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Oxidative delignification: The roles of lignin reactivity and accessibility

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ABSTRACT

This study compared oxidative delignification of birch kraft pulp fibers to pulp fibers from acid hydrotropic fractionation (AHF) using *p*-toluenesulfonic acid (*p*-TsOH). Under oxygen delignification at 20% consistency, AHF pulps with lower hemicellulose content showed higher delignification than kraft pulps with similar lignin content despite its residual lignin (cellulosic enzymatic lignin, CEL) being less reactive with fewer β-O-4 ether aryl linkages based on 2D ^{13}C-^{1}H nuclear magnetic resonance (NMR) spectroscopy. The water retention value (WRV) of AHF pulp fibers, a measure of fiber accessibility to water or oxidative chemicals, was substantially greater than that of kraft pulp fibers. Similar comparison of various AHF pulps further suggested that fibers with lower hemicellulose content were easier to delignify (bleach) despite having more lignin with lower reactivity (fewer β-O-4 linkages). Additionally, the present study also indicated that oxygen delignification was more effective at high fiber consistency, which can be attributed to thinner water films on the fiber surfaces at higher fiber loadings. These results indicated that mass transfer was the rate controlling process in oxidative delignification of wood fibers.

1. Introduction

Oxidative delignification is an important chemistry in the processing of plant biomass for clean production of biomaterials, biofuels, and biochemicals (Bujanovic et al., 2010; Ma et al., 2015b; Palonen et al., 2004; Schmidt and Thomsen, 1998). Currently, oxidative delignification using oxygen and peroxide is commercially practiced in pulp mills for producing fibers (Dence and Reeve, 1996; Ji, 2007) and is considered a green process for its minimal negative impact on the environment. Therefore, it is expected that oxidative delignification will play a more important role in future plant biomass utilization. It is well known commercial manufacturing of white paper and dissolving grade pulp (for producing cellulose derivative products such as viscose rayons, acetates, etc. (Chen et al., 2016; Sixta et al., 2013) requires a series of oxidative delignification stages of considerable complexity (Argyropoulos, 2001). Removing residual lignin from fibers often requires extensive bleaching, a term used to describe removal of residual lignin after bulk delignification, using strong chemicals (Gierer, 1986) which is not only expensive, but also can cause adverse environmental impact depending on the chemical(s) used. Therefore, understanding oxidative delignification not only has immediate environmental and commercial benefits, but also has significant importance to sustainable biorefinery. Studies on understanding oxidative delignification of fibers can provide direct knowledge for developing sustainable technologies for plant biomass utilization through the biorefinery concept.

Lignin is primarily composed of guaiacyl (G), syringyl (S), and *p*-hydroxyphenyl (H) subunits which are connected by uncondensed α/β-aryl-ether (α-O-4, α-O-γ and β-O-4) and condensed C-C (β-β, β-1 and β-5) linkages. It is an amorphous polymer with a supramolecular structure that, in native state, is mostly physically embedded in the carbohydrate matrix instead of being chemically bonded to carbohydrates as lignin-carbohydrate complex (LCC) (Kang et al., 2019). LCCs do exist in residual lignin in pulp fibers, even though the amount is small. Extensive studies on the properties of residual lignin in pulp fibers and its effects on bleaching (Bujanovic et al., 2010; Chang et al., 1975; Froass et al., 1996a; Lachenal et al., 1995; Ma et al., 2020; Sealey et al., 1998; Sixta, 2006) have shown that amount, condensed structure, reactivity, and LCC characteristics can negatively affect pulp fiber bleaching (Sixta, 2006; Suess, 2010).

