Green Chemistry

Selective conversion of lignin in corncob residue to monophenols with high yield and selectivity†

Zhicheng Jiang, Ting He, Jianmei Li* and Changwei Hu*

The conversion of lignin to monophenols is regarded as a promising approach to produce high-quality biofuel from renewable feedstocks, because of the higher H/C_{eff} of lignin than that of cellulose and hemi-cellulose. In this work, the selective conversion of lignin in corncob residue to monophenols was achieved *via* a two-step process without significant degradation of cellulose. In the first step, the lignin component in corncob residue was selectively degraded to oligomers in the H_2O–tetrahydrofuran (THF) (3 : 7, v/v) co-solvent system, and the percentage of delignification reached up to 89.8%. Further reaction of the filtrate in the THF solvent led to further depolymerization of oligomers to monophenols, and the yield of total monophenols reached up to 24.3 wt% without hydrogen addition under the optimized conditions. 4-Ethylphenol (10.5 wt%), 2,6-dimethoxyphenol (6.6 wt%), and 4-ethylguaiacol (4.0 wt%) were the predominant products, which occupied 86.8% of the identified monophenols. This approach achieved high yield and selectivity to monophenols directly from corncob residue, simplifying the separation process. The obtained reaction residue with high content of cellulose (83.5%) is possibly a preferable feedstock to produce biofuel such as ethanol by fermentation.

1. Introduction

With accelerating depletion of worldwide fossil fuel and the related environmental pollution, lignocellulose, as the most abundant component of biomass, was generally recognized as the alternative renewable resource to replace fossil resources.[1–3] Extensive research has been focused on the production of biofuel directly from lignocellulosic biomass-based feedstocks.[4–6] However, the obtained biofuel usually has low stability, resulting from the high oxygen content and low hydrogen content of lignocellulose. The H/C_{eff} ratio, proposed by Huber, was used to estimate the hydrogen content of a particular resource.[7] Higher H/C_{eff} ratio implied higher intrinsic hydrogen content of the biomass-derived feedstocks, which allowed a higher theoretical yield of aromatic hydrocarbons and olefins, because less carbon was used for the deoxygenation.[7] The H/C_{eff} ratio of lignocellulosic biomass is between 0 and 0.5, which is much lower than that of petroleum-based feedstocks (1.0 to 2.0). Among the three main components in lignocellulosic biomass, lignin has the highest H, C and lowest

O contents.[8,9] Furthermore, lignin is the polymer of differently substituted aromatics, and maintaining the naturally formed aromatic structure in monomers derived from lignin will be beneficial for the production of high-quality fuel from biomass. Thus, lignin in lignocellulosic biomass is regarded as the most potential feedstock for the production of high-quality biofuel.[10–13] Monophenols from the depolymerization of lignin, such as phenol, 4-ethylphenol, guaiacol, and 2,6-dimethoxyphenol, are recognized as the promising basic resource to produce high-quality biofuel with C_8–C_9 alkanes *via* a hydrodeoxygenation process.[14,15] Therefore, efficient depolymerization of the lignin component to monophenols with high yield is very important for the production of high-quality biofuel directly from biomass.

Lignin is also regarded as the most difficult component to be degraded among the lignocellulosic biomass, because of its high degree of polymerization and random, three-dimensional network structure.[16,17] At present, some efforts were made to degrade lignin to monophenols, and hydrogenolysis was the most employed method.[18,19] Typically, high yield of monophenols was achieved *via* the catalytic hydrogenation process.[20] For the catalytic hydrogenation process, plenty of expensive hydrogen was necessary. Recently, several reports indicated that some monophenols were produced from lignin in the solvothermal system with or without a catalyst in the absence of hydrogen. However, only 10% monophenols were obtained from softwood under hydrothermal conditions, and many

Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China.
E-mail: changweihu@scu.edu.cn, gchem@scu.edu.cn, lijianmei@scu.edu.cn;
Fax: +86-28-85411105; Tel: +86-28-85411105
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oligomers were detected.[21,22] Yoshikawa *et al.* presented a two-step process including depolymerization and catalytic cracking to produce phenols from lignin, and a high yield (17%) of monophenols was achieved at 400 °C for 2–4 h.[23] Because this process converted lignin without hydrogen, it was considered to be an economically and environmentally promising approach to produce monophenols from lignin.

For the production of monophenols directly from biomass, another key challenge is the low selectivity to monophenols obtained, because of the simultaneous conversion of other components in biomass such as cellulose, hemicellulose, and proteins, resulting in difficult separation. Thus, effective strategies to selectively convert lignin to monophenols with high yield and selectivity directly from biomass, avoiding significant degradation of the cellulose and hemicellulose, are urgently needed. Because of the removal of the lignin component, the retained cellulose can be easily hydrolyzed by cellulase to produce ethanol.[24,25] To selectively degrade lignin, solvothermal treatment is becoming an alternative approach. Tetrahydrofuran (THF), relatively nontoxic, is a promising green solvent to extract lignin, due to its high solubility for lignin and it can be easily synthesized directly from furfural.[26,27] In our previous work,[13] the selective degradation of lignin in pubescens was investigated in the ethanol solvothermal system. 45.3% of lignin was degraded at 220 °C for 2 h, while significant conversion of hemicellulose and cellulose was avoided. The maximum yield of 10.6 wt% to 4-ethyl phenols based on the converted lignin in pubescens was obtained under optimized conditions. Nearly half of lignin was still retained in pubescens after treatment, and many phenolic oligomers were detected in reaction solution. In the present work, the objective is to further promote the delignification and the degradation of phenolic oligomers to produce more monophenols. Corncob residue, a typical process waste from the production of xylose by converting the hemicellulose component in corncob,[5,6] is used as the raw material. Cellulose and lignin are the predominant components in corncob residue. A new approach was developed to selectively convert the lignin component in corncob residue to monophenols with high yield and selectivity *via* a two-step process without the use of hydrogen.

