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Dissolution of less-processed wood fibers without bleaching in an ionic liquid: Effect of lignin condensation on wood component dissolution

Huihui Wang [a,b], Kolby Hirth [b], Junjun Zhu [c], Qianli Ma [a,b], Chuanfu Liu [a], J.Y. Zhu [b,d,*]

[a] State Key laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China
[b] Forest Products Laboratory, U.S. department of Agriculture Forest Service, Madison 53726, USA
[c] Jiangsu Co-Innovation center of Efficient Processing and Utilization of Forest Resources, Nanjing Forestry University, Nanjing, China
[d] Department of Biological Systems Engineering, University of Wisconsin-Madison, Madison, WI 53706, USA

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ABSTRACT

This study evaluated the solubility of low-processed wood fibers produced from a low temperature acid hydrotropic fractionation (AHF) in an ionic liquid (IL) 1,5-diazabicyclo[4.3.0]non-5-enium acetate (DBNH[OAc]. Unbleached wood fibers produced from AHF using *p*-Toluenesulfonic acid (*p*-TsOH) with or without post-treatments with lignin and hemicelluloses content up to 15% and 25%, respectively, were dissolved directly into the IL DBNH[OAc]. Post-AHF treatments using dilute alkaline and glycerol swelled the cellulose and partially removed residual lignin resulting in improved dissolution. Semi-quantitative 2D HSQC NMR analyses revealed that the undissolved wood fiber residues were enriched with G units and condensed S units (S_{cond}), demonstrating, as expected, that G units and condensed lignin substructures have a negative effect on dissolution in DBNH[OAc]. Therefore, AHF with rapid fractionation at low temperatures offers a promising advantage over existing high temperature pulp dissolving fiber (PDF) processes in terms of reducing energy input, lowering lignin content as well as reducing lignin condensation for producing man-made cellulosic fibers (MMCF).

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1. Introduction

Population growth resulted in rising demand for textiles over the past several decades. Unfortunately, the cultivation of cotton has reached its maximal capacity and the production of cotton declined 4.1% during the period 2012–2013 primarily due to the shrinkage of cotton growing land [1]. Estimated market shortage of native cellulosic textile fibers is at least 1.7 kg per capita by 2030[2]. Producing man-made cellulosic fibers (MMCF) from wood dissolving pulp fibers (DPF) could address this market shortage.

There are only two commercial processes for the production of MMCF from wood: the viscose and Lyocell process [3,4] and both have drawbacks. The use of substantial CS_2 during the viscose process leads to serious environmental concerns and the Lyocell process requires high energy input and expensive stabilizers [5,6]. Furthermore, both processes require DPF of high purity, i.e., free of lignin and hemicelluloses, which requires further processing, such as caustic extraction and bleaching, in order to achieve satisfactory spinning performance and textile fiber quality. This results in substantial reductions in DPF yield, increases processing cost and adverse environmental impacts, and limits the utilization of less-processed and unbleached cellulosic materials [7–9]. Specifically, commercial DPF are produced by extensive bleaching of chemical pulps from either sulfite or hot-water pre-hydrolysis followed by kraft pulping, with both requiring high temperatures and pressures, e.g., 130 °C for 4–6 h (sulfite), 170 °C for total of 4 h (hot-water pre-hydrolysis and kraft). The metal base in sulfite pulping is very difficult to be recovered unless magnesium is used. Air emissions of SO_2 from sulfite pulping is an environmental concern. Hot-water pre-hydrolysis with kraft pulping is energy intensive and the hemicellulosic sugars from hot-water pre-hydrolysis are often discarded to save energy in commercial operations, which increases biological oxygen demand in pulp mills. Kraft pulping chemicals are recovered through combustion of concentrated spent pulping liquor in expensive Tomlinson recovery boilers, and has had incidents of catastrophic explosion when small leaks allowed black liquor smelt to come into contact with water (recent explosion in September 2017 in Canada).

In view of these considerations, novel MMCF processes capable of utilizing less-processed DPF with low energy input would add real value and promote sustainability. It would also require novel solvent systems and the development of efficient processes to produce high yield (unbleached) DPF which are suitable for dissolution and spinning to produce quality textiles. In searching for novel cellulose solvent systems, acidic lithium bromide trihydrate (ALBTH, LiBr·3H2O) system exhibited the capability of dissolving cellulose and even depolymerizing it

* Corresponding author at: Forest Products Laboratory, U.S. Department of Agriculture Forest Service, Madison 53726, USA.
E-mail address: junyong.zhu@usda.gov (J.Y. Zhu).

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to sugars [10], but the system has not been tried for producing textile fibers. Cold alkaline with urea process was able to solubilize cellulose with potential to producing textile fibers [11], however chemical recovery remains a hurdle. Ionic liquids (ILs) have shown significant potential in solubilizing cellulose for a variety of applications [12] with good recyclability through simple evaporation [13,14]. The Ioncell process, based on the IL 1,5-diazabicyclo[4.3.0]non-5-enium acetate (DBNH[OAc]) [1,15,16], demonstrated promising performance in dissolving less-refined cellulosic materials, such as recycled waste paper and cardboard, at moderate processing temperatures (70–80 °C) [17]. The dissolving cellulose dope was spinnable to fibers with excellent mechanical and physiological properties [1,15,17]. However, the Ioncell system cannot solubilize newsprints fibers, even after kraft cooking, to produce dopes with good spinnability. The remaining lignin is tightly bonded with the carbohydrate matrix after kraft cooking, which leads to an aggregated polymer structure with unfavorable rheological properties in IL systems [17]. It is also known that kraft cooking resulted in lignin condensation through repolymerization due to the high reaction temperature of 170 °C [18,19].

