Sequential Fractionation of Lignocellulosic Biomass Using CO_2-Assisted Hydrolysis Combined with γ-Valerolactone Treatment

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A biomass biorefinery strategy for the selective fractionation of poplar into its three main compositions (hemicellulose sugars, lignin, and high-purity cellulose) with a two-step process is developed. The first step consists of the selective hydrolysis of hemicellulose at mild conditions in a CO_2/H_2O system. This leads to various hemicellulose sugars and other intermediates in the water-soluble fraction, with more than 87.90% of the hemicellulose being extracted from the original poplar (180 °C, 2.0 MPa CO_2, 10 min). The pretreated sample is subsequently used for extracting lignin in a γ-valerolactone (GVL)/H_2O with acid catalysts for the next step. Meanwhile, four acid catalysts, including sulfuric acid and solid heteropoly acids (phosphomolybdic acid, silicotungstic acid, and phosphotungstic acid), are studied for the selective delignification in the GVL/H_2O system, resulting in more than 91.35% of the original lignin being removed in the cellulose-rich substrates (140 °C, 30 mM silicotungstic acid, 3 h). Overall, the biorefinery approach fractions the poplar wood into three primary components: 1) various oligosaccharides, monosaccharides, and other intermediates derived from hemicellulose; 2) cellulose-rich substrate with a purity of cellulose as high as 90.76%, which has great potential as biochemicals or biomaterials; and 3) high-purity and proportion lignin recovered from biomass.

1. Introduction

Lignocellulosic biomass, a fixed renewable and abundant source of carbon, could be used as a promising resource to replace fossil-based products [1,2]. Its three main polymeric components, cellulose, hemicellulose, and lignin, account for more than 90% of its dry weight and form a complex rigid matrix in the cell wall.[3] To achieve the sustainable and green production of renewable fuels and chemicals, an effective biorefinery strategy must be developed to convert biomass into useful products with high yield and high purity. Numerous studies highlight the integrated biorefinery of an entire bio-based plant. A well-known example is the pyrolysis or liquefaction of lignocellulosic biomass for the production of bio-oils, resulting in hundreds of complex components because of the different chemical structures of the biomass constituents, which hinder downstream separation and further conversion.[4–6] Other biorefinery strategies propose the prefractionation of the lignocellulose biomass into different streams (e.g., cellulose, hemicellulose, and lignin), thereby reducing the complexity of the obtained production.[7]

Biomass pretreatment is an intensive research field where various greener methods are sought. Among them, the hydrothermal process is one of the most promising pretreatments and is considered an ecofriendly technology because it utilizes hot water as the reaction medium, does not require a chemical catalyst, and can be conducted at relatively low temperature.[8–10] The main goal of the hydrothermal process is to selectively dissolve the hemicellulose fraction to sugars (i.e., xylose, arabinose) or intermediates (i.e., furfural, formic acid).[11] The release of acetic acid from acetyl groups in hemicellulose can enhance the hydrolytic

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efficiency during hydrothermal processing. However, this technology still exhibits low selectivity and poor recovery of hemicellulose. Recently, the idea of using CO_2—H_2O as a green and sustainable solvent has received considerable attention for the enhancement of hemicellulose hydrolysis.[12,13] In the pressured CO_2—H_2O system, the formation of in situ carbonic acid results in a decrease in the pH of the reaction mixture and facilitates the hydrolysis of biomass under mild conditions. Furthermore, the CO_2 in the hydrothermal process can be easily recovered and recycled, thereby avoiding any corrosion or acid pollution problems.[14]

Lignin is the most abundant resource of renewable aromatics on the planet and is a highly branched polyphenolic macromolecule material composed of phenylpropane subunits.[15] Its isolation process has a great impact on its physical and chemical properties due to the complex structure and various functional groups in lignin. Current industrial delignification strategies apply sulfite, chlorite, or alkaline solutions as solvents to extract lignin from the lignocellulosic matrix.[16,17] Under such severe conditions, lignin undergoes irreversible polymerization, and the alterations result in lignin having limited use in low-value material applications or a raw material for energy generation.[18,19] Until now, several solvent delignification systems have been developed to isolate lignin, including ammonia-based fractionation,[20,21] ionic liquid fractionation,[22,23] and mild organosolv techniques.[24–26] Recently, γ-valerolactone (GVL) and water mixtures have been demonstrated to be ideal green media for the fractionation of the lignocellulose.[27,28] The proper solvent system can achieve the almost complete isolation of lignin from biomass in mild processing conditions with negligible degradation of cellulose, which can improve the preservation of β—O—4 bonds in lignin and decrease the condensation of lignin derivatives.[27,29] Sulfuric acid is the most common catalyst in the GVL/H_2O system for the fractionation of biomass. However, its corrosiveness to equipment and possible acid contamination will limit its use. Heteropoly acids have also been widely applied in biomass conversion, owing to their strong Bronsted acidity, higher proton mobility, and their good solubility in most common organic solvents.[30,31] In addition, they possess higher catalytic activity than other acid catalysts due to their uniform acid sites.[32] In the present study, three solid heteropoly acids (silicotungstic acid, phosphotungstic acid, and phosphomolybdic acid), which are considered as environmentally friendly solid acid catalysts, are used as catalysts in the GVL/H_2O system for the dissolving of lignin in biomass.

Herein, we propose a methodology that integrates lignocellulosic biomass fractionation with the stepwise extraction of the three main components (**Figure 1**). A CO_2-assisted hydrothermal treatment was used to release the hemicellulose fractions from poplar wood, providing water-soluble hemicellulose sugars. Then, the solvent treatment of the pretreated samples in the GVL/H_2O system with acid catalysts was conducted. Furthermore, four acid catalysts, sulfuric acid, and three solid heteropoly acids (phosphomolybdic acid, silicotungstic acid, and phosphotungstic acid), were studied for the selective delignification in GVL/H_2O system. The lignin fraction can be solubilized in a GVL/H_2O cosolvent, leaving behind a solid substrate mostly composed of cellulose that has great potential for biomaterials or biochemicals.

2. Results and Discussion

2.1. Pretreatment of Poplar Wood in CO_2/H_2O System

2.1.1. Analysis of Pretreated Solid Fraction

The pretreatment of poplar wood was conducted in a CO_2/H_2O system. The mixture of CO_2 and H_2O results in an acidic environment due to the in situ formation and dissociation of unstable carbonic acid. The goals of this step is to maximize hydrolyzed hemicellulose while retaining as much cellulose and lignin as possible. A series of hydrothermal experiments were performed under various operational conditions, for example, reaction time, initial CO_2 pressure, and temperatures, to assess the

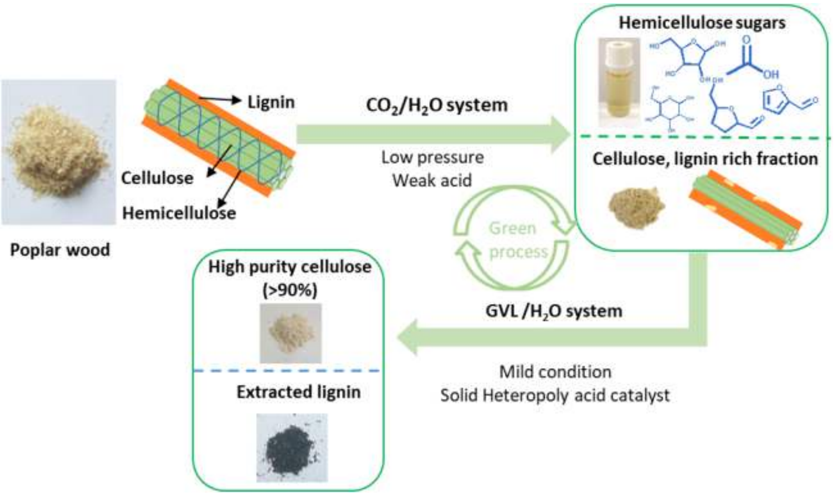

Figure 1. Process scheme for the selective fractionation of lignocellulosic biomass into its three main compositions: hemicellulose sugars, high-purity cellulose, and lignin.