2. Experimental

2.1 Materials

The corncob residue sample, including 17.2 wt% of lignin, 62.4 wt% of cellulose, 0.1 wt% of hemicellulose, 4.5 wt% of ash and 15.8 wt% of others unknown, was obtained from Shandong Futaste Investment Co., Ltd (Shandong Province in China),[28] and the content of hemicellulose is negligible. Before use, it was ground into powder between 40 and 80 meshes and dried in an oven at 110 °C overnight. THF (A. R.) used was from a commercial source without further purification.

2.2 Solvothermal liquefaction

The solvothermal liquefaction of corncob residue was carried out in a 250 mL stainless-steel autoclave reactor equipped with a stirrer. The dried corncob residue powder was placed in the reactor with 100 mL solvent. Air in the reactor was replaced by nitrogen for 3 minutes, and the initial pressure in the reactor was maintained at 2.0 MPa. By heating the reaction system, the temperature was raised up to the designated one. When the reaction was complete, the reactor was cooled down to ambient temperature by cooling water. The mixture in the reactor was poured out, and the reactor was washed with the reaction solvent three times. The reaction mixture was filtered to separate the solid residue from the liquid phase. The remaining residue was dried in an oven at 100 °C overnight before weighing for conversion calculation. By adding NaCl to the liquid mixture, the THF phase was separated in a separatory funnel. The lignin fraction dissolved in the H_2O phase was extracted with dichloromethane three times, and all the organic phase was collected together. The organic phase was evaporated to remove the THF solvent, and the retained liquid products were further analyzed. The separated THF phase was subjected to further reaction at a higher temperature and longer reaction time.

2.3 Characterization of the solid residue

2.3.1 Chemical titration. The analysis of corncob residue indicated that nearly all hemicellulose contained in corncob was removed by the industrial process, thus the conversion of hemicellulose in corncob residue was not discussed. The components (cellulose and lignin) in corncob residue and reaction residue were analyzed using classical chemical titration methods. The experimental details could be obtained from ref. 13 and 29. Every sample was tested three times, and the error was less than 3%.

2.3.2 XRD. The crystalline forms of corncob residue and the residues after liquefaction under different reaction conditions were examined by XRD measurements on the Dandong Fangyuan DX-1000 instrument. The diffracted intensity of Cu Kα radiation ($k = 0.1540$ nm; 40 kV and 25 mA) was measured over the 2θ range of 5° to 40°. The crystallinity index (CI) of cellulose in the samples was calculated according to the literature.[13]

2.3.3 Elemental analysis. The contents of C, H and N elements in corncob residue and reaction residue were determined using an EA flash1112 elemental analyzer. The content of element O was calculated by difference.

2.3.4 SEM. To characterize the surface morphology of corncob residue and the reaction residue after treatment, SEM (FEIINSPECT F) analysis was performed. The instrument was run at an acceleration voltage of 20 kV.

2.3.5 ^{13}C CPMAS NMR. The ^{13}C Cross-Polarization Magic Angle Spinning Nuclear Magnetic Resonance (CPMAS NMR) of corncob residue and reaction residue was conducted with a Bruker Avance III 500 MHz instrument. A total of 800 scans were accumulated for each sample. The spinning rate was

37 878 Hz, and the relaxation delay was 5 s. Spinal 128 decoupling was used during acquisition.

2.4 Characterization of the liquid products

2.4.1 GC-FID. The liquid products were dissolved in acetonitrile for quantitative detection using a GC equipped with a flame ionization detector (Fuli 9750). The GC-FID was equipped with an HP-5 column (30 m × 0.25 mm × 0.25 μm) and the temperature program was set as rising from 50 °C to 250 °C by 5 °C min^{-1}, holding for 10 min. Benzyl alcohol was used as an internal standard to quantify the content of the products. Every sample was tested three times, and the error was less than 5%.

2.4.2 GPC. The molecular weight and distribution of liquid products were analyzed using a gel permeation chromatograph (GPC, HLC-8320) with a TSK gel Super HM-H (6.0 mm × 15 cm × 2) pump and a RI detector. Both the columns and RI detector were maintained at 40 °C during analysis. THF was used as the eluent with a flow rate of 0.6 mL min^{-1} and an injection volume of 10 μL was used. A calibration curve was obtained using monodisperse polystyrene standards.