Much work on lignin dissolution in IL systems have been carried out [20,21], however, a good understanding of the effects of lignin structure on dissolution of individual lignocellulosic components in IL systems suitable for textile production is not available. It is critical to improve the utilization of less-processed fibers for producing MMCF using IL based green solvent systems. The objective of this study is to investigate the effects of lignin content and chemical structure, especially lignin condensation, on dissolution of individual lignocellulosic components (cellulose, lignin, and hemicelluloses) of less-processed DPF in an IL. Specifically, this study will use acid hydrotropic fractionation (AHF) [22,23] to produce DPFs in the spirit of searching novel and more sustainable PDF production processes. Rapid delignification at low temperatures (≤90 °C) with excellent selectivity makes AHF promisingly more efficient than commercial wood pulping and existing delignification processes, such as organic solvents [24,25], ILs [26–28], and sulfite [29], in terms of both energy input and lignin solubilization. The dissolved hemicelluloses by AHF can be dehydrated into furfurals catalyzed by the *p*-TsOH in the spent liquor [30] after lignin precipitation through dilution using water to the minimal hydrotrope concentration of 11.5% [22,23,31], and the *p*-TsOH can then be reused [22]. Importantly, the rapid AHF fractionation at low reaction temperatures significantly reduces lignin condensation in the resultant PDF [32], which is critical to achieve dissolution of the less-processed AHF DPF. Therefore, the present study has significance for sustainable, green, and efficient processing of lignocelluloses for producing MMCF.

2. Materials and methods

2.1. Materials

A birch (*B. papyrifera*) tree of approximately 35 years of age harvested from the Rhinelander Experimental Forest in Rhinelander, WI, USA, was provided by Dr. Ronald Zalesny, Jr. (Northern Research Station, Institute for Applied Ecosystem Studies, USDA Forest Service). The birch logs, 1.2–1.8 m in length and 15–23 cm in diameters, were transported to the USDA Forest Products Laboratory, Madison, WI then manually debarked and chipped using a 127 cm diameter, 45 kW knife-chipper (Carthage Machine Co, Carthage, NY). The chips were screened to remove particles larger than 38 mm and <6 mm. The screened chips were 1–5 mm thick with 61% moisture content and were kept frozen at −16 °C until use.

Birch medium density fiberboard fibers (MDF) were produced by pre-steaming the wood chips at 165 °C for 10 min with a steam pressure of 0.72 MPa. The pre-steamed chips were fiberized in a 30.5 cm pressurized disk refiner (Sprout-Bauer, model 1210P, Muncy, PA) at a feed rate of approximately 1 kg/min in oven dry (OD) weight base with a disk gap of 0.178 mm. The disk plate pattern was D2B505. The refining energy consumption was 127 W/kg OD chips, and the resulting pulp fibers were stored at room temperature in a plastic bag until use.

p-TsOH, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), acetic acid, and dimethyl sulfoxide (DMSO) of ACS reagent grade and dialysis bags with 14,000 Da molecular weight cut-off (Product No. D9402-100FT) were purchased from Sigma Aldrich (St. Louis, MO). NaOH of ACS reagent grade and Filter paper (15 cm, slow) were purchased from Fisher Scientific Inc. (Pittsburgh, PA). Glycerol of 99% purity was purchased from Alfa Aesar (Tewksbury, MA). All the chemicals and materials were used as received without further purification.

2.2. Delignification of MDF using AHF

AHF of MDF and dissolution of delignified MDF were carried out according to the experimental flow schematics shown in Fig. 1. Aqueous *p*-TsOH solutions of desired mass concentrations were prepared by adding the required amounts of *p*-TsOH and deionized (DI) water to a 150-mL flask. 100 mL of acid solution was added into a three-neck flask and heated in a glycerol bath to the desired temperature, then 5 g of MDF (in OD weight) was manually fed into the flask. The fiber suspension was constantly mixed using a mechanical mixer at 200 rpm at various acid concentration between 55 and 80 wt% and temperatures between 80 and 90 °C. At the end of the preset time, 100 mL of DI water was added to terminate the reaction. The water insoluble solids (WIS) of the suspension were separated by vacuum filtration. The WIS was further dialyzed using DI water until the conductivity of the liquid approached that of DI water at approximately 1.5 μS/cm, and then freeze-dried. The filtrate was also collected to recover the acid and dissolved lignin.

2.3. Dilute alkaline and glycerol treatments

1 g of AHF WIS (in OD weight) was soaked in 10 mL of NaOH solution (0.01 mmol/L, pH = 12) at ambient temperature for 1 h. The fiber suspension was filtered by vacuum filtration and the separated solids were dialyzed with DI water until the conductivity of the liquid approached to that of DI water at approximately 1.5 μS/cm. The resultant solids were freeze-dried for later use.

20 g of glycerol was added into a three-neck flask, and heated to 120 °C in a glycerol bath. 1 g of AHF WIS (OD weight) was added into the flask. The glycerol treatment was performed at 120 °C for 4 h with stirring using a mechanical mixer at 200 rpm. After the treatment, 100 mL of DI water was added to quench the reaction. The suspension was filtered by vacuum filtration and the separated solids were dialyzed using DI water until the conductivity of the liquid approached to that of DI water at approximately 1.5 μS/cm. The resultant solids were freeze-dried for later use. The filtrate was collected for recovery of glycerol.

2.4. IL synthesis and fiber dissolution

DBNH[OAc] was synthesized according to Parvianen et al. [33]. Briefly, acetic acid was slowly added into equimolar amounts of DBN with stirring. After the addition was complete, the mixture was further stirred for 1 h at 80 °C.

30 mg freeze-dried treated or untreated MDF sample was added to a vial containing 3 mL of DBNH[OAc] melted at 70 °C stirred at 400 rpm for 4 h at 80 °C. At the end of the preset time, 3 mL of DMSO was added to the mixture and stirred for 5 min at room temperature. The mixture was vacuum filtered through a 450 nm pore size nylon filter membrane. The separated unsolubilized solid residue was washed with DI water three times (total 300 mL), and freeze-dried to preserve fluffiness for later ball-milling. The filtrate was diluted with 100 mL of DI water to precipitate the dissolved lignocellulose, then the suspension was vacuum filtered, and the filtered cellulosic solids were washed with