CO_2-assisted hydrothermal treatment. The hemicellulose extraction and cellulose and lignin retention from poplar wood were used to evaluate the hydrolysis efficiency in CO_2/H_2O system.

The initial CO_2 pressure plays an essential role in the control of acidity in the hydrothermal treatment process. The effect of CO_2 pressure on the hydrolysis of poplar wood was studied to determine the optimal acidity condition for the removal of hemicellulose. The CO_2 pressure varied from 0 to 4 MPa at 180 °C for 10 min of reaction time (**Table 1**). The hydrolysis degree and hemicellulose extraction significantly increased from 23.19% and 51.56% without CO_2 to 28.53% and 79.97%, respectively, with a CO_2 pressure of 1 MPa. Clearly, the presence of CO_2 effectively improved the hemicellulose removal from biomass owing to the in situ formation carbonic acid. The hemicellulose extraction increased to 87.90% with a 2 MPa initial CO_2 pressure in the system. Increasing the CO_2 pressure to 3 and 4 MPa led to a moderate increase in hemicellulose extraction, but a significant decrease in lignin and cellulose retention from 84.96% to 75.00% and 69.41%, and from 90.19% to 85.12% and 82.02%, respectively. Thus, a 2 MPa CO_2 pressure was used for further studies to remove hemicellulose fraction from poplar wood and preserve the cellulose and lignin fractions as much as possible.

The CO_2-assisted hydrothermal treatment of poplar was also conducted at five different temperatures from 140 to 220 °C. It was found that increasing temperature in the process led to an obvious improvement of the in the extent of hydrolysis (Table 1). At 2 MPa of initial CO_2 pressure, approximately 39.28 % of hemicellulose was extracted at 140 °C. Increasing the temperature to 160 °C led to a significant increase in hemicellulose extraction from 39.28% to 71.54%. At 180 °C, the hemicellulose extraction reached more than 87.90%; meanwhile, 90.19% of cellulose and 84.93% of the lignin fraction were retained in the pretreated poplar. In fact, the higher the reaction temperature, the lower the density and dielectric constant of water, which makes the solubility of water, together with the acidity and permeability of CO_2, destroy the recalcitrant structure of lignocellulosic fibers, resulting in easier hydrolysis of biomass components, especially hemicellulose. A further increase in temperature to 200 and 220 °C resulted in a slight increase in the hemicellulose extraction. However, only 81.28% and 73.10% of cellulose, and 73.97% and 65.43% of lignin, respectively, were be preserved in feedstock along with hemicellulose extraction.

The reaction time varied at an increment of 0–30 min while maintaining the temperature at 180 and 200 °C with 2 MPa of CO_2 pressure. As shown in **Table 2**, the hydrolysis degree and the hemicellulose extraction increased with prolonging the reaction time. In particular, it has been observed that the hemicellulose extraction significantly increased from 71.17% without reaction time to 78.09% with 5 min at 180 °C. When the reaction time was further extended from 10 to 30 min, the hemicellulose extraction varied from 87.90% to 90.60%. Meanwhile, the lignin retention decreased from 84.93% to 76.61% and the cellulose retention decreased from 90.19% to 82.73%, suggesting that a prolonged reaction time during the hydrolysis mainly caused depolymerization of the lignin fraction. At 200 °C, the hemicellulose extraction varied from 81.07% to 92.85% when prolonging the reaction from 0 to 30 min. Meanwhile, the lignin retention decreased from 80.86% to 66.14% and cellulose retention decreased from 90.50% to 74.07%, indicating that a prolonged reaction time mainly accelerated the depolymerization of the cellulose fraction during the hydrolysis at 200 °C in the CO_2/H_2O system. After considering the cost of energy, hemicellulose removal and cellulose and lignin retention, it was decided that 180 °C, 2.0 MPa of CO_2 initial pressure, and 10 min of reaction time would be served to further studies and analysis.

Fourier-transform infrared spectroscopy (FT-IR) spectroscopy of the feedstock and pretreated samples at various temperatures contributed to further understanding the removal of hemicellulose and revealed the structural transformation (**Figure 2**a). The unique region of the spectrum of the three main fractions in biomass ranged from 2000 to 700 cm^{-1}. In an FT-IR spectrum of

Table 1. The influence of initial CO_2 pressure and temperatures on hydrolysis degree and composition of solid phase after CO_2 assisted hydrothermal treatment.

Reaction conditions[a]		Hydrolysis degree [%]	Solid composition [%]			Hemicellulose Extraction [%][b]	Lignin retention[%][b]	Cellulose retention [%][b]
Initial CO_2 Pressure [MPa]	Temp. [°C]		Hemicellulose	Lignin	Cellulose			
Poplar			21.82	22.36	48.40	0	100	100
0 (without CO_2)	180	23.19	13.58	25.83	58.21	51.56	89.89	93.57
1	180	28.53	6.11	27.62	62.81	79.97	88.28	92.75
2	180	32.42	3.91	28.10	64.59	87.90	84.93	90.19
3	180	37.97	3.37	27.04	66.34	90.42	75.00	85.02
4	180	41.11	2.63	26.35	67.41	92.90	69.41	82.02
2	140	15.07	15.60	24.27	54.96	39.28	92.17	96.45
2	160	25.41	8.33	26.83	60.44	71.54	89.49	93.14
2	180	32.42	3.91	28.10	64.59	87.90	84.93	90.19
2	200	40.16	3.18	27.64	65.74	91.29	73.97	81.28
2	220	48.43	2.43	27.83	67.30	94.13	65.43	73.10

[a] Reaction conditions: 6 g poplar wood, 60 g deionized water, and 10 min of reaction time. [b] Extraction and retention (%) is based on the original hemicellulose, lignin, and cellulose.

Table 2. The influence of reaction time on the composition of solid phase after CO_2-assisted hydrothermal treatment.