2.4.3 2D HSQC NMR. The 2D HSQC NMR spectra of liquid products were qualitatively determined on a Bruker Avance 400 MHz spectrometer. About 50 mg samples for analysis were prepared by fully dissolving the viscous liquid products from the reaction liquid fraction after removing solvents H_2O and THF in 0.5 mL deuterated dimethyl sulfoxide (DMSO-d$_6$). Heteronuclear single quantum coherence (HSQC) experiments were performed with 10 to 0 ppm and 220 to 5 ppm in ^{1}H- and ^{13}C-dimensions, respectively. For the ^{1}H-dimension, 1024 data points were used for an acquisition time of 64 ms, while 256 data points were used for the ^{13}C-dimension. The $^1J_{C-H}$ used was 145 Hz. Besides, 1.5 s pulse delay and 16 scans were also adopted. The DMSO solvent peak (δ_c 39.5 ppm and δ_H 2.5 ppm) was used for the chemical shift calibration.

3. Results and discussion

3.1 Separation of lignin in corncob residue in the H_2O–THF solvent

3.1.1 Effect of the ratio of H_2O–THF. To remove lignin from corncob residue and retain cellulose, the depolymerization of lignin from corncob residue was performed under solvothermal conditions. Ethanol, methanol, DMSO, and dioxane were usually adopted as the reaction solvent,[26,30–33] while THF was seldom used. THF was a promising green solvent with low boiling point (66 °C) and high solubility for lignin.[26] Furthermore, THF could be synthesized directly from furfural with high selectivity through catalytic decarbonylation to furan followed by ring hydrogenation.[27] Thus, the selective degradation of lignin from corncob residue was carried out in the H_2O–THF co-solvent system with different ratios of H_2O–THF (Fig. 1). To reveal the delignification function of the H_2O–THF co-solvent system, control experiments were conducted in
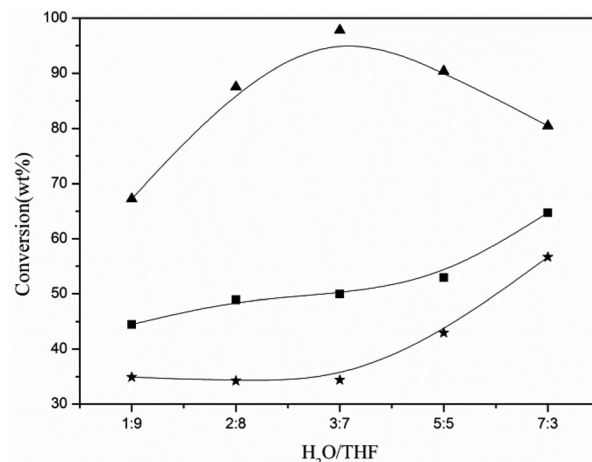
Fig. 1 Effect of the ratio of H_2O–THF on the conversion of corncob residue (■ raw material, ★ cellulose converted/cellulose contained, ▲ lignin converted/lignin contained; reaction conditions: corncob residue: 4.0 g, reaction temperature: 220 °C, reaction time: 2.0 h).

the H_2O and THF single solvent system, respectively. In the THF system, most of the lignin and cellulose in corncob residue remained, and the conversion was only 17.2% and 4.9%, respectively. Likewise, the conversion of lignin was very low in the H_2O system, while 67.2% cellulose in corncob residue was converted. In the H_2O–THF co-solvent system, the conversion of lignin in corncob residue initially increased with an increasing ratio of H_2O–THF, and had a maximum at the ratio of 3 : 7 (v/v), then decreased. The conversion of cellulose in corncob residue remained unchanged with an increasing ratio of H_2O–THF to 3 : 7, and increased dramatically when the ratio of H_2O–THF was beyond 3 : 7 (v/v). This result indicated that the H_2O–THF co-solvent system was more favorable for the selective conversion of lignin in corncob residue than a single solvent, while more H_2O was more effective to convert cellulose in corncob residue. Control experiments were conducted using pure cellulose as the material under identical conditions. The results indicated that pure cellulose was hardly converted in the single THF solvent, and the conversion of pure cellulose in the H_2O–THF (3 : 7) co-solvent was only 4.7% under the identical reaction conditions. It further confirmed that the addition of THF was not favorable for the conversion of cellulose. According to the literature, it seemed that H_2O could disrupt numerous intermolecular and intramolecular hydrogen bonds of cellulose, ascribing to its high hydrogen bond acceptor ability.[34,35] Because the hydrogen bond acceptor ability of THF was much lower than that of H_2O, THF or H_2O–THF was not as effective as single H_2O to convert cellulose. Therefore, efficient delignification from corncob residue could be achieved in the H_2O–THF (3 : 7, v/v) co-solvent system, and the conversion of cellulose and lignin was 34.4% and 97.8%, respectively. This result was further proved by the elemental analysis of reaction residues (Fig. S1†). It was reported that the co-solvent system such as H_2O–ethanol co-solvent exhibited better delignification

capacity than a single solvent.[31] The co-solvent system had a synergistic capability to promote the liquefaction of biomass, even to inhibit the formation of solid residue. These co-solvents could be consisting of two solvents with different polarities (1) an electron acceptor solvent with high polarity, always containing a hydroxyl group and (2) an electron donor solvent with middle polarity.[36] When H_2O–THF was used as the co-solvent, H_2O acted as a nucleophile agent to react with the activated centers in lignin, and THF contributed to impregnate the plant tissue and dissolve the liberated fragments.[27]