Biomass cell walls are mostly made of cellulose, hemicelluloses, and lignin. Therefore, hemicelluloses will inevitably influence fractionation, purification, oxidative delignification, as well as microbial and enzymatic deconstruction of lignocellulosic fibers (Busse-Wicher et al., 2014; Kang et al., 2019; Leu and Zhu, 2013; Zhang et al., 2012; Zhu et al.,

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2009, 2021a). Hemicelluloses are polysaccharide heteropolymers with side chains composed of hexoses (mannose and galactose), pentoses (xylose and arabinose) and uronic acids (D-glucuronic acid and 4-O-methyl-D-glucuronic acid). In cell walls, they are present in two forms: either as surface coatings on cellulose fibrils or as crosslinkers to cellulose chains (Busse-Wicher et al., 2014; Kang et al., 2019; Zhu et al., 2021a). It is well recognized that sulfite pulps with lower hemicellulose content have better bleachability than kraft pulps with higher hemicellulose content (Sixta, 2006), however the effect of hemicelluloses on mass transfer and pulp fiber oxidative bleachability has seldom been studied. Xylanase pretreatment to remove xylan has been reported to facilitate subsequent chemical bleaching of kraft pulp fibers (Ma et al., 2015a; Paice et al., 1992). Nevertheless, when enzymatic pretreatment was applied to softwood sulfite pulps with varied xylan and mannan content, obtained from both acidic and alkaline sulfite pulping, hemicellulose reduction did not improve fiber bleachability (Buchert et al., 1995). Several studies showed that dissolution of hemicelluloses have a substantial impact on cellulose accessibility and enzymatic digestibility of cellulose (Ishizawa et al., 2007; Leu and Zhu, 2013; Zhu et al., 2012). Analogously, removal of hemicelluloses should also increase accessibility of lignin to bleaching chemicals. Hemicellulose removal can facilitate the loosening and breakdown of the lignocellulosic structure and increase the pore volume and pore size of biomass (Wang et al., 2012). Hemicelluloses are susceptible to acidic treatments and can be easily dissolved, therefore acid pulps, such as acidic sulfite pulps, often have lower hemicellulose content than kraft pulps under equivalent extent of delignification; this can be used to evaluate the effect of hemicellulose removal on the bleachability of fibers.

Acid hydrotropic fractionation (AHF), developed recently in our laboratory, has attracted interest (Cai et al., 2020; Chen et al., 2017; Zhu et al., 2021b). *p*-Toluenesulfonic acid (*p*-TsOH), as an hydrotrope, can rapidly (≤30 min) fractionate lignocelluloses at a low temperature (≤90 °C) (Chen et al., 2017). The resultant fractionated water insoluble cellulosic solids (WISs) can be used to produce lignocellulosic nanofibrils (LCNFs) (Bian et al., 2017). Moreover, WISs showed good enzymatic cellulose digestibility in producing glucose for biorefinery applications (Chen et al., 2017). Previously, we reported that *p*-TsOH fractionation resulted in more reactive structures in both the dissolved (Cheng et al., 2019; Wang et al., 2019) and residual lignins (Ma et al., 2020). Furthermore, using single stage oxidative bleaching, we demonstrated that the resultant *p*-TsOH AHF fibers had good bleachability and, therefore, may be suitable for dissolving pulp production.

The objective of this study is twofold: (1) To conduct sequential bleaching of *p*-TsOH pulp fibers using oxygen-chlorine dioxide-H_2O_2 (O-D-P). The bleaching is commercially relevant, and the pulp fibers produced would meet cellulose purity and brightness requirements for potential utilization as dissolving pulp or for papermaking; (2) To understand the importance of lignin reactivity and accessibility to oxidative delignification. This would be accomplished by comparing the bleachability of an AHF pulp sample with a kraft pulp sample of the same lignin content. Lignin reactivity was characterized by the amount of β-O-4 aryl ether linkages semi-quantified from 2D NMR analysis of the residual lignins. Fiber lignin accessibility was characterized by pulp fiber length, fine (fibers short than a few hundred micrometers) content, hemicellulose content, and water retention value (WRV). Consideration was also given to the effect of improving oxygen mass transfer during oxygen bleaching by using a high-solid loading to improve lignin accessibility. The goal of the study is to identify the key rate controlling processes on oxidative delignification to decrease chemical usage and environmental impact in processing lignocellulosic biomass for sustainable production and biomaterials, bioproducts, and biochemicals through biorefinery.

