ACS Sustainable Chemistry & Engineering

Research Article

Cite This: ACS Sustainable Chem. Eng. 2019, 7, 526−536

pubs.acs.org/journal/ascecg

Integrated Separation Process of C5 Sugars and Phenolics from Poplar Wood Using CO_2-Assisted Hydrolysis Followed by Hydrogenolysis

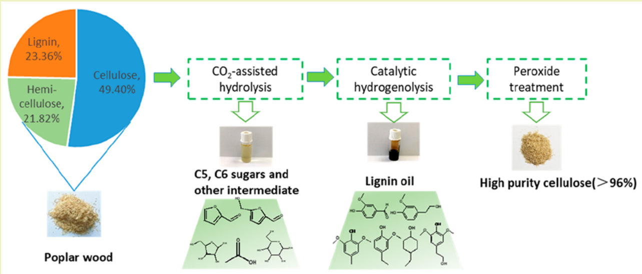
Qiaolong Zhai,[†] Fanglin Li,[†] Feng Long,[†] Fei Wang,[†] Jianchun Jiang,[†] Chung-yun Hse,[‡] and Junming Xu*,[†]

[†]Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry; National Engineering Laboratory for Biomass Chemical Utilization; Key and Open Laboratory on Forest Chemical Engineering, SFA; Key Laboratory of Biomass Energy and Material, Nanjing 210042, China

[‡]Southern Research Station, United States Department of Agriculture (USDA) Forest Service, Pineville, Louisiana 71360, United States

Supporting Information

ABSTRACT: This study presents an efficient methodology to remove hemicellulose and lignin from lignocellulosic biomass by a three-step process to obtain C5 sugars, phenolics and high purity cellulose. The first step, a CO_2-assisted hydrolysis pretreatment was conducted for the selective extraction of the hemicellulose fraction. The process effectively extracted hemicellulose at 180 °C with CO_2 at 20 bar initial pressure for 10 min, during which a variety of monosaccharides and other intermediates were obtained. The second step, the catalytic hydrogenolysis of the pretreated feedstock, was performed in a cosolvent isopropyl alcohol−water system with Raney Ni as the catalyst, which can catalyze the depolymerization of lignin components for phenolic products. A variety of phenolic components with lower molecular weights were detected via GC−MS and HSQC. Further treatment with alkaline hydrogen peroxide was used to extract the remaining small amount of lignin and hemicellulose fractions in biomass and to obtain high purity cellulose (>96%). Characterization results indicated that 96% of the lignin and 99% of the hemicellulose could be fractionated by the three-step treatment. This method can be used for the efficient fractionation of hemicellulose, cellulose and lignin, thus achieving high valorization of the entire biomass.



KEYWORDS: *Biomass fractionation, Hemicellulose, Hydrolysis, Lignin, Catalytic hydrogenolysis, High-purity cellulose*

INTRODUCTION

Growing global energy demands and diminishing fossil fuel resources have driven research toward the utilization of lignocellulosic biomass resources as a sustainable and renewable feedstock to create chemicals, materials and other products to replace fossil-based products.[1−3] Lignocellulosic biomass primarily consists of three main polymeric components: cellulose, hemicellulose and lignin, which account for 40−50%, 20−30% and 15−30%, respectively.[4] Effective biorefinery strategies are required before a selective conversion of lignocellulosic biomass components toward value-added products is possible. However, the structural complexity of biomass and the significant differences in the physical and chemical properties of cellulose, hemicellulose and lignin have created obstacles for the refining process of biomass.[5] Numerous research studies have explored an integrated biorefinery of an entire biobased feedstock via pyrolysis or liquefaction for the production of bio-oils, obtaining complex mixtures containing a variety of aldehydes, organic acids, esters, phenolics and oligomers, which create a huge barrier to the separation and refining process of the products.[6−8] Therefore, a prior fractionation of the lignocellulosic matrix into their different components (i.e., carbohydrates, lignin), might be an effective pathway for the reduction of the complexity of downstream refining processes.[9,10]

The most common lignocellulosic biomass fractionation strategies such as pulping use a sulfite, chlorite or alkaline solution as the solvent to fractionate the biomass.[11,12] These processes for the fractionation of biomass mainly focus on the production of high-quality cellulosic fibers, while most of the lignin and hemicellulose become waste streams. Unfortunately, due to the condensed and degraded nature of biorefinery lignin, it is typically burned for energy recovery or is used in low value material applications.[13,14] Various newly proposed fractionation strategies aim to obtain value-added chemicals and materials from the whole biomass, including lignin. Lignin

Received: August 16, 2018
Revised: December 1, 2018
Published: December 13, 2018

DOI: 10.1021/acssuschemeng.8b04077

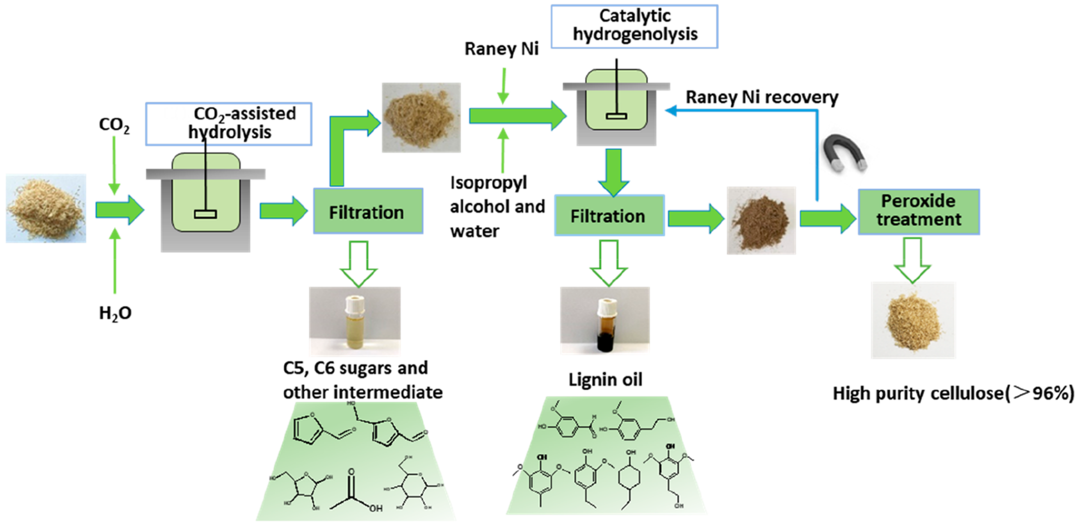


Figure 1. Schematic representation of stepwise extraction of hemicellulose and lignin from lignocellulosic biomass.

can provide a source for the production of aromatic liquid fuel.[15,16] Multiple new solutions have been reported for the isolation of lignin. Lignin can be fractionated from lignocellulosic biomass with some media in mild conditions, such as ionic liquids,[17,18] eutectic solvent,[19,20] γ-valerolactone,[21−23] or organic solvent systems.[24] The application of these media can achieve the deconstruction of biomass under mild conditions, which yield a reactive type of isolated lignin compared with traditional lignin (e.g., Kraft).[25] A new class of lignin fractionation technology, Reductive Catalytic Fractionation (RCF), is an active stabilization technique using reduction catalysts to stabilize reaction intermediates to prevent lignin condensation.[26−28] During RCF, it involves an initial solvolysis step that extracts the lignin fraction from biomass, followed by depolymerization and reductive stabilization.[12,29] The depolymerization and reductive stabilization process requires the presence of redox catalysts (e.g., Raney Ni, Ru/C, Pd/C, Ni/C) and a reducing agent, which contains pressurized H_2, an external hydrogen donor or an internal hydrogen donor (e.g., formic acid) derived from biomass.[27] The lignin fractionation technology results in highly depolymerized lignin oil comprising monomers, dimers and short lignin oligomers. The carbohydrates are recovered from biomass and retained in the solid fraction after RCF. Moreover, it has been reported that the depolymerization of hemicellulose and lignin simultaneously during RCF, while keeping cellulose in the solid fraction. The depolymerized lignin and hemicellulose can be separated based on their difference in polarity.[28]

The extraction of hemicellulose from lignocellulosic biomass has increasingly become the focus of recent studies. Hemicellulose can be a feedstock for chemicals (such as bioethanol and biopolymers), polymeric materials and even medicinal applications.[30−32] A variety of methods have been applied for the extraction of hemicellulose, such as dilute acid,[33] alkaline,[34] enzymatic hydrolysis,[35] autohydrolysis in hot water[36] and steam explosion versus steam treatment[37] techniques. Autohydrolysis in hot water extraction is an environmentally benign process, which has been widely used for lignocellulosic biomass pretreatment. Pontes et al. achieved 62% recovery of hemicellulose from corncobs in an autohydrolysis system at 206 °C under highly severe conditions (S_0 = 4.15).[38] Unfortunately, autohydrolysis in hot water without a catalyst results in low recovery of hemicellulose from biomass. In this paper, weak acids (carbonic acid) was used as the catalyst for extracting hemicellulose, which can be formed by pressurized carbon dioxide, wherein the carbonic acid formed in situ dissociates and causes the gradual acidification of the reaction mixture.[39,40] The hydrolysis of hemicelluloses makes the reaction proceed more rapidly under mild conditions and is environmentally friendly without acid pollution.

