Molecular Structure of Poplar Lignin Obtained by *p*-Toluene Sulfonic Acid (p-TsOH) and Formic Acid Delignification

Songlin Wang,[a,b,]* Zongjia Song,[b] Hui He,[a] and Qian Wang [b]

Poplar wood sawdust was chemically modified and separated into fractions using a mixture of p-toluene sulfonic acid (p-TsOH) and formic acid under different conditions. The optimum conditions of poplar lignin separation were determined by single-factor experiment. The mixed acid lignin (MAL) and the solid residues were subjected to comprehensive structural characterization by Fourier-transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (^{1}H-NMR), X-ray diffraction (XRD), and scanning electron microscope (SEM). At the mass ratio of 5:1 of p-TsOH and formic acid, temperature of 80 °C, acid concentration of 75%, and reaction time of 20 min, more than 80% of lignin was removed, and almost all of the cellulose was retained in the solid residue. The results indicated that the p-TsOH/formic acid achieved rapid and nearly-complete dissolution of wood lignin below the water boiling temperature by enhancing the cleavage of interunitary bonds in lignin (β-O-4' bond) and the 4-hydroxy-3-methoxy cinnamic acid structure in the lignin.

Keywords: Lignin; p-Toluenesulfonic acid; Formic acid; Separation; FTIR; SEM; Crystallinity index

Contact information: a: Guangxi Key Laboratory of Clean Pulp & Papermaking and Pollution Control, College of Light Industry and Food Engineering, Guangxi University, Nanning 530004; b: College of Marine Science and Biological Engineering, Shandong Provincial Key Laboratory of Biochemical Engineering, Qingdao University of Science & Technology, Qingdao, Shandong 266042 China;
** Corresponding author: wangsongl@126.com*

INTRODUCTION

As the most abundant biopolymer after cellulose present in lignocellulosic biomass, lignin is expected to play an important role in the production of renewable high-value added chemicals and new materials. The three-dimensional network structure of lignin is formed by three types of phenylpropane units connected by ether and carbon-carbon bonds.

In addition to its use as heavy oil viscosity reducer, high temperature baking agent, dispersing agent in concrete, and oil-water coagulant, *etc*. (Dessbesell *et al*. 2020), lignin has significant aromaticity, and it can be used to produce biofuels (Bi *et al*. 2015), hydrogels (Thakur *et al*. 2017; Sathawong *et al*. 2018), adsorbent materials (Supanchaiyamat *et al*. 2019), urea formaldehyde adhesives, surfactants, and various polymer composites (Thakur *et al*. 2014). In recent years, the separation and utilization of lignin has attracted attention from academic and industrial researchers (Yuan *et al*. 2013; Kumar *et al*. 2020). Acid (Yasuda *et al*. 2001), alkali (Sipponen *et al*. 2013), supercritical liquid (Pasquini *et al*. 2005), electrochemical methods (Haddad *et al*. 2017), ionic liquid (Achinivu *et al*. 2014; Achinivu 2018), and gels (Cai *et al*. 2001) are widely used in academic laboratories to separate lignin from biomass.

Nearly all commercial lignin products come from sulphite pulping, and the spent liquor is called "brown liquor". However, the lignin obtained has a broad molecular weight distribution and does not have a constant thermal transition temperature (Yuan *et al*. 2009; Rautiainen and Alén 2010). These drawbacks limit the lignin for further development and utilization. Acid is also widely used for delignification. Acid lignin includes Klason lignin, periodate lignin, phosphoric acid lignin, *etc*. Significant chemical structure modification of Klason lignin makes it difficult for further utilization. Lignin from periodate delignification is usually over-oxidized. However, acid lignins are only produced in lab-scale quantities, but they are not commercially produced. The only “acidic lignin” commercially produced is lignosulphonate.

Organic solvent lignin is easily prepared with minimal degradation (Zhao *et al*. 2009). New lignocellulosic fractionation technologies using organic solvents, which can easily be recovered and reused, such as alcohols, organic acids, cresols, and phenols, have been developed to obtain cellulose, hemicelluloses, and lignin without serious degradation (Zhang *et al.* 2017). Among the organic solvents, formic acid used in organosolv fractionation process demonstrates high efficiency on different biomass materials. It can simultaneously separate cellulose, hemicelluloses, and lignin and allow further conversion of fractions into value added chemicals and materials (Kupiainen *et al.* 2012). Fractionation of lignocellulose by acetic and formic acid conducted at atmospheric pressure and above the water boiling temperature (>100 °C) achieved 96% lignin removal from wheat straw (Snelders *et al.* 2014), 88.9% lignin removal from bamboo (Li *et al.* 2012), and 85% lignin removal from rice straw (Lam *et al. 2*001). Increasing the reaction pressure yields higher degrees of delignification than the treatment of the same raw material at atmospheric pressure (Dapía *et al.* 2000). However, using a high temperature and pressure with organic solvents means that the process requires a high energy input and causes environmental issues, which in turn, impedes commercial deployment of the technology.