2. Materials and methods

2.1. Materials

Birch logs were obtained from the USDA Forest Service, Rhinelander Experimental Forest. The logs were harvested in October 2016 and had breast height diameter of 15–20 cm. Wood logs were provided by Dr. Ronald Zalesny, Jr. at the USDA Forest Service, Northern Research Station. The wood logs were debarked and chipped at the USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin. The wood chips were used to produce medium density fiberboard fibers (MDF) in a 30.5-cm pressurized disk refiner (Sprout-Bauer, model 1210P, Muncy, PA, USA) by pre-steaming the wood chips at steam pressure of 0.72 MPa and 165 °C for 10 min. The disk plate pattern was D2B505 with a gap of 0.18 mm. The chip feeding rate was approximately 1 kg/min. The resulting pulp fibers were stored in a plastic bag for further processing.

p-TsOH from Alfa Aesar (Ward Hill, MA), sodium hydroxide from LabChem (Pittsburgh, PA), hydrogen peroxide from Sigma-Aldrich (Burlington, MA), and magnesium sulfate from Mallinckrodt, Inc. (Phillipsburg, NJ) were used as received. All chemicals were ACS reagent grade. 0.02 mol/L $KMnO_4$ and 0.1 mol/L $Na_2S_2O_3$ solution purchased from Fisher Scientific (Ottawa, ON) were used for kappa number (KN) determination. 1 mol/L copper-ethylenediamine solution (CED) purchased from Acros Organics of Fisher Scientific (NJ) was used for pulp fiber intrinsic viscosity testing. Bottle oxygen of 99.0% purity was purchased from Badger Welding Supplies, Inc. (Madison, WI). Chlorine dioxide was prepared in house by reacting sodium chlorite ($NaClO_2$) with sulfuric acid (H_2SO_4) with a final concentration of 8 g/L.

2.2. Pulping and fractionation

AHF of birch MDF using p-TsOH. AHFs of birch MDF were carried out in batch (Ba) and flow-through (FT) using *p*-TsOH. Fractionation conditions were abbreviated as PxxTyytzzDD to represent reactions at *p*-TsOH concentration xx wt% and reaction temperature yy °C for zz min with DD = FT or Ba for flow-through and batch runs, respectively.

Flow-through fractionation was conducted in an 800 mL flow-through reactor with a 200-mesh steel screen at both the inlet and outlet ends of the reactor and equipped with a peristatic pump (WZ1R057, Masterflex, Vernon, IL). 100 g oven dry (OD) birch MDF were preloaded and heated to the target temperature (80–90 °C) using a hot water bath. Aqueous *p*-TsOH solutions (40–60 wt%) were first pumped into the reactor at the highest flow rate of 200 mL/min to rapidly flood the biomass in the reactor, then the flow rate was lowered to 40 mL/min for fractionation. At the end of the preset reaction time the spent fractionation liquor was collected in a flask containing ice-water to stop the reaction and prevent condensation reactions of the dissolved lignin, then fresh water was pumped into the reactor at the flowrate of 200 mL/min to wash the pulp fibers until the effluent stream reached neutral pH.

For batch runs, 50 g OD birch MDF and 500 mL *p*-TsOH solution (50–60 wt%) were added to a 2-L flask and heated to the target temperature (80–90 °C) in an oil bath. The fresh *p*-TsOH solution was preheated to the reaction temperature before mixing with the MDF and the mixture was stirred by a Eurostar 40 digital overhead stirrer (IKA, Germany) at 300 rpm for 20–60 min. At the end of the preset reaction time, the mixture was rapidly separated by vacuum filtration with water washing.

The collected washing filtrates from both flow-through and batch runs were diluted to a concentration of 4 wt% *p*-TsOH to precipitate the dissolved lignin (DL) through centrifugation at 11,000 rpm for 10 min. The collected DL was then dialyzed and freeze dried. The fractionated water insoluble cellulosic solids (WISs) were thoroughly washed using DI water until neutral pH and kept at 4 °C until use.

