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Facile Fractionation of Bamboo Wood Toward Biomass Valorization by *p*-TsOH-Based Methanolysis Pretreatment

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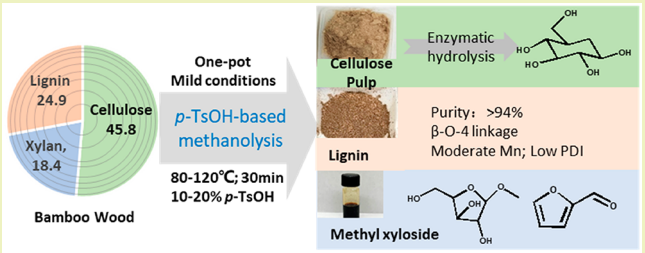
Supporting Information

ABSTRACT: A mild methanolysis pretreatment strategy was developed with a recyclable acid, *p*-TsOH, as the catalyst for the fractionation of lignocellulosic biomass toward its main components. Bamboo fiber was fractionated in one step with dissolution of more than 88% lignin and 90% xylan with most of the cellulose (86.8%) retained in pretreated bamboo at mild conditions (110 °C, 30 min, and 10% *p*-TsOH). Enzymatic hydrolysis of the cellulose-rich fraction was enhanced to 89.2% at an enzyme loading of 15 FPU g^{-1} substrate, nearly 4-fold higher than the untreated bamboo. Most of the xylan (hemicellulose) and lignin in the biomass were extracted and dissolved into the spent liquor. The extracted lignin had higher purity (>94%) and a moderate and homogeneous molecular weight, which could be adapted to add value to lignin. *p*-TsOH can be effectively recovered by recrystallization technology after concentrating the spent liquor. Hemicellulose (xylan) was transformed into methyl xyloside and furfural during the pretreatment. Overall, the described process showed practical significance for the effective fractionation and comprehensive utilization of lignocellulosic biomass components.



KEYWORDS: *p-Toluenesulfonic acid, Delignification, Methanolysis, Lignocellulose valorization, Enzymatic hydrolysis*

INTRODUCTION

Recently, much attention has been focused on developing biorefinery technologies to harvest biochemicals and biofuels from lignocellulosic biomass to reduce the dependence on fossil fuel resources.[1,2] Lignocellulosic biomass, a nonedible and renewable plant material, is primarily composed of polysaccharides (cellulose and hemicellulose) and aromatic polymer (lignin), with each component having its own special characteristics.[3] Extensive research has been devoted to the development of biorefinery processes of fractionating lignocellulose into its individual components and selectively converting each component for the manufacture of fuels and materials.[4−6] To improve the fractionation performance, biomass pretreatment is an essential step to break down the strongly interlinked lignocellulose structure in the plant cell walls and allow the valorization of the entire biomass.

In traditional carbohydrates, the first strategy of lignocellulose biorefinery, such as in the papermaking industry and the production cellulosic biofuels, is to remove as much lignin as possible to facilitate cellulose and hemicellulose valorization.[7,8] Typical delignification processes occur at harsh treatment conditions with a temperature of appropriately 150 °C for more than 2 h using sodium sulfide, sulfite, or sodium hydroxide to yield irreversible degradation of lignin with highly condensed structures. Therefore, these lignin fractions are difficult to valorize.[9,10] Various innovative fractionation techniques have been developed to overcome the recalcitrance of plant cell walls in breaking down and to isolate the relatively reactive lignin fraction under mild conditions. These techniques include ionic liquid and deep eutectic solvents fractionation,[11−13] ammonia-assisted fractionation,[14,15] γ-valerolactone fractionation,[16,17] and mild organosolv techniques.[18,19] For example, ionic liquids have been considered as a novel solvent in biomass fractionation. Agnieszka et al.[11] reported that 85% of the lignin and almost 100% of the hemicellulose were solubilized into the IL solution (triethy-

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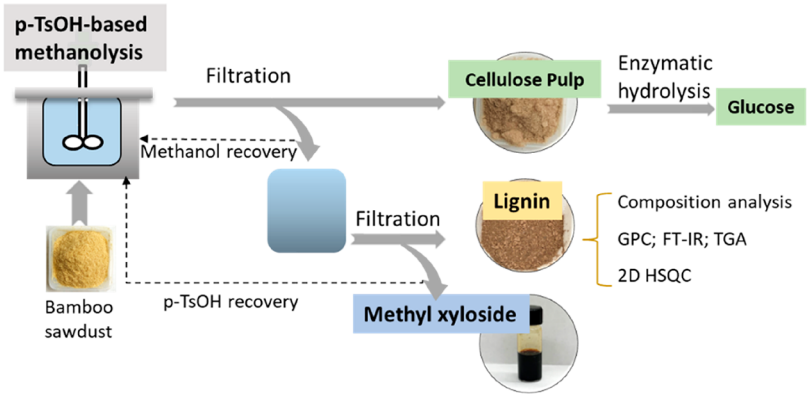

Figure 1. Process scheme for the fractionation of bamboo in the *p*-TsOH-based methanolysis system.

lammonium hydrogen sulfate [TEA][HSO4]), and up to 77% of the glucose was contained in the solid pulp at 120 °C. However, ionic liquids are generally expensive and some ionic liquids such as imidazoles and pyridines are toxic, which make them difficult to be used in large-scale industrialization. A long treatment time (typical more than 8 h) was required during the fractionation process because the poor thermal stability of ionic liquids prevents the process to be conducted at temperatures higher than 130 °C.[20,21]

Recently, Zhu et al.[22] reported an acid hydrotrope, *p*-toluenesulfonic acid (*p*-TsOH), that exhibited outstanding performance during the delignification of poplar biomass at mild conditions. Approximately 90% lignin and 85% hemicellulose from poplar wood can be dissolved with a minimal glucan loss at 80 °C for only 20 min. *p*-TsOH, a strong organic acid (pK_a = −2.8 at 20 °C), is soluble in water, alcohols, and other polar solvents. The group indicated that the sulfonic acid group at the hydrophilic end of *p*-TsOH catalyzes the cleavage of ether and ester bonds, and the lipophilic nonpolar part (toluene moiety) forms a micellar aggregate with lignin by hydrophobic interaction. In addition, *p*-TsOH can be easily recycled due to its low solubility in water at ambient temperatures.[23,24] However, the fractionation process requires a higher *p*-TsOH concentration (more than 70%), and the self-condensation of lignin was evident in the reaction process, which reduces the potential of high-value utilization of lignin. We considered using organic solvents instead of water with *p*-TsOH as an acid catalyst to fractionate lignocellulose components. In recent years, alcohol-based organosolv technology with an acid catalyst for the pretreatment of lignocellulosic biomass has been extensively studied.[25−27] In this study, methanol was used instead of water as a solvent with *p*-TsOH as the acid catalyst to investigate the fractionation of lignocellulosic biomass, with the following considerations. (1) The solubility of *p*-TsOH in methanol is better than that in water, and *p*-TsOH can dissolve more fully in a reaction solvent. (2) Methanol provides higher solubility for decomposition products from the biomass, especially for high molecular weight lignin, due to the relatively low dielectric constant.[28] (3) Alcohol-derived decomposition products (e.g., hydrogen, alkoxy moieties) can be quenched during the reaction by some intermediates to reduce the repolymerization of lignin.[29]

Recently, the application of bamboo wood in energy production has received notable attention. Bamboo is an easily propagated and fast-growing lignocellulosic species that is widely distributed around the world. Its cultivation can effectively utilize land and obtain a large amount of biomass resources per unit area compared with most other plant species.[30,31] In the present work, we report on the methanolysis process in the presence of *p*-TsOH with the potential to achieve efficient lignocellulose (bamboo wood) fractionation at relatively mild conditions (<120 °C). The schematic workflow for the experiment is presented in Figure 1. Three clean fractions consisting of a cellulose-rich substrate, homogeneous lignin fraction, and depolymerized hemicellulose sugars were obtained during the one-step *p*-TsOH-based methanolysis pretreatment. The cellulose-rich fractions were directly transformed to glucose by enzymatic saccharification. The extracted lignin was recovered and characterized in terms of structure and thermochemistry to assess its potential application value. The released sugars and derivatives, methyl xyloside and furfural, from hemicellulose were important platform chemicals. The described synergy shows practical implications for the fractionation and valorization of lignocellulosic biomass.