The aim of this study was to develop a methodology for the fractionation of lignocellulosic biomass. First, H_2O was used as a green medium for the CO_2-assisted hydrolysis treatment of the feedstock under mild conditions to remove the hemicellulose fraction. Second, catalytic hydrogenolysis of pretreated samples after CO_2-assisted hydrolysis was performed in an isopropyl alcohol and water medium with Raney Ni as the catalyst to extract the lignin fraction. As a result, fractionation of the hemicellulose and lignin compositions occored to obtain C5 sugars, phenolics and high purity cellulose was expected. The fractionation efficacy was evaluated by component analysis and combinational Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric (TG) and X-ray diffraction (XRD). The analysis of the liquor and solid fractions under various temperatures, times and initial pressures of CO_2 after the CO_2-assisted hydrolysis process was carried out. The phenolics derived from the depolymerization of lignin were characterized by two-dimensional HSQC-NMR, GC−MS, and GPC. The properties of the obtained high purity cellulose in terms of component analysis, crystallinity and thermal degradation were comprehensively investigated. This method can be used for the efficient fractionation of hemicellulose and cellulose for value-added chemicals and high purity cellulose, thus achieving the valorization of the entire biobased feedstock.

■ EXPERIMENTAL SECTION

Materials. In this study, poplar biomass was purchased from a local farm (Nanjing, China), passed through a 250−425-μm sieve and dried to a constant weight at 105 °C. The absolute-dried particles were kept in sealed bags until they were needed. All other chemical reagents were of analytical grade and used without further modification. The chemical composition (wt %) of the poplar was 49.40% cellulose, 21.82% hemicellulose, 20.62% acid insoluble lignin and 2.74% acid soluble lignin.

DOI: 10.1021/acssuschemeng.8b04077
ACS Sustainable Chem. Eng. 2019, 7, 526−536

CO_2-Assisted Hydrolysis Pretreatment. The CO_2-assisted hydrolysis treatment in a H_2O medium was conducted in a 250 mL high pressure reactor (Figure 1). The reaction mixture was filled with 8 g of poplar sawdust along with 80 mL of water. The CO_2 was flushed from the CO_2 high pressure gas cylinder into the reactor, the reactor was heated to the set temperature and maintained at the desired temperature for the time determined by the experimental design with a stirring rate of 350 rpm. After hydrolysis, the reactor was rapidly cooled to room temperature before opened. The exhaust valve was opened to slowly release carbon dioxide. The hydrolysis mixtures (pretreated materials and water-soluble fractions) were separated by filtration through filter paper. The pretreated materials after hydrolysis were washed with 100 mL of hot distilled water (100 °C) and stored at 4 °C.

$$\text{The degree of hydrolysis} = \left(1 - \frac{m_s}{m_0}\right) \times 100\% \tag{1}$$

$$\text{Delignification rate} = \left(1 - \frac{m_{L_d}}{m_{L_0}}\right) \times 100\% \tag{2}$$

$$\text{Re-cellulose rate} = \frac{m_{C_d}}{m_{C_0}} \times 100\% \tag{3}$$

$$\text{De-hemicellulose rate} = \left(1 - \frac{m_{H_d}}{m_{H_0}}\right) \times 100\% \tag{4}$$

Where m_0 was the mass of the raw poplar wood; m_s was the mass of the solid residues; m_{L_0}, $m_{\ C_0}$, m_{H_0}were the mass of the lignin, cellulose, hemicellulose in raw poplar wood, respectively; m_{L_d}, m_{C_d}, m_{H_d} were the mass of lignin, cellulose, hemicellulose respectively, in samples with the chemical treatment (CO_2-assisted hydrolysis or catalytic hydrogenation or alkaline hydrogen peroxide treatment). Thedelignification rate, de−cellulose rate and de- hemicellulose rate were the degree of lignin, cellulose and hemicellulose removal in feedstock, respectively. Recellulose was the retention of cellulose in feedstock.

Catalytic Hydrogenolysis of Pretreat Samples. After the CO_2-assisted hydrolysis pretreatment of the poplar feedstock, the catalytic hydrogenolysis of the pretreated materials was conducted to remove the lignin fraction. The pretreated sample (8 g) was combined with 70 g of isopropyl alcohol and 30 g of water cosolvent, reaching a mass ratio of cosolvent and pretreated sample of 12.5 with 2 g of Raney Ni as a reaction catalyst in a 250 mL high pressure reactor. 4 MPa of H_2 was loaded into the reactor from a H_2 high pressure gas cylinder. The reaction was performed at 180, 200, 220, and 240 °C with a stirring speed of 350 rpm for 6 h. The reactor was rapidly cooled to room temperature after reaching the desired time. Raney Ni could be easily removed from the suspension with a magnet. The mixture after hydrogenolysis was separated by filtration and 80 mL of isopropyl alcohol were used to wash the solid residue to remove any remaining lignin products on the surface of the solid. For convenience, the solid residues derived at 180, 200, 220, and 240 °C were marked as HGN180, HGN200, HGN220, and HGN240, respectively. The lignin oil derived at 180, 200, 220, and 240 °C are marked as OIL180, OIL200, OIL220, and OIL240, respectively. The yield of lignin oil products and solid residues were calculated by formulas 5 and 6).

$$\text{Yield of lignin oil} = \frac{m_l}{m_o} \times 100\% \tag{5}$$

$$\text{Yield of solid residues} = \frac{m_s}{m_o} \times 100\% \tag{6}$$

Where m_l was the mass of the lignin oil.

Analytical Methods. *Composition Analysis of Samples.* The cellulose, hemicellulose, and lignin contents in biomass or processed samples were analyzed by following NREL standard laboratory analytical procedure.[41]

XRD Analysis. The crystallinity analysis of the samples after the CO_2-assisted hydrolysis and catalytic hydrogenolysis was performed using XRD with an XRD-6000 X-ray diffract meter with monochromatic Cu/Kα radiation (λ = 0.154 18 nm). The diffracted intensity was measured from 10 to 60° (2θ) using a counting speed of $2° \ \text{min}^{-1}$ with a step of 0.02°. The crystallinity index (CrI) of cellulose in biomass was calculated from formula 7:[42]

$$\text{CrI\%} = (I_{002} - I_{am})/I_{002} \times 100\% \tag{7}$$

Where I_{002} is the peak intensity of the (002) lattice diffraction at 2θ = 22.4° and I_{am} is the diffraction intensity of the amorphous region at 2θ = 18.0°.

FT-IR Spectroscopic Analysis. The functional groups of the samples with treatment were analyzed by FT-IR spectroscopy with a Thermo 208 Nicolet (NEXUS 670) spectrometer. The analysis was completed from 600 to 4000 cm^{-1} at a resolution >0.4 cm^{-1} and a wavenumber accuracy of >0.01 cm^{-1}.

GPC Analysis. The molecular weight of the lignin oil was determined on a Waters 1515 system equipped with a manually packed column. The injection volume was 20 μL with tetrahydrofuran as the eluent. Polystyrene was used as an internal standard.

2D-HSQC NMR Spectroscopy Analysis. The lignin oil were characterized by 2D HSQC NMR spectra to analyze the specific structures of the complex compounds. The NMR samples were prepared by dissolving the lignin oil in DMSO-d_6 at 30 °C with benzaldehyde as an internal reference. All NMR experiments were recorded on a Bruker DRX 500 NMR spectrometer operated at 500 MHz. The spectral widths for the 1H and 13C dimensions were 8.5 and 120 ppm, respectively.

Thermogravimetric (TG) Analysis. The TGA of the samples with the CO_2-assisted hydrolysis and catalytic hydrogenolysis treatment was conducted using a Pyris6 TG analyzer (PerkinElmer, Waltham, MA). The samples (~10 mg) were heated from room temperature to 800 °C at a heating rate of 10 °C/min with a flow of 50 mL min^{-1} of N_2.

High-Performance Liquid Chromatography (HPLC) Analysis. The water-soluble components (xylose, arabinose, glucose, acetic acid, furfural, and HMF) after hydrolysis were detected using a HPLC instrument (Waters 2414, America) with a Bio-Rad Aminex HPX-87H (300 mm × 7.8 mm) column and a refractive index detector. The mobile phase was 5-mM H_2SO_4 at a flow rate of 0.5 mL/min and the column temperature was maintained at 50 °C. The amounts of xylose, arabinose, glucose, acetic acid, furfural, and HMF were calculated based on external standard curves constructed with authentic standards.