3.1.2 Effect of reaction temperature and time. As illustrated in Fig. 1, the lignin in corncob residue was nearly converted at 220 °C in the H_2O–THF (3 : 7, v/v) system, while 34.4% cellulose in corncob residue was also converted. To decrease the cellulose conversion, the liquefaction of corncob residue was performed at lower reaction temperature. When the reaction temperature was decreased from 220 °C to 200 °C, the conversion of lignin and cellulose decreased from 97.8% and 34.4% to 92.2% and 21.5%, respectively. Further decreasing the reaction temperature to 180 °C greatly decreased the conversion of both lignin and cellulose, which was only 67.5% and 11.0%, respectively. Then, the reaction was conducted at 200 °C with different reaction times. As illustrated in Fig. 2, the conversion of lignin showed a sharp increment with increasing reaction time to 1.0 h, and then increased slowly with time. The conversion of cellulose in corncob residue almost remained unchanged before 1.0 h, and distinctly increased with reaction time after 1.0 h. It implied that the selective conversion of lignin in corncob residue could be achieved at 1.0 h, without significant degradation of cellulose. The conversion of lignin at 1.0 h reached 89.8%, while the conversion of cellulose was just 13.5%. Namely, the content of lignin and cellulose in reaction residue changed from 17.2% and 62.4% to 2.7% and 83.5%, respectively. The high content of cellulose in the produced reaction residue was a possible

resource to produce ethanol by biological conversion, or HMF and/or levulinic acid by further thermochemical conversion.

3.2 Characterization of reaction residue

3.2.1 SEM analysis. The reaction residues treated in different ratios of H_2O–THF systems were distinctly different in color. As shown in Fig. 3, the color of reaction residue in the THF system had no obvious change compared to corncob residue. However, the reaction residue became shallower when the ratio of H_2O–THF increased to 3 : 7. A light gray residue was obtained in the H_2O–THF (3 : 7) co-solvent system, which was possibly ascribed to the high percentage of cellulose after removal of lignin. While further increasing the ratio of H_2O–THF resulted in the deeper color of reaction residue, and a weak black reaction residue was obtained in the H_2O system. To deeply investigate the reaction residue after treatment, SEM analysis was conducted. From Fig. 3, it could be found that the surface of reaction residues after treatment became rougher with an increasing ratio of H_2O–THF to 3 : 7, which suggested that more lignin was peeled off from corncob residue. The bundle structure of cellulose in reaction residue after treatment in the H_2O–THF (3 : 7) co-solvent system was found to be more clear than corncob residue, which implied that the crystalline structure of cellulose remained and the cellulosic crystal structure became neater after the removal of lignin and some cellulose existed in amorphous regions.[37,38] However, the bundle structure of cellulose was observed to be damaged when the percentage of H_2O was beyond 70%. It implied that the cellulose component was more easily destroyed in the H_2O solvent, resulting from the disruption of hydrogen bonding in cellulose by H_2O. This result proved that lignin was efficiently removed without obvious cellulose damage in the H_2O–THF (3 : 7) co-solvent system. In addition, the reaction residues at different reaction times were also analyzed by XRD (Fig. S2†) and SEM (Fig. S3†). The results indicated that the crystal structure of cellulose in corncob residue was not disrupted by treatment for 1.0 h, and the crystallinity index increased slightly from 78.0% to 80.1% resulting from the removal of lignin and amorphous cellulose.