Reaction conditions[a]		Hydrolysis degree [%]	Solid composition [%]			Hemicellulose extraction [%]	Lignin retention [%]	Cellulose retention [%]
Reaction time [min]	Temp. [°C]		Hemicellulose	Lignin	Cellulose			
Poplar		0	21.82	22.36	48.40	0	100	100
0	180	27.82	8.71	26.85	62.16	71.17	87.67	92.71
5	180	30.07	6.84	27.33	63.05	78.09	85.47	91.10
10	180	32.42	3.91	28.10	65.59	87.90	84.93	90.19
20	180	36.07	3.86	28.53	65.89	88.68	81.57	87.02
30	180	38.75	3.35	27.97	65.37	90.60	76.61	82.73
0	200	31.25	6.01	26.30	63.71	81.07	80.86	90.50
5	200	36.69	3.59	27.26	65.66	89.60	77.19	85.89
10	200	40.16	3.18	27.64	65.74	91.29	73.97	81.28
20	200	44.13	3.02	28.23	67.59	92.25	70.53	78.02
30	200	46.45	2.90	27.62	66.95	92.85	66.14	74.07

[a] Reaction condition: 6 g poplar wood, 60 g deionized water, and 2.0 MPa CO_2 initial pressure.

typical wood feedstock, the prominent absorbance peaks at ≈1735 and 1245 cm^{-1} were attributed to carboxylic acid and the stretching vibration of C═O in xylan (hemicellulose), respectively.[33] It was noted that the two absorbance peaks significantly decreased as the temperature rose from 140 to 180 °C, and even disappeared after treatment at 200 and 220 °C. The disappearance of these peaks demonstrated the almost full removal of the hemicellulose fraction from poplar wood. The absorbance peaks at 2900, 1423, 1370, 1160, 1105, 1060 and 897 cm^{-1} are related to the typical characteristics of cellulose.[34] The presence of the aforementioned absorbance peaks was consistent with the cellulose structure, and the spectra of cellulose in the pretreated samples showed no apparent differences at various temperatures. The results suggested that crystallized cellulose was not significantly affected by the hydrolysis in the CO_2/H_2O system. The absorbance peaks at 1601 and 1508 cm^{-1} were associated with the typical features of lignin.[35] FT-IR spectroscopy analysis of the pretreated samples at different temperatures revealed that lignin was still present in the solid components. However, slight amounts of lignin were also removed during the cleavage of intermolecular linkages between hemicellulose and lignin mentioned earlier.

The structural transformation of pretreated samples and feedstock was further studied using ^{13}C CP/MAS nuclear magnetic resonance (NMR) spectroscopy (Figure 2b). The spectrum of poplar feedstock represents a typical spectral pattern of lignocellulose. Two signals with rather weak intensities were assigned to hemicellulose: the carbonyl carbons (173.8 ppm) and the methyl carbons (20.8 ppm) in the acetyl group.[36] The signals from 60 to 110 ppm were attributed to cellulose fragments (containing crystalline and amorphous cellulose). The signals at 153.1 and 56.1 ppm were attributed to lignin.[37,38] ^{13}C CP/MAS solid-state NMR results also provided evidence for the efficient extraction of hemicellulose in poplars with temperatures over 180 °C, and the solid pretreated samples were enriched in cellulose and lignin fractions. Furthermore, the absence of the signals in disordered cellulose region at 220 °C indicated that higher temperature led to the depolymerization of the amorphous cellulose.

The thermogravimetry (TG) and derivative thermogravimetry (DTG) curves of the feedstock and pretreated samples are shown in Figure 2c,d. Hemicellulose is the most reactive component of the feedstock. According to the literature, the pyrolysis peak of hemicellulose, cellulose, and lignin is at ≈220–315, ≈300–400, and ≈300–500 °C, respectively.[39,40] As shown in Figure 2d, the DTG curve of the feedstock exhibited a broad peak at ≈280 °C, which was attributed to hemicellulose decomposition. Compared with the raw feedstock, the broad peak at ≈280 °C significantly decreased with the increasing temperature and even disappeared at >180 °C. It contributed to hemicellulose gradually diminishing with the increasing temperatures and was almost completely removed at >180 °C during the CO_2-assisted hydrothermal process, which was consistent with the analysis results of the FT-IR and ^{13}C CP/MAS NMR.

To study the effect of CO_2-assisted hydrothermal treatment on the morphological structure of poplar wood, scanning electron microscopy (SEM) analysis was performed on the poplar before and after treatment at various temperatures (Figure 2e). The CO_2-assisted treatments resulted in noticeable changes in morphological structure of the processed solids. Compared with the raw feedstock, the pretreated sample at 140 °C showed minor differences at the surface of the dense catheter-like structure. The surface of the pretreated sample became rough, whereas cellulose bundles were still intact after the treatment at 180 °C. The cellulose bundle structure was obviously destroyed at 220 °C. Based on the composition analysis of the pretreated samples mentioned earlier, in addition to the easily degraded hemicellulose, a considerable portion of cellulose and lignin also undergone depolymerization.

2.1.2. Composition Analysis of Water-Soluble Fraction

Hemicellulose is most easily removed by hydrothermal treatment among the three major biomass components. The