p-Toluene sulfonic acid (p-TsOH) is an organic acid with strong reactivity and low price. It is a good solvent for the removal of lignin through proton-catalyzed hydrolysis of polysaccharides, lignin, and ether or ester bonds in aqueous solution. p-TsOH has good selective degradation on hemicelluloses and oligosaccharides in the amorphous zone of fiber structure (Bian *et al*. 2017). *p*-Toluene sulfonic acid removes approximately 85% of lignin from birch wood after only 20 min at 80 °C, resulting in a cellulose-rich water-insoluble solids (WIS) fraction and a spent acid liquor stream containing mainly dissolved lignin (Bian *et al.* 2017). Due to the low water solubility of p-TsOH at ambient temperature, efficient recovery of p-TsOH can be achieved by cooling the spent acid solution. This method holds great potential in achieving commercial success.

This research took advantage of the high efficiency of formic acid and its strong reactivity, low price, and good selective degradation on different biomass materials. Formic acid and p-TsOH were mixed and used to separate lignin from poplar material. To use lignin and cellulose obtained from this new fractionation process as raw materials for the production of high-value chemicals in a future biorefinery industry, their structure and properties were characterized by Fourier-transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (^{1}H-NMR), X-ray diffraction (XRD), and scanning electron microscope (SEM). The establishment of an effective fractionation process is also of great significance to the conversion and the utilization of lignin of lignocellulosic biomass. Thus, the optimum conditions of poplar lignin separation were determined.

EXPERIMENTAL

Materials

Analytical grade p-TsOH and 98% formic acid, purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China), was used directly without further purification. The poplar wood sawdust was provided by Shandong Chenming Paper Group Co., Ltd. (Shandong, China). The moisture of the poplar wood chips was 2.75%. Chemical analysis showed that it had 40.6% cellulose, 19.7% hemicelluloses, and 31.6% Klason lignin (KL) on a dry weight basis determined by nitric acid - ethanol method by GB/T 745-1989 (1989).

Methods

Poplar wood sawdust fractionation by mixed p-TsOH acid and formic acid

Poplar wood sawdust fractionation by mixed p-TsOH acid and formic acid was conducted in different reaction conditions. The desired concentration and ratio of acid was prepared by mixing the required amounts of p-TsOH and formic acid in a three-necked flask. The p-TsOH/formic acid solution in the flask was heated in a water bath to the predetermined temperature (Bian *et al. 2*017). Next, 5 g (oven-dry weight) of poplar wood sawdust (the solid-liquid mass ratio was 1:20 (g mL^{-1})) was added to the acid solution. The reaction was allowed to proceed according to the pre-designed experimental conditions. At the end of reaction, 100 mL of distilled and deionized water was added to quench the reaction. A Buchner funnel was used to separate the water-insoluble solid from pulping liquor by vacuum filtration and pressing in order to recover as much lignin as possible. The water-insoluble solid was repeatedly washed to neutral pH with deionized water and dried at 50 ℃ in a convection drying oven (101-2AB, Shanghai Kuntian Laboratory Instrument Co., Ltd.) for 24 h. The filtrate and the washing liquids were evaporated and concentrated to near dryness (black liquor). Water was then poured into the concentrated black liquor to precipitate the dissolved lignin. The crude lignin was separated by centrifugation at 3000 rpm for 10 min and washed with water three times at room temperature. The crude lignin was purified by washing with deionized water until neutrality and then dried at 50 ℃ for 24 h. The effects of acid ratio, acid concentration, reaction temperature, and reaction time on the yield of lignin and solid residues were investigated.

Recovery of formic acid and p-TsOH

As depicted in Fig. 1, the formic acid and p-TsOH in the waste liquid were recovered by vacuum distillation and crystallization, respectively. After the black liquor was concentrated in an glycerol bath at 100 ℃, it was transferred to a RE-52CS rotary evaporator (Shanghai Yanhe Instrument Equipment Co., Ltd, Shanghai, China), where a vacuum degree of -0.1 MPa and a temperature of 60 ℃ was used to recover the formic acid. The p-TsOH was recovered using commercially proven crystallization technology by simply cooling the re-concentrated spent acid solution after formic acid recovery as p-TsOH has low solubility at ambient temperature. The precipitated p-TsOH crystals were weighed, and the proportional recovery was calculated.