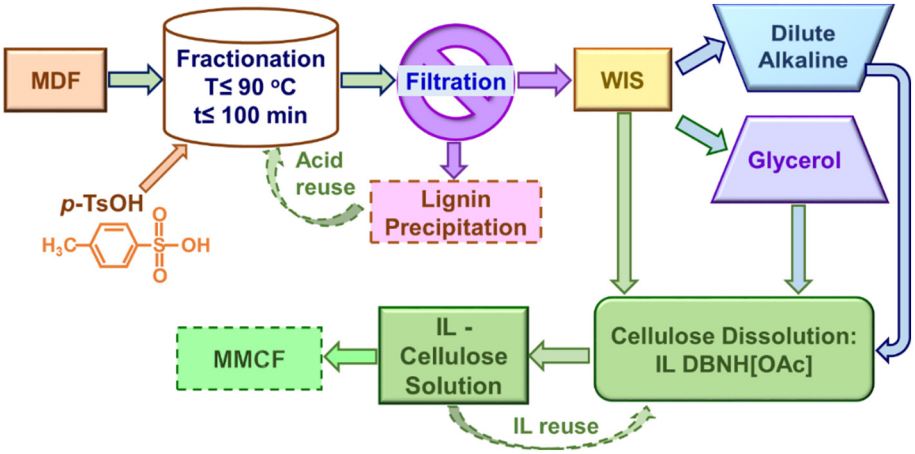

Fig. 1. Schematic flow diagram shows fractionation of birch MDF and dissolution in ionic liquid DBNH[OAc] for the production of MMCF. Processes with dashed lines were not carried out in this study.

DI water three times (total 600 mL), and freeze-dried. The first filtrate was collected to recover the DBNH[OAc].

2.5. Chemical compositional analyses

The treated and untreated MDF and precipitated dissolved lignocellulosic solid samples were oven-dried at 105 °C for 4 h and ground to 20-mesh powder, then analyzed for carbohydrate and lignin according to previous literature with few modifications [34]. Briefly, the 2-step sulfuric acid hydrolysis conditions were 72% (v/v) at 30 °C and 3.6% (v/v) at 120 °C for the first and second stages, respectively, with 1 h for both stages. The hydrolysate was then analyzed in duplicate for carbohydrates using a Thermo Scientific (Sunnyvale, CA) Dionex Ultimate 3000 ion chromatographic system equipped with a refractive index detector and Aminex HPX87H ion exclusion guard and analytical (300 mm × 7.8 mm) columns at 50 °C. Eluent was 0.005 mol/L H_2SO_4 delivered at 0.6 mL/min^{-} for 60 min runtime.

2.6. Optical and scanning electron microscopy

The morphologies of fibers before and after dissolution in the IL system were examined using an optical microscope (Eclipse Ci, Nikon, Japan). The fibers before dissolution were also evaluated by a scanning electron microscope (Zeiss Leo Evo-40) at an accelerating voltage of 10 kV after sputter-coating.

2.7. ^{13}C—^{1}H 2D nuclear magnetic resonance (NMR) analyses

Approximately 500 mg of the untreated MDF and the AHF fractionated WISs from various treatments were ball-milled for 23 cycles (each cycle contains a 10-min interval with a 10-min interval break) at 600 rpm using a planetary ball mill (PM 100, Retch, Haan, Germany) equipped with a zirconium dioxide (ZrO_2) grinding jar (50 mL) containing ZrO_2 balls (10*10 mm). The undissolved WIS residues from various treatments (approximately 30 mg) were ball-milled for 7 cycles.

NMR spectra were recorded on a Bruker (Billerica, MA) AVANCE III HD spectrometer at 27 °C from the ball-milled samples (75 mg) swollen in 0.5 mL of DMSO d_6/Pyridine d_5 (v/v, 4:1). NMR data was processed with TopSpin 3.0 software. The central DMSO solvent peak was used as internal reference (δ_C, 39.5 ppm; δ_H, 2.49 ppm). Two-dimensional heteronuclear single-quantum coherence (HSQC) spectra were recorded at 25 °C using the standard hsqcetgpsisp 2.2 standard pulse program with the following parameters: acquisition time (AQ) of 85 msec using spectral width of 12 ppm in F2 (1H) dimension with 1024 data points (TD1) and 215 ppm in F1 (13C) with 256 non-uniformly sampled data points (TD2); a 1 s interscan delay; and number of scans (NS) for a total acquisition time (expt) of 16–24 h. The spectral images were colored with Adobe Illustrator CS6 and the chemical structures were created with ChemDraw Pro 14.0.

3. Results and discussion

3.1. Chemical composition of AHF WIS

Birch MDF was fractionated using *p*-TsOH solutions at three reaction conditions represented by PxxTyytzz, i.e., *p*-TsOH concentration of xx wt% at yy °C for zz min. The chemical compositions and yields of the three fractionated WISs (1, 2, and 3) are listed in Table 1. Pn-PxxTyytzz represent AHF fractionated WISs with $n = 1, 2$, or 3 stands for fractionation condition number. The results show WIS from P65T80t20 retained approximately 90% cellulose and solubilized approximately 75% and 65% of lignin and hemicelluloses, respectively. Increasing AHF severity had only slight effect on cellulose degradation but improved hemicelluloses and lignin dissolution, in agreement with our early studies using poplar wood and wheat straw [22,30]. Under P55T90t100, both hemicelluloses and lignin dissolution increased to approximately 85% and retained 88% cellulose. These results clearly indicate that AHF has excellent selectivity for dissolution of lignin and hemicelluloses, and a cellulose-rich fraction was successfully obtained from MDF, important for producing DPF.

Post delignification treatment using alkali or glycerol to further remove lignin or swell cellulosic fibers, respectively, have been found effective for improving cellulose dissolution in NNMO/H_2O [35,36] and IL DBNH[OAc] [17]. We, therefore, treated AHF WISs and report chemical compositions of alkaline- and glycerol-treated AHF WISs, An-PxxTyytzz and Gn-PxxTyytzz, respectively, in Table 1. Alkaline treatment reduced solid yield, i.e., solubilized additional amounts of lignin as well as cellulose and hemicelluloses, in agreement with literature [37,38]. Glycerol treatment is dominated by physical swelling. Chemical composition of glycerol-treated samples, Gn, was not much changed with slight decreases in solid yields resulting from the minor degradation of lignin and hemicelluloses [39]. The observed higher lignin content (or lower delignification) in G2 than P2 is within the measurement error margin.