EXPERIMENTAL SECTION

Material. Bamboo stems were provided by the USDA Forest Service, Pineville, LA, USA. Bamboo was ground in a Wiley mill, passed through a 250−425 μm sieve (60−80 mesh), and dried at 105 °C overnight before fractionation. The chemical composition of bamboo sawdust was 45.79% cellulose, 18.42% xylan, and 24.91% lignin in terms of dry weight. *p*-TsOH (98%) was purchased from Sigma-Aldrich. All other chemicals were of analytical grade.

Fractionation using *p*-TsOH. A schematic representation of bamboo sawdust fractionation is given in Figure S1. Lab-scale pretreatment experiments were performed using 500 mL reactors. Typically, a mixture of bamboo sawdust, methanol, and *p*-TsOH was heated to 80−120 °C, with the preset temperature maintained for 5−60 min and with a stirrer speed of 300 rpm. At the end of the experiment, the reactor was cooled to below 30 °C. The solid fraction (cellulose-rich fraction) was separated from the liquid mixture by filtration and washed twice with methanol. The solid fraction was air-dried and then further dried at 105 °C for 12 h. Methanol solvent was separated from the filtrate mixtures by rotary evaporation under negative pressure of 0.1 MPa at 45 °C, and then evaporated methanol could be recycled and reused as the fractionation solvent. Next, deionized (DI) water was added into the slurry to precipitate lignin fragments and to separate water-insoluble lignin and water-soluble sugars and *p*-TsOH (spent acid liquor) by filtration, followed by thoroughly washing the lignin using DI water until a neutral pH was reached. *p*-TsOH could be recovered using crystallization technology from the spent liquor. Detailed crystallization steps of *p*-TsOH are as follows. The spent liquor solution was concentrated to the concentration of *p*-TsOH of about 90% by an evaporation process,

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Table 1. Chemical Composition of CRF and Untreated Sample under Various Conditions

		solid composition (%)					
reaction condition	solid recovery (%)	cellulose	lignin	xylan	cellulose loss (%)	delignification (%)	xylan loss (%)
T80-A10-t30	79.46	55.73	20.84	13.36	3.29	36.71	42.37
T80-A50-t30	62.82	68.41	10.16	7.08	6.15	74.38	75.85
T80-A50-t60	58.62	71.25	9.97	5.87	8.79	76.54	81.32
T90-A10-t30	69.22	63.35	16.91	11.21	4.23	53.01	57.87
T90-A50-t30	53.7	76.62	8.54	5.33	10.14	81.59	84.46
T90-A50-t60	51.57	77.02	8.44	4.37	13.26	82.53	87.77
T100-A10-t30	57.42	73.15	10.76	6.02	8.27	75.20	81.23
T100-A20-t30	53.64	75.14	9.79	5.81	11.98	78.92	83.08
T100-A20-t60	51.07	77.53	8.33	3.94	13.53	82.59	89.08
T110-A5-t30	65.67	67.51	15.12	9.58	3.18	60.14	65.85
T110-A7.5-t30	54.46	77.51	9.72	6.14	7.81	78.75	81.85
T110-A10-t30	49.18	80.84	5.73	3.63	13.18	88.69	90.31
T110-A15-t30	46.40	83.78	5.33	2.11	15.10	90.07	94.68
T110-A20-t30	44.21	84.78	4.21	2.19	18.15	92.53	94.74
T110-A10-t5	53.81	76.96	8.52	5.92	9.56	81.60	82.71
T110-A10-t10	50.66	80.13	7.76	4.24	11.35	84.22	88.34
T110-A10-t60	46.26	83.06	4.96	2.32	16.09	90.79	94.17
T120-A5-t10	56.71	71.14	14.12	7.94	11.89	67.85	75.55
T120-A5-t30	52.42	74.62	12.69	6.73	14.58	73.30	80.85
T120-A10-t30	43.03	88.76	4.16	1.85	16.59	92.81	95.68

[a]CRF samples labeled using the fractionation conditions. T = temperature (°C); A = acid concentration (g/100 mL); t = time (min). For example, T80-A10-t30 is the CRF after the pretreatment of bamboo wood at 80 °C with the *p*-TsOH concentration of 10 g/100 mL for 30 min of reaction time. The final pressure was shown in Table S1.

during which glass rods were continuously stirred, and then cooled to ambient temperature. *p*-TsOH was crystallized from spent liquor, thus realizing the separation of *p*-TsOH and hemicellulose sugars.

$$\text{delignification (\%)} = \left(1 - \frac{m_{L_P}}{m_{L_O}}\right) \times 100\% \quad (1)$$

$$\text{cellulose loss} = \left(1 - \frac{m_{C_P}}{m_{C_O}}\right) \times 100\% \quad (2)$$

$$\text{hemicellulose loss} = \left(1 - \frac{m_{H_P}}{m_{H_O}}\right) \times 100\% \quad (3)$$

$$\text{lignin yield} = \left(\frac{m_L}{m_O}\right) \times 100\% \quad (4)$$

where m_{C_O}, m_{L_O}, and m_{H_O} are the mass of cellulose, lignin, and hemicellulose in the original bamboo sawdust; m_{C_P}, m_{L_P}, and m_{H_P} are the mass of cellulose, lignin, and hemicellulose in pretreated samples (cellulose-rich fractions). The variable m_O is the mass of the original bamboo sawdust; m_L is the mass of precipitant lignin.

Enzymatic Hydrolysis of Cellulose-Enriched Fractions. Enzymatic hydrolysis of untreated and pretreated bamboo samples was carried out on a shaking incubator (250 rpm) at 50 °C for 72 h. Next, 2% of sample (w/v) and 1 mL of tetracycline chloride solution (40 mg/mL) were loaded into a 15 mL vial. Acetate buffer (pH = 5) was subsequently added to make the final liquid volume of 12 mL with 5, 10, 15, 20 FPU/g substrate of cellulase for samples. A 200 μL sample was taken from the mixture and analyzed by HPLC for sugar yield determination.