Reprecipitated lignin washing. Because dissolved lignin in the spent liquor can partially reprecipitate onto the cellulosic fiber surface

during fractionation, an aliquot of water washed WISs was subjected to alkaline extraction at NaOH charge of 0.5 or 1.0% (on WIS OD basis) with liquor-to-WIS ratio of 20:1 or 40:1 at room temperature for 5 min. The WISs were then separated through filtration with washing using DI water until neutral pH to obtain alkaline extracted WISs.

Kraft pulping of birch MDF. Kraft delignification was performed using 50 g OD birch MDF in a 1.3 L stainless steel bomb digester mounted in a 21 L rotating reactor in an autoclave heated by a steam jacket, as described previously (Tian et al., 2011). All runs were carried out at the same liquor-to-wood ratio of 10:1 and sulfidity of 20% with varied effective alkali charge of 17–23% (both sulfidity and effective alkali are as Na_2O). The digester temperature was raised from ambient temperature to a maximum temperature of 160 or 165 °C in 20 min. Reaction durations at maximum temperatures were varied to obtain pulps with different lignin content as measured by KN. At the end of the preset reaction time, the digesters were cooled with tap water before opening. The delignified pulp fibers were separated from spent liquor through filtration and washed with tap water. The collected spent liquor was concentrated by vacuum rotary evaporation to total solids of approximately 40% and then heated to 80 °C with the addition of 20% H_2SO_4 to adjust the mixture pH to 2.0. The mixture was cooled in an iced water bath overnight. The supernatant was decanted and centrifuged repeatedly, then the combined precipitated lignin was washed twice with water and freeze dried. The delignified birch pulp fibers were thoroughly washed using DI water until neutral pH.

2.3. Oxidative delignification (bleaching)

The sequence bleaching was carried out using oxygen (O), chlorine dioxide (D), and peroxide (P). O-D-P bleaching conditions were as follows: O: 0.75 MPa O_2 with 3% NaOH and 0.5% $MgSO_4$ charge on OD pulp fibers at 20% consistency and 110 °C for 60 min; D: 1% ClO_2 charge on OD pulp fibers at 10% consistency and 70 °C for 90 min with the ending pH 2.5–3.5. P: 1.0% H_2O_2, 1.0% NaOH and 0.5% $MgSO_4$ charge on OD pulp fibers at 10% consistency and 70 °C for 90 min.

2.4. Analytical methods

All lignocellulosic solid samples were oven-dried at 105 °C overnight and then Wiley-milled to 40 mesh. For chemical analysis, the conventional two-step sulfuric acid hydrolysis procedure was applied. The hydrolysates were analyzed for carbohydrates. Klason lignin was determined gravimetrically (Sluiter et al., Revised August 2012)

Thick pulp pads (250 g/m^2) were prepared according to TAPPI Standard Test Method T218 sp-97. Diffuse brightness of the pulp pads was obtained according to TAPPI T525 om-92on using a ColorTouch PC instrument (Technidyne Corporation, USA). Reported brightness numbers are the average of six measurements.

All pulp KN were measured according to TAPPI Useful Method 246, Micro-Kappa number due to the limited amount of the samples available.

The fractionated pulp intrinsic viscosities ([η]) were determined after dissolving in copper-ethylenediamine solution (CED), using ISO 5351:2010. 0.125 g OD pulp and 12.50 mL of distilled water were added to a dissolving tube and the suspension was stirred for 30 s using a motor-driven copper bar. After purging the dissolving tube with nitrogen for 1 min, 12.50 mL of the CED solution of 1.00 ± 0.02 mol/L was added. The mixture was stirred for 15 min at approximately 400 rpm, then the viscosity of the dissolved pulp solution was measured.

Hexeneuronic acid (HexA) content of pulps was measured according to TAPPI Standard Test Method T282 om-13 using a dual-wavelength spectroscopic technique on a UV–Vis spectrophotometer (Model 8453, Agilent Technologies, Palo Aalto, CA) (Chai et al., 2001).

Fiber lengths and widths were determined using a Fiber Quality Analyzer (FQA, OpTest Equipment, Canada). Total 5000 fibers were analyzed for each sample at the speed of 30–60 fibers/s (Wanrosli et al., 2007).