3.2. Dissolution of AHF WISs in DBNH[OAc] with and without post-treatments

The freeze-dried WISs from AHF birch with and without alkaline or glycerol treatment were directly dissolved in IL DBNH[OAc], at 1% consistency and 80 °C for 4 h, to evaluate the suitability of WISs from *p*-

Table 1
Yields and chemical compositions of WISs from AHF birch MDF using *p*-TsOH under three conditions, without and with subsequent alkaline or glycerol treatment, and of the unfractionated MDF. Numbers in parentheses are component mass retained on WISs based on component mass in the unfractionated MDF.

Sample label[a]	Solid yield (%)	Cellulose (%)	Hemicelluloses (%)	Lignin (%)	BET surface area (m^2/g)
MDF	100	38.6	22.8	23.5	0.7 ± 0.0
P1-P65T80t20	52.9	67.8 ± 0.2 (92.9)	14.4 ± 0.1 (33.3)	11.6 ± 0.2 (26.2)	2.3 ± 0.7
P2-P80T80t20	45.6	74.9 ± 0.9 (88.4)	12.5 ± 0.4 (24.9)	8.2 ± 1.7 (15.9)	2.4 ± 0.2
P3-P55T90t100	41.9	81.5 ± 2.3 (88.4)	9.5 ± 0.1 (17.4)	8.4 ± 0.7 (14.9)	2.9 ± 0.2
A1-P65T80t20	43.1	71.6 ± 1.1 (79.9)	14.2 ± 0.2 (26.8)	9.3 ± 0.8 (17.0)	3.4 ± 0.0
A2-P80T80t20	40.2	79.1 ± 1.2 (82.3)	11.5 ± 0.3 (20.2)	6.1 ± 0.9 (10.4)	2.5 ± 0.1
A3-P55T90t100	33.9	79.7 ± 3.8 (70.0)	9.6 ± 0.8 (14.3)	6.9 ± 0.8 (9.9)	2.5 ± 0.2
G1-P65T80t20	49.5	69.1 ± 2.1 (88.6)	13.2 ± 0.1 (28.6)	11.5 ± 3.1 (24.3)	3.1 ± 0.1
G2-P80T80t20	44.0	74.5 ± 0.3 (84.9)	11.5 ± 0.3 (22.1)	9.1 ± 0.4 (17.0)	2.7 ± 0.0
G3-P55T90t100	38.5	81.0 ± 1.9 (80.8)	10.1 ± 0.1 (17.0)	8.2 ± 1.3 (13.5)	3.2 ± 0.1

[a] PxxTyytzz stands for *p*-TsOH concentration of xx wt% at yy °C for zz min.

TsOH AHF as DPF using the Ioncell solvent system. The solubility of these WIS samples was measured from the amounts of cellulosic solids regenerated from the WIS-IL solutions (Fig. 2A).

The solubility of P1 from the mild AHF was over 72% despite P1 having a lignin content of 26% and hemicelluloses content of 33% (Table 1). Increasing delignification and hemicelluloses removal by using a more severe AHF resulted in improved WIS solubility in DBNH[OAc], i.e., the solubility of P2 and P3 was increased to approximately 80%, with both P2 and P3 having a lignin and hemicelluloses content over 8% and 17%, respectively. These results indicate that WIS from AHF can be well dissolved in the IL.

Similar results were observed in the samples after dilute alkaline or glycerol treatment. Alkaline treatment slightly improved dissolution by removing lignin (Fig. 2A) and, interestingly, the glycerol treatment without significantly altering sample chemical composition resulted in higher dissolution than alkaline treatment. WIS dissolution of G2 and G3 was over 85%. Glycerol treatment swells fibers and loosens fiber bundles thereby improving IL accessibility to the cellulosic substrate. This is in agreement with measured BET surface area as listed in Table 1. In general, AHF fractionation substantially increased BET surface area from 0.7 m^2/g (MDF) before fractionation to over 2.0 m^2/g due to significant dissolution of lignin and hemicelluloses; glycerol treatment further increased surface area to result in a higher BET surface area for G samples than their corresponding P samples. Cold alkaline treatment increased surface area of P1 sample due to a substantial increase in delignification from 74% to 83% (Table 1), but minimally changed or slightly reduced surface area for P2 and P3 samples despite alkaline extraction slightly increased delignification from approximately 85% to 90% (Table 1). This perhaps is due to the fact that delignification does not play a major role in opening-up the sample structure for these two samples with lignin content below 10%. On the contrarily, further remove lignin by alkaline extraction exposed cellulose surface and facilitated drying-induced (samples need to be dried for BET analyses) hydrogen bonding (hornification) to cause fiber pore collapse [40,41]. Both P and G samples had higher lignin content than their corresponding A samples, therefore lower degrees of hornification than A samples.

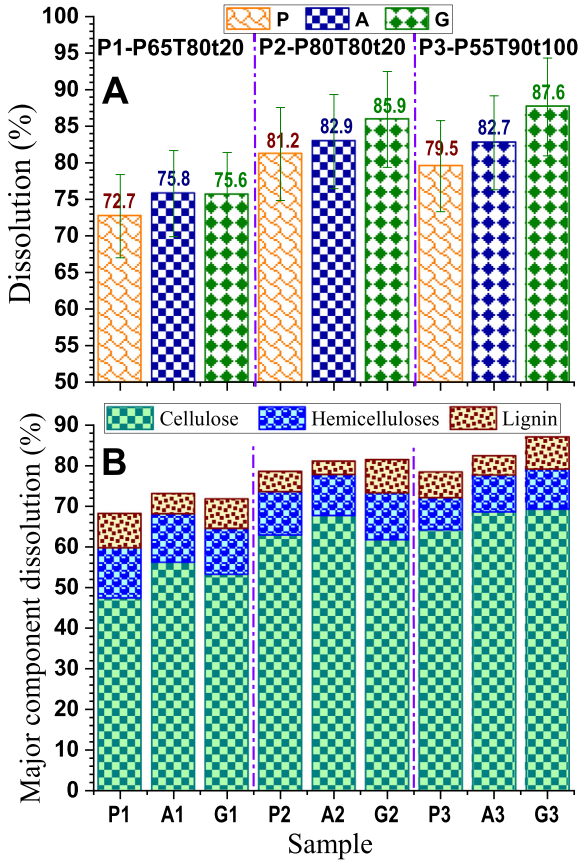

Fig. 2. Dissolution of AHF birch MDF with and without post treatments. A: total dissolution; B: component dissolution.