Analytical Methods. The chemical compositions of the cellulose-rich substrates from different pretreatment conditions were determined using the two-step hydrolysis method for chemical composition analysis based on NREL/TP-510-42618.[32] The ^{13}C CP/MAS solid-state NMR analysis of the cellulose-rich fractions was recorded with a Bruker AVIII 400 HD instrument using a relaxation delay of 2.5 s. Each sample was scanned 800 times in total. The crystallinity analysis of the cellulose-rich substrates was performed on an XRD-6000 X-ray diffractometer (monochromatic Cu/Kα radiation, 2θ varied from 10° to 50°). The crystallinity index (CrI) was determined by the formulate of eq 4.[33]

$$\text{CrI (\%)} = \left(\frac{I_{002} - I_{am}}{I_{002}}\right) \times 100\% \quad (5)$$

where I_{002} is the intensity of the crystalline peak corresponding to the 002 plane at $2\theta \approx 22.4°$ and I_{am} is the peak intensity of the amorphous cellulose at $2\theta \approx 18.0°$.

FT-IR spectra of lignin were measured using a Thermo 208 Nicolet (NEXUS 670) spectrometer. The spectra of samples were recorded in ATR mode, and data were recorded ranging from 600 to 4000 cm^{-1} with a resolution of 2 cm^{-1}. The weight-average (Mw) and number-average (Mn) molecular weights of lignin were measured using gel permeation chromatography (GPC) with a UV−vis detector at 254 nm. GPC was carried out using tetrahydrofuran as the mobile phase with a flow rate of 1 mL/min at 25 °C. The polydispersity index (M_w/M_n) was calculated. The thermal properties of the extracted lignin and cellulose-rich fraction were studied using TGA (PerkinElmer, Waltham, MA). Approximately 10 mg of the sample was placed into the pan of the instrument and heated from room temperature to 700 °C with a heating rate of 10 °C/min. The lignin fragments (90 mg) were dissolved in DMSO-d6 (0.5 mL) for 2D HSQC NMR characterization to analyze the specific structures of the complex compounds. The 2D-HSQC NMR spectra were measured using a Bruker DRX 500 NMR spectrometer. The spectral widths were 8.5 and 120 ppm for the ^{1}H and ^{13}C dimensions, respectively.

The hemicellulose sugars in spent liquor, including methyl xylose and methyl glycoside, were analyzed via HPLC for characterization. A quantitative analysis of the methyl glycosides (methyl α-D-xylopyranoside, methyl β-D-xylopyranoside, methyl α-D-glucopyranoside, and methyl β-D-glucopyranoside) was conducted using an HPLC instrument equipped with a Bio-Rad Aminex HPX-87H (300 × 7.8 mm) column and a refractive index detector. Next, 5 mM H_2SO_4 was used as the mobile phase at a flow rate of 0.5 mL/min. A quantitative analysis of the methyl glycosides was based on an external standard

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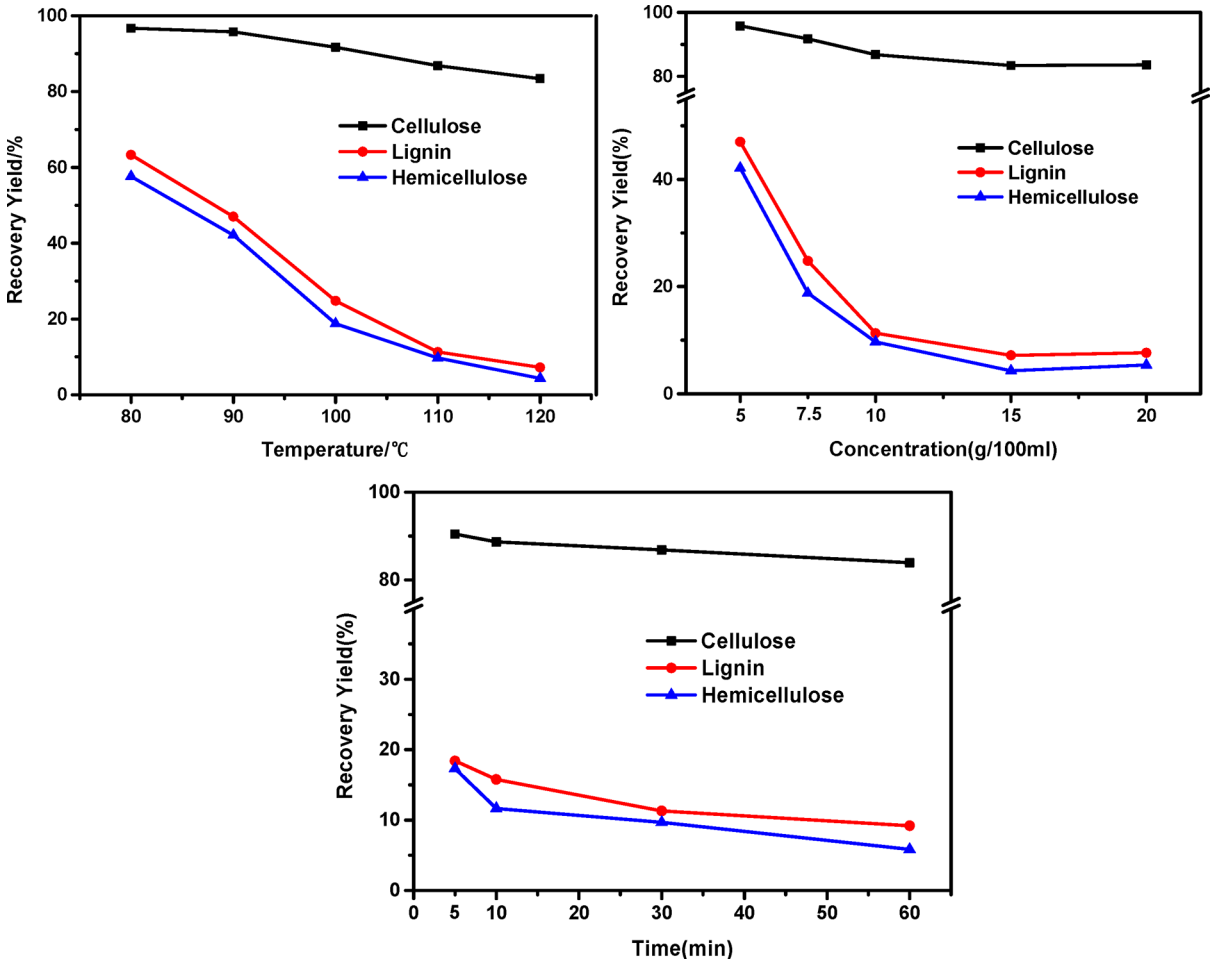

Figure 2. Effect of temperature (a), *p*-TsOH concentration (b), and holding time (c) on cellulose, lignin, and xylan recovery yield during the *p*-TsOH-based methanolysis pretreatment.

with methyl α-D-xylopyranoside, methyl β-D-xylopyranoside, methyl α-D-glucopyranoside, and methyl β-D-glucopyranoside as the model compounds. Figure S2 shows the standard curves of the methyl xyloside and methyl glucoside.