A commercial Fourier-transform infrared spectrometer (FTIR) (Spectrum Two, PerkinElmer, UK) was used to analyze pulp samples after freeze drying.

Water retention values (WRV) were obtained as described previously (Gu et al., 2018; Luo et al., 2011). Briefly, 1 g OD pulp fibers was transferred to a stainless-steel jar with a stainless steel membrane with mesh size of 100 μm inserted at the bottom of the jar. The jar was then centrifuged at 3000 g for 15 min. WRV was reported as the amount of water retained in the fibers after centrifugation in percentage of OD fiber weight.

The sequentially bleached AHF and kraft pulp samples were analyzed by Raman spectroscopy. Pulp sample pellets were made using a pellet press. Raman spectra were recorded using a Bruker MultiRam spectrometer (Bruker Instruments Inc., Billerica, Massachusetts) equipped with a 1064-nm 1000-mW continuous wave (CW) diode pumped Nd:YAG laser. The laser power was 660 mW. 1024 scans were obtained from three different locations for each pellet. Spectra were obtained in the region 50 and 3700 cm^{-1}. Instrument software OPUS 7.2 was used to find peak positions and process the spectral data. For additional processing, Excel program was used. The crystallinity (CrI) of sequence bleached pulps was calculated on their peak intensity ratios at 380 and 1096 cm^{-1} (Agarwal et al., 2010).

$$\mathrm{CrI}_{380-\mathrm{Raman}} = \frac{\left(\left(\frac{\left(I_{380}/I_{1096}\right)-0.0212)}{0.0065}\right)+2.0212\right)}{0.8222} \quad (1)$$

where, I_{380} and I_{1096} are the Raman peak intensities of bleached pulps at 380 and 1096 cm^{-1}, respectively.

Milled wood lignin (MWL) of birch MDF and cellulosic enzymatic lignin (CEL) of AHF and kraft pulp fibers were analyzed using two-dimensional ^{1}H-^{13}C nuclear magnetic resonance (2D NMR) spectroscopy. Birch MDF was first extracted with acetone/water (95:5, v/v) for 8 h using a Soxhlet apparatus at approximately 70 °C. The extractive-free birch MDF and pulp fibers were ball-milled using PM 100 Planetary Ball Mill (Retsch, German) at 600 rpm in a 50 mL vessel containing ZrO_2 balls (10 mm × 10 mm). The milling duration for all samples was 23 cycles, with each cycle having 10-min milling and 10-min break to avoid approaching the glass transition temperature of lignin. The ball milled sample was then enzymatically hydrolyzed to remove carbohydrates and enrich the lignin (Chang et al., 1975; Lou et al., 2013). Novozymes CTec3 at 20 FPU/g glucan was used for hydrolysis at pH 6.0 (Lan et al., 2013; Lou et al., 2013), then the hydrolyzed sample was filtered and dried. The dried residue was ball-milled for 23 cycles, then refluxed in dioxane-water (85:15, v/v) with 0.05 mol/L HCl at 3% consistency for 2 h at approximately 86 °C and then filtered. The solid residue was repeatedly washed with fresh dioxane until clear, and the filtrates were combined. 10 times of DI water was added to the filtrate and sit overnight to precipitate the MWL and CEL. The precipitated lignin was collected and washed with DI water until free of acid, then collected and freeze-dried. Lignin was solubilized in 0.5 mL DMSO-d_6 for liquid state NMR.