GC−MS Analysis. The composition of lignin oil was analyzed by GC−MS. All samples were dissolved in the methanol solvent. The GC−MS was equipped with an HP-5 column (30 m × 0.25 μm × 0.32 nm i.d. capillary column), a hydrogen flame ion detector, and a WSC meteorological chromatography workstation. The specific detection conditions were as follows. The injection mode was split at a rate of 35, the carrier gas was He at a flow rate of 1.5 mL/min, and the column was heated to 30 °C and maintained for 5 min. It was then further heated to 250 °C at a rate of 10 K/min and held for 20 min. The inlet temperature of the sample was 250 °C and the injection volume was 0.2 μL.

RESULTS AND DISCUSSION

CO_2-Assisted Hydrolysis of Poplar. *Analysis of Solid Residues after CO_2-Assisted Hydrolysis.* For the first step, the hydrolysis of poplar was conducted in a CO_2-H_2O system, wherein the carbonic acid formed in situ dissociates, leading to a weak acid environment in the system. The purpose of the CO_2-assisted hydrolysis was to hydrolyze the hemicellulose fraction while retaining the cellulose and lignin as much as possible. The effect of hydrolysis conditions, such as initial pressure, reaction time and temperature, on the degree of

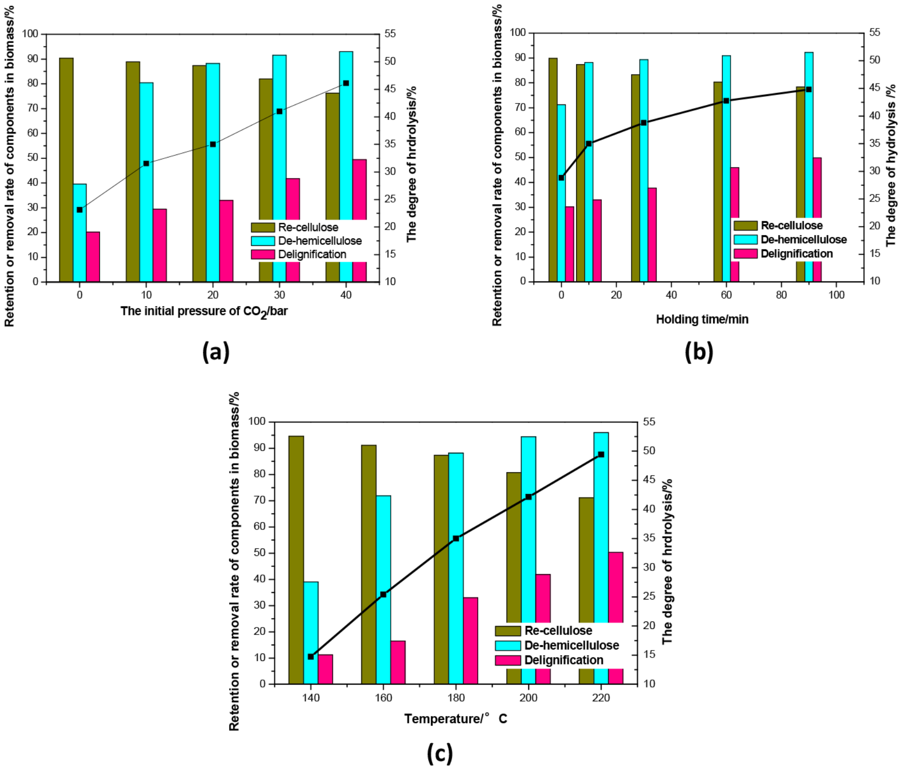


Figure 2. Degree of retention or removal of components in biomass and degree of hydrolysis with CO_2-assisted hydrolysis affected by (a) initial CO_2 pressure, (b) holding time, and (c) temperature. Reaction condition of panel a: maintain a temperature of 180 °C and holding time of 10 min. Reaction condition of panel b: maintain a temperature of 180 °C and initial CO_2 pressure of 20 bar. Reaction condition of panel c: maintain a holding time of 10 min and initial CO_2 pressure of 20 bar.

hydrolysis and the composition of cellulose, hemicellulose, and lignin in solid residues were determined.

It was essential to control the initial pressure of CO_2 in order to prevent the system from being overly acidic by the high initial pressure, and decreasing the depolymerization of the cellulose and lignin fractions. The influence of the initial pressure of CO_2 on the hydrolysis of poplar was investigated to identify the optimal conditions for extracting hemicellulose. As can be seen from Figure 2a, the degree of hydrolysis could be significantly improved in the presence of CO_2 in the system (maintaining a short holding time of 10 min and a low temperature of 180 °C). The conversion of poplar at 180 °C could be increased from low conversion of only 23.14% without CO_2 to a high value of 31.53% with an initial CO_2 pressure of 10 bar. Meanwhile, the dehemicellulose rate after hydrolysis increased from 38.59% to 80.42%. The results indicated that the presence of CO_2 effectively enhanced the hydrolysis of the hemicellulose fraction in feedstock. The degree of hydrolysis increased from 31.53% to 46.11% as the initial pressure of CO_2 increased from 10 to 40 bar. Comparison to the hemicellulose content (21.82%) in poplar feedstock suggested that part of the cellulose and lignin had been depolymerized during the CO_2-assisted hydrolysis process. The dehemicellulose rate increased from 80.42 to 88.18% with the increase of CO_2 pressure from 10 to 20 bar. Upon further increasing the pressure to 30 and 40 bar, the dehemicellulose rates only increased by 3.14% and 4.83%, respectively, compared with the 20 bar CO_2 pressure. Meanwhile, the delignification rate increased from 32.97% to 41.78% and 49.44%, and the recellulose rate decreased from 87.37% to 81.93% and 76.23%. This was due to the higher CO_2 pressure (30 and 40 bar), leading to higher acidity in the system, resulting in degradation of more lignin and cellulose components in the feedstock. Thus, it was decided to use 20 bar as the initial pressure for the study.

The holding time was an important factor for investigating the hydrolysis of poplar (Figure 2b). The holding time was increased from 0 to 90 min, while keeping the temperature at 180 °C and using a low pressure of CO_2 of 20 bar. As the holding time increased, so did the degree of hydrolysis, and the hemicellulose content in the solid residue decreased. In particular, it was found that the dehemicellulose rate could be increased from 71.20% without holding time to 88.18% with a 10 min holding time. When further prolonging the holding time from 10 to 90 min, the dehemicellulose rate varied from 88.18% to 92.23%. Meanwhile, the delignification rate increased from 32.97% to 49.86% and recellulose rate decreased from 87.37% to 78.32%, indicating that it was mainly the depolymerization of the lignin fraction for a long holding time during the hydrolysis process. Taking into account the energy consumption and component (cellulose, hemicellulose, and lignin) content in the solid residues, it was decided that a 10 min holding time would be used for further study.

In general, increasing the temperature promoted the conversion of biomass and accelerated the rate of hydrolysis. It was found that the conversion of poplar gradually increased with temperature from 140 to 220 °C (maintaining a short holding time of 10 min and using a low pressure of CO_2 of 20 bar) (Figure 2c), with a maximum degree of hydrolysis of 49.43% at 220 °C. Meanwhile, the dehemicellulose rate was significantly increased from 39.04% to 95.99% as the

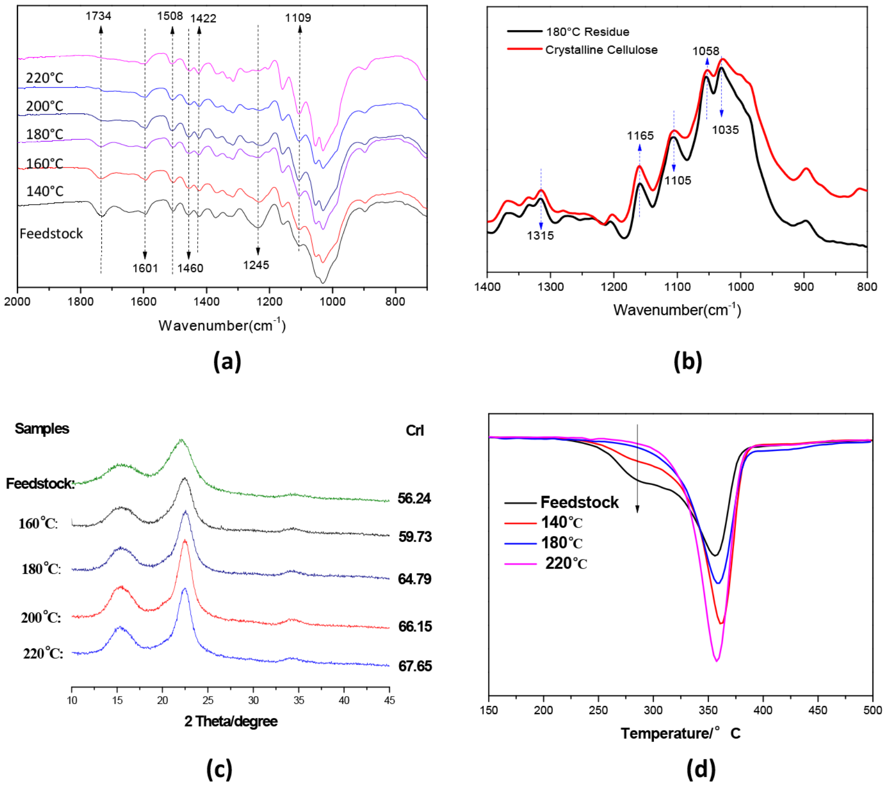


Figure 3. (a) FT-IR spectra of feedstock and solid residues obtained after CO_2-assisted hydrolysis at various temperatures from 2000 to 700 cm^{-1}. (b) FT-IR spectra of microcrystalline cellulose and solid residue obtained after CO_2-assisted hydrolysis at 180 °C. (c) XRD analysis of feedstock and samples with CO_2-assisted hydrolysis treatment at various temperatures. (d) DTG analysis of feedstock and solid residues obtained after CO_2-assisted hydrolysis at various temperatures.