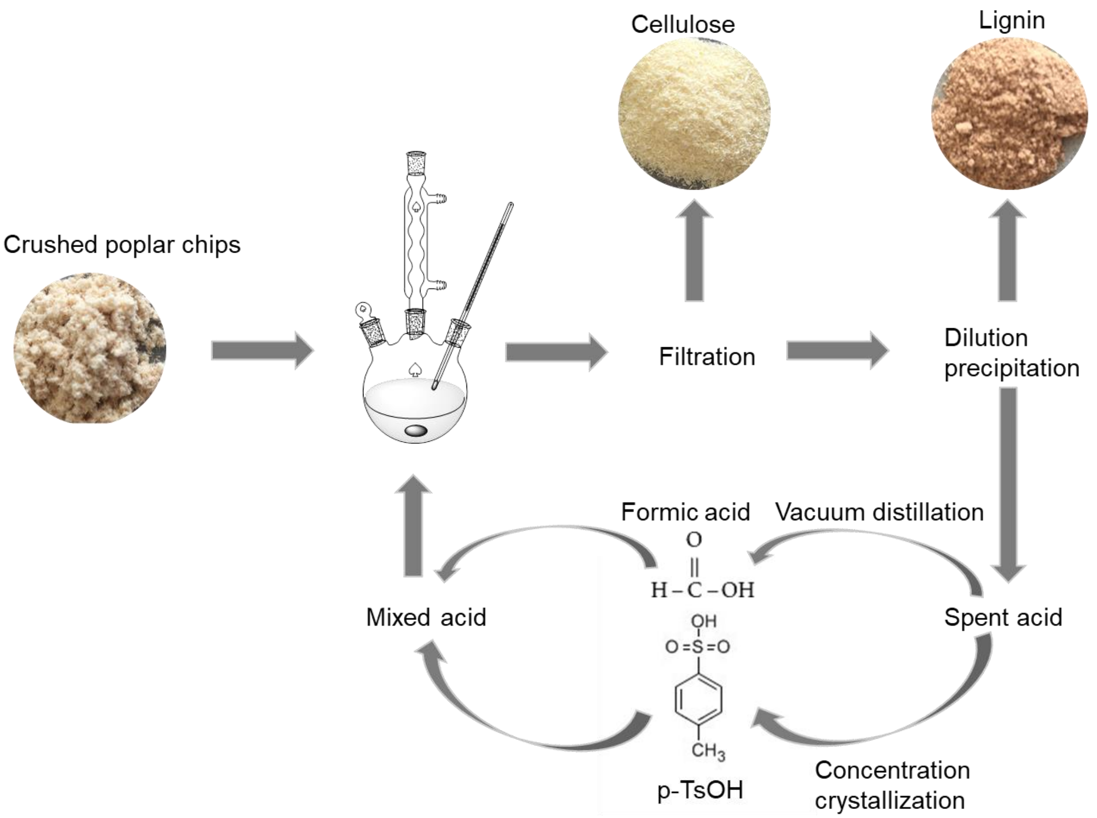


Fig. 1. Schematic diagram of poplar fractionation process

Characterization

Fourier-transform infrared spectroscopy

The FTIR spectra were collected by Fourier transform infrared spectrometer (VECTOR22, Bruker, Ettlingen, Germany) using a KBr disc containing finely ground samples (1%). The resolution of infrared spectrum was 4 cm^{-1}, the collection range was 500 to 4000 cm^{-1}, and the spectrum was obtained from 8 scans in transmission mode.

Nuclear magnetic resonance hydrogen spectrum

^{1}H-NMR spectra of the lignin samples dissolved in deuterated dimethyl sulfoxide (DMSO-d6) was recorded by a Bruker Avance II instrument. The samples were scanned at least 8 times with a scanning width of 400 MHz, a collection time of 2.0 s, and a relaxation delay time of 3.0 s. All operations were carried out at 25 °C. The spectra were analyzed by MestReNova (Brook, Germany).

Crystallinity indices analysis by X-ray diffraction (XRD)

The crystallinity indices of cellulose were analyzed using wide-angle X-ray diffraction on a Bruker D8 130 Discover system under the condition of 40 kV, 30 mA, and Cu-Kα radiation (I = 0.154 nm). Scattering radiation from a pellet made of freeze-dried cellulose was detected in a 2θ range from 5° to 60° in steps of 0.02° with a scanning speed of 5° min^{-1}. As previously reported (Segal *et al*. 1959), the crystallinity index (*CrI*) of cellulose was calculated as follows,

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \tag{1}$$

where I_{002} is the maximum diffraction intensity of the 002 lattice diffraction, and I_{am} is the diffraction intensity in the same units at $2\theta = 18°$.