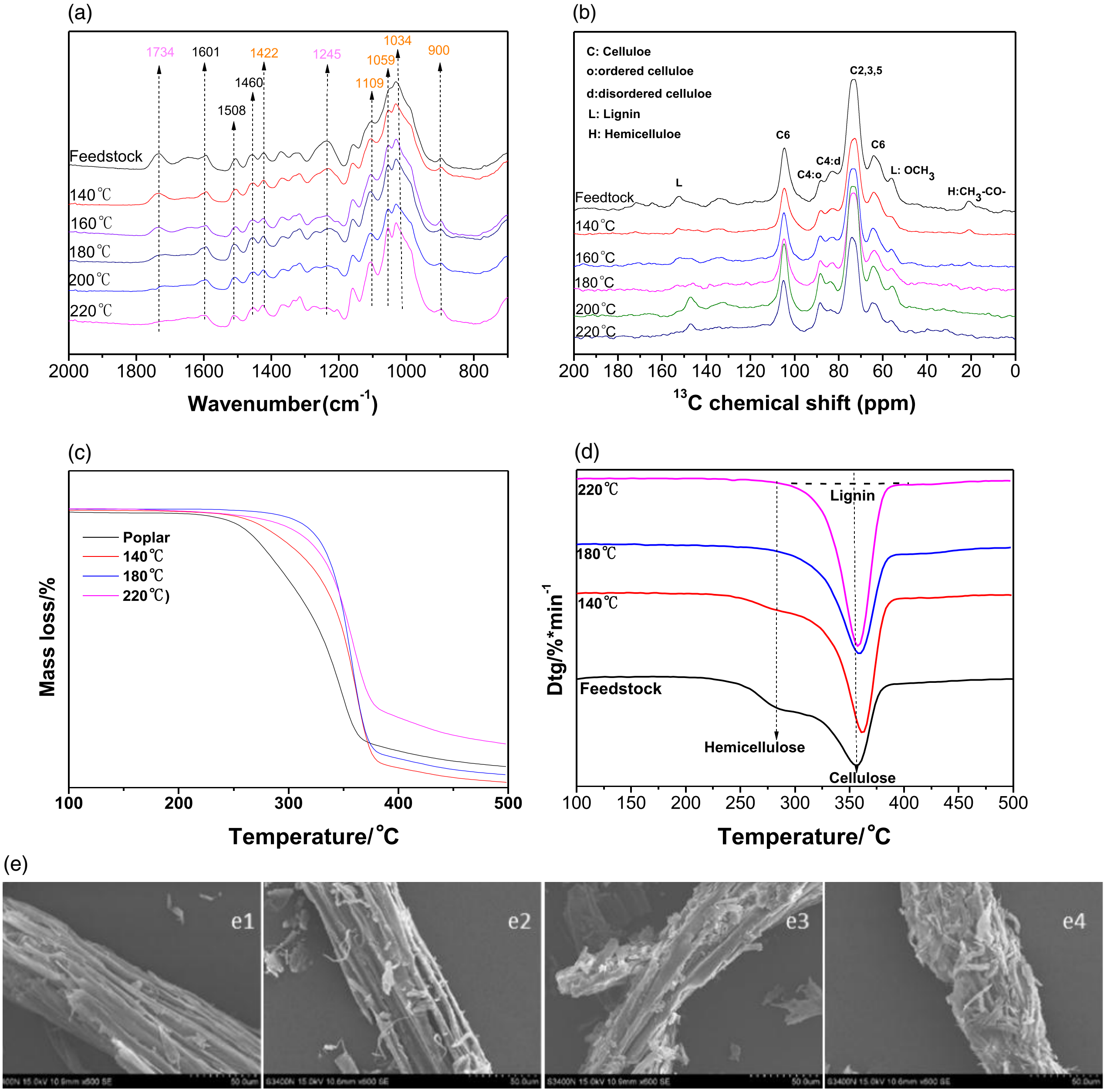

Figure 2. a) FTIR spectra of feedstock and pretreated samples at various temperatures from 2000 to 700 cm^{-1} b) ^{13}C CP/MAS solid-state NMR spectra of feedstock and pretreated samples. c) TG analysis results of feedstock and pretreated samples at different temperatures. d) DTG corresponding to (c) SEM image of feedstock and pretreated samples with CO_2-assisted hydrothermal treatment at various temperatures. e) SEM images of the feedstock (e1) and pretreated samples at 140 °C (e2), 180 °C (e3), and 220 °C (e4).

high-performance liquid chromatography (HPLC) results of the liquid phase indicated that the products comprise a mixture of oligosaccharides (xylooligosaccharides [XOS] and glucooligosaccharides [GluOS]), monosaccharides (xylose, arabinose, and glucose), acetic acid, furfural, and 5-hydroxymethylfurfural (HMF). The formation of these chemicals is dependent on the severity of hydrothermal conditions. The composition of the water-soluble fraction after pretreatment in CO_2/H_2O with different temperatures and initial CO_2 pressures is shown in **Figure 3**. It was found that the yield of oligosaccharide and monosaccharide gradually increased with the increasing CO_2 pressure and temperature. XOS and GluOS were the major components in the water-soluble fraction in all reactions. The present data in Figure 3 show that the presence of CO_2 can significantly promote the hydrolysis of hemicellulose to XOS even at lower CO_2 pressures (1 MPa) due to the in situ formation of unstable carbonic acid in the reaction system. The main small molecular products were xylose and acetic acid. Acetic acid came from the hydrolysis of acetyl groups in O-acetyl-4-O-methylglucuronoxylan in hemicellulose. The CO_2 pressure and temperatures play an important role in the

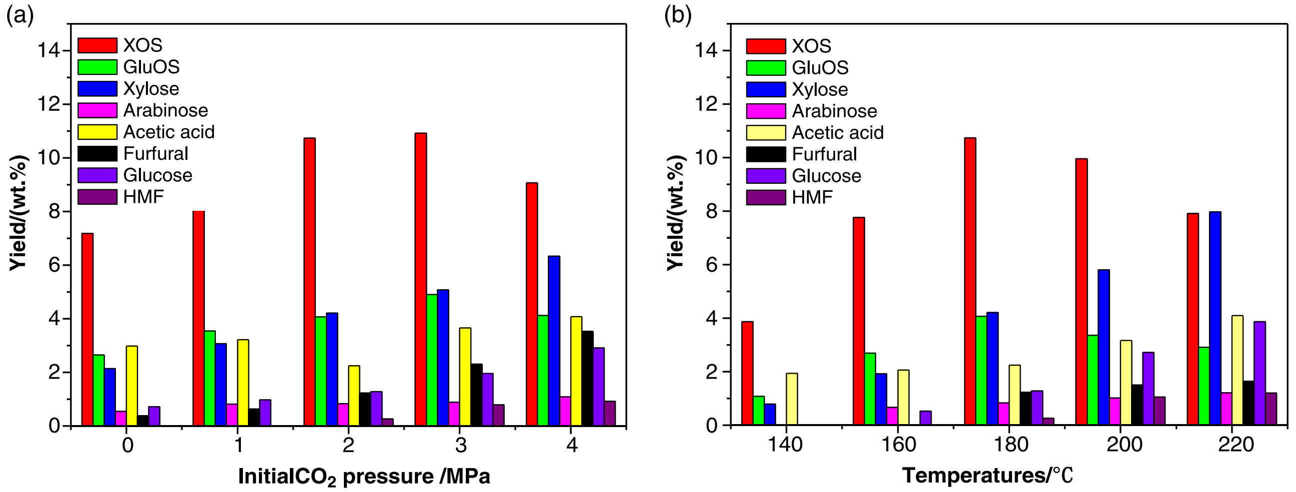

Figure 3. Composition of liquid fractions from CO_2-assisted hydrothermal treatment under various temperatures a) and different initial CO_2 pressures b). (The yield of the products was calculated based on the entire poplar.)

formation of furfural and HMF, but their yield was relatively low. Furthermore, the yield of glucose (mainly from the hydrolysis of cellulose) significantly increased with higher temperatures (>200 °C) and CO_2 pressure (>3 MPa), indicating, as expected, that the more severe reaction conditions enhanced the reaction kinetics of cellulose. In addition, it is noteworthy that in all experiments the total content of hemicellulose sugars detected by HPLC was always less than the hydrolysis degree, which may be mainly due to some water-soluble lignin and a small amount of extractives in the water-soluble fraction.

2.2. Delignification Process in GVL/H_2O System

The poplar wood pretreated by the CO_2-assisted hydrothermal treatment (180 °C, 2.0 MPa of CO_2 initial pressure for 10 min) was subsequently used for lignin extraction in GVL/H_2O system. Four catalysts, H_2SO_4, and three solid heteropoly acids (PHTU, SITU, and PHMO) were prepared to improve the selectivity of fractionation. Treatment of the pretreated samples by each catalyst was conducted at five different concentrations: 10, 20, 30, 40, and 50 mM; four different treatment temperatures of 120, 130, 140, and 150 °C; and a reaction time of 2 h. The treatment in the GVL/H_2O system resulted in the fractionation of the biomass into two parts, the cellulose-rich substrate (cellulose pulp) and the extracted lignin, which were analyzed to better understand the treatment process. Delignification, cellulose retention, and cellulose purity were the important indicators to evaluate the efficiency of delignification in the GVL/H_2O system at various conditions.