temperature increased. However, the lignin content in the solid residues decreased from 160 to 220 °C with increasing the delignification rate from 16.51% to 50.25% and decreasing recellulose rate from 91.14% to 71.08%. At 180 °C, 88.18% of the hemicellulose fraction was extracted; meanwhile, 87.37% of cellulose and 67.03% of lignin were kept in solid residues. With further elevation of the temperature to 200 and 220 °C, the dehemicellulose rate had a high value of 94.41 and 95.99%, respectively. While the recellulose rate was less than 81% and the delignification rate was over 41% in solid residues. Therefore, 180 °C was the optimum reaction temperature for the extraction of hemicellulose.

To further understand this observation, the FT-IR spectra of poplar feedstock and solid residues obtained after the CO_2-assisted hydrolysis treatment at various temperatures are displayed in Figure 3a. The absorbance bands at ∼1735 and 1245 cm^{-1} were attributed to the carbonyl (C═O) stretch in unconjugated ketone, ester, or carboxylic groups in xylose.[43,44] These two absorbance bands gradually decreased with increasing temperature and they greatly weakened after the CO_2-assisted hydrolysis treatment at 180 °C and disappeared at 220 °C, which indicated that most of the hemicellulose had been extracted over 180 °C. The absorbance peaks at 1603, 1512, 1460, 1422, 1111, and 833 cm^{-1} were related to the typical features of lignin, and the peaks at 2900, 1423, 1370, 1160, 1115, 1060, and 897 cm^{-1} contributed to the absorbance peaks in cellulose.[45] From the FT-IR spectra of poplar at different temperatures, it was found that lignin remained in the solid residues after the cleavage of intermolecular linkages between hemicellulose and lignin.[46] Furthermore, there was almost no change in the characteristic peaks after hydrolysis at 180 °C were compared with microcrystalline cellulose (Figure 3b.). Indicating that crystallized cellulose was not significantly affected during the hydrolysis treatment. The above results confirmed an enrichment of cellulose and lignin in the pretreated feedstock due to the extraction of the hemicellulose fraction.

In order to study the changes in the crystal structure and crystallinity of cellulose before and after hydrolysis treatment. The samples obtained at various temperatures during the CO_2-assisted hydrolysis process were analyzed with XRD (Figure 3c). The XRD patterns displayed three broad peaks at ∼16°, 22°, and 35°, which represented the (110), (002), and (004) planes, respectively. The CrI, as a key factor in influencing the mechanical and thermal properties, was calculated according to the Segal method. The CrI of the solid residues increased with increasing temperatures. Furthermore, the CrI of the samples after hydrolysis treatment showed a 3.49−7.92% enhancement compared with poplar feedstock. Undoubtedly, the increase in CrI was due to the removal of the noncrystalline components, especially hemicellulose in samples with increased treatment based on sample component and XRD analysis.

Figure 3d shows the derivative mass loss curves for samples with different temperature treatments. It was reported that the hemicellulose pyrolysis peak is at 220−315 °C and the maximum mass loss rate is ∼250−300 °C. The pyrolysis peak of cellulose pyrolysis was between 300 and 400 °C and the maximum mass loss rate is usually ∼350 °C.[47,48] It can be seen that the DTG curves of the sample showed one broad peak at low temperature (∼280 °C). It was clear that the broad peak was due to the decomposition of hemicellulose in biomass. It was found that the hemicellulose component in the hydrolyzed

Table 1. Composition of Liquors from CO_2 Hydrolysis of Poplar and Yields of Each Product under Various Conditions

reaction conditions		composition in the liquors/yields[a] derived from hemicellulose and cellulose							
T (°C)	pCO_2 (bar)	xylose	arabinose	acetic acid	furfural	glucose	HMF	total yield[a]	total yield[b]
140	20	1.50	–	2.72	–	–	–	4.23	3.01
160	20	3.09	1.11	4.30	0.41	0.74	–	9.65	6.87
180	0	2.13	0.72	4.18	0.94	1.01	–	8.99	6.4
	10	2.42	1.42	4.62	1.29	1.36	–	11.11	7.91
	20	4.59	1.43	5.73	2.13	1.80	0.37	16.05	11.43
	30	4.89	1.59	5.95	2.25	2.53	1.11	18.31	13.04
	40	5.07	1.80	6.32	2.56	3.66	1.29	20.70	14.74
200	20	6.37	1.70	7.50	2.51	3.40	1.47	22.96	16.35
220	20	7.40	2.11	10.40	2.84	5.29	1.68	29.72	21.17

[a] The yield was calculated based on the content of the hemicellulose and cellulose in feedstock. [b] The yield was calculated based on the entire feedstock.

Table 2. Chemical Composition Analysis of Samples with Catalytic Hydrogenolysis Treatment[a]

			composition of the solid residues after hydrogenolysis (%)				
temp. (°C)	yield of lignin oil[b] (%)	yield of solid residues[b] (%)	cellulose	hemicellulose	lignin	delignification rate (%)	dehemicellulose rate (%)
180	7.67	51.64	83.79	2.16	10.62	78.01	95.21
200	10.88	48.9	85.64	1.74	8.33	81.78	95.93
220	14.61	42.79	91.50	1.09	4.01	90.18	97.14
240	14.87	42.16	91.63	0.94	3.79	90.62	97.51

[a] The pretreated sample for the catalytic hydrogenolysis treatment was derived from the samples after the CO_2-assisted hydrolysis at a temperature of 180 °C, a retention time of 10 min and an initial CO_2 pressure of 20 bar. Reaction condition: 8 g of pretreat samples combined with 70 g of isopropyl alcohol and 30 g of water cosolvent, Raney Ni (2 g) as catalyst, 4 MPa of H_2 for 6 h of holding time. [b] The yield of lignin oil and solid residues were calculated based on the entire poplar feedstock.

solid residue gradually decreased as the temperature was raised from 140 to 220 °C compared with the raw material. It almost completely disappeared at 180 and 220 °C, indicating that most of the hemicellulose was removed during the CO_2-assisted hydrolysis over 180 °C.

Composition of Liquors after CO_2-Assisted Hydrolysis. The composition of the liquors was examined in this study using HPLC analysis. A variety of small molecular products were detected, including xylose, arabinose, acetic acid, furfural, glucose and HMF. The CO_2-assisted hydrolysis system forms *in situ* carbonic acid, which promotes the cleavage of hemicellulose bonds into C5 monosaccharides, such as xylose, arabinose, and acetic acid. Acetic acid was mainly derived from the hydrolysis of acetyl groups in *O*-acetyl-4-*O*-methylglucuronoxylan in hemicellulos.[9] Meanwhile, the cellulose in the amorphous region also can be depolymerized into C6 monosaccharides, such as glucose. Additionally, these monosaccharides can be further converted to degradation products, such as furfural and hydroxyl methyl furfural (HMF). The composition of liquors obtained from the CO_2-assisted hydrolysis treatment under various temperatures and initial pressures is depicted in Table 1.

The yield of C5 monosaccharides (xylose and arabinose) and acetic acid deriving from hemicellulose increased with increasing temperature and the initial CO_2 pressure. Furthermore, it was found that xylose and acetic acid were the main small molecule hydrolyzates obtained by CO_2-assisted hydrolysis at various temperatures and initial pressures. The yield of the C5 monosaccharide derivative (furfural) gradually increases with increasing temperature (140−220 °C) and pressure (10−40 bar), but its yield was quite low. The yield of the C5 monosaccharide and its derivatives accounts for more than 76% of the total yield of the water-soluble liquor after CO_2-assisted hydrolysis, indicating that the CO_2-assisted hydrolysis treatment results in the effective depolymerization of hemicellulose with the increase of temperature and initial pressure.

The higher temperatures and pressures increased the yield of the C6 monosaccharide (glucose) and its derivatives (HMF) mainly deriving from cellulose. Furthermore, it was observed that the yield of glucose increased rapidly when the temperature exceeded 200 °C, indicating that the depolymerization of cellulose began to depolymerize more rapidly due to the high temperature and acidic environment at this condition. The goal of the hydrolysis was to extract the hemicellulose fraction and retain the cellulose and lignin components. Thus, a hydrolysis temperature below 200 °C was a more suitable choice.