3.2.2 ^{13}C CPMAS solid-state NMR. To further investigate the change of cellulose and lignin in corncob residue after treatment, the ^{13}C CPMAS solid-state NMR experiment was performed, because its signals could recognize different carbons of the main components in corncob residue. Fig. 4 presents the ^{13}C CPMAS NMR spectra of corncob residue and reaction residue at 1.0 h in the H_2O–THF (3 : 7, v/v) co-solvent system. The NMR signals were assigned to different lignocellulosic components according to the literature.[39–41] For cellulose, the signals of C-6, C-2, 3, 5, C-4 disordered, C-4 ordered and C-5 were presented at 63, 74, 84, 89, and 105 ppm, respectively, while aryl methoxy carbon in lignin was at 56 ppm. As shown in Fig. 4, the signals assigned to lignin almost disappeared after solvothermal treatment and it showed delignification. However, the signals of characteristic peaks assigned to cellulose (C-1, C-2, C-3, C-5 and C-6) increased significantly, indicating the rise of the cellulose percentage in reaction
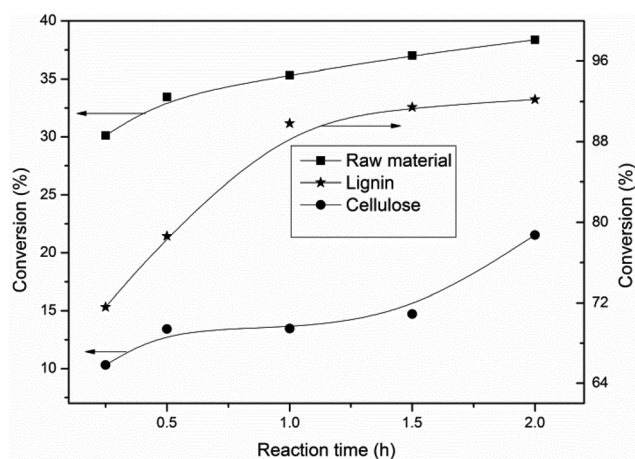
Fig. 2 Effect of reaction time on the conversion of corncob residue (reaction conditions: corncob residue: 4.0 g, reaction temperature: 200 °C, H_2O–THF: 3 : 7, v/v).
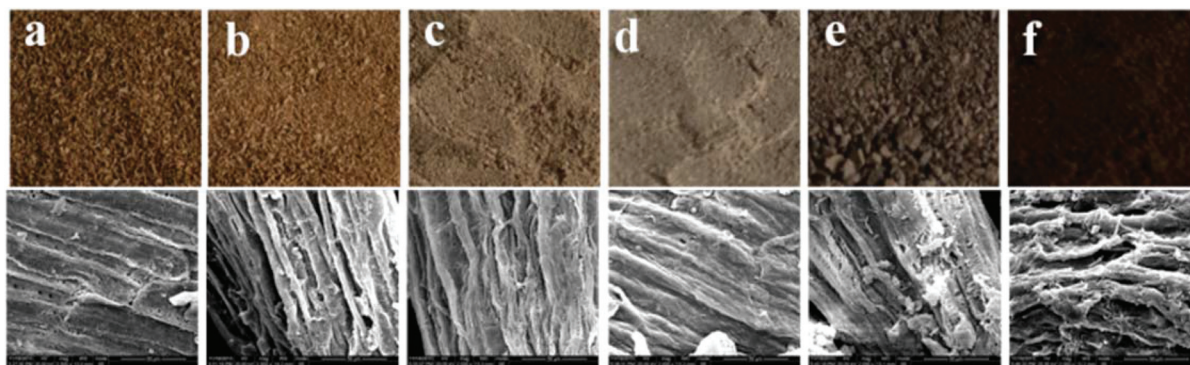
Fig. 3 Photograph and SEM micrographs of residues treated in different reaction systems ((a) corncob residue, (b) THF, (c) H_2O–THF (1 : 9, v/v), (d) H_2O–THF (3 : 7, v/v), (e) H_2O–THF (7 : 3, v/v), (f) H_2O).
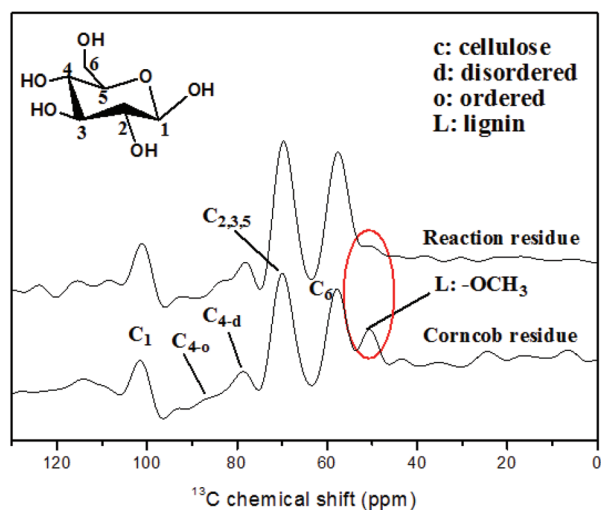

Fig. 4 ^{13}C CPMAS solid-state NMR spectra of corncob residue and reaction residue.

residue after co-solvent treatment. Furthermore, the increase of the signal of C-4 ordered demonstrated the consumption of amorphous cellulose, while the crystal structure of cellulose remained original. These results were in accordance with the chemical titration and elemental analysis.

3.3 Further reaction of the filtrate in the THF solvothermal system

3.3.1 Effect of reaction temperature. Based on the results above, the selective conversion of lignin in corncob residue was achieved in the H_2O–THF (3 : 7, v/v) co-solvent system. Most of the lignin (89.8%) was degraded at 200 °C for 1.0 h, avoiding significant degradation of cellulose. However, few monomers of lignin were detected in the filtrate, which implied that the lignin fraction in the filtrate existed possibly as oligomers. The THF phase with lignin fraction was successfully separated from the H_2O phase by the addition of NaCl. To obtain more monophenols, the lignin fraction in the THF phase of the filtrate was further subjected to higher temperature reaction. As demonstrated in Table 1, temperature played

an important role in the improvement of the yield of monophenols. There were trace monophenols obtained in the reaction solution treated at 220 °C. A small amount of monophenols was detected in the reaction solution treated at 240 °C, including 4-ethylphenol, 4-ethylguaiacol, 2,6-dimethoxyl-phenol, phenol, guaiacol, vanillin, syringaldehyde and 2,3-dihydrobenzofuran. With further increasing reaction temperature from 260 to 300 °C, a large increase of the yield of monophenols was observed, especially for 4-ethylphenol, 4-ethylguaiacol, and 2,6-dimethoxylphenol. The total yield of identified monophenols markedly increased to 11.7 wt% at 300 °C, which suggested that high temperature was favorable for the cleavage of the lignin bond to yield monophenols. It should be pointed out that the 15.8 wt% unknown fraction might have an effect on the yields as well as on the mass balances of the process. However, the effects of the unknown fraction on the reaction would be systematic, and the tendency of lignin degradation would not vary if those effects were included. The great improvement of the yield of monophenols beyond 260 °C was probably ascribed to the special properties of the THF solvent system under this reaction condition, where THF, a supercritical fluid (critical temperature 268 °C, critical pressure 5.19 MPa), was obtained.[27] Thus, the THF reaction system was favorable for the depolymerization of