Figure S1, Supporting Information, shows the cellulose-rich substrates recovery gradually declined as the acid concentration increased from 10 to 50 mM. The significant reduction of the lignin in cellulose-rich substrates confirmed the extraction of lignin and into the GVL/H_2O cosolvent. As shown in **Figure 4**a, the delignification yield in the presence of heteropoly acid catalyst was higher than with H_2SO_4 as the catalyst at the same acid concentration from 10 to 50 mM (while maintaining a reaction time of 3 h and a low temperature of 140 °C). This finding indicated that the heteropoly acids have an excellent ability of catalytic extraction of lignin from biomass in the GVL/H_2O system. At 10 mM of acid catalyst, ≈65.40%, 76.41%, 72.04%, and 70.33 % of lignin were extracted with the H_2SO_4, SITU, PHTU, and PHMO as catalysts, respectively. Increasing the acid concentration to 20 mM led to a significant increase in lignin extraction with all four catalysts. When the acid concentration increased to 30 mM, the delignification yield reached a high value of 82.87% and 85.12% with the PHTU and PHMO catalysts, respectively. The maximum lignin extraction yields were observed with the SITU catalyst, where 91.35% of lignin was extracted based on the original poplar feedstock. Increasing the acid concentration to 40 mM led to a significant increase (90.91% and 90.37%) in lignin extraction with the PHTU and PHMO catalysts, respectively. Further increasing the acid concentration to 50 mM led to a moderate increase in lignin extraction for the heteropoly acids catalysts. However, there was a decrease in the cellulose extraction yield with higher heteropoly acid concentration. SITU seemed to be the best catalyst for lignin extraction in GVL/H_2O system with a 91.35 % lignin extraction yield while preserving more than 84.29% of cellulose still in solid cellulose pulp with a 30 mM acid concentration at 140 °C. The results can be explained by the fact that protons are the main active elements of heteropoly acids that catalyze the degradation of lignin in the GVL/H_2O system. SITU ($H_4[Si(W_3O10)_4]$) can be considered as a tetrahydrogen acid, whereas PHTU ($H_3[P(W_3O_{10})_4]$) and PHMO ($H_3[P(Mo_3O_{10})_4]$) are trihydrogen acids. SITU releases more H^+ when fully ionized, thus it exhibited a better catalytic ability under the same acid concentration.

The delignification and cellulose retention in the solid substrate after the GVL/H_2O treatment of poplar are shown in Figure 4b. The delignification yield with H_2SO_4 significantly increased with the increasing temperature from 120 to 150 °C with the highest lignin extraction of 87.73% and the cellulose retention yield of 78.83% at 150 °C. A higher delignification yield

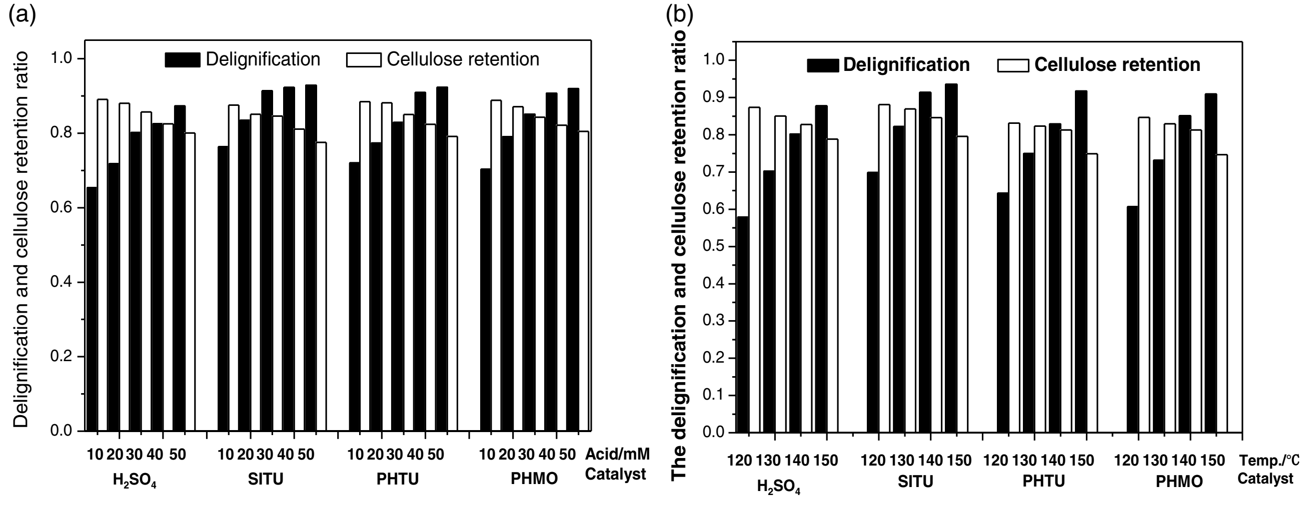

Figure 4. Delignification and cellulose retention yield from pretreated sample under different treatment conditions: a) 3 h at 140 °C with different catalyst concentrations; b) 30 mM of catalyst concentration for 2 h with different temperatures.

for heteropoly acids than H_2SO_4 was obtained at the same temperature. Specifically, at 120 °C, approximately 69.87%, 64.30%, and 60.65 % of lignin were extracted with the SITU, PHTU, and PHMO catalysts, respectively, meaning that the extraction of lignin was insufficient at this condition. Increasing the temperature to 130 and 140 °C led to a significant increase in lignin extraction obtained from the three heteropoly acids. The delignification yield reached 91.35%, 83.61%, and 85.12% with SITU, PHTU, and PHMO, respectively, as the catalyst in the GVL/H_2O system at 140 °C. A further increase in temperature to 150 °C resulted in up to 90% delignification with PHTU and PHMO as the catalysts. Therefore, the SITU catalyst was used as the optimal catalyst for further analysis.

The effect of temperature on the fractionation of pretreated biomass in a GVL/H_2O system with SITU as a catalyst is analyzed in detail in **Table 3**. As the temperature increased from 120 to 150 °C, the extracted lignin increased from 10.45% to 15.04%. Meanwhile, the cellulose-rich substrate yield decreased from 53.26% to 39.45%. The delignification and purity of cellulose significantly increased from 69.87% and 78.91% to 93.73% and 92.47%, respectively. Overall, cellulose and lignin were almost completely fractioned at 140 °C with 30 mM SITU as the catalyst for a 2 h reaction time in the GVL/H_2O system.

2.2.1. Characteristic of the Cellulose-Rich Substrates

The cellulose-rich substrates are the undissolved material recovered with the GVL/H_2O treatment (SITU catalyst). Herein, X-ray diffraction (XRD) was performed to determine the changes in the crystallinity index (CrI) and the crystal structure after the treatment in the CO_2/H_2O and GVL/H_2O systems. As shown in **Figure 5**a, the CrI of the original poplar feedstock was determined to be 56.24 %, whereas the CrI of the CO_2-assisted hydrothermal pretreatment sample (2 MPa CO_2 initial pressure for 10 min at 180 °C) increased to 64.79 %, which contributed to the removal of amorphous components (mainly hemicellulose) during pretreatment, as also revealed by the compositional analysis of the samples. Further processing of the pretreated sample with a GVL/H_2O cosolvent and SITU catalyst resulted in cellulose-rich substrates. From 120 to 140 °C, the CrI of the cellulose-rich substrates showed a 2.62–11.46% enhancement from the hydrolysis pretreated samples. This increasing trend is due to the removal of amorphous lignin fraction from the GVL/H_2O system, and confirmed by the compositional analysis of the cellulose-rich substrates. In addition, it was found that the CrI of the cellulose-rich substrate slightly decreased from 76.25% to 76.07% as the temperature increased from 140 to 150 °C, which

Table 3. The delignification process in GVL/H_2O system with SITU catalyst at different temperatures.