In addition, for all experiments, there were differences between the degrees of hydrolysis and the total yield of products in the liquor based on the HPLC analysis. For example, the degree of hydrolysis at 180 °C and 20 bar CO_2 was 35.02%, while the total yield of monosacharaides and its derivatives based on the whole feedstock in the liquor displayed in Table 1 were only 11.43%. This 23.59% difference might be due to the presence of C5, C6 polysaccharides, water-soluble lignin, and small amount of extractives in the liquor.

Selective Catalytic Hydrogenolysis of Pretreated Samples. The CO_2-assisted hydrolysis treatment removed most of the hemicellulose, during which monosaccharides and other intermediates were obtained. Meanwhile, most of the cellulose and lignin was retained in the solid residues. Depolymerization of the lignin into low molecular weight aromatics might be an effective solution for the valorization of lignin. Selective catalytic hydrogenolysis of samples after the CO_2-assisted hydrolysis treatment was conducted to selectively extract the lignin composition in biomass and high purity cellulose is expected.

To achieve the extraction of lignin in high yields, the effects of temperature on the fractionation of pretreated feedstock were examined. The catalytic hydrogenolysis process was performed under an isopropyl alcohol and water (7:3, w/w) cosolvent system with Raney Ni as the hydrogenolysis catalyst at various temperatures (Table 2). The yield of lignin oil derived from the depolymerization lignin was increased from 7.67% to 14.87%, and the lignin content in solid residues after hydrogenolysis was decreased from 10.62% to 3.79% from 180 to 240 °C. The results indicated that the lignin fraction was effectively extracted during the catalytic hydrogenolysis process. In addition, the delignification and dehemicellulose rate reached more than 90% and 97%, respectively, at 220 °C. The purity of cellulose in solid residues reached more than 91% after the hydrogenolysis treatment at 220 °C, suggesting that a substantial part of the hemicellulose and lignin was successfully removed using CO_2-assisted hydrolysis followed by the hydrogenolysis process. The yield of lignin oil and purity of cellulose in the solid residues obtained at 220 °C was similar to that at 240 °C. Thus, 220 °C was selected for the extraction of lignin in the hydrogenolysis process.

Figure 4 displays a GC−MS analysis image of the lignin oil obtained from catalytic hydrogenolysis of poplar in the presence of Raney Ni in an isopropyl alcohol/H_2O system at 220 °C for 6 h. Numerous types of phenolic monomers and naphthenic were identified in the products (Table S1), mainly including 4-(2-hydroxyethyl)-2,6-dimethoxyphenol (15.54%), benzene, 2,6-dimethoxy-4-methylphenol (14.64%), homovanillyl alcohol (9.86%), 4-ethylcyclohexanol (6.12%), 4-(2-hydroxyethyl)-2-methoxyphenol (5.50%), 1-methoxybutan-2-ol (5.10%), and 4-ethyl-2-methoxyphenol (4.34%). This suggested a successful depolymerization of lignin toward soluble phenolics and a small portion of naphthenic. In addition, 1-methoxybutan-2-ol, cyclopentane-1,2-diol, hexane-2,5-diol, and other diols were derived from the hydrogenolysis of hemicellulose. Therefore, the hydrogenolysis process not only removed most of the lignin in biomass, but also depolymerized lignin into a small molecule phenolics and naphthenic products.

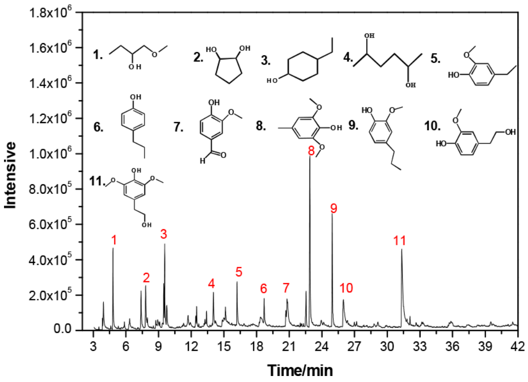


Figure 4. GC−MS results of lignin oil obtained from catalytic convention of pretreated poplar in the presence of Raney Ni.

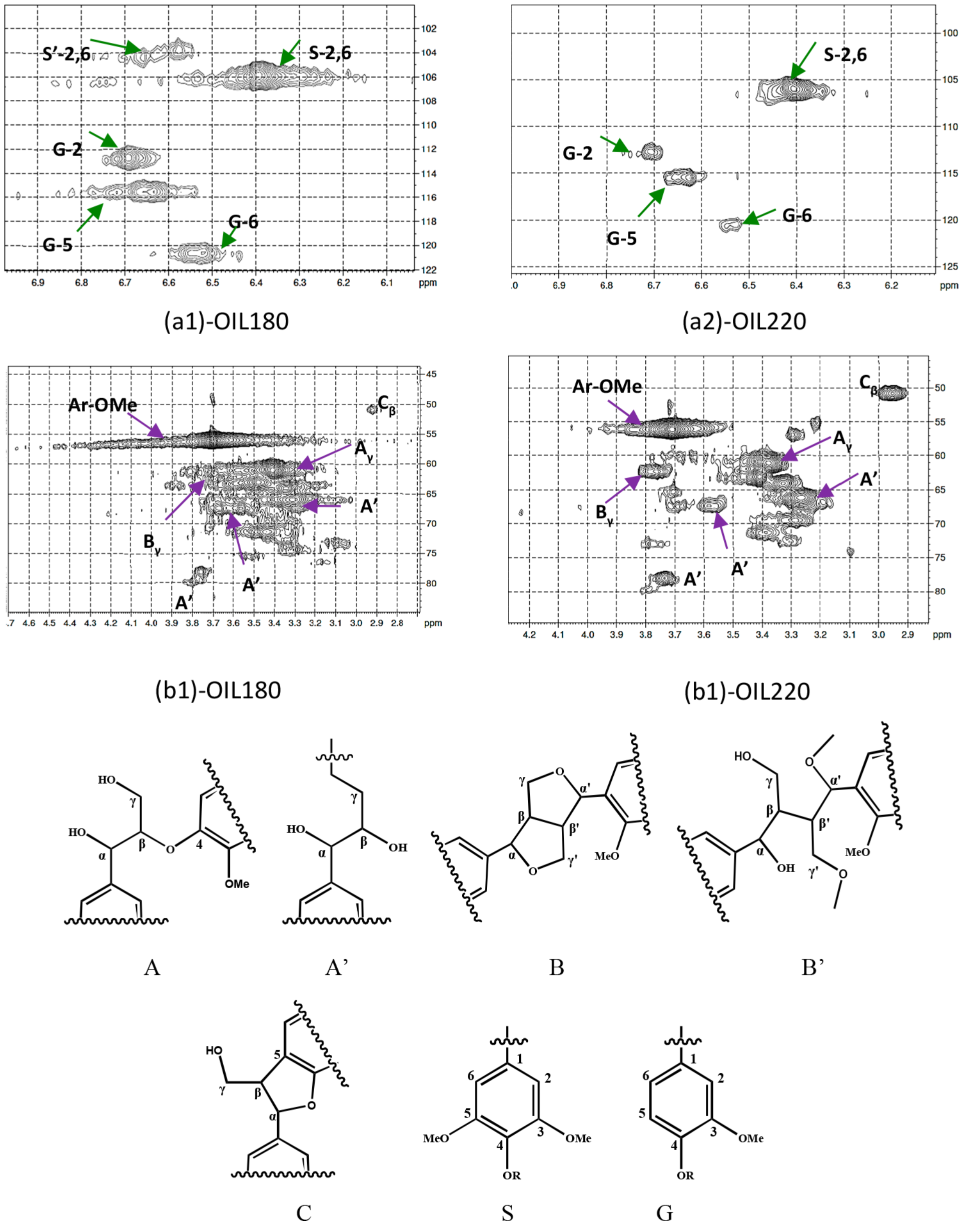
The weight-average (Mw) and number-average (Mn) molecular weights of lignin oil were analyzed using gel permeation chromatography (Figure S1). The results demonstrated that lignin was depolymerized into products with much lower weight-average (Mw) (TableS2). The distribution of apparent Mw values continually shifted toward lower values (from 467 to 343) with an increase in temperature from 180 to 220 °C, indicating the further decomposition of lignin with the increasing temperatures.

To gain further information about the compositional and structural features of the lignin oil. 2D HSQC NMR were performed to characterize the samples. The OIL180 and OIL220 subjected to the hydrogenolysis process were selected as representatives. The HSQC spectra of the lignin oil are shown in Figure 5. The HSQC spectra of the lignin oil can be divided up into three regions: the aromatic region ($\delta C/\delta H$ 110−130/6.0−8.0 ppm), the aliphatic C−O side chain region ($\delta C/\delta H$ 50−90/2.5−5.0 ppm), and the aliphatic C−C side-chain region ($\delta C/\delta H$ 10−40/0.5−2.8 ppm). Additionally, the cross signals at $\delta C/\delta H$ 91−105/3.9−5.4 ppm are mainly attributed to the lignin-carbohydrate complex (LCC) structure[49,50] and the absence of signal in this region indicated LCC bonds were cleaved during the catalytic hydrogenolysis process.