Optical microscopic images of the undissolved solid residues are shown in Fig. 3. Compared with the residue from P1, there were much less undissolved residues from P2 and P3. This is consistent with the better dissolution of P2 and P3 in DBNH[OAc] (Fig. 2). The lignin content of P1 of 11.6% was substantially higher than the approximately 8% in both P2 and P3. More lignin can form a tighter structural network containing covalent linkages with carbohydrates [39], which negatively affects the formation of hydrogen bonds between lignocellulose and IL, critical to the dissolution of lignocelluloses [33,42,43]. The images in Fig. 3 also show that both alkaline and glycerol treatments reduced solid residue, with G2 and G3 showing best dissolution and consistent with the measured dissolution data (Fig. 2A).

3.3. Component dissolution

Unlike commercial production using high purity DPF, use of less-processed DPF, such as AHF WISs evaluated in this study, for MMCF production requires examining the potential effects of all dissolved components. Solids regenerated from IL-WIS solutions, denoted as rPn, rAn, and rGn, were analyzed for cellulose, hemicelluloses and lignin (Table 2). As expected, the major component is cellulose, as shown in Fig. 2B, however total dissolution of hemicelluloses and lignin was substantial at approximately 20%, more than half of which was hemicelluloses. The effect of dissolved hemicelluloses and lignin on dissolving dope spinnability and textile fiber performance needs yet to be investigated, however literature study using unbleached kraft cooked deinked newsprint wood fibers (containing upto 6% lignin and 20% hemicelluloses) produced textile fibers with excellent performance [17].

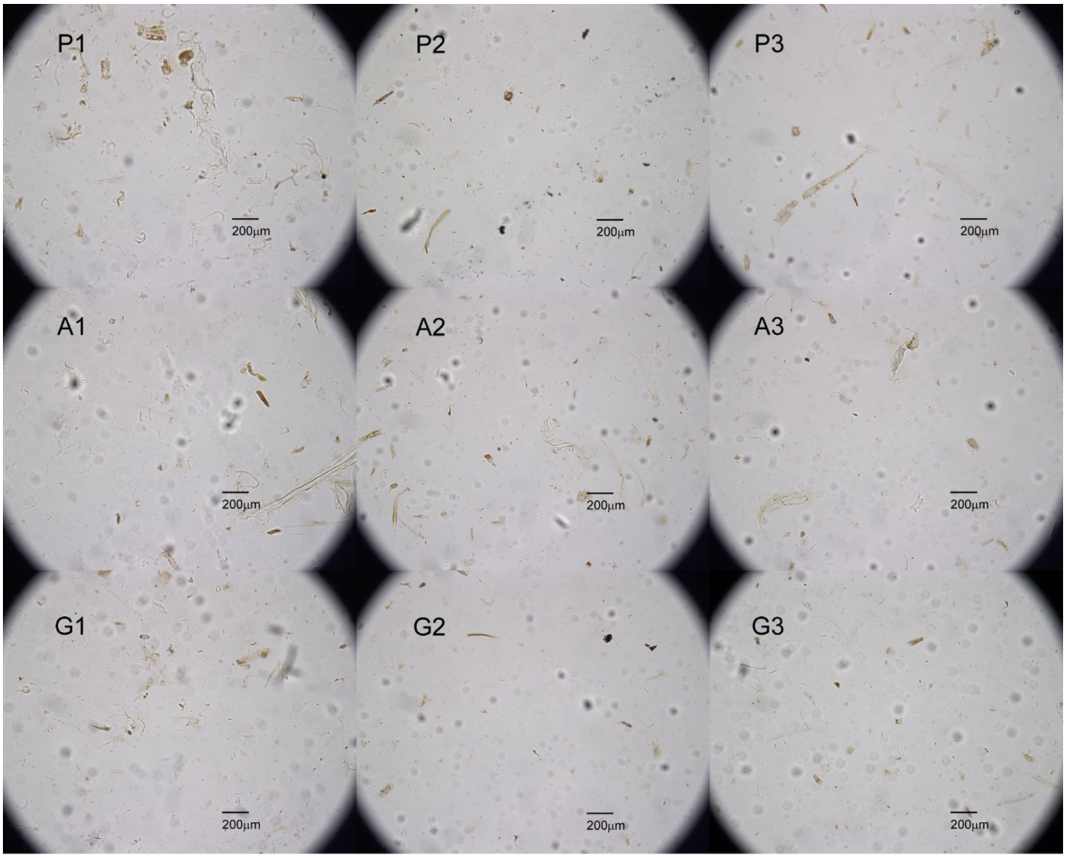

Fig. 3. Optical microscopic images of AHF WIS samples, with and without post-treatment, after dissolving in the ionic liquid DBNH[OAc] at 80 °C for 4 h.

Cellulose content in rP2 and rP3 (77.4% and 81.4%) was higher than that in rP1 (65.3%), while the lignin content in P1 (11.6%, Table 1) was higher than in P2 (8.2%, Table 1) and P3 (8.4%, Table 1). This suggested that a higher lignin content negatively affected dissolution of the cellulose fraction in the ionic liquid DBNH[OAc]. To more closely examine the effects of residue hemicelluloses and lignin in AHF on component dissolution in IL, the percentages of component dissolution based on the component mass in the feeding samples were plotted in Fig. 4. The results clearly show that cellulose dissolution was hindered with increasing residue hemicellulose (Fig. 4A) and lignin (Fig. 4B) and that the residual lignin has a more pronounced impact. Furthermore and notably, a small change of only a few percent lignin content generated up to a 30% decrease in dissolution of cellulose, with the drop beginning at about 8% lignin close to the 6% of lignin content reported for producing excellent MMCF through spinning [17]. Additionally, further decreases in lignin content did not improve cellulose dissolution. Hemicelluloses dissolution, by contrast, did not demonstrate any discernable trend or inflection point influenced by residual hemicelluloses (Fig. 4C) or lignin (Fig. 4D).