RESULTS AND DISCUSSION

***p*-TsOH-Based Methanolysis Pretreatment.** For a typical pretreatment, bamboo sawdust was fractionated in a methanol medium using a recyclable acid, *p*-TsOH, as the catalyst under various conditions. After the reaction, the reaction mixture was subjected to filtration to separate the lignin and hemicellulose sugars from the cellulose-rich fraction (CRF), which was the undissolved intermediate for the production of glucose by enzymatic hydrolysis. The chemical compositions of the CRF and untreated samples were analyzed following standard procedures in order to evaluate the fractionation efficiency under different pretreatment conditions (Table 1). The solid yield and recovery of cellulose, lignin, and xylan (based on the weight of its individual components in the untreated sample) in the CRF are presented in Figure 2. The solid recovery declined from 79.46% to 43.03% as the temperature increased from 80 to 120 °C (30 min, 10% *p*-TsOH concentration). It was observed that the increased temperature greatly improved the solubilization of lignin and xylan as evidenced by greatly decreased lignin and xylan amounts in the CRF. For example, the extraction amount of lignin and xylan was 34.36% and 42.37%, respectively, at a condition of T80-A10-t30. A substantial amount of lignin (88.69% and 92.81%) and xylan (90.31% and 95.68%) was extracted after the pretreatment at 110 °C (T110-A10-t30) and 120 °C (T120-A10-t30), respectively, indicating that the *p*-TsOH-based methanolysis system led to the notable extraction of lignin and xylan at relatively mild conditions. We investigated the fractionation conditions under "higher *p*-TsOH concentration and lower temperature" (T80-A50-t30 and T90-A50-t30) and "lower *p*-TsOH concentration and higher temperature" (T110-A10-t30 and T120-A10-t30). It was found that "lower *p*-TsOH concentration and higher temperature" was more favorable for the dissolution of xylan and lignin.

To further optimize pretreatment conditions, combinations of different acid concentrations and pretreatment times were also studied. The *p*-TsOH concentration also plays an important role in lignin and xylan solubilization. The recovery yield of xylan dropped from 34.15% to 9.69%, and the recovery yield lignin reduced from 39.86% to 11.31%, as the concentration increased from 5% (T110-A5-t30) to 10% (T110-A10-t30). Therefore, increasing the concentration of *p*-TsOH can effectively improve the extraction of lignin and xylan in the CRF. The relatively low acidity of a *p*-TsOH methanolysis system might be difficult to break the linkage in LCC and lignin macromolecules at relatively mild temperature. Further increasing the *p*-TsOH concentration from 10% to 20% resulted in an increase in 3.84% xylan and 4.43% lignin

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solubilization. The holding time was an important factor for investigating the fractionation efficiency. It was found that the increase of reaction time mainly improved the dissolution of xylan under the "higher *p*-TsOH concentration and lower temperature" conditions by comparing T80-A50-t30, T80-A50-t60 or T90-A50-t30, and T90-A50-t60. Under the "lower *p*-TsOH concentration and higher temperature" conditions, the increase of reaction time enhanced the dissolution of xylan and lignin at the same time. However, we observed that reaction time had a lesser effect on the extraction of xylan and lignin compared with the reaction temperature and acid concentration. Our finding suggested that 30 min might be the optimal reaction time among these survey time frames at 110 °C and 10% of acid concentration based on the lignin and xylan extraction in the CRF after comparing these four different time conditions.

Furthermore, a significant enhancement of cellulose content was observed in the pretreated samples with the increase of reaction severity due to the removal of lignin and xylan fractions. The removal of xylan and lignin seemed to be synchronous with the increase of severity of reaction conditions. It was found that temperature, acid concentration, and reaction time had a minimal effect on the amount of cellulose (expressed as glucan) remaining in the CRF, confirming that cellulose was not obviously hydrolyzed or degraded during the reaction. The cellulose loss was approximately 5−17% under the given conditions. The relative lower cellulose loss might be attributed to the mild processing conditions. It also can be inferred that *p*-TsOH-based methanolysis was more selective in solubilizing the hemicellulose (xylan) and lignin and left most of the cellulose fraction in the CRF. Based on these findings and taking the cellulose retention, delignification, and the energy consumption into consideration, the pretreatment at 110 °C of 10% *p*-TsOH concentration for 30 min were considered to be optimal conditions for further investigation. In general, the *p*-TsOH-based methanolysis system provided a rapid and effective approach for the fractionation of biomass by synergistic removal of hemicellulose and lignin fractions in mild conditions.

Lignin Characterization. *Yield and Chemical Composition.* In order to comprehensively assess the potential value and application of extracted lignin, the conversion and structural characteristics of lignin (obtained with 10% *p*-TsOH concentration for 30 min at different pretreated temperatures) were analyzed using chemical composition, GPC, FTIR, TGA, and 2D HSQC NMR analysis. The result of yield, theoretical yield (based on the above calculation of delignification results), and the chemical composition of the extracted lignin are shown in Table 2. The yield of extracted lignin increased from 47.17% to 83.65% as the temperature increased. Small amounts of carbohydrates (glucan and xylan) were detected, and xylan accounted for a high proportion in extracted lignin. The xylan content exhibited a decreasing trend, which may be due to the gradual breakage of LCC bonds with increasing temperature. Overall, the high recovery yield and high purity of lignin make it possible to use it for industrial applications without the need for further purification processes.

Molecular Weight Distribution. To further understand the depolymerization of lignin, the average molecular weights (Mw and Mn) of extracted lignin were measured with GPC (Figure S3). The value of Mn showed a decreasing trend changing from 5503 g mol^{-1} to 3094 g mol^{-1} as the temperature increased from 90 to 120 °C, which might be related to cleavage of ester linkages in lignin under higher temperatures, resulting in depolymerization of lignin macromolecules. The polydispersity index (PDI) was calculated to understand the molecular weight distribution of the lignin fraction. All the lignin fraction exhibited a narrow molecular distribution with a PDI of less than 2.5. Thus, it could be inferred that lower temperature pretreatment could obtained uniform lignin fragments. The PDI gradually decreased from 90 to 110 °C, which might be associated with the higher carbohydrates content at lower temperature and was in agreement with the results in Table 2. Since the PDI obviously increased at 120 °C and the cleavage of ester linkages mainly occurred at higher temperature, the recondensation reaction of lignin probably occurred under these conditions leading to relatively higher PDI. In addition, the solubility of the four lignin fractions was investigated in organic solvents, i.e., methanol, acetone, and tetrahydrofuran (Figure S4). It was found that all lignin fractions had good solubility in tetrahydrofuran, while the solubility of L-90, L-100, L-110, and L-120 samples in methanol and acetone was gradually reduced, which may be due to the condensation reaction of lignin under higher temperature and acidic conditions.

Table 2. Chemical Composition and Molecular Weight of Lignin Samples

		chemical composition			molecular weight		
sample[a]	yield (%)	lignin (wt %)	glucan (wt %)	xylan (wt %)	Mn (g/mol)	Mw (g/mol)	PDI
L-90	47.17	93.37	0.37	3.54	2283	5503	2.41
L-100	69.91	96.82	0.09	3.02	2121	4157	1.96
L-110	78.83	95.23	1.12	2.55	1929	3472	1.80
L-120	84.65	96.15	0.91	2.76	1412	3094	2.19

[a]The extracted lignin obtained at 90, 100, 110, and 120 °C labeled as L-90, L-100, L-110, and L-120, respectively.