The S and G, which are the basic lignin structures, provided correlations of the aromatic C−H group in the two conglomerates. As can be seen in Figure 5a, the cross signals at $\delta C/\delta H$ 107.0/6.50 ppm were attributed to the $C_{2,6}/H_{2,6}$ correlations of S units and the cross signals at $\delta C/\delta H$ 107.5 ppm/7.25−7.35 ppm were attributed to the $C_{2,6}/H_{2,6}$ correlations of the oxidized syringyl (S′) units. The signals at $\delta C/\delta H$ 114.5 ppm/6.70−6.80 and 115.5 ppm/6.65 ppm were attributed, respectively, to the C_5/H_5 and C_6/H_6 correlations in the G unit. Furthermore, obviously, the spectrum of the OIL180 has a higher ratio of G and S units than that of OIL220 and the signals in the former are much broader than in the latter, the S′ group signals in OIL220 sample even was not detected, which was due to its higher molecular weight and slower molecular motion.[29]

The aliphatic C−O side-chain regions provide structural information regarding the interunit linkages of lignin oil (Figure 5b). Correlation signals at $\delta C/\delta H$ 53−58 ppm/3.15−3.95 ppm were attributed to the methoxyl groups, which were obviously the most prominent units in this region. They were connected to the aromatic rings or aliphatic carbons. Those connected to the aromatic rings derived mainly from S−3−OMe, G−3−OMe, S−5−OMe, and G−5−OMe linkages present in the original lignin structure. While the methoxyl groups, which connected to aliphatic carbons, mainly contributed by the decomposition of the β−5, β−β', and β−O−4 linkages in lignin.

Peroxide Treatment of Samples after Catalytic Hydrogenolysis. The aim of the hydrolysis and hydrogenolysis treatment of poplar was the removal of the hemicellulose and lignin fractions. In the HGN220 sample, the contents of cellulose, hemicellulose and lignin were 91.50%, 1.09%, and 4.01%, respectively, and 90.18% of the total lignin and 97.14% of the hemicellulose were extracted from the poplar feedstock. In order to further improve the purity of cellulose, additional treatment should be adopted to fractionate lignin and hemicellulose (mainly lignin) as completely as possible without destroying the cellulose component. Peroxide oxidation is more aggressive with lignin and hemicellulose, the peroxide superoxide radical can oxidize the aromatics of lignin and hemicellulose to carboxylic acid compounds.[51,52] Conversely, cellulose is less easily decomposed by peroxide under mild conditions.



(a1)-OIL180 (a2)-OIL220

(b1)-OIL180 (b1)-OIL220

Figure 5. 2D-HSQC NMR spectra of lignin oil: (a) the aromatic region (δC/δH 110−130/6.0−8.0 ppm), (b) the aliphatic C−O side chain region (δC/δH 50−90/2.5−5.0 ppm).

After the alkaline hydrogen peroxide treatment of the HGN220 sample, the cellulose, hemicellulose and lignin contents in the cellulose rich solid residue (cellulose pulp) were 96.13%, 0.27% and 1.06%, respectively. The delignification and dehemicellulose rate reached more than 96% and 99%, respectively. This indicated that the peroxide contributed to further fractionation of biomass, resulting in higher purity cellulose (>96%).

Characteristic of Obtained Cellulose Pulp. In order to study the changes in the crystal structure and crystallinity of cellulose before and after hydrolysis, catalytic hydrogenolysis and peroxide treatment. The samples with different treatments were analyzed with XRD (Figure 6a). The fact that the CrI of the sample after CO_2-assisted hydrolysis (64.79%) was higher than the raw material (56.24%) was due to the extraction of noncrystalline fractions, especially hemicellulose. The CrI of the samples after catalytic hydrogenolysis showed a 5.36−10.10% enhancement from the hydrolysis pretreated sample. Undoubtedly, the increase in CrI was mainly due to the removal of the lignin fraction in poplar. The CrI of the HGN220 sample was very close to that of microcrystalline cellulose, indicating that the HGN220 sample had reached a high content of cellulose. Then, after the treatment of alkaline hydrogen peroxide, the CrI of the cellulose pulp was slightly decreased compared to the HGN220 sample, which suggested the alkaline hydrogen peroxide had a negative effect on the crystalline region of cellulose.

The DTG curves, which represent the rate of weight loss of the sample, are shown in Figure 6b. Compared with the microcrystalline cellulose, the fact that the lower starting decomposition temperature and maximum degradation rate of the DTG curves of the HGN180 and HGN200 samples contributed to some of the hemicellulose and lignin (mainly lignin) not having been extracted in samples. The DTG curves of the HGN220 showed that the starting decomposition temperature occurred at 335 °C, and the maximum

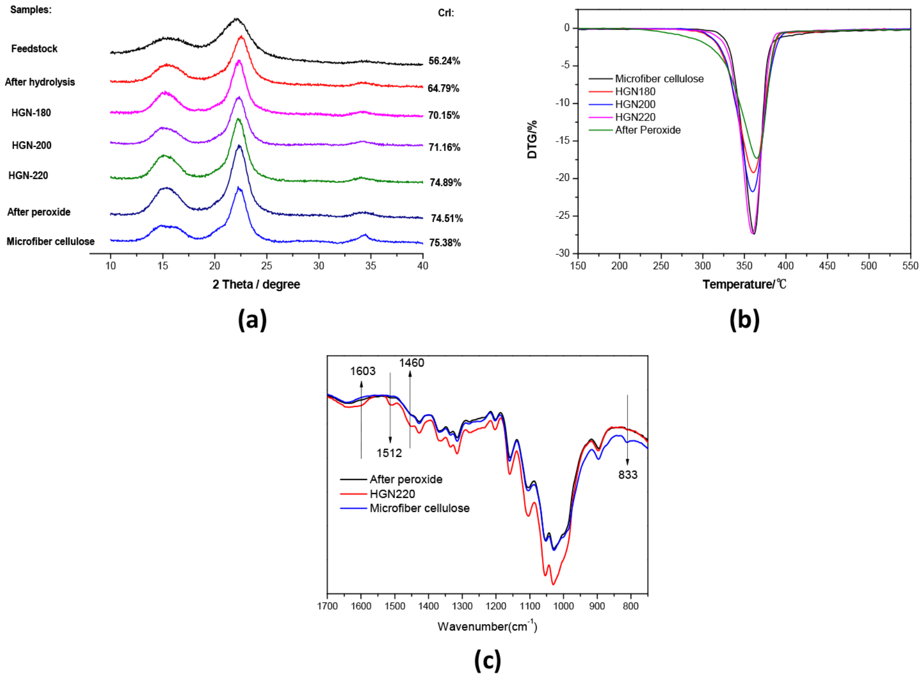


Figure 6. (a) XRD analysis of feedstock and samples with hydrogenolysis and alkaline hydrogen peroxide treatment. (b) DTG analysis results of solid samples with hydrogenolysis and peroxide treatment. (c) FT-IR spectra of commercial cellulose and solid residue obtained after hydrogenolysis and peroxide treatment from 1700 to 800 cm^{-1}.

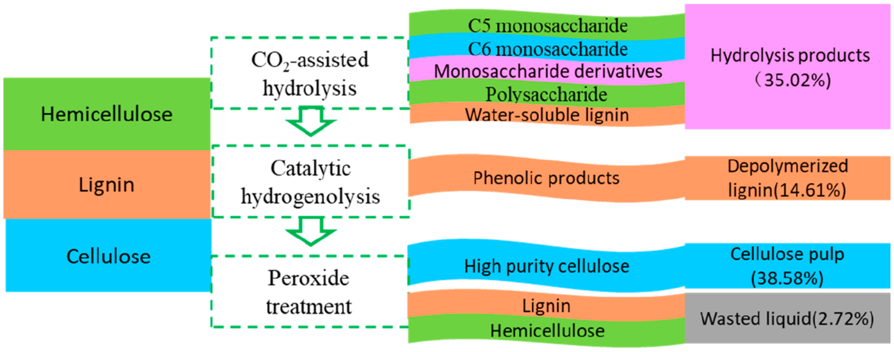


Figure 7. Mass balance of poplar feedstock with CO_2-assisted hydrolysis, catalytic hydrogenolysis, and peroxide treatment.

degradation rate reached 25 °C/min at ~360 °C, which was consistent with the loss of microcrystalline cellulose, showing the high purity of cellulose in the HGN220 sample. In addition, the curve of the sample after the alkaline hydrogen peroxide treatment showed an earlier weight loss that started at ~220 °C, indicating that the alkaline hydrogen peroxide treatment had destroyed the crystalline region of cellulose, consistent with the XRD analysis.