Table 2
Chemical compositions of regenerated cellulosic samples from dissolved AHF WISs in ionic liquid DBNH[OAc]. The number in the parentheses are component dissolution yield based on component mass in the unfractionated MDF.

Sample label	Cellulose (%)	Hemicelluloses (%)	Lignin (%)
rP1-P65T80t20	65.3 ± 4.2 (65.0)	16.9 ± 4.8 (28.5)	17.8 ± 2.1 (19.0)
rP2-P80T80t20	77.4 ± 1.6 (74.3)	13.2 ± 0.5 (21.4)	9.4 ± 2.7 (9.6)
rP3-P55T90t100	81.4 ± 4.7 (69.7)	10.0 ± 0.6 (14.5)	8.6 ± 2.5 (11.3)
rA1-P65T80t20	74.1 ± 6.5 (62.7)	15.8 ± 0.9 (22.6)	10.1 ± 4.5 (9.2)
rA2-P80T80t20	81.6 ± 3.1 (70.5)	12.2 ± 0.7 (17.8)	6.2 ± 2.3 (5.6)
rA3-P55T90t100	82.8 ± 3.6 (60.2)	11.0 ± 0.3 (13.5)	6.2 ± 2.4 (6.8)
rG1-P65T80t20	70.4 ± 0.6 (68.3)	15.0 ± 2.3 (24.6)	14.6 ± 1.6 (15.2)
rG2-P80T80t20	79.1 ± 1.2 (70.4)	11.3 ± 1.1 (22.1)	13.7 ± 1.4 (15.4)
rG3-P55T90t100	79.1 ± 0.9 (69.1)	11.2 ± 0.3 (16.5)	9.8 ± 0.4 (12.9)

Apparently, reducing WIS lignin content such as by alkaline treatment improved cellulose dissolution, which contributed to the improved total material dissolution (Fig. 2A) as discussed early. Comparing the data trends of Pn and Gn samples in Fig. 3B, substrate swelling by glycerol treatment improved cellulose dissolution, which also contributed to total material dissolution (Fig. 2A). The results also indicate that dissolution of hemicelluloses was approximately 90%, higher than cellulose dissolution. The effects of residue hemicelluloses (Fig. 4C) and lignin (Fig. 4D) contents on hemicelluloses dissolution are small, cannot be discerned from the data and are within measurement errors of approximately ±3–7% (Table 2).

Large variations in lignin dissolution were observed among different sample sets Pn, An, and Gn. For Gn, the less residual lignin present, then the greater percentage was dissolved (Fig. 4F). The same trend was observed for residual hemicelluloses (Fig. 4E), which can be explained by lignin-carbohydrate complex. It is interesting to note that alkaline treatment resulted in the lowest lignin dissolution of approximately 50%, independent of residue hemicelluloses or lignin contents in the substrates, i.e. lignin dissolution of AHF WISs Pn without treatment was higher than alkaline treated samples An. Glycerol treatment resulted in the greatest lignin dissolution as long as hemicelluloses and lignin content was low of approximately 8%, which was the same observed inflection point for cellulose dissolution.

3.4. Lignin chemical structure analyses by 2D ^{1}H—^{13}C HSQC NMR spectroscopy

2D ^{1}H—^{13}C HSQC NMR spectroscopy was used to analyze the lignin remaining on the AHF WISs from the least harsh condition (P1, A1, G1) as compared to the most harsh condition without subsequent treatment