Scanning electron microscopy

The morphology of poplar cellulose raw fiber, nitrate ethanol cellulose (C) and mixed acid cellulose (MAC) were observed and recorded by JSM-6700F scanning electron microscope (JEOL Ltd., Japan). All SEM samples were sputter-coated with gold to improve the conductivity of the sample and the quality of the SEM image.

RESULTS AND DISCUSSION

Yields of Water Insoluble Solids (WIS) and Lignin Removal at Different Hydrolysis Conditions

Figure 2 shows the yields of water insoluble solids (cellulose-rich fraction) and lignin removal at different formic acid and p-TsOH acid ratios, acid concentrations, hydrolysis temperatures, and times. The p-TsOH/formic acid removed more than 60% wood lignin with more than 35% cellulose-rich water-insoluble solids (WIS) under all investigated conditions.

As shown in Fig. 2(a), the change of acid concentration had an influence on the removal of lignin and the yield of water insoluble solids. The increase of acid concentration promoted the fracture of lignin macromolecular ether bond and thus the removal of lignin from the poplar woodchips but caused more cellulose degradation as indicated by the lower WIS yield.

Figure 2(b) shows that the increase of the ratio of mixed acid had little effect on lignin removal but negative effect was observed for cellulose degradation. The higher the concentration of p-TsOH in the mix acid resulted in a lower yield of WIS, because of excessive hydrolysis of cellulose. Thus, with the increase of p-TsOH concentration in the mixed acid, more hemicelluloses and some disordered cellulose were hydrolyzed, leading to the reduced yield of WIS (Bian *et al. 2*017).

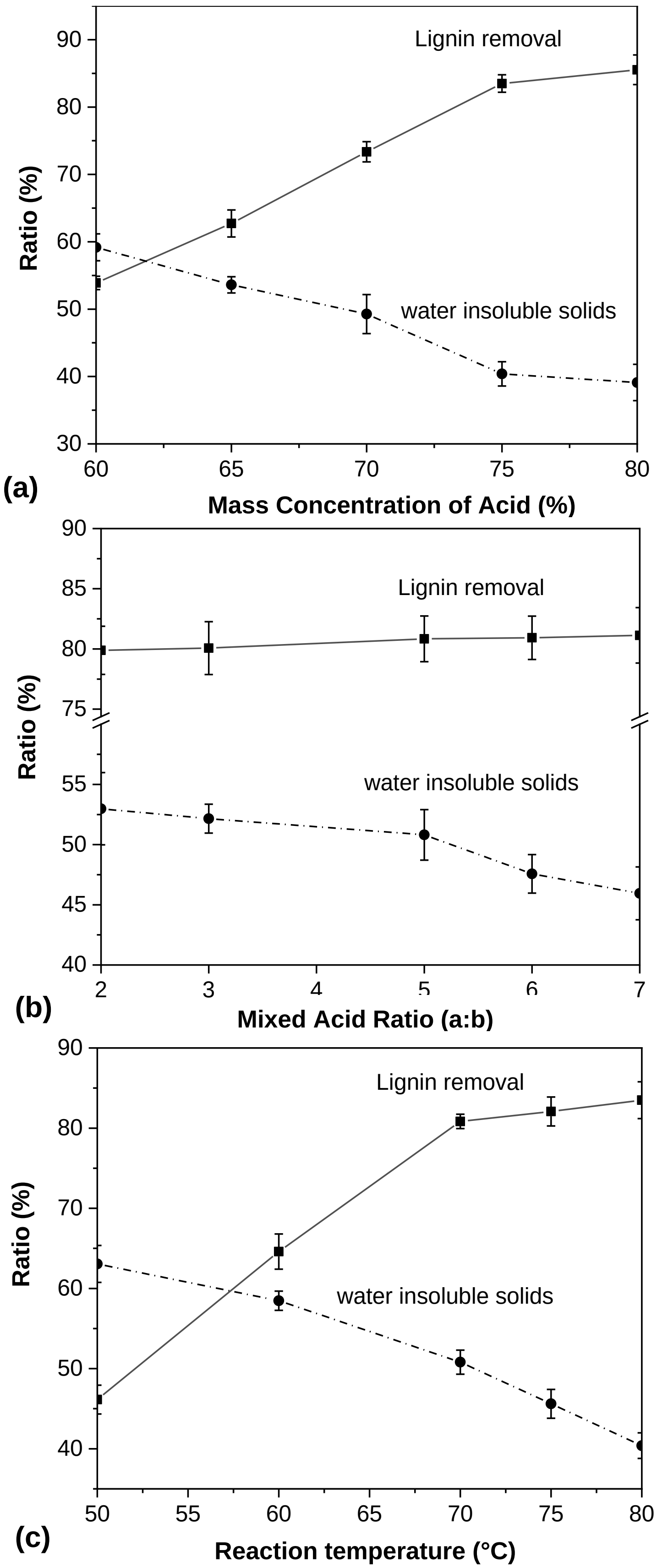
Figure 2(c) shows the increase of temperature improved the lignin removal and reduced the yield of water-insoluble solids as more cellulose was degraded. This result indicates p-TsOH is not effective in removing lignin and hydrolyzing cellulose at low temperatures even with high concentrations.