The HGN220 sample and cellulose pulp were further analyzed by FT-IR spectroscopy (Figure 6c). Comparing the FT-IR of the two samples (HGN220 sample and cellulose pulp) with the microcrystalline cellulose, it was found that the hemicellulose absorption peak in the HGN220 sample was not detected, and the lignin still had obvious absorbance peaks at 1603, 1512, 1460, and 833 cm^{-1}. This indicated that the hemicellulose in the sample was almost completely removed, but some of the lignin remained in the sample. The absorbance peaks of the cellulose pulp were consistent with that of microcrystalline cellulose, and the absorption peaks of hemicellulose and lignin were not detected. This indicated that most of the noncellulosic component had been extracted in the cellulose pulp.

Mass Balance of Whole Treatment of Poplar Feedstock. Figure 7 displays the mass balance of the fractionation of the whole feedstock using CO_2-assisted hydrolysis followed by catalytic hydrogenolysis and peroxide treatment. The optimal CO_2-assisted hydrolysis of poplar feedstock was achieved under a shorter reaction time of 10 min, a moderate temperature of 180 °C, and an initial pressure of 20 bar with a yield of hydrolysis of 35.02%. More than 88.18% of hemicellulose was removed from the feedstock, and 87.3% of cellulose and 67.03% of lignin kept in solid residues after the CO_2-assisted hydrolysis. The yield of monosaccharide (xylose, arabinose, and glucose) and monosaccharide derivatives (acetic acid, furfural, and HMF) after hydrolysis treatment at 180 °C of poplar was 11.43% according to the HPLC analysis. The yield of lignin oil was 14.61% based on the original feedstock. A wide variety of phenolic products and small amounts of naphthenic components were obtained. The HGN220 was selected for further bleaching treatment with 5 wt % H_2O_2 and 4 wt % NaOH to remove the remaining hemicellulose and lignin components. The result was the removal of 99% of the hemicellulose and 96% of the lignin from feedstock via the above process. The yield of cellulose pulp reached 38.58% based on the whole feedstock with the purity of cellulose of more than 96%. This can achieve the integrated utilization of the whole biomass and obtain the saccharide and derivatives, phenolics and high purity cellulose.

CONCLUSIONS

We developed an efficient strategy for achieving the extraction of hemicellulose and lignin from poplar sawdust for C5 sugars, phenolics, and high purity cellulose production. More than 88.18% of hemicellulose was removed by the CO_2-assisted hydrolysis process at 180 °C with CO_2 of 20 bar initial pressure for 10 min. The obtained monosaccharides and other intermediates have great potential for biomaterials or biochemicals. Catalytic hydrogenolysis was performed after the CO_2-assisted hydrolysis, using isopropyl alcohol/water (7:3 w/w) as the cosolvent and Raney Ni as the catalyst in the presence of H_2 to extract the lignin fraction, the lignin oil containing various phenolics were obtained. More than 90% of lignin and 97% of hemicellulose was fractionated, and the purity of cellulose reached 91.50% in solid residues after the catalytic hydrogenolysis process at 220 °C. In order to obtain a higher purity of cellulose, additional treatment with alkaline hydrogen peroxide removed the remaining small amount of lignin and hemicellulose, resulting in high purity cellulose (>96%). The above results showed that this strategy can be an effective alternative scheme to the fractionation of biomass and provides the possibility for the valorization of the biobased feedstock.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b04077.

GC–MS analysis of the OIL220 obtained from catalytic hydrogenolysis, molecular weight analysis of lignin oil derived from the hydrogenolysis of pretreated poplar at different temperatures, GPC image of lignin oil obtained from the catalytic hydrogenolysis of pretreated poplar at various temperatures (PDF)

AUTHOR INFORMATION

Corresponding Author

*J. Xu. Tel. +86 2585482478; Fax: 025-85482485; E-mail: xujunming@icifp.cn.

ORCID

Junming Xu: 0000-0002-1398-2336

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the financial support provided by the National Natural Science Foundation of China (31530010) for this investigation.

REFERENCES

(1) Sun, Z.; Bottari, G.; Afanasenko, A.; Stuart, M. C.; Deuss, P. J.; Fridrich, B.; Barta, K. Complete lignocellulose conversion with integrated catalyst recycling yielding valuable aromatics and fuels. *Nat. Catal.* **2018**, *1* (1), 82–92.

(2) Tuck, C. O.; Pérez, E.; Horváth, I. T.; Sheldon, R. A.; Poliakoff, M. Valorization of biomass: deriving more value from waste. *Science* **2012**, *337* (6095), 695–699.

(3) Shi, N.; Liu, Q.; Zhang, Q.; Wang, T.; Ma, L. High yield production of 5-hydroxymethylfurfural from cellulose by high concentration of sulfates in biphasic system. *Green Chem.* **2013**, *15* (7), 1967–1974.

(4) Agirrezabal-Telleria, I.; Gandarias, I.; Arias, P. L. Heterogeneous acid-catalysts for the production of furan-derived compounds (furfural and hydroxymethylfurfural) from renewable carbohydrates: A review. *Catal. Today* **2014**, *234* (10), 42–58.

(5) Yat, S. C.; Berger, A.; Shonnard, D. R. Kinetic characterization for dilute sulfuric acid hydrolysis of timber varieties and switchgrass. *Bioresour. Technol.* **2008**, *99* (9), 3855–3863.

(6) Jacobs, P. A.; Dusselier, M.; Sels, B. F. Will Zeolite-Based Catalysis be as Relevant in Future Biorefineries as in Crude Oil Refineries? *Angew. Chem., Int. Ed.* **2014**, *53* (33), 8621–8626.

(7) Li, R.; Li, B.; Yang, T.; Kai, X.; Wang, W.; Jie, Y.; Chen, G. Sub-supercritical liquefaction of rice stalk for the production of bio-oil: Effect of solvents. *Bioresour. Technol.* **2015**, *198*, 94–100.

(8) Bai, Y. Y.; Xiao, L. P.; Sun, R. C. Microwave-assisted conversion of biomass derived hemicelluloses into xylo-oligosaccharides by novel sulfonated bamboo-based catalysts. *Biomass Bioenergy* **2015**, *75*, 245–253.

(9) Luo, Y.; Fan, J.; Budarin, V. L.; Hu, C.; Clark, J. H. Microwave-assisted hydrothermal selective dissolution and utilisation of hemicellulose in Phyllostachys heterocycla cv. pubescens. *Green Chem.* **2017**, *19* (20), 4889–4899.

(10) Galkin, M. V.; Samec, J. S. Lignin valorization through catalytic lignocellulose fractionation: a fundamental platform for the future biorefinery. *ChemSusChem* **2016**, *9* (13), 1544–1558.

(11) Schutyser, W.; Renders, T.; Van den Bosch, S.; Koelewijn, S. F.; Beckham, G. T.; Sels, B. F. Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation, and upgrading. *Chem. Soc. Rev.* **2018**, *47* (3), 852–908.

(12) Liu, Y.; Chen, L.; Wang, T.; Zhang, Q.; Wang, C.; Yan, J.; Ma, L. One-pot catalytic conversion of raw lignocellulosic biomass into gasoline alkanes and chemicals over LiTaMoO6 and Ru/C in aqueous phosphoric acid. *ACS Sustainable Chem. Eng.* **2015**, *3* (8), 1745–1755.

(13) Calvo-Flores, F. G.; Dobado, J. A. Lignin as renewable raw material. *ChemSusChem* **2010**, *3* (11), 1227–1235.

(14) Ragauskas, A. J.; Beckham, G. T.; Biddy, M. J.; Chandra, R.; Chen, F.; Davis, M. F.; Langan, P. Lignin valorization: improving lignin processing in the biorefinery. *Science* **2014**, *344* (6185), 1246843.

(15) Rinaldi, R.; Jastrzebski, R.; Clough, M. T.; Ralph, J.; Kennema, M.; Bruijnincx, P. C.; Weckhuysen, B. M. Paving the Way for Lignin Valorisation: Recent Advances in Bioengineering, Biorefining and Catalysis. *Angew. Chem., Int. Ed.* **2016**, *55* (29), 8164–8215.

(16) Zhang, X.; Zhang, Q.; Wang, T.; Ma, L.; Yu, Y.; Chen, L. Hydrodeoxygenation of lignin-derived phenolic compounds to hydrocarbons over Ni/SiO2–ZrO2 catalysts. *Bioresour. Technol.* **2013**, *134* (4), 73–80.

(17) Kim, K. H.; Simmons, B. A.; Singh, S. Catalytic transfer hydrogenolysis of ionic liquid processed biorefinery lignin to phenolic compounds. *Green Chem.* **2017**, *19* (1), 215–224.

(18) Fu, D.; Mazza, G.; Tamaki, Y. Lignin extraction from straw by ionic liquids and enzymatic hydrolysis of the cellulosic residues. *J. Agric. Food Chem.* **2010**, *58* (5), 2915–2922.