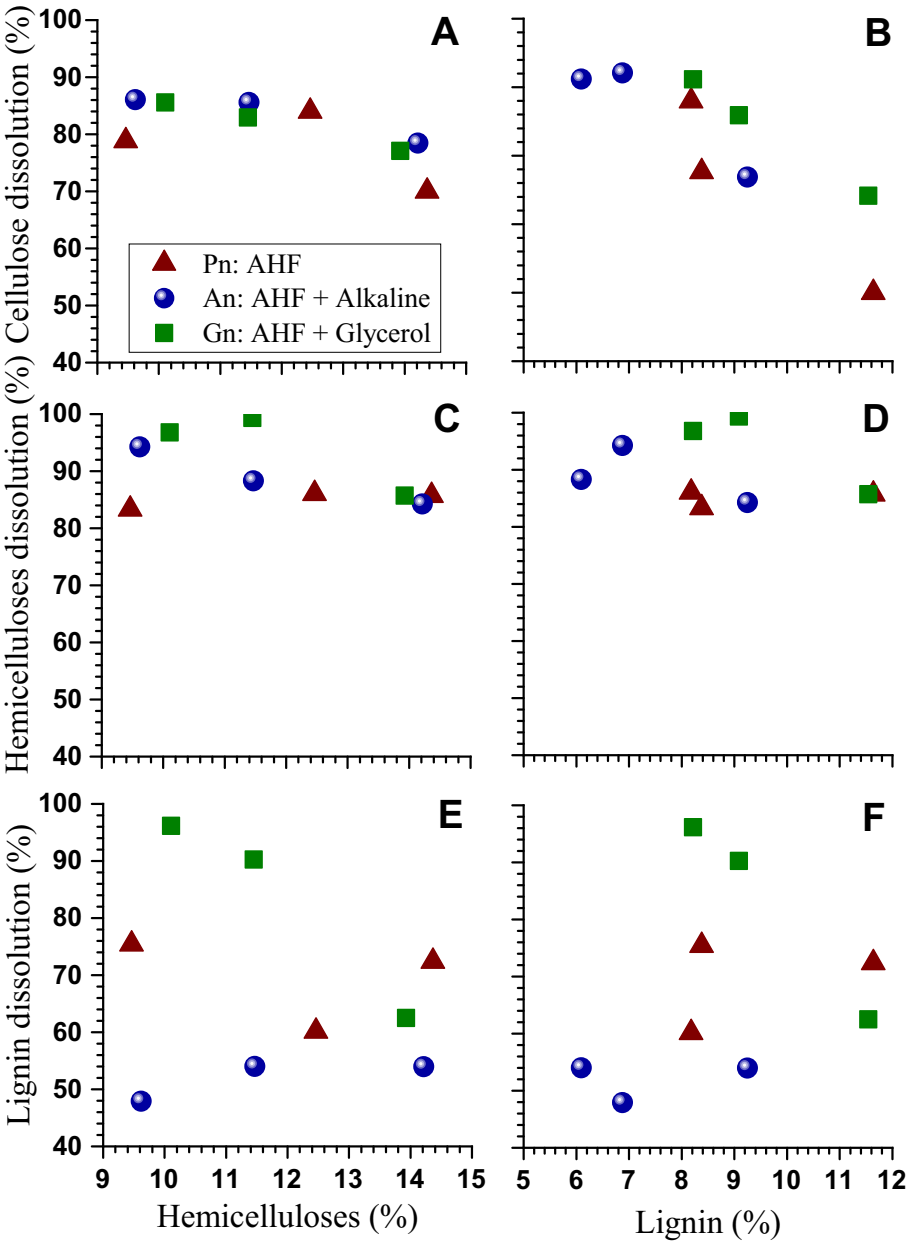

Fig. 4. Effects of hemicelluloses and lignin content on component dissolution of different AHF MDF samples with and without post treatments.

(P3). The undissolved solid residues P1, A1 were also examined. G1 was not included because it should have a similar lignin structure as that of P1 as glycerol treatment simply swells cellulose for increasing accessibility of the IL and did not modify lignin.

Assignment of the NMR signals and the semi-quantitative analyses were according to literature (Table S1) [44–46]. As shown in Fig. 5, the cross-peaks from lignin substructures and subunits (including β-aryl ether (A), phenylcoumaran (B), and resinol (C) linkages, syringyl (S), guaiacyl (G), and *p*-hydroxyphenyl (H)) and β-D-xylan of hemicelluloses main-chains were well resolved in the six samples.

The relative quantities of lignin substructures and subunits are presented in Table 3. The WIS from low severity treatment (P1) had comparatively higher β-O-4′ content because these linkages in the lignin remaining on the cellulosic solids were not destroyed during treatment. This is in agreement with our earlier study [22] that showed the *dissolved* lignin from poplar wood under low severity treatments such as P65T80t20 was almost unchanged from that in the original material, i.e. not condensed with a similar level of β-*O*-4′ linkages as the whole cell wall. The WIS from alkaline post-treatment (A1), by contrast, had reduced β-*O*-4′ linkages (from 86% for P1 to 78% for A1). Furthermore, A1 also had reduced S units (from 77% for P1 to 60% for A1) and increased oxidized (S′) and condensed (S_{cond}) units (from 5% and 17% for P1 to 10% and 20% for A1, respectively). These results are in agreement with literature [47], which suggests that lignin condensation contributed to reduced lignin dissolution as discussed earlier.

Glycerol treatment did not significantly affect β-O-4′, (S′) or condensation (S_{cond}), however it did increase both β-5′ and β-β' linkages from 3.3/100Ar in the sample P1 to 6.9/100Ar in the sample G1. This indicates that the elevated temperature (120 °C) involved in the glycerol treatment initiated condensation of lignin side-chains. The fact that the solubility of lignin in G1 is higher than in A1 suggests that oxidation and condensation of the aromatic units, especially S units, negatively affected the dissolution of lignin in the IL.

It is very interesting to note that the undissolved solid residues P1res and A1res from dispersing P1 and A1 into IL DBNH[OAc] had substantially lower β-*O*-4′ linkages of 25% and 15% than their feedstock P1