Figure 2(d) shows the removal of lignin slightly decreased with the increase of reaction time probably because of the aggregation of dissolved lignin and its deposition on the cellulose surface (Chen *et al*. 2017). Increased reaction time lowered the yield of water insoluble solid, indicating that more cellulose was degraded (Chen *et al*. 2016).

The results showed that 84% lignin was removed when the reaction was carried out at the mass ratio of p-TsOH and formic acid of 5:1, concentration of 75%, temperature of 80, and time of 20 min.

Recovery of p-TsOH Acid and Formic Acid

Approximately 36.4% formic acid and 53.7% p-TsOH were recovered.


Lignin removal
water insoluble solids
Ratio (%)
90
80
70
60
50
40
30
60
65
70
75
80
(a)
Mass Concentration of Acid (%)
Lignin removal
water insoluble solids
Ratio (%)
90
85
80
75
55
50
45
40
2
3
4
5
6
7
(b)
Mixed Acid Ratio (a:b)
Lignin removal
water insoluble solids
Ratio (%)
90
80
70
60
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(c)
Reaction temperature (°C)

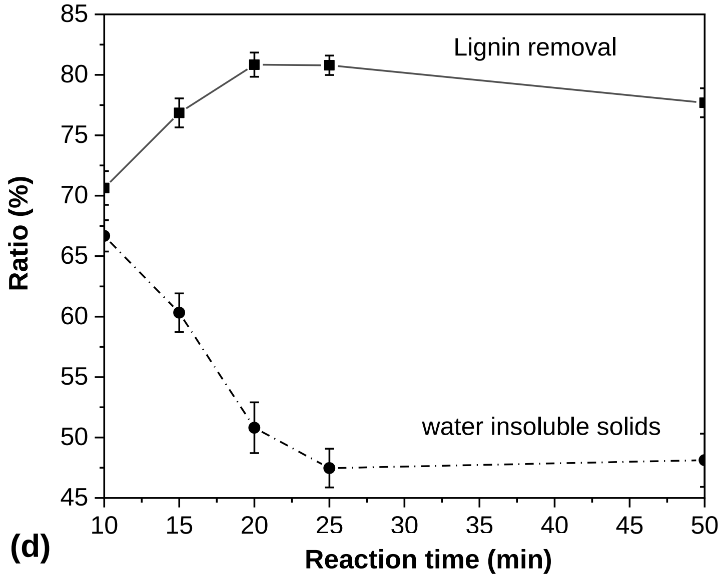

Fig. 2. Yields of water insoluble solids (WIS) and lignin removal at different (a) concentrations of acid, (b) mixed acid ratios, (c) temperatures, and (d) reaction times

Characterization of Solid Residues

FTIR spectra of solid residues

Figure 3 shows the FTIR spectrum of solid residues from mixed acids treatment. The characteristics of cellulose (Thomas *et al*. 2015; Benini *et al*. 2018) are revealed by the presence of the bands associated with the stretching vibration of the OH group (3408 cm^{-1}) and the CH group (2900 cm^{-1}). Vibration at 1640 cm^{-1} is associated with O-H bond, as cellulose is hydrophilic and interacts strongly with water at the molecular level. No C=O group (1717 cm^{-1}) vibration was observed, indicating that no esterification occurred on the cellulose surface.