Table 1 Effect of reaction temperature on the yield[a] of monophenols by further reaction of the filtrate[b]

	Temperature				
Phenols	220 °C	240 °C	260 °C	280 °C	300 °C
Phenol	—	0.12	—	0.50	0.50
2,3-Dihydrobenzofuran	—	—	—	0.19	0.32
Guaiacol	—	0.10	—	0.42	0.63
4-Ethylphenol	—	0.27	1.31	1.66	6.00
4-Ethylguaiacol	—	0.19	0.72	0.64	2.16
2,6-Dimethoxylphenol	—	0.14	0.65	0.99	1.01
Vanillin	—	0.85	—	0.75	0.68
Syringaldehyde	—	0.37	—	—	0.38
Total monophenols	Trace	2.04	2.68	5.16	11.69

[a] wt%, based on the lignin content in corncob residue. [b] Reaction conditions: THF 100 mL, reaction time: 2.0 h.

lignin oligomers to produce monophenols at higher temperature. Wyman also pointed out that THF promoted the extraction and deconstruction of lignin.[27]

3.3.2 Effect of reaction time. To further improve the yield of monophenols, further reaction of the filtrate was conducted at 300 °C with longer reaction time (Fig. 5). With increasing reaction time to 8.0 h, the yield of 4-ethylphenol and 4-ethylguaiacol gradually increased. The yield of 2,6-dimethoxylphenol had no obvious change initially, and sharply increased from 1.1 to 6.6 wt% after treatment for 8.0 h. This result indicated that 2,6-dimethoxylphenol was easily formed at longer reaction time. Other monophenols such as vanillin, syringaldehyde, and phenol exhibited no obvious change. The yield of 4-ethylphenol, 4-ethylguaiacol, and 2,6-dimethoxylphenol at 8.0 h was 10.5 wt%, 4.0 wt%, and 6.6 wt%, respectively. The yield of total monophenols reached up to 24.3 wt% after 8.0 h treatment, which was higher than that reported in the literature without hydrogen addition.[23,42] 4-Ethylphenol, 4-ethylguaiacol, and 2,6-dimethoxylphenol occupied 86.8% of the identified monophenols, which provided the possibility to simplify the separation process and was favorable for the further reaction to produce high-quality biofuel. However, further increasing the reaction time to 12.0 h resulted in the decrease of the yield of total monophenols especially 4-ethylphenol, 4-ethylguaiacol, and 2,6-dimethoxylphenol, possibly ascribing to the repolymerization of monophenols.[36] However, the amount of other monophenols had a little increase at 12.0 h. Thus, high yield and selectivity of 4-ethylphenol, 4-ethylguaiacol and 2,6-dimethoxylphenol was achieved in the THF solvent at 300 °C for 8.0 h.

3.3.3 Molecular weight distribution. Table 2 shows the average molecular weight and polydispersity of the filtrate and the liquid from further reaction. The molecular weight (M_w) of the lignin fraction in the filtrate after delignification treatment was 706 g mol^{-1}, which was much lower than that

Table 2 Weight-average (M_w) and number-average (M_n) molecular weights and polydispersity (M_w/M_n) of lignin fraction