FT-IR Analysis. Functional group information for the extracted lignin at different temperatures was detected by Fourier transform infrared spectroscopy, and the signals were identified based on previous publications.[34−36] As shown in Figure 3(a), it was observed that all curves showed typical characteristic peaks for lignin in the FT-IR spectra. The broad peak at 3350 cm^{-1} was related to the stretching of phenolic hydroxyls in the aromatic and aliphatic regions of the lignin fractions. The appearance of peaks at 2938 and 2843 cm^{-1} corresponded to the C−H vibration of the methyl and methylene groups, respectively. The characteristic peaks at about 1595, 1508, and 1419 cm^{-1} were attributed to aromatic skeletal vibrations, and the peak at 1458 cm^{-1} was ascribed to C−H deformation and aromatic ring vibration. The vibration of syringyl and guaiacyl unit were evident at 1326 and 1219 cm^{-1}, respectively. The absorption peaks at 1028 and 836 cm^{-1} were attributed to the in-plane deformation and vibration of aromatic C−H and to the out-of-plane stretching of C−H. It was also determined that the lignin in bamboo belonged to a GSH-type feature. Overall, the lignin fractions extracted at different temperatures exhibited similar stretching vibrations. It was observed that the intensities of the characteristic peaks gradually weakened with increasing temperatures. This finding indicates that the lignin fractions maintained an analogous and

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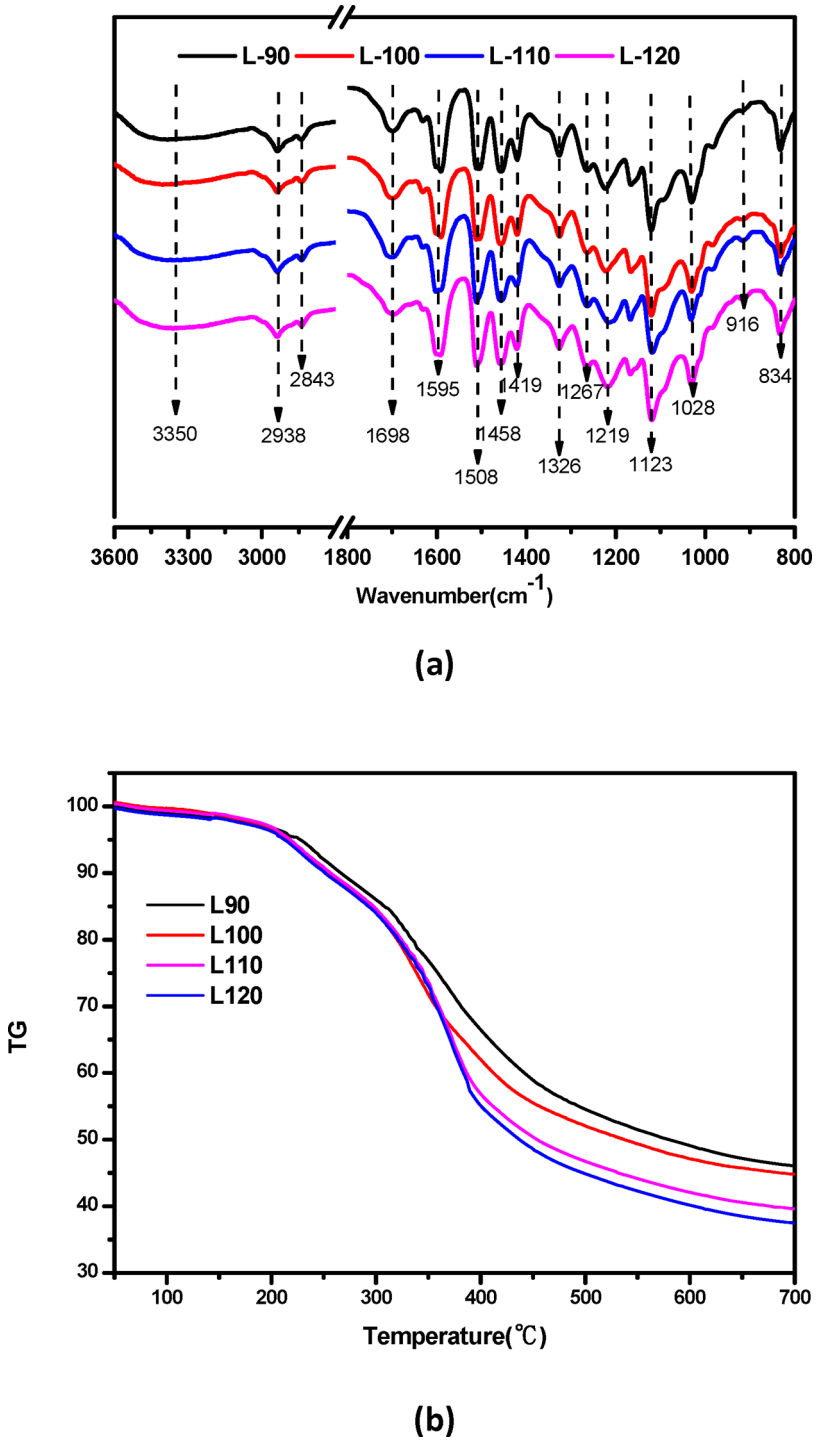

Figure 3. (a) FT-IR analysis and (b) TG curves of extracted lignin.

functional group but slight changes occurred under different pretreatment condition.

TGA Analysis. The thermal stability of the extracted lignin was determined using TGA to understand the relationship between its inherent chemical features and thermal properties. The TG curves recorded in the temperature range from 50 to 600 °C are presented in Figure 3(b). The initial pyrolysis degradation stage at ≤200 °C was mainly related to small molecular weight lignin and the weak C−O bond in the β-O-4 linkage. Then, the aryl ether bond linkages were broken under 350 °C. Next, the side chain oxidation decomposition and dehydrogenation of the lignin began to occur at ∼350−400 °C. The aromatic ring and C−C bonds began to cleave as the pyrolysis temperature increased above 400 °C. Finally, as the pretreatment temperature elevated above 500 °C, the TGA curve flattened due to the formation of char.[37,38] It was found that all lignin fractions exhibited similar thermal profiles. The pyrolysis degradation rate of lignin was faster and the residue mass decreased and with less variability (range of 25%−48%) as the temperature increased from 90−120 °C. The molecular weight of lignin was proportional to the residual mass due to