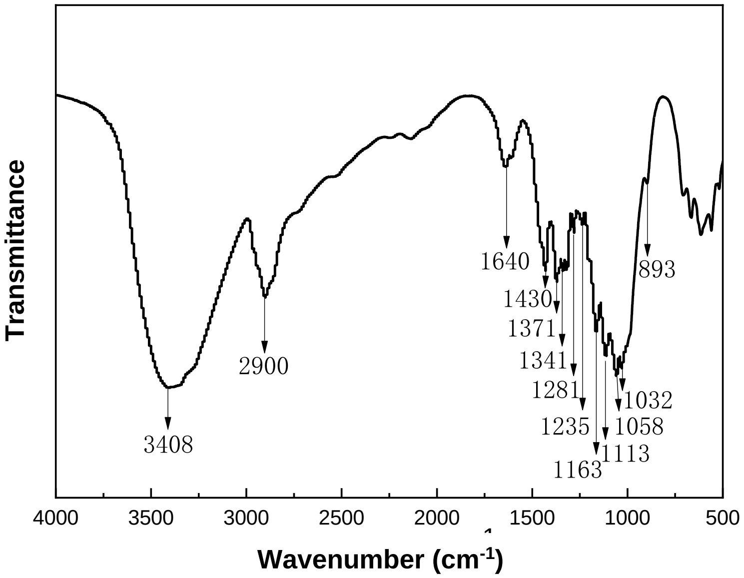

Fig. 3. FTIR spectra of solid residues treated by mixed acid

The bands at 1430 cm^{-1} correspond to the crystalline regions in cellulose. In addition, bands corresponding to C-H bending vibration (1371 cm^{-1}), to O-H or C-H bending vibration (1281 cm^{-1}) in arabinoxylan, to C-O stretching vibration (1032 cm^{-1}) in the cellulose, and to β-glycosidic linkage (893 cm^{-1}) connecting the glucose units in the cellulose were identified.

The FTIR spectra also show characteristic absorption bands of lignin. The band at 1341 cm^{-1} is attributed to the C-O stretching vibration of the ether bond. The band at 1235 cm^{-1} corresponding to the asymmetric stretching vibration of -C=O in the ether, ester, and phenol groups of lignin, 1163 cm^{-1} and 1058 cm^{-1} corresponding to the C-O stretching vibration, and 1113 cm^{-1} corresponding to the C-H bending in the syringa-base structure of lignin were identified. The presence of these absorption peaks indicates that the cellulose retained a small amount of lignin.

Crystallinity index

Figure 4 shows measured XRD patterns of the ethanol-nitrocellulose (C) and mixed acid cellulose fibrils (MAC). They had similar diffraction patterns and diffraction angle, grain strength, and crystallization area. At approximately 16.4° and 22.6°, there are two characteristic peaks corresponding to the (110) and (200) reflective planes of the typical cellulose I structure, revealing that mixed acid hydrolysis did not destroy or alter the intrinsic crystalline structure of the cellulose (Sun *et al*. 2010; Sun *et al*. 2007). After mixed acid treatment, the XRD peaks became sharp, especially the diffraction peaks at 2θ=16.4°and 22.6°, indicating that the proportion of the crystalline regions of cellulose increased.

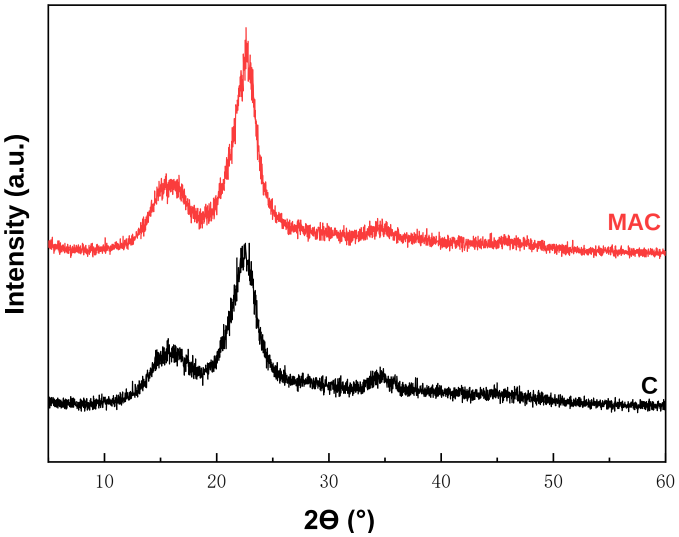

Fig. 4. Measured XRD patterns of ethanol-nitrocellulose (C) and mix acid cellulose fibrils (MAC)

The crystallinity index (*CrI*) of the cellulose showed that ethanol-nitrocellulose had a crystallinity index of 40.3% and mixed acid cellulose had a crystallinity index of 58.8%. This result indicated that mixed acid is effective in hydrolyzing the amorphous regions of cellulose and thus producing cellulose with higher crystallinity index.

Scanning electron microscopy

Figure 5 shows the SEM images of cellulose fibrils, ethanol-nitrocellulose, and solid residues treated by mixed acid at 60 ℃ and solid residues treated by mixed acid at 75 ℃. As shown in Fig. 5 (a), hemicelluloses and lignin are attached to the cellulose before acid treatment. Cellulose structure was clearly exposed after acid treatment as shown in Fig. 5(b), (c), and (d).