Samples[a]	Fraction yield [wt%]		Cellulose-rich substrate composition [wt%][b]			Delignification [%]	Purity of cellulose [%]
	Extracted lignin	Cellulose-rich substrate	Cellulose	Hemicellulose	Lignin		
CO_2-treated sample			43.65	2.64	18.99		
SITU-120	10.45	54.26	42.65	1.13	7.04	69.87	78.60
SITU-130	11.27	49.77	42.07	0.98	4.15	82.24	84.53
SITU-140	15.16	45.13	40.96	0.65	2.02	91.35	90.76
SITU-150	16.04	41.45	38.51	0.40	1.50	93.73	92.91

[a] Reaction condition: 2 g pretreated poplar sample, 20 g GVL/H_2O (w/w 7:3) solvent, and 30 mM SITU, 2 h. [b] Based on the entire feedstock.

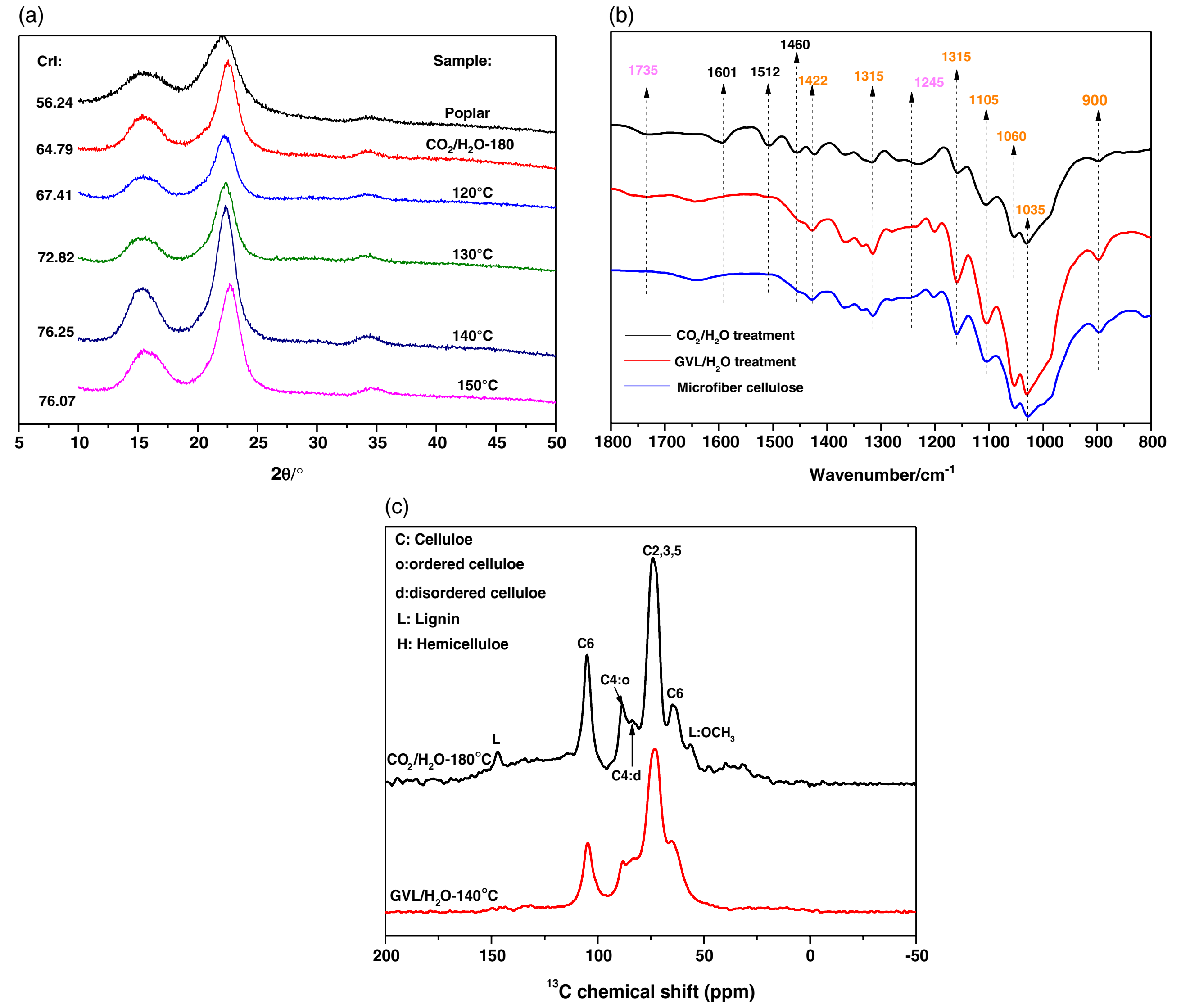

Figure 5. a) XRD analysis of poplar wood and samples with the treated in CO_2/H_2O and GVL/H_2O systems. b) FT-IR spectra of samples treated in CO_2/H_2O and GVL/H_2O systems from 2000 to 800 cm^{-1}. c) ^{13}C CP/MAS solid-state NMR spectra of solid samples after treatment in CO_2/H_2O and GVL/H_2O systems.

may be due to the high treatment temperature leading to the cleavage of hydrogen bonds in the poplar wood.

FT-IR spectroscopy of the cellulose-rich substrates was further analyzed to understand the functional groups with the GVL/H_2O treatment (Figure 5b). Compared with the FI-IR of the CO_2/H_2O pretreated samples, the disappearance of the absorbance peaks at 1601, 1512, and 1460 cm^{-1} is associated with lignin removal from the GVL/H_2O treatment. The absorbance peaks at 2900, 1423, 1370, 1160, 1105, 1060, and 897 cm^{-1} were related to the typical characteristics of cellulose. It was observed that the absorption peaks of cellulose-rich substrates were consistent with those of microcrystalline cellulose, and the typical absorption peaks of hemicellulose and lignin were not detected, which confirmed that almost all of the noncellulosic components have been removed in the cellulose-rich substrates. ^{13}C CP/MAS solid-state NMR results (Figure 5c) also confirmed that the efficient removal of hemicellulose and lignin in cellulose-rich substrates was achieved and the dominant structure of crystalline cellulose was not affected significantly.

2.2.2. Characteristics of Extracted Lignin

Most of the lignin dissolving in the GVL/H_2O solvent after delignification process can be precipitated by adding water. The composition analysis of the extracted lignin at treatment temperatures is shown in **Table 4**. The lignin precipitated from GVL/H_2O had a higher purity due to the limited carbohydrate content. The weight distribution of the extracted lignin was determined using GPC. The values of average molecular weight (M_w and M_n) and polydispersity index (PDI) of the extract lignin

Table 4. The composition analysis and weight distribution of the extracted lignin after GVL/H_2O treatment.