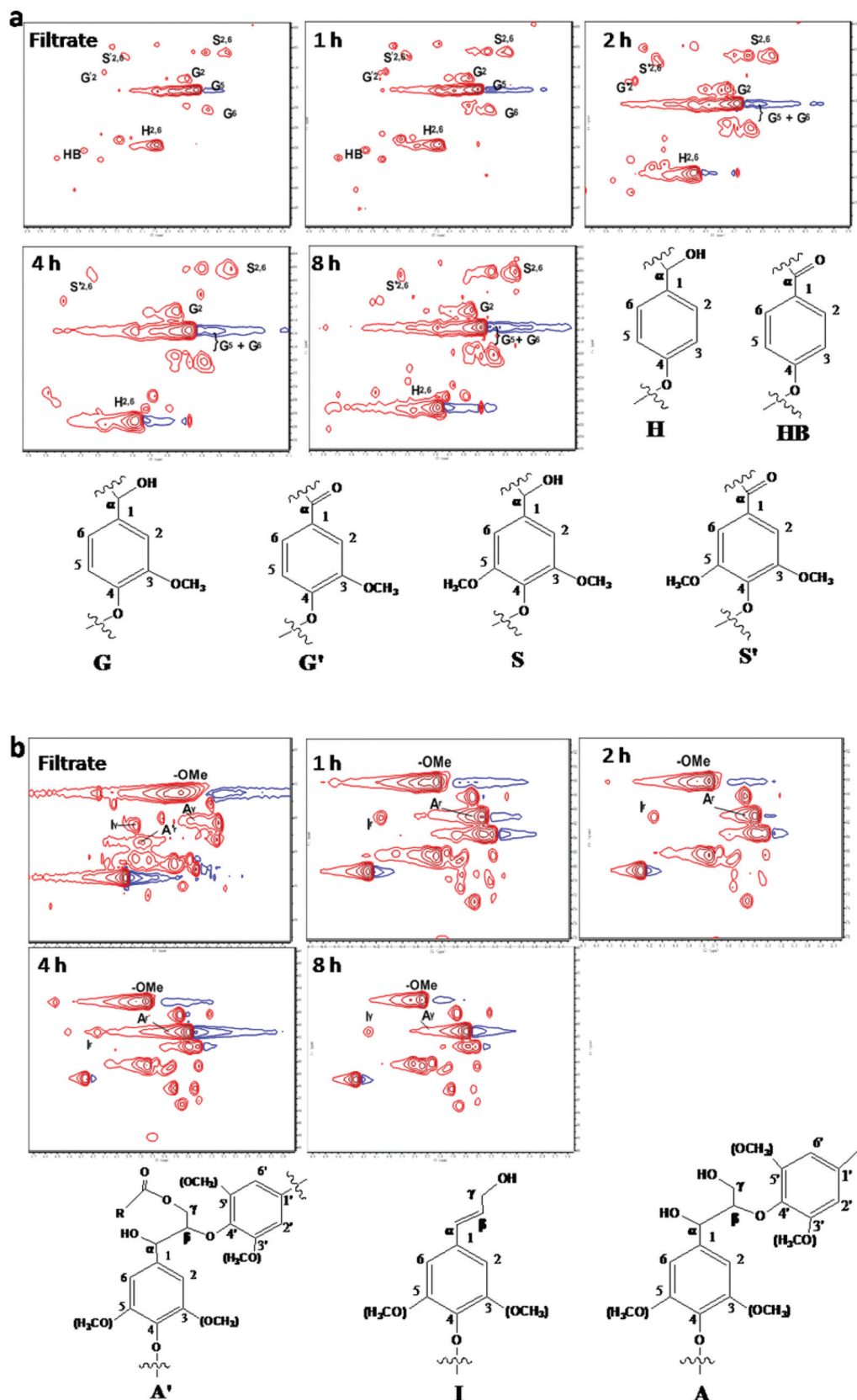|	M_w (g mol^{-1})	M_n (g mol^{-1})	M_w/M_n
Filtrate	706	295	2.40
Liquid (260 °C, 2 h)	392	157	2.50
Liquid (300 °C, 8 h)	323	146	2.27

(2050–2430 g mol^{-1}) extracted from corncob in the ionic liquid/organic solvent system by Sun.[43] This implied that the industrial process for xylose production and delignification treatment in the H_2O–THF co-solvent system improved the depolymerization of lignin. When the reaction temperature was increased to 260 °C in further reaction of the filtrate, M_w decreased from 706 to 392 g mol^{-1}, and M_n decreased from 295 to 157 g mol^{-1}. With a continuous increment of the reaction temperature and the treatment time, M_w and M_n of liquid products after treatment at 300 °C for 8.0 h further decreased to 323 and 146, respectively, which was near to the molecular weight of 4-ethylphenol and 2,6-dimethoxylphenol. The polydispersity of liquid products after treatment at 300 °C for 8.0 h had a significant decrease to 2.27, suggesting an increasing amount of monophenols. These results demonstrated that a higher reaction temperature and a longer treatment time could facilitate the depolymerization of the oligomer intermediates, and the average degree of polymerization decreased from 5–6 to 2–3.