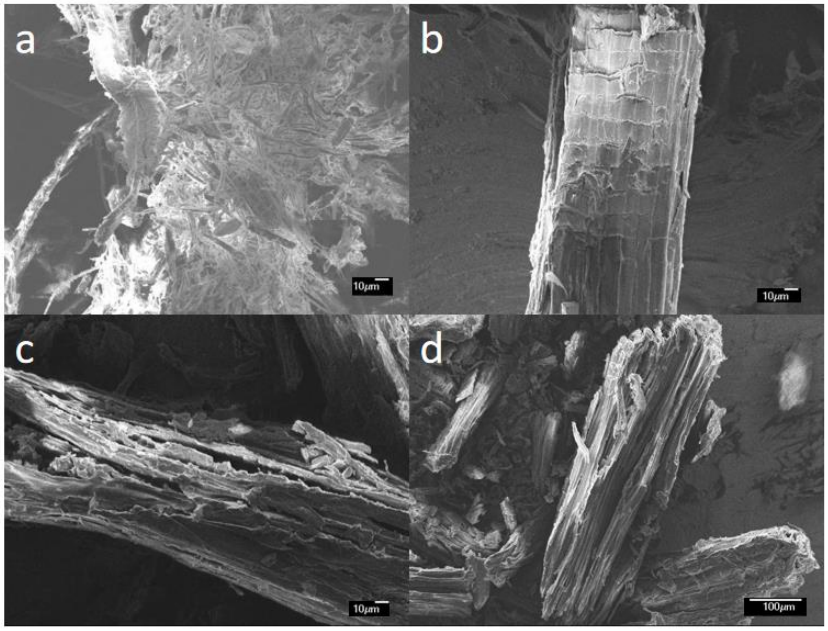

Fig. 5. SEM images of (a) cellulose fibrils, (b) ethanol-nitrocellulose, (c) solid residues treated by mixed acid at 60 °C and (d) solid residues treated by mixed acid at 75 °C

The surface of the cellulose fibril was more fluffy and rougher than that of ethanol-nitrocellulose. Peeling, fluffing, and sliding were observed between the layers after mixed acid treatment due to the efficient removal of hemicelluloses and lignin by mixed acids.

Characterization of Lignin

FTIR spectra of lignin

The FT-IR spectra of mixed acid lignin (MAL) and KL are shown in Fig. 6. The absorption bands and relative strength of lignin fingerprint regions of both lignins were similar (Zhang *et al*. 2010). Signals observed at 1607 cm^{-1}, 1512 cm^{-1}, and 1422 cm^{-1} corresponded to the aromatic skeleton vibrations, indicating that the chemical structure of lignin was not changed during the mixed acid treatment process. The band at 3421 cm^{-1} was assigned to the O-H stretching vibration of the phenolic hydroxyl group and the alcoholic hydroxyl group. The bands at 2936 cm^{-1}, 2840 cm^{-1}, and 1462 cm^{-1} corresponded to C-H groups of methyl and methylene in lignin. Typical absorption bands of guaiacyl (G) and syringyl (S) of lignin basic units were also found in the FT-IR spectra (Zhang *et al*. 2017). The absorption peaks at 1330 to 1320 cm^{-1} corresponded to syringyl (S), and the absorption peaks at 1274 to 1250 cm^{-1} corresponded to the C=O stretching vibration of guaiacyl (G). Compared with KL, the MAL showed a strong absorption peak located at 1714 cm^{-1}, which is the -C=O vibration peak of non-conjugated ketones, carbonyl compounds, and ester groups. This might be due to the esterification of the aromatic groups and alcohols in the propane chain during lignin removal (Jahan *et al*. 2007).

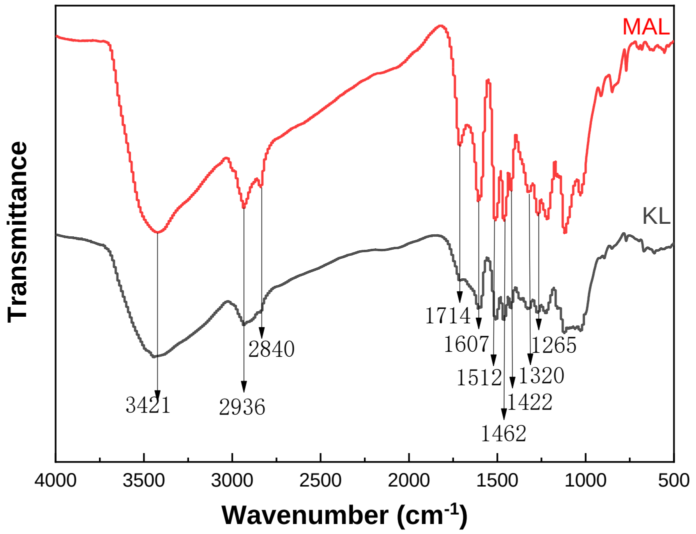

Fig. 6. FTIR spectra of mixed acid lignin (MAL) and Klason lignin (KL)