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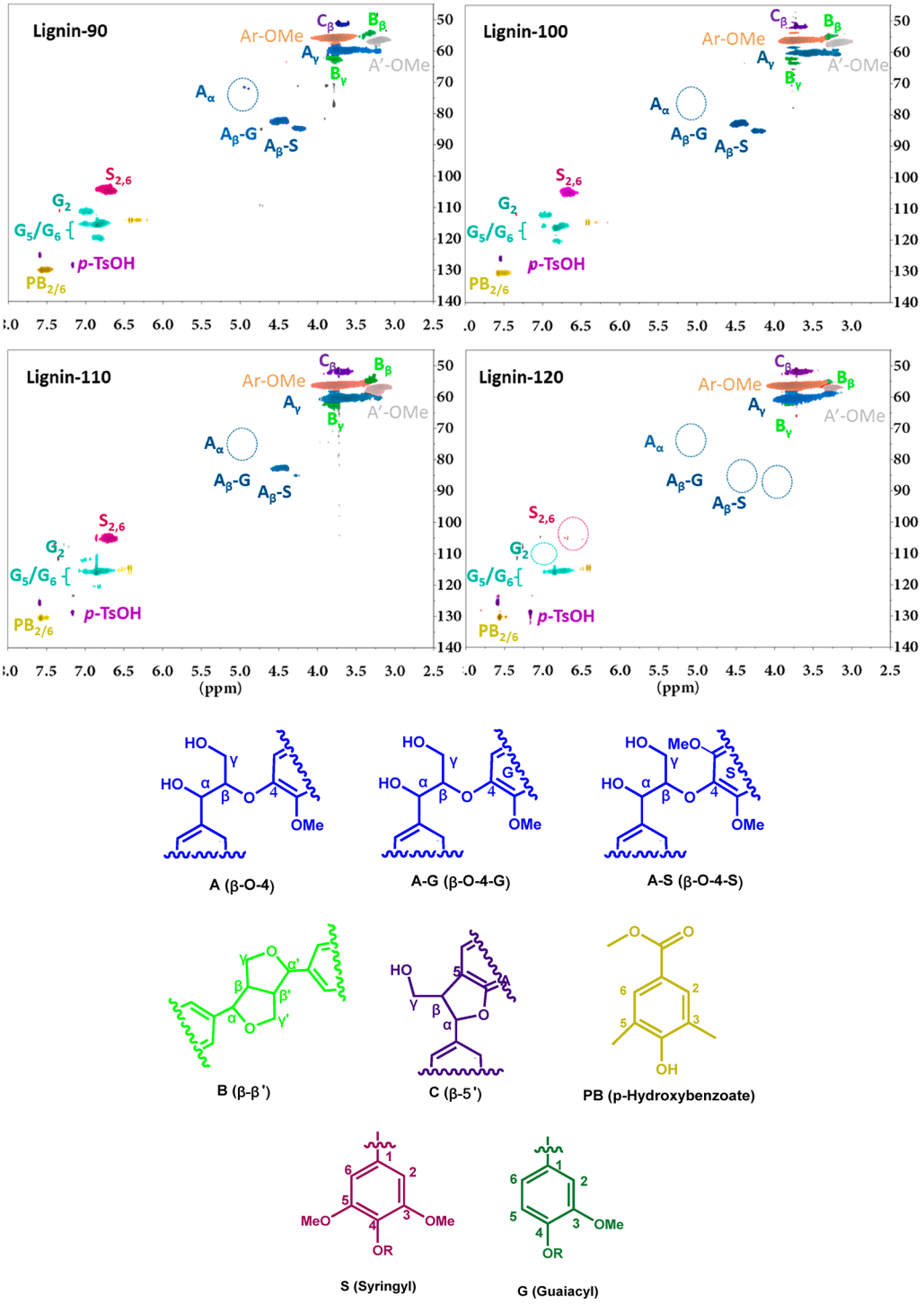

Figure 4. 2D HSQC NMR spectra of lignin fractions and the main structures.

the high molecular weight lignin being relatively easily condensed to form char.

2D HSQC NMR Analysis. We further analyzed the lignin isolated with different pretreatment temperatures using 2D HSQC NMR for a better understanding of the conversion and structural information for these lignin. The cross-signals in the spectra were annotated according to previous studies.[39−42] Figure 4 shows the NMR spectra and depicts two main cross-signal regions, namely, the side-chain (δC/δH 40−90/2.6−6.0) and aromatic (δC/δH 100.0−140.0/5.5−8.5) regions. The signals at the carbohydrate's regions (δC/δH 90−105/4.0−5.5) were not detected in all lignin samples which indicated the cleavage of the lignin-carbohydrate complex (LCC) structure during the pretreatment. However, it was observed in the side-chain regions that the C−H correlation in methoxy groups at δH/δC 3.73/55.6 ppm was the most prominent in all lignin fractions. The appearance of signals at δC/δH 84.6/4.5 ppm (A_β-G), 85.6/4.4 ppm (A_β-S), and 60.3/3.7 ppm (A_γ) related to the β-O-4′ substructure (A) in lignin samples. However, a typical signal of β-O-4′ aryl ether linkages, A_α, could not be detected in all lignin samples. It might due to the grafting of methanol to the A_α position in the β-O-4′

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substructure, which could be proved by the presence of the A′-OMe signal at $\delta C/\delta H$ 58.1/3.6 ppm. The cross signals at $\delta C/\delta H$ 53.5/3.25 ppm were assigned to the Cβ−Hβ in β−β' substructure (B). The C−H correlation in the β-5′ substructure (C) was found at $\delta C/\delta H$ 51.5/3.75 ppm. The pretreatment greatly promoted the depolymerization of lignin, as evidenced by the gradual decrease in β-aryl ether content with the increase of temperature. By comparison, the extracted lignin at 110 °C of pretreatment temperature maintained a relatively complete chemical structure and higher delignification yield and were superior to other temperature conditions.

In the aromatic regions, the C_2/H_2, C_5/H_5 and C_6/H_6 correlations in the G unit were detected at $\delta C/\delta H$ of 105.0/7.10, 119.5/6.98, and 121.5/6.83, respectively. The signal at $\delta C/\delta H$ 130.0/7.6 was assigned to the cross-link characteristic signals of $C_{2,6}/H_{2,6}$ in PB. The contours of the S and G units significantly decreased with increasing temperature, and the S unit even disappeared in the Lignin-120 sample, probably due to the condensation of lignin at the 2, 5, and 6 positions. The reason was the new aromatic linkages at 2, 5, and 6 positions would lack hydrogens, making it less visible in the NMR spectrum with the pretreated temperature increasing from 90 to 120 °C. Severe conditions effectively depolymerized highly complex lignin structures and also led to lignin condensation during the pretreatment, consistent with GPC and TGA analyses. For comparison, milder temperatures of 100 and 110 °C proved to be efficient for separating carbohydrate fractions with lignin but with limited impact on the structural of lignin compared with 120 °C.

Hemicellulose Derivatives. After the isolation of the cellulose-rich fraction and lignin, the water-soluble fraction was collected containing most of the hemicellulose sugars and its derivatives (mainly furfural). We quantitatively analyzed the methyl glycoside components in spent liquor by HPLC with two model compounds (i.e., methyl xyloside and methyl glucoside). The chemical composition of the spent liquor is shown in Figure 5. A low methyl glucoside yield (range of 0.5−4%) was detected in all spent liquor samples because of minimal glucan loss in the CRF during the pretreatment. Lower furfural was detected with pretreated temperatures of 90 and 100 °C due to the minimal transformation of methyl xyloside to furfural at lower temperature. The yield of methyl xyloside increased with increasing temperature from 90 to 100 °C, and decreased from 100 to 120 °C, which was partly due to the formation of furfural at higher temperature. Furthermore, we found there was great mass loss of xylan (based on the yield of methyl xyloside and furfural) compared to the amount of xylan removed in the CRF. Thus, an investigation of the conversion of purity xylose and furfural in the *p*-TsOH-based methanolysis system was performed to further understand the transformation during the pretreatment (Table S2). It was found that coke was formed at higher temperature because furfural is highly reactive to polymerization.[43] Almost all xylose was converted to methyl xylose at 90 to 100 °C, and the yield of furfural and coke was lower. At 110 and 120 °C, the yield of coke significantly increased due to the formation of more furfural. It was found that more than 78% of furfural was transformed into coke with a 10% *p*-TsOH concentration at 120 °C for 30 min. So, it was inferred that the mass loss of xylan mainly contributed to the polymerization of furfural at higher temperature. Overall, these data indicated that *p*-TsOH-based methanolysis at mild conditions can efficiently transform xylan toward methyl xyloside.