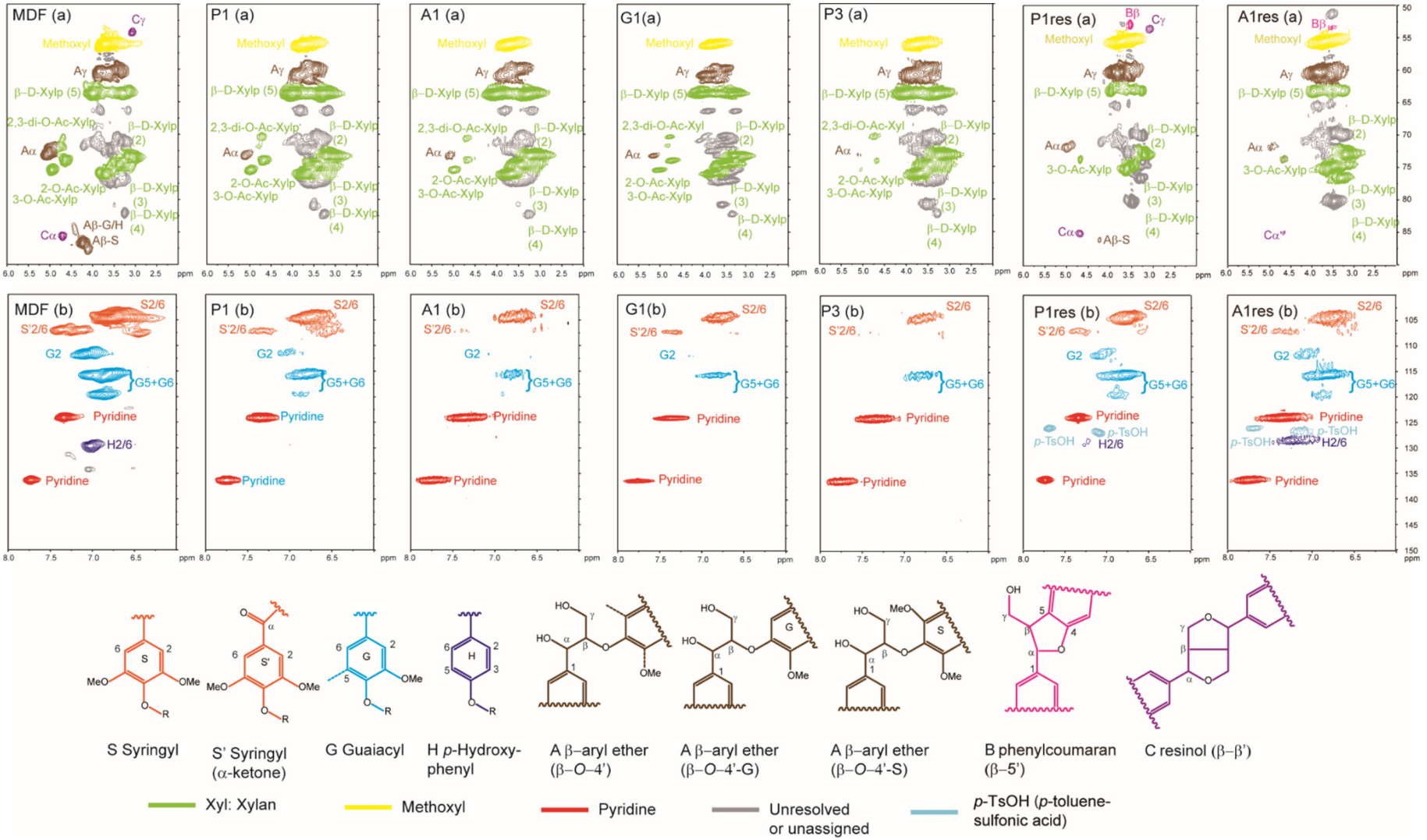

Fig. 5. Side-chain (δ_C/δ_H 50–90/2.0–6.0 ppm) and aromatic (δ_C/δ_H 100–150/8.0–6.0 ppm) regions of ^{13}C–^{1}H 2D HSQC NMR spectra of AHF WISs with and without post treatments and regenerated cellulosic samples dissolved in ionic liquid DBNH [OAc].

Table 3
Structural characteristics (interunit linkages, aromatic units, and S/G ratio) of lignin remaining on the AHF WISs from integration of ^{1}H–^{13}C correlation peaks in the HSQC spectra of the samples.

	MDF	P1	A1	G1	P3	P1res	A1res
Lignin interunit linkages (results expressed per 100Ar)							
β-*O*-4′ aryl ether (A)	78	86	78	84	22	25	15
Phenylcoumaran (β-5′, B)	0.5	0	0	0.6	2.2	13	5.6
Resinol (β-β', C)	8.4	3.3	3.8	6.9	0	9.8	4.9
Lignin aromatic units [0.5(S S′) S_{cond} G = 100%]							
S (%)	72	77	60	81	47	57	41
S′ (%)	7	5	10	5	9	6	10
S′/S	0.1	0.1	0.2	0.1	0.2	0.1	0.2
S_{cond} (%)	3	17	20	14	44	23	21
S_{cond}/S	0.04	0.2	0.3	0.2	0.9	0.4	0.5
G (%)	1.7	0.8	8.8	0.6	0	13.4	27.9
G/S	0.02	0.01	0.1	0.007	0	0.2	0.7

and A1 of 86% and 78%, respectively (Table 3). P1res and A1res also had a slightly higher content of condensed S units than their corresponding feedstock P1 and A1. However, the quantity of β-5′ and β-β' linkages obviously increased compared with that in their corresponding feedstock P1 and A1. This suggests that lignin side-chain condensation occurred during dissolution in the IL. This also indicates that condensed lignin with low β-*O*-4′ linkages and higher β-5′ and β-β' were less soluble in IL and ended up in the undissolved solid residue.

To further illustrate the effect of lignin condensation on lignin dissolution in DBNH[OAc], we compared the lignin component dissolution between P1 and P3. Increasing AHF severity under P55T90t100 improved delignification (Table 1) but condensed lignin in the retained WIS (P3) mostly due to elevated temperature of 90 °C and prolonged treatment time of 100 min [32]. P3 obtained from a severer AHF (P55T90t100) had a lower content of β-*O*-4′ linkages of only 22% than P1 (P65T80t20) of 86% (Table 3). Both oxidized units (S′) and condensed units (S_{cond}) were substantially increased from 5% and 17% for P1 to 9% and 44% for P3, respectively. P3 had a lower amount of lignin dissolution 6.3% than P1 had of 8.4% (Fig. 2B) to result in a much higher lignin content of 17.8% in the regenerated dissolved cellulosic solids rP1 than 8.6% in rP3 (Table 2). P3 also had a lower overall lignin component dissolution of 11.3% based on lignin in MDF than P1 of 19.0%. These indicate that avoiding lignin condensation using mild AHF can improve lignin dissolution for using less-processed DPF to produce MMCF.

As shown in Table 2, birch wood has a very low content of G units, only 1.7% in MDF. G units was pretty much unchanged after AHF under P65T80t20. Alkaline treatment removed some S units which enriched G units to 8.8% for A1. The severer treatment under P55T90t100 condensed G units to result in G content below the detection limit in P3. It is interesting to note G units was substantially enriched in the undissolved solid residues P1res and A1res to 13.4% and 27.9%, respectively, which suggesting that G units is less soluble than S units. The fact that birch has low content of G units makes it suitable for DPF to produce MMCF through dissolution using DBNH[OAc].

4. Conclusions

Hydrotropic *p*-TsOH can rapidly remove approximately 85% of lignin at 80 °C within 20 min. Approximately 80% of the water insoluble solids after *p*-TsOH fractionation without grinding could be well dissolved in the ionic liquid DBNH[OAc]. Residue content of hemicelluloses and lignin had negative effects on cellulosic solids dissolution with residue lignin content had a more pronounced effect on cellulose dissolution. The undissolved solid residues in the ionic liquid DBNH[OAc] was mainly composed of hemicelluloses and lignin. Dilute alkaline and glycerol treatment increased dissolution in the ionic liquid by further delignification and swelling carbohydrates (cellulose and hemicelluloses), respectively. Semi-quantitative 2D HSQC NMR results showed lignin condensation occurred at a higher AHF severity and through alkaline treatment. The undissolved residues were enriched with more condensed lignin with lower content of β-O-4′ linkages, as well as G lignin units compared with the corresponding feed fibers. It can be concluded that lignin condensation has a negative effect on lignin dissolution in the ionic liquid DBNH[OAc]. G units are more difficulty to be dissolved than S units. Using AHF can eliminate lignin condensation and promote dissolution of AHF PDF for more sustainable MMCF production.

Declaration of Competing Interest

Zhu is a co-inventor of the acid hydrotropic fractionation process.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijbiomac.2019.05.074.

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