. L.; Zhou, S.; Wang, Z. H.; O'Fallon, J.; Li, C. Z.; Garcia-Perez, M. Separation, hydrolysis and fermentation of pyrolytic sugars to produce ethanol and lipids. *Bioresour. Technol.* **2010**, *101*, 9688−9699.

(12) Luque, L.; Oudenhoven, S.; Westerhof, R.; van Rossum, G.; Berruti, F.; Kersten, S.; Rehmann, L. Comparison of ethanol production from corn cobs and switchgrass following a pyrolysis-based biorefinery approach. *Biotechnol. Biofuels* **2016**, *9*, 242.

(13) So, K. S.; Brown, R. C. Economic analysis of selected lignocellulose-to- ethanol conversion technologies. *Appl. Biochem. Biotechnol.* **1999**, *79*, 633−640.

(14) Kuzhiyil, N.; Dalluge, D.; Bai, X. L.; Kim, K. H.; Brown, R. C. Pyrolytic sugars fromcellulosic biomass. *ChemSusChem* **2012**, *5*, 2228−2236.

(15) Jiang, L. Q.; Zheng, A. Q.; Zhao, Z. L.; He, F.; Li, H. B.; Wu, N. N. The comparison of obtaining fermentable sugars from cellulose by enzymatic hydrolysis and fast pyrolysis. *Bioresour. Technol.* **2016**, *200*, 8−13.

(16) Carpenter, D.; Westover, T. L.; Czernik, S.; Jablonski, W. Biomass feedstocks for renewable fuel production: a review of the impacts of feedstock and pretreatment on the yield and product distribution of fast pyrolysis bio-oils and vapors. *Green Chem.* **2014**, *16*, 384−406.

(17) Bai, X. L.; Brown, R. C. Modeling the physiochemistry of levoglucosan during cellulose pyrolysis. *J. Anal. Appl. Pyrolysis* **2014**, *105*, 363−368.

(18) Jiang, L. Q.; Zheng, A. Q.; Zhao, Z. L.; He, F.; Li, H. B. Comprehensive utilization of glycerol from sugarcane bagasse pretreatment to fermentation. *Bioresour. Technol.* **2015**, *196*, 194−199.

(19) Zheng, A. Q.; Zhao, K.; Jiang, L. Q.; Zhao, Z. L.; Sun, J. W.; Huang, Z.; Wei, G. Q.; He, F.; Li, H. B. Bridging the gap between pyrolysis and fermentation: improving anhydrosugar production from fast pyrolysis of agriculture and forest residues by microwave assisted organosolv pretreatment. *ACS Sustainable Chem. Eng.* **2016**, *4*, 5033−5040.

(20) Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D.; Crocker, D. *Determination of Structural Carbohydrates and Lignin in Biomass. Laboratory Analytical Procedure*. National Renewable Energy Laboratory, 2008.

(21) Kuo, C. H.; Lee, C. K. Enhancement of enzymatic saccharification of cellulose by cellulose dissolution pretreatments. *Carbohydr. Polym.* **2009**, *77*, 41−46.

(22) Sun, S. L.; Chen, W. J.; Tang, J. N.; Wang, B.; Cao, X. F.; Sun, S. N.; Sun, R. C. Sygergetic effect of dilute acid and alkali treatments on fractional application of rice straw. *Biotechnol. Biofuels* **2016**, *9*, 217.

(23) Fahmi, R.; Bridgwater, A. V.; Donnison, I.; Yates, N.; Jones, J. M. The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability. *Fuel* **2008**, *87*, 1230−1240.

(24) Piskorz, J.; Radlein, D. S. A. G.; Scott, D. S.; Czernik, S. Pretreatment of wood and cellulose for production of sugars by fast pyrolysis. *J. Anal. Appl. Pyrolysis* **1989**, *16*, 127−142.

(25) Oudenhoven, S. R. G.; Westerhof, R. J. M.; Kersten, S. R. A. Fast pyrolysis of organic acid leached wood, straw, hay and bagasse: improved oil and sugar yields. *J. Anal. Appl. Pyrolysis* **2015**, *116*, 253−262.

(26) Muller-Hagedorn, M.; Bockhorn, H.; Krebs, L.; Muller, U. A comparative kinetic study on the pyrolysis of three different wood species. *J. Anal. Appl. Pyrolysis* **2003**, *68*−*69*, 231−249.

(27) Liu, Q.; Wang, S. R.; Luo, Z. Y.; Cen, K. F. Catalysis mechanism study of potassium salts on cellulose pyrolysis by using TGA-FTIR analysis. *J. Chem. Eng. Jpn.* **2008**, *41*, 1133−1142.

(28) Zhu, C.; Maduskar, S.; Paulsen, A. D.; Dauenhauer, P. J. Alkaline-earth- metal-catalyzed thin-film pyrolysis of cellulose. *ChemCatChem* **2016**, *8*, 818−829.

(29) Fuentes, M. E.; Nowakowski, D. J.; Kubacki, M. L.; Cove, J. M.; Bridgeman, T. G.; Jones, J. M. Survey of influence of biomass mineral matter in thermochemical conversion of short rotation willow coppice. *J. Energy Inst.* **2008**, *81*, 234−241.

(30) Patwardhan, P. R.; Satrio, J. A.; Brown, R. C.; Shanks, B. H. Influence of inorganic salts on the primary pyrolysis products of cellulose. *Bioresour. Technol.* **2010**, *101*, 4646−4655.

(31) Wang, K. G.; Zhang, J.; Shanks, B. H.; Brown, R. C. The deleterious effect of inorganic salts on hydrocarbon yields from catalytic pyrolysis of lignocellulosic biomass and its mitigation. *Appl. Energy* **2015**, *148*, 115−120.

(32) Hosoya, T.; Sakaki, S. Levoglucosan formation from crystalline cellulose: importance of a hydrogen bonding network in the reaction. *ChemSusChem* **2013**, *6*, 2356−2368.

(33) Khelfa, A.; Finqueneisel, G.; Auber, M.; Weber, J. V. Influence of some minerals on the cellulose thermal degradation mechanisms-thermogravimetic and pyrolysis-mass spectrometry studies. *J. Therm. Anal. Calorim.* **2008**, *92*, 795−799.

(34) Le Brech, Y.; Ghislain, T.; Leclerc, S.; Bouroukba, M.; Delmotte, L.; Brosse, N.; Snape, C.; Chaimbault, P.; Dufour, A. Effect of potassium on the mechanisms of biomass pyrolysis studied using complementary analytical techniques. *ChemSusChem* **2016**, *9*, 863−872.

(35) Wang, S. R.; Guo, X. J.; Liang, T.; Zhou, Y.; Luo, Z. Y. Mechanism research on cellulose pyrolysis by Py-GC/MS and subsequent density functional theory studies. *Bioresour. Technol.* **2012**, *104*, 722−728.