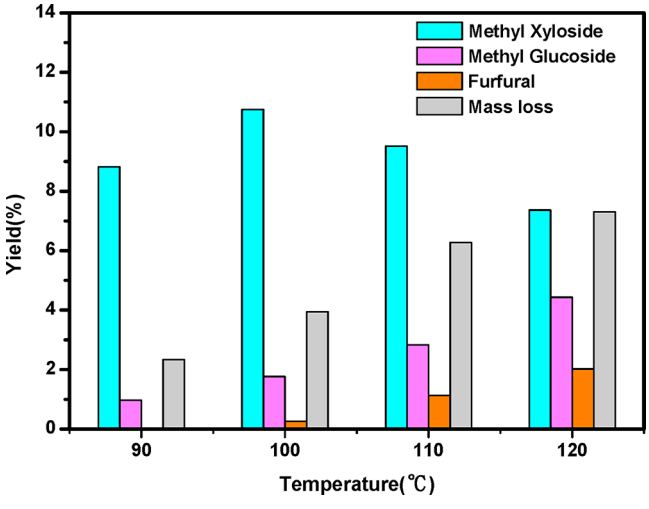

Figure 5. Yield of hemicellulose sugars and its derivatives under different pretreatment temperatures.

Dissolution Mechanism of Lignin and Hemicellulose and the Recovery of *p*-TsOH. Glycosidic bonds are the dominate linkages between hemicellulose and cellulose sugar units. The possible reaction mechanism of the methanolysis of xylan is shown in Figure S5. *p*-TsOH, as an organic strong acid, can readily release protons in methanol solution, protonating the O atoms in the glycosidic bonds to make them electrophilic. Then, the hydroxyl group in methanol acts as a nucleophile to attack the electrophilic C atom adjacent to the glycosidic bond, which in turn cleaves the glycosidic bond to produce a leaving group and a neutral hydroxyl group, resulting in the release of C5 and C6 sugars, e.g., methyl xyloside and methyl glucoside from xylan and cellulose, respectively, which can be evidenced by the compositions determined in the spent liquor. The depolymerization of lignin-carbohydrate complex (LCC) and lignin in biomass have a similar mechanism of cleaving the ether and ester bonds. However, the cellulose loss was significantly lower than xylan removal, which was because the crystalline cellulose was resistant to methanolysis at relatively mild conditions. Zhu et al. believed that the outstanding delignification performance of *p*-TsOH aqueous solution at mild conditions was attributed to the hydrotropic properties of *p*-TsOH for solubilizing the lignin fraction. The effective dissolution of lignin was achieved under low temperature (≈80 °C) with a high *p*-TsOH concentration (>70%). However, *p*-TsOH must aggregate above the minimal hydrotrope concentration (11.5%) to solubilize lignin.[23,24] In this study, lignin was effectively dissolved in a 10% *p*-TsOH methanol solution, probably because with the high solubility of *p*-TsOH in methanol, the density of the solution was relatively low, which facilitated the dissolution of lignin and hemicellulose sugars. Higher solubility of lignin in methanol allowed rapid lignin dissolution during the pretreatment.

We evaluated the recoverability of *p*-TsOH by fractionating bamboo wood under two conditions (T80-a50-t30 and T110-a10-t30) (Table S3). *p*-TsOH could be recovered by recrystallization technology after concentrating spent acid liquor because of its low water solubility at ambient temperature. Further, 53.4% of *p*-TsOH was recovered under the condition of T80-A50-t30. The fractionation experiment of bamboo wood was conducted using the same raw material/recovered *p*-TsOH/methanol ratio. The solid recovery

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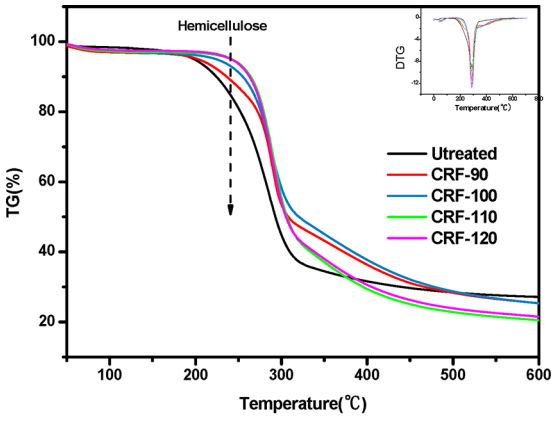
(76.35%) was slightly higher than that using fresh *p*-TsOH (62.82%). The secondary recovered *p*-toluenesulfonic acid has a lower recovery yield than the primary recovery. In order to better separate *p*-TsOH, in the process of concentrated crystallization, the content of water in the spent acid solution cannot be too low due to the high viscosity of methyl glycoside, which may hinder the crystallization of some acid, so it has a low *p*-TsOH recovery in low acid concentration process. Methanol could be easily recovered through the rotary distillation process, and the recovery rate was more than 90%, which could realize the recycling of methanol solvent.

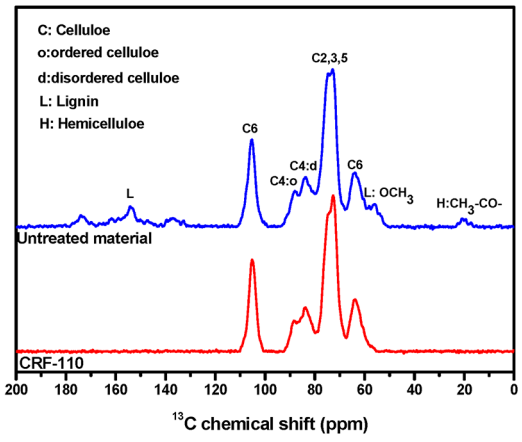
Cellulose-Rich Fraction. *TGA and ^{13}C Analysis CPMAS Solid-State NMR of CRF.* The thermal behavior of the CRF was measured by TG and DTG analyses. According to the literature, the mass loss at temperature ranges of ∼220−315, ∼300−350, and ∼300−500 °C contributed to the pyrolysis of hemicellulose, cellulose, and lignin, respectively.[44,45] The different thermal behaviors of the three main components can provide a better understanding of the conversion of the biomass composition. As can be seen in Figure 6 (a), the weight of untreated bamboo rapidly decreased at ∼280 °C, which contributed to the decomposition of hemicellulose. The hemicellulose in the CRF was gradually removed as the temperature increased from 90 to 120 °C, which was consistent with the previous composition analysis of the CRF samples. The main weight loss at about 300 °C was caused by the pyrolysis of cellulose, with the further pyrolysis corresponding to the decomposition of lignin. Lignin is prone to generating char at high pyrolysis temperatures (>600 °C). The CRF-110 and CRF-120 samples exhibited a lower residual level at the end of degradation, which contributed to the effective extraction of lignin. ^{13}C CPMAS solid-state NMR results (Figure 6(b)) also confirmed the efficient removal of xylan and lignin, while the dominant structure of the crystalline cellulose was not significantly affected.