Samples[a)]	Composition [b)]		Weight distribution		
	Carbohydrate [wt%]	Lignin [wt%]	M_w	M_n	PDI
SITU-120	4.47	92.15	3430	2415	1.42
SITU-130	2.56	94.38	3227	2055	1.57
SITU-140	3.56	93.21	2946	1619	1.82
SITU-150	3.18	91.43	2845	1635	1.74

[a)] Reaction condition: 30 mM SITU concentration for 2 h. [b)] The composition (carbohydrate and lignin) analysis of the extracted lignin was determined following the two-step hydrolysis method which was consistent with the chemical analysis of the feedstock.

are shown in Table 4. It was found that the lignin had a relatively narrower and lower molecular weight distribution ranging from 1619 to 2612 g mol^{-1}. The average molecular weight (M_w) of the extracted lignin decreased from 3430 to 2845 as the temperature increased from 120 to 150 °C. In fact, the dominant cleavage group in lignin with the GVL/H_2O treatment was β—O—4 linkages and the molecular weight is positively related to the content of β—O—4 linkages [41]. Therefore, the cleavage of the β—O—4 bond in lignin increases with the increasing temperature.

2.2.3. The Mass Balance of the Whole Poplar Wood

Figure 6 depicts the mass balance of the fractionation strategy for poplar wood with the CO_2-assisted hydrothermal treatment combined with GVL/H_2O treatment. As a target for extracting hemicellulose in a CO_2/H_2O system, 87.90% hemicellulose removal, 90.19 % cellulose retention, and 84.93 % lignin retention were achieved in the pretreated samples under the optimal condition (180 °C and 2.0 MPa initial CO_2 pressure for 10 min). Hemicellulose was substantially hydrolyzed to a mixture of oligosaccharides (mainly XOS, 10.74%), monosaccharides (mainly xylose and arabinose, 5.04%), acetic acid (2.25%), and furfural (1.23%). In addition, GluOS (4.07%), glucose (1.28%), and HMF (0.26%) were also detected. The pretreated sample was then used for extracting lignin in a GVL/H_2O system for the next step. This led to 91.35 % removal of the original lignin and 84.63 % retention of the original cellulose in the solid cellulose-rich substrates under mild conditions (140 °C, 30 mM SITU acid for 2 h). The yield of the cellulose-rich substrates was 43.85 % based on the original feedstock with the cellulose purity of up to 90.76%. Meanwhile, 15.16% lignin with high purity was precipitated from GVL/H_2O solvent.

3. Conclusion

Due to the different structural and chemical properties of cellulose, hemicellulose, and lignin, an efficient fractionation strategy is essential to separate each component without reducing the value of any of the components. This study proposed a lignocellulose biorefinery approach for the fractionation of poplar biomass into its individual components. The poplar wood was first pretreated in the CO_2/H_2O system for the extraction of hemicellulose. Approximately 87.90% of hemicellulose could be removed from the original feedstock at 180 °C in 10 min with 2 MPa of CO_2. The presence of CO_2 effectively improved the hemicellulose removal from biomass owing to the in situ formation carbonic acid compared with the non-CO_2 hydrothermal. Next, the selective dissolution of the lignin from the pretreated samples in a GVL/H_2O cosolvent with acid catalyst was conducted. It was found that SITU exhibited higher catalytic delignification ability among four catalysts (sulfuric acid, SITU, PHTU, and PHMO). More than 91.35% of the original lignin was removed from the pretreated samples at the mild condition

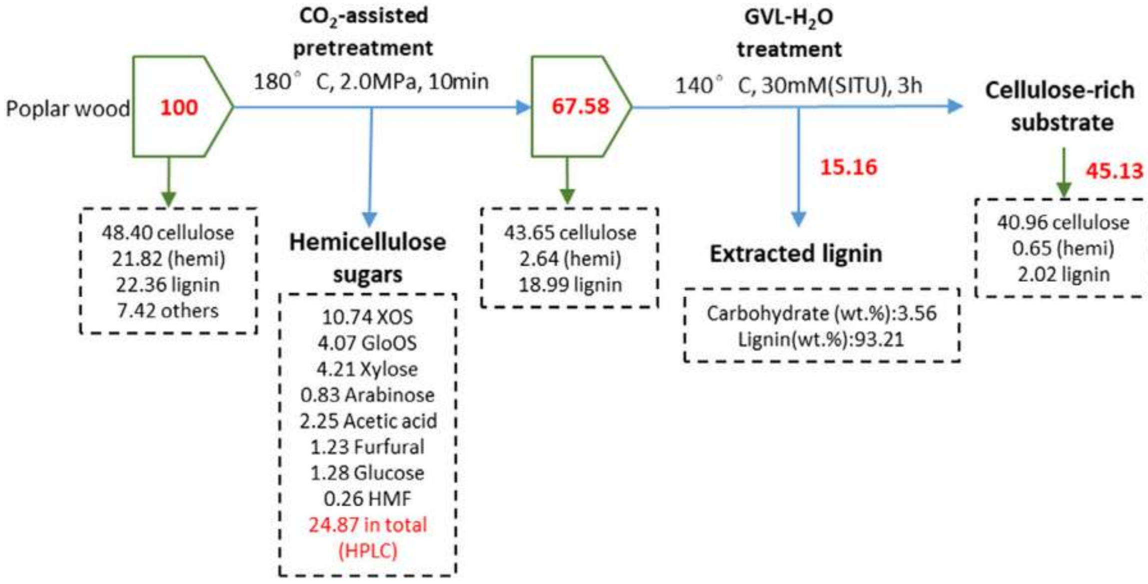

Figure 6. Mass balance of integrated conversion of poplar wood with the CO_2/H_2O treatment followed by GVL/H_2O treatment.

(140 °C and 30 mM silicotungstic acid catalyst for 2 h) and the cellulose purity in cellulose-rich substrates (cellulose pulp) reached a high value of 90.76%. Furthermore, the reagent, solvent, and catalyst in the whole process are considered as environmentally friendly chemicals and can be recycled in the whole process. Overall, the present strategy with simple and green conditions may offer an alternative option for the efficient fractionation lignocellulosic biomass.

4. Experimental Section

Materials: Poplar (*Populus* sp.) chips were acquired from a local sawmill (Nanjing, China). The chips were milled into a 60 mesh powder and dried for 12 h at 105 °C. The composition (wt%) of the poplar wood was determined following the NREL/TP-510-42618, and the cellulose, hemicellulose, and lignin contents were 48.40%, 21.82%, and 22.36 %, respectively, in terms of dry weight (detailed composition analysis of the poplar wood is available in Table S1, Supporting Information). CO_2 gas with a purity of 99.99% (w/w) was purchased from Tianze Gas, Nanjing, China. Silicotungstic acid hydrate ($H_4[Si(W_3O_{10})_4]{\cdot}xH_2O$), phosphotungstic acid hydrate ($H_3[P(W_3O_{10})_4]{\cdot}xH_2O$), and phosphomolybdic acid hydrate ($H_3[P(Mo_3O_{10})_4{\cdot}xH_2O]$) and other chemical reagents were purchased from Sigma-Aldrich, of analytical grade and used without further purification. For convenience, phosphotungstic acid, silicotungstic acid, and phosphomolybdic acid are abbreviated as PHTU, SITU and PHMO, respectively.