^{1}H-NMR spectra of lignin

The ^{1}H-NMR spectra of MAL in Fig. 7 shows the aliphatic region (0.80 to 3.00 ppm), lignin side chain region (3.00 to 6.00 ppm), and aromatic region (6.00 to 8.00 ppm) in lignin. The lignin side chain region includes the methoxy group in the aldehyde group and possible polysaccharides.

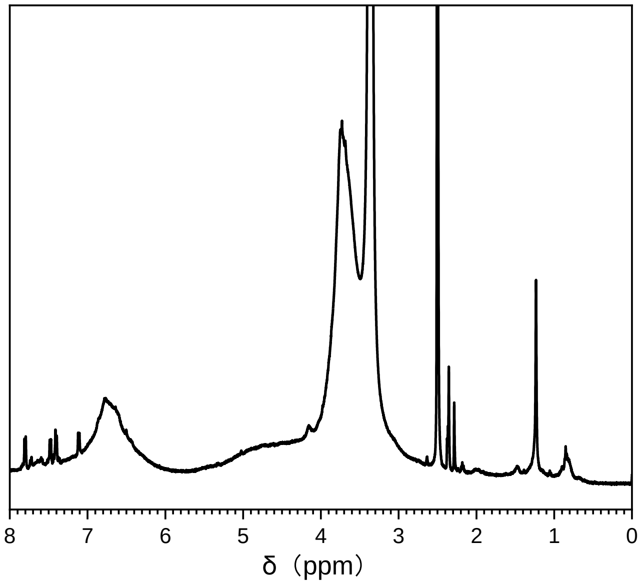

Fig. 7. ^{1}H NMR spectra of mixed acid lignin

Resonance between 7.00 ppm and 8.00 ppm originated from the aromatic protons in the structures of p-hydroxyphenyl (H), p-hydroxycinnamate, and 4-hydroxy-3-methoxy cinnamate. The signal between 6.20 ppm and 6.80 ppm was attributed to aromatic protons in the structures of syclo-propane and guaiac-propane, indicating the relative content of S and G in lignin. The signal at 6.78 ppm and 7.44 ppm were associated with hydrogen at C-

3 and C-5 positions in the hydroxy cinnamate. The signal at 7.49 ppm originated from the protons at C-2 and C-6 positions in the p-hydroxycinnamate structure. The signal at 7.47 ppm corresponded to the proton at C-β in the hydroxyl cinnamate. The typical resonance of protons on C-6 and C-β of 4-hydroxy-3-methoxy cinnamic acid at 6.35 ppm and 7.06 ppm showed did not appear in the ^{1}H spectrum of MAL, indicating the structure of 4-hydroxy-3-methoxy cinnamic acid was destroyed during the process of delignification by mixed acid. The signals at 5.58 ppm were attributed to benzyl aryl ether H-α, and the signals between 4.80 ppm and 5.00 ppm corresponded to the H-β of β-O-4 'structure (Xu *et al*. 2006). However, these signals did not appear in the spectra of MAL, indicating that the benzyl aryl ether and β-aryl ether bond were broken during the delignification process. In addition, signals between 0.80 and 2.20 ppm originated from the CH_3 and CH_2 in S-aliphatic chain of lignin (Oliveira *et al*. 2009), indicating that the mixed acid treatment process could not remove free fatty acids.

CONCLUSIONS

1. Poplar wood was fractionated efficiently into lignin and solid residue (mainly cellulose) by mixed acid of para-toluene-sulfonic acid (p-TsOH) and formic acid at low temperature. At a mass ratio of 5:1 of p-TsOH and formic acid, acid concentration of 75%, temperature of 80 °C, and time of 20 min, more than 80% of the lignin was removed and 50% of the cellulose was retained as solid residue.
2. Lignin and hemicelluloses that had been present between the fibers was removed by the mixed acid treatment, as characterized by Fourier transform infrared (FTIR) spectrometry, scanning electron microscopy (SEM), and nuclear magnetic resonance (NMR). The crystallinity index of cellulose increased from 40.3% to 58.8% after mixed acid treatment.
3. The structure of lignin was changed by mixed acid treatment mainly through destruction of β-O-4' bonds and 4-hydroxy-3-methoxy cinnamic acid structures in lignin.

ACKNOWLEDGMENTS

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