(19) Liu, Y.; Guo, B.; Xia, Q.; Meng, J.; Chen, W.; Liu, S.; Yu, H. Efficient cleavage of strong hydrogen bonds in cotton by deep eutectic solvents and facile fabrication of cellulose nanocrystals in high yields. *ACS. Sustain. Chem. Eng.* **2017**, *5* (9), 7623–7631.

(20) Alvarez-Vasco, C.; Ma, R.; Quintero, M.; Guo, M.; Geleynse, S.; Ramasamy, K. K.; Zhang, X. Unique low-molecular-weight lignin with high purity extracted from wood by deep eutectic solvents

(DES): a source of lignin for valorization. *Green. Chem.* **2016**, *18* (19), 5133−5141.

(21) Alonso, D. M.; Hakim, S. H.; Zhou, S.; Won, W.; Hosseinaei, O.; Tao, J.; et al. Increasing the revenue from lignocellulosic biomass: maximizing feedstock utilization. *Sci. Adv.* **2017**, *3*(5), DOI DOI: 10.1126/sciadv.1603301.

(22) Luterbacher, J. S.; Rand, J. M.; Alonso, D. M.; et al. Nonenzymatic sugar production from biomass using biomass-derived γ-valerolactone. *Science* **2014**, *343* (6168), 277−280.

(23) Luterbacher, J. S.; Azarpira, A.; Motagamwala, A. H.; et al. Lignin monomer production integrated into the γ-valerolactone sugar platform. *Energy Environ. Sci.* **2015**, *8* (9), 2657−2663.

(24) Deuss, P. J.; Lancefield, C. S.; Narani, A.; et al. Phenolic acetals from lignins of varying compositions via iron (iii) triflate catalysed depolymerisation. *Green Chem.* **2017**, *19* (12), 2774−2782.

(25) da Costa Sousa, L.; Foston, M.; Bokade, V.; Azarpira, A.; Lu, F.; Ragauskas, A. J.; Balan, V. Isolation and characterization of new lignin streams derived from extractive-ammonia (EA) pretreatment. *Green Chem.* **2016**, *18* (15), 4205−4215.

(26) Feghali, E.; Carrot, G.; Thuery, P.; et al. Convergent reductive depolymerization of wood lignin to isolated phenol derivatives by metal-free catalytic hydrosilylation. *Energy Environ. Sci.* **2015**, *8* (9), 2734−2743.

(27) Anderson, E. M.; Stone, M. L.; Katahira, R.; et al. Flowthrough Reductive Catalytic Fractionation of Biomass. *Joule* **2017**, *1* (3), 613−622.

(28) Renders, T.; Cooreman, E.; Bosch, S. V. D.; Schutyser, W.; Koelewijn, S. F.; Vangeel, T.; et al. Catalytic lignocellulose biorefining in n-butanol/water: a one-pot approach toward phenolics, polyols, and cellulose. *Green. Chem.* **2018**, DOI: 10.1039/C8GC01031E.

(29) Den Bosch, S. V.; Schutyser, W.; Vanholme, R.; et al. Reductive lignocellulose fractionation into soluble lignin-derived phenolic monomers and dimers and processable carbohydrate pulps. *Energy Environ. Sci.* **2015**, *8* (6), 1748−1763.

(30) Sella Kapu, N.; Trajano, H. L. Review of hemicellulose hydrolysis in softwoods and bamboo. *Biofuels, Bioprod. Biorefin.* **2014**, *8* (6), 857−870.

(31) Gilani, B.; Stuart, P. R. Life cycle assessment of an integrated forest biorefinery: hot water extraction process case study. *Biofuel. Bioprod. Bior.* **2016**, *9* (6), 677−695.

(32) Zhong, C.; Wang, C.; Huang, F.; Wang, F.; Jia, H.; Zhou, H.; Wei, P. Selective hydrolysis of hemicellulose from wheat straw by a nanoscale solid acid catalyst. *Carbohydr. Polym.* **2015**, *131*, 384−391.

(33) Gaur, R.; Soam, S.; Sharma, S.; et al. Bench scale dilute acid pretreatment optimization for producing fermentable sugars from cotton stalk and physicochemical characterization. *Ind. Crops Prod.* **2016**, *83*, 104−112.

(34) Sabiha-Hanim, S.; Noor, M. A. M.; Rosma, A. Fractionation of oil palm frond hemicelluloses by water or alkaline impregnation and steam explosion. *Carbohydr. Polym.* **2015**, *115*, 533−539.

(35) Finore, I.; Poli, A.; Donato, P. D.; et al. Hemicellulose extract from Cynara cardunculus: a source of value-added biomolecules produced by xylanolytic thermozymes. *Green. Chem.* **2016**, *18* (8), 2460−2472.

(36) Krogell, J.; Korotkova, E.; Eränen, K.; et al. Intensification of hemicellulose hot-water extraction from spruce wood in a batch extractor–effects of wood particle size. *Bioresour. Technol.* **2013**, *143* (17), 212−220.

(37) Martinsampedro, R.; Eugenio, M. E.; Moreno, J. A.; et al. Integration of a kraft pulping mill into a forest biorefinery: pre-extraction of hemicellulose by steam explosion versus steam treatment. *Bioresour. Technol.* **2014**, *153* (2), 236−244.

(38) Pontes, R.; Romaní, A.; Michelin, M.; et al. Comparative autohydrolysis study of two mixtures of forest and marginal land resources for co-production of biofuels and value-added compounds. *Renewable Energy* **2018**, *128*, 20.

(39) Toscan, A.; Morais, A. R.; Paixao, S. M.; et al. High-pressure carbon dioxide/water pre-treatment of sugarcane bagasse and elephant grass: Assessment of the effect of biomass composition on process efficiency. *Bioresour. Technol.* **2017**, *224*, 639−647.

(40) Fockink, D. H.; Morais, A. R.; Ramos, L. P.; et al. Insight into the high-pressure CO_2 pre-treatment of sugarcane bagasse for a delivery of upgradable sugars. *Energy* **2018**, *151*, 536−544.

(41) Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J. *Determination of structural carbohydrates and lignin in biomass. Laboratory Analytical Procedures (LAP)*; National Renewable Energy Laboratory (NREL), Golden, CO. Revised version Jul 2011. There is no corresponding record for this reference 2012, 1−15.

(42) Segal, L. G. J. M. A.; Creely, J. J.; Martin, A. E., Jr; Conrad, C. M. An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. *Text. Res. J.* **1959**, *29* (10), 786−794.

(43) Jiang, Z.; Yi, J.; Li, J.; et al. Promoting Effect of Sodium Chloride on the Solubilization and Depolymerization of Cellulose from Raw Biomass Materials in Water. *ChemSusChem* **2015**, *8* (11), 1901−1907.

(44) Pan, H.; Shupe, T. F.; Hse, C. Y. Characterization of liquefied wood residues from different liquefaction conditions. *J. Appl. Polym. Sci.* **2007**, *105*, 3740−3746.

(45) Liao, Y.; Liu, Q.; Wang, T.; Long, J.; Ma, L.; Zhang, Q. Zirconium phosphate combined with ru/c as a highly efficient catalyst for the direct transformation of cellulose to c6 alditols. *Green Chem.* **2014**, *16* (6), 3305−3312.

(46) Long, J.; Li, X.; Guo, B.; et al. Simultaneous delignification and selective catalytic transformation of agricultural lignocellulose in cooperative ionic liquid pairs. *Green Chem.* **2012**, *14* (7), 1935−1941.

(47) Chinaie, M.; Zafarani, J. Investigation on thermochemical behaviour of low rank Malaysian coal, oil palm biomass and their blends during pyrolysis via thermogravimetric analysis (TGA). *Bioresour. Technol.* **2010**, *101* (12), 4584−4592.

(48) Poletto, M.; Zattera, A. J.; Forte, M. M.; et al. Thermal decomposition of wood: influence of wood components and cellulose crystallite size. *Bioresour. Technol.* **2012**, *109* (1), 148−153.

(49) Si, X.; Lu, F.; Chen, J.; et al. A strategy for generating high-quality cellulose and lignin simultaneously from woody biomass. *Green Chem.* **2017**, *19* (20), 4849−4857.

(50) Wen, J.; Yuan, T.; Sun, S.; et al. Understanding the chemical transformations of lignin during ionic liquid pretreatment. *Green Chem.* **2014**, *16* (1), 181−190.

(51) Sun, J.; Sun, X.; Sun, R.; et al. Fractional extraction and structural characterization of sugarcane bagasse hemicelluloses. *Carbohydr. Polym.* **2004**, *56* (2), 195−204.

(52) Li, Y.; Liu, Y.; Chen, W.; et al. Facile extraction of cellulose nanocrystals from wood using ethanol and peroxide solvothermal pretreatment followed by ultrasonic nanofibrillation. *Green Chem.* **2016**, *18* (4), 1010−1018.