XRD Analysis. Crystallinity of the CRF is a major criterion for assessing the suitability of cellulose for enzymatic hydrolysis. The untreated bamboo and CRF at various temperatures were subjected to XRD analysis to compare their CrI values. XRD patterns and their CrI values are shown in Figure 6(c). All the XRD patterns showed the typical diffraction peaks at 2θ = 16°, 22°, and 34°, which confirmed that original crystalline cellulose form was preserved although it had gone through the pretreatment. Untreated bamboo exhibited the lowest CrI value of 51.5%. Whereas the samples were subjected to the treatment using *p*-TsOH-based methanolysis pretreatment, the CrI of CRF pretreated samples was in the range of 59.6−65.8%, showing an 8−14% enhancement from the untreated samples, which indicated a large number of amorphous components, such as xylan (hemicellulose) and lignin, were removed and led to an increase in CrI of the CRF samples.

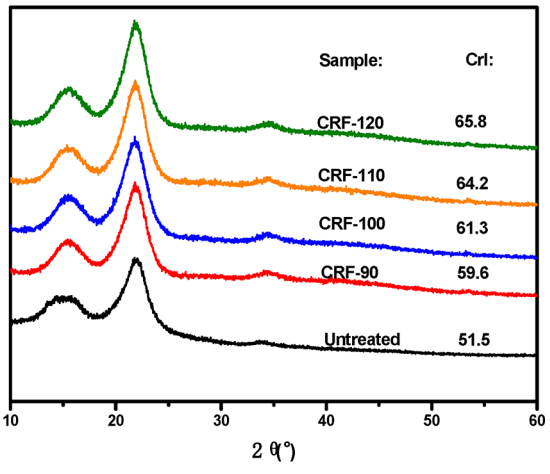
Enzymatic Saccharification. The enzymatic digestibility of cellulose to glucose is an important approach for cellulose valorization. Therefore, the left CRF samples were directly hydrolyzed by enzymatic saccharification for the evaluation of pretreatment behavior. The untreated bamboo wood exhibited the highest resistance to enzymatic hydrolysis, and a low enzymatic conversion of 24.1% was obtained (Figure 7(a)). After the pretreatment, the cellulose enzymatic conversion rate of the CRF samples pretreated from 90 to 120 °C increased to 67.7%, 79.4%, 89.2%, and 91.2% with a cellulase loading of 15 FPU/g glucan, respectively. The highest enzymatic digestibility



(a)



(b)



(c)

Figure 6. (a) TGA analysis results, (b) ^{13}C CPMAS solid-state NMR spectra, and (c) XRD analysis of untreated bamboo and pretreated samples at different temperatures.

was more than 60% higher than the untreated material, indicating that the pretreatment led to a dramatical enhancement in enzymatic digestibility of cellulose. The glucose yield showed a positive correlation with pretreatment temperature.

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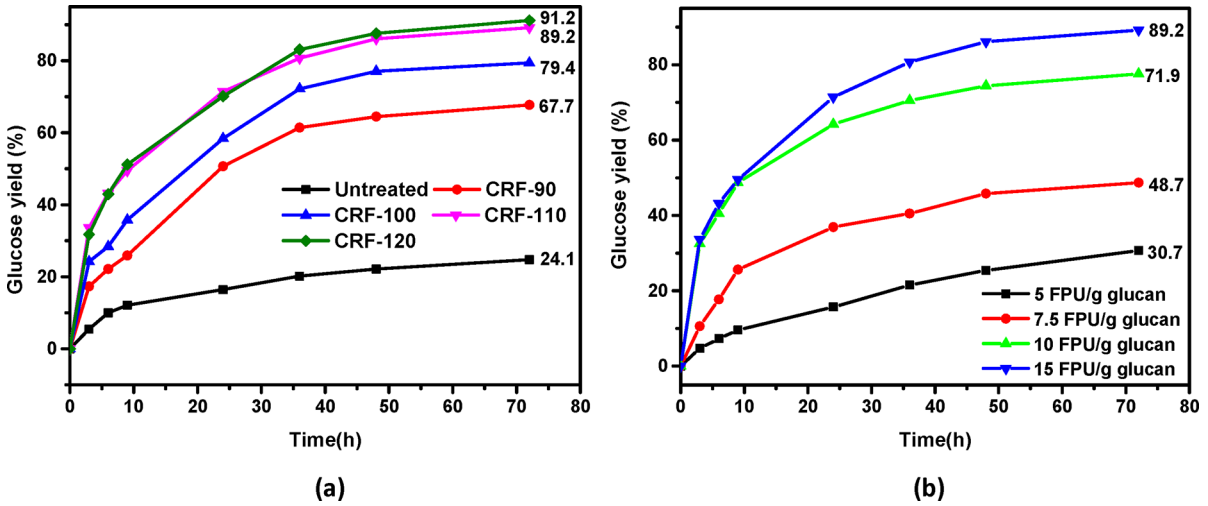

Figure 7. Comparison of enzymatic digestibility of CRF at various conditions. (a) Untreated sample and CRF from different temperatures with cellulase loading of 15 FPU/g glucan, and the (b) 110-A10-t30 sample with different cellulase loading.

The enhancement of the enzymatic hydrolysis was attributed to the removal of hemicellulose and lignin which created a better accessibility of the surface for enzyme adsorption. The enzymatic digestibility of T110-A10-t30 sample with different cellulase loading (5, 7.5, 10, and 15 FPU/g glucan) was tested, as shown in Figure 7(b). The results indicated that more than 10 FPU/g glucan of cellulase loading could achieve a better glucose yield.

CONCLUSION

The present study comprehensively demonstrates the effective fractionation of lignin and hemicellulose from bamboo fiber in a *p*-TsOH-based methanolysis system at mild conditions. The leftover solid cellulose-rich fraction could be hydrolyzed to glucose by enzymatic digestion. The sugar yield was significantly increased to 89.2% (15 FPU/g glucan) at the selected condition (110 °C, 30 min, and 10% *p*-TsOH concentration), which exhibited great enhancement compared with untreated bamboo (24.1%). A variety of analytical methods (GPC, FI-IR, TGA, HSQC, component analysis) further confirm that lignin was effectively separated with carbohydrates under mild conditions, and the extracted lignin exhibited a intact structure with a representative structure such as *β*-O-4′, high purity, and moderate molecular weight distribution, which could be adapted to add value to lignin. Hemicellulose was mainly transformed into methyl xyloside with the yield of 9.51% during the pretreatment. The proposed strategy provides a simple, efficient way to fraction lignin, hemicellulose, and lignin in mild conditions and has great potential for future large-scale industrialization processing.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b05392.

(Figure S1) Detailed process for the fractionation of bamboo and the recovery of methanol and *p*-TsOH in the *p*-TsOH/methanol system; (Figure S2) the standard curve of concentration of methyl xyloside and methyl glucoside; (Figure S3) GPC analysis of the molecular distribution of extraction lignin at various temperatures; (Figure S4) dissolution of lignin in tetrahydrofuran and methanol; (Figure S5) possible reaction mechanism for the methanolysis of hemicellulose (xylan) in biomass; (Table S1) the operating pressure during the *p*-TsOH-based methanolysis at various conditions; (Table S2) the conversion of xylose and furfural in the *p*-TsOH methanolysis system; and (Table S3) the recovery of *p*-TsOH experiments under different treatment conditions (PDF)

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Notes

The authors declare no competing financial interest.

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