3.3.4 2D HSQC NMR analysis of liquid fractions. Due to the complexity of the lignin structure, it is necessary to investigate the mechanism of lignin degradation, which can provide more information concerning the degradative rules and more guiding significance for the utilization of lignin to obtain biofuel. Herein, the liquid products in the filtrate by delignification treatment and the further reaction solution were subjected to 2D HSQC NMR analysis (Table S1† and Fig. 6).[44–46] The 2D NMR spectra exhibited two regions, which were aromatic C–H correlation (δ_C/δ_H 95–150/5.5–8.0 ppm, Fig. 6a) regions and the aliphatic side-chain C–H correlation (δ_C/δ_H 50–95/2.5–6.0 ppm, Fig. 6b). Because of the presence of ferulic acid and *p*-coumaric acid in the cell walls of herbaceous crops, corncob had more correlations in the aromatic region than softwood and hardwood.[42] Signals from *p*-hydoxyphenyl (**H**), guaiacyl (**G**), and syringyl (**S**) lignin units were observed, which confirmed that a large amount of lignin intermediates was present in the liquid fraction. The signal of the **H** unit was observed for the $C_{2,6}$–$H_{2,6}$ correlation. The $C_{3,5}$–$H_{3,5}$ correlation signal of the **H** unit overlapped with the signal of C_5–H_5 correlation of the **G** unit. The **G** unit presented correlations for C_2–H_2, C_5–H_5 and C_6–H_6. The **S** unit showed a major signal for $C_{2,6}$–$H_{2,6}$ correlation. **H**-type and **G**-type were the main unit structures in the liquid fraction, and the **S**-type was low. This confirmed the products detected by GC. In addition, the C_α-oxidized **S** unit (**S′**) and C_α-oxidized **H** unit (**HB**) were also observed. This implied that lignin in corncob residue was destroyed after treatment in the H_2O–THF co-solvent system.
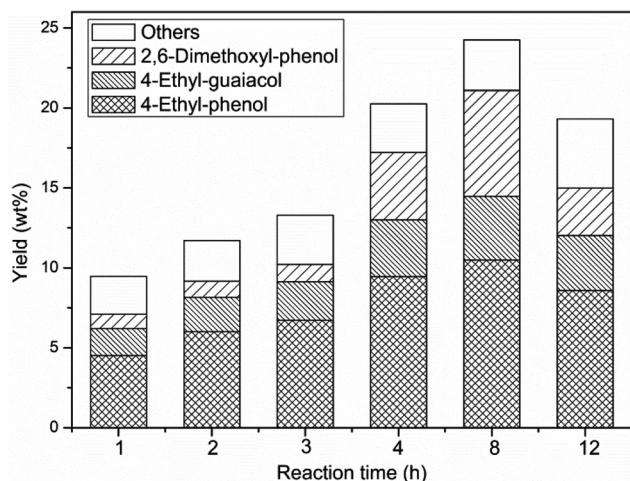
Fig. 5 Effect of reaction time on the yield of monophenols (based on the lignin content in the corncob residue) by the further reaction of the filtrate (reaction conditions: THF 100 mL, reaction temperature: 300 °C).

Fig. 6 The 2D HSQC NMR spectra ((a) aromatic regions and (b) aliphatic side-chain) of the liquid product from further reaction of the filtrate at different reaction times and 300 °C.

With increasing reaction time for further reaction of the filtrate, the signals of **H** and **G** units in the lignin substructure strengthened gradually, especially for the **H** unit, which suggested that the further reaction improved the depolymerization of **H** and **G** lignin oligomers to produce 4-ethylphenol and 4-ethylguaiacol. The signal of the **S** unit exhibited a great enhancement when treated for 4.0 and 8.0 h, which resulted in the great increase of 2,6-dimethoxylphenol yield. These results indicated that **H** and **G** units of lignin could be depolymerized at the initial stage of reaction under the reaction conditions, while the **S** unit was favorable to form with longer reaction time. It was well consistent with the GC results. In addition, the C_α-oxidized **H** unit (**HB**) gradually disappeared with increasing reaction time.

In the aliphatic side-chain C–H correlation region (Fig. 6b), methoxyl correlation was the most prominent signal. β-O-4′ (**A**) of lignin was enriched in corncob residue, while the phenylcoumaran (β-β′), resinol (β-5′), and spirodienone (β-1) were not observed. This was significantly different from that of raw lignocelluloses such as pubescens, sugarcane bagasse, and cotton stalk, because corncob residue was from the reaction residue of the xylose production process.[13,16,43] Likewise, Cheng reported that neither phenylcoumaran and resinol nor spirodienone were found in the solution of corn stem lignin.[47] The main signal correlations to β-O-4′ (**A** and **A′**) and C_γ–H_γ were observed. However, the signals for C_α–H_α and C_β–H_β were not found, which was possibly ascribed to further oxidation of C_α–H_α and C_β–H_β by the industrial process for xylose production and treatment in the H_2O–THF reaction system. This could be proved by the presence of structure unit **I** in the filtrate, which demonstrated that the aliphatic side-chain of lignin was also damaged by treatment. The signals of the aliphatic side-chain weakened gradually with increasing reaction time in the further reaction of the filtrate, which further confirmed the degradation of lignin oligomers. The 2D HSQC NMR results proved that the treatment of corncob residue in the THF–H_2O co-solvent system solubilized lignin and most of the chemical bonds in the lignin aliphatic side-chain remained without cracking, and further reaction of the filtrate at a higher reaction temperature and longer reaction time promoted the cracking of the chemical bond in the lignin aliphatic side-chain, enhancing the depolymerization of lignin oligomers to monophenols.

4. Conclusions

A new approach was developed to selectively convert lignin to monophenols in corncob residue, avoiding significant degradation of the cellulose component. High delignification was achieved in the H_2O–THF (3 : 7, v/v) co-solvent system, and the conversion of lignin reached up to 89.8% at 200 °C for 1.0 h. High yield of monophenols (24.3 wt%) was obtained by the further reaction of the filtrate at 300 °C for 8.0 h without hydrogen addition. 4-Ethylphenol (10.5 wt%), 2,6-dimethoxylphenol (6.6 wt%), and 4-ethylguaiacol (4.0 wt%) occupied 86.8% of the identified monophenols. 2D HSQC NMR analysis proved that the treatment of corncob residue in the H_2O–THF co-solvent system solubilized lignin, and lignin oligomers were obtained, while further reaction of the filtrate promoted the cracking of the chemical bond in the lignin aliphatic side-chain to produce monophenols. This approach achieved high yield and selectivity to monophenols directly from corncob residue, and the obtained reaction residue with high content of cellulose (83.5%) was a promising feedstock to produce biofuel such as ethanol.

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