CO_2-Assisted Hydrothermal Pretreatment Process: The pretreatment of poplar was performed in the CO_2—H_2O mixture system. For a typical procedure, 6 g of poplar wood and 60 g deionized water (DI) were loaded in a 150 mL stainless autoclave equipped with mechanical agitation. Air was thrice displaced from the reactor with pressurized CO_2 and then the reactor was loaded with CO_2 with the designed pressure. Afterward, the reactor was heated with designed temperature (140–220 °C) and maintained for desired time (10–60 min) under stirring of 300 rpm. Once the reaction time was achieved, the autoclave was cooled down using flowing water and CO_2 was slowly released until the temperature dropped below 30 °C. The solid fractions (pretreated samples) and water-soluble liquor were separated using filter paper. The water-soluble liquor was stored at 4 °C. The solid fractions was washed three times with hot water (90 °C) and dried for 12 h at 105 °C for further analysis.

$$\text{Hydrolysis degree(wt\%)} = \left(1 - \frac{m_s}{m_0}\right) \times 100\%$$

$$\text{Hemicellulose extraction yield(wt\%)} = \left(1 - \frac{m_{H_D}}{m_{H_0}}\right) \times 100\%$$

$$\text{Delignification(wt\%)} = \left(1 - \frac{m_{L_D}}{m_{L_0}}\right) \times 100\%$$

$$\text{Lignin retention yield(wt\%)} = \left(\frac{m_{L_D}}{m_{L_0}}\right) \times 100\%$$

$$\text{Cellulose retention yield(wt\%)} = \left(\frac{m_{C_D}}{m_{C_0}}\right) \times 100\%$$

where m_0 is the mass of the feedstock (poplar); m_s is the mass of the pretreated samples after hydrothermal treatment; m_{C_0}, m_{H_0}, and m_{L_0} are the mass of the original cellulose, hemicellulose, and lignin in feedstock, respectively; andm_{C_D}, m_{H_D}, and m_{L_D} are the mass of cellulose, hemicellulose, and lignin, respectively, in samples after CO_2/H_2O hydrothermal treatment or GVL/H_2O treatment.

Delignification Process in GVL/H_2O System: After the hydrothermal treatment of poplar wood in the CO_2/H_2O system, the pretreated samples were subjected to further delignification in the GVL/H_2O system. In a typical reaction process, 2 g of pretreated sample and 20 g of GVL/H_2O (7/3 by weight) and an acid catalyst were added to the reactor. The reactor was heated to the designated temperatures with different acid catalysts for 3 h. At the end of the reaction, the reactor was cooled down to room temperature and the slurry was separated through vacuum filtration. The solid cellulose-rich fraction was washed with additional fresh GVL/H_2O three times and then washed with water and dried at 105 °C for further analysis. DI water (500 mL) was added into the filter and solid lignin can be precipitated from the solution. The precipitated lignin was separated from the liquid solvent by centrifugation, thoroughly washed with DI water and then ultrasonic treatment for 20 min to remove any remaining impurities, and dried by freeze drying overnight.

$$\text{Extracted lignin yield(wt\%)} = \left(\frac{m_L}{m_0}\right) \times 100\%$$

$$\text{Cellulose rich substrate yield(wt\%)} = \left(\frac{m_R}{m_0}\right) \times 100\%$$

where m_L and m_R are the mass of extracted lignin and cellulose-rich substrate, respectively.

The composition (cellulose, hemicellulose, and lignin) contents in cellulose-rich substrate were calculated as follows:

$$\text{Cellulose(wt\%)} = \left(\frac{m_{C_R}}{m_0}\right) \times 100\%$$

$$\text{Hemicellulose(wt\%)} = \left(\frac{m_{H_R}}{m_0}\right) \times 100\%$$

$$\text{Lignin(wt\%)} = \left(\frac{m_{L_R}}{m_0}\right) \times 100\%$$

where m_{C_R}, m_{H_R}, and m_{L_R} are the mass of cellulose, hemicellulose, and lignin in the cellulose-rich substrate, respectively.

Analytical Methods: *Chemical Composition Determination*: The chemical composition of feedstock, the samples with hydrothermal pretreatment and GVL/H_2O treatment, was analyzed by using the two-step hydrolysis method based on NREL/TP-510-42618.[42a,b] Each sample was tested at least three times and the mean values were reported.

FT-IR: FT-IR spectra of the feedstock and solid samples were measured using a Thermo 208 Nicolet (NEXUS 670) spectrometer. The spectra of samples were recorded in ATR mode, and data recorded ranging from 600 to 4000 cm^{-1} with a resolution of 2 cm^{-1}.

XRD Analysis: XRD patterns were obtained using an X-ray diffract meter with Ni-filtered Cu/Ka radiation ($\lambda = 0.154$ nm) at a counting rate of $2° min^{-1}$ from 10 to 60° (2θ). The relative CrI was determined by the Segal method using the following equation[43a,b]:

$$\text{CrI\%} = \frac{(I_{200} - I_{am})}{I_{200}} \times 100\%$$

where I_{200} and I_{am} are the peak intensity of the crystalline region of cellulose at $2\theta = 22.4°$ and the amorphous cellulose region at $2\theta = 18.0°$.

Gel Permeation Chromatography Analysis: To determine the molecular weight distribution of the extracted lignin, the freeze-dried lignin sample was measured by GPC using a Waters 1515 system equipped with a manually packed column. Polystyrene and tetrahydrofuran were used as an internal standard and solvent, respectively.

TG Analysis: The TG analysis of the solid samples was performed using a TG analyzer (Pyris6 PerkinElmer, Waltham, MA). In general, 10 mg of sample was heated from 25 to 800 °C at a heating rate of 10 °C min^{-1} in a constant N_2 flow of 50 mL min^{-1}.

^{13}C CP/MAS NMR Spectroscopy: The ^{13}C CP/MAS solid-state NMR analysis on the samples with CO_2-assisted hydrolysis and GVL/H_2O treatment was recorded with a BRUKER AVIII 400 HD instrument (at room temperature) using a relaxation delay of 2.5 s. Each sample was scanned 800 times in total.

SEM Analysis: The micrographs of the feedstock and pretreated samples were observed by SEM (5–10 kV accelerated voltage). Prior to observation, the samples were platinum plated by vacuum sputtering coating machine.

HPLC Analysis: The water-soluble liquor after CO_2-assisted hydrothermal treatment was quantitatively measured by a HPLC instrument (Waters 2414, America) with a refractive index detector and a Bio-Rad Aminex HPX-87H (300 × 7.8 mm) column. A 5 mM H_2SO_4 solution was used as the mobile phase. The flow rate was 0.6 mL min^{-1} and the column temperature was maintained at 50 °C. Determination of the concentration of oligosaccharides in the liquid phase: hydrolyzed liquor sample and sulfuric acid (4% (w/w)) was performed at 121 °C in an autoclave to convert oligosaccharides into monosaccharides according to NREL/TP-510-42623 procedure.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

biomass fractionation, delignification, high-purity cellulose, heteropoly acids, hydrothermal

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