A Bruker BioSpin AVANCE III 500 MHz NMR spectrometer fitted with a 5 mm, z-gradient Prodigy TCI cryoprobe was used to acquire ^{13}C-^{1}H short-range correlation (heteronuclear single-quantum coherence (HSQC)) experiments using the Bruker standard pulse program hsqcetgisisp2.2. Spectra were acquired using 40 scans and 1 s interscan delay for a total time of 3 h, with 12 ppm sweep width (SW) in F2 (^{1}H) using 1024 data points for an acquisition time of 85 ms and 215 ppm SW in F1 (^{13}C) using 512 increments with 50% NUS sampling density. Data processing used Gaussian multiplication (LB -0.1, GB = 0.01) in F2 and squared cosinebell (QSine SSB = 2) with 1 zero-fill and linear forward prediction of 40 coefficients in F1 resulting in a 1024 × 1024 data matrix. Topspin 3.5pl7 was used for interactive integration of the cross peaks after the central DMSO solvent peak was referenced at δ ^{13}C, 39.5 ppm; δ ^{1}H, 2.49 ppm. Spectral images were colored using Adobe

Table 1
Chemical composition of AHF and kraft pulp fibers and their corresponding bleached samples. Numbers in the parentheses are component yields based on the Klason lignin, glucan, and xylan content in birch MDF.

Sample label	Fractionation; washing conditions	Yield (%)[b]	Klason lignin (%)[c]	Cellulose (%)[c]	Hemicelluloses (%)[c]	KN
Birch MDF [a]			20.8	38.2	20.6	
P40FT	P40T90t20FT; no alkaline	56.3	14.8 (40.2)	59.2 (87.3)	12.8 (35.0)	81.1
P50FT	P50T90t20FT; no alkaline	44.8	7.0 (15.0)	68.9 (80.8)	10.7 (23.3)	38.5
P60FT	P60T90t20FT; no alkaline	43.0	4.2 (8.60)	71.7 (80.7)	9.0 (18.7)	23.0
P50Ba	P50T90t20Ba; no alkaline	48.7	8.0 (18.8)	67.2 (85.7)	9.3 (22.0)	44.3
P60t3Ba	P60T90t30Ba; no alkaline	47.2	6.8 (15.5)	67.6 (83.5)	9.5 (21.7)	37.6
P60t6Ba	P60T90t60Ba; no alkaline	45.2	7.4 (16.1)	69.1 (81.8)	8.0 (17.4)	40.9
$P50BaW_{05}$	P50T90t20Ba; 0.5% NaOH	48.7	8.0 (18.6)	67.2 (85.7)	9.3 (22.0)	43.8
$P60t3BaW_1$	P60T90t30Ba; 1% NaOH	47.2	4.70 (10.7)	67.6 (83.5)	9.5 (21.7)	25.9
$P60t6BaW_1$	P60T90t60Ba; 1% NaOH	45.2	3.83 (8.32)	69.1 (81.8)	8.0 (17.4)	21.1
KP1 [e]	EA = 17% @165 °C for 60 min	51.8	7.31 (18.2)	61.3 (83.1)	17.2 (43.3)	42.7 (40.3)[d]
KP2 [e]	EA = 17% @160 °C for 90 min	44.6	6.05 (13.0)	60.7 (70.9)	18.4 (39.8)	36.7 (33.4)[d]
KP3 [e]	EA = 23% @165 °C for 60 min	43.1	3.52 (7.29)	61.3 (69.2)	17.4 (36.4)	22.7 (19.4)[d]

[a] Arabinan, galactan and mannan were not detected in birch MDF.
[b] The numbers in parentheses are total solid yields based on original birch MDF.
[c] The numbers in parentheses are component retained in cellulosic solid fiber samples after AHF and kraft process based on original birch MDF.
[d] The numbers in parentheses are the KNs subtracted the HexA contribution to KN (= 0.084HexA (μMol/g pulp)) (Chai et al., 2001).
[e] Sulfidity = 20% and no alkaline washing for all three kraft runs.

Table 2
KN and Brightness of unbleached, O and sequence bleached (at 20% fiber solids loading unless indicated) fibers.

Sample	KN			Brightness %ISO	
	Unbleached	O-bleached:20%; 12%; 10% solids	Sequence bleached	Unbleached	Sequence bleached
P40FT	81.1	48.0; 69.7; 71.8	26.0	26.6 ± 0.2	46.3 ± 0.2
P50FT	38.5	15.8; 25.8; 26.6	1.7	15.7 ± 0.1	80.3 ± 0.3
P60FT	23.0	4.1; 14.8; 15.6	ND	15.9 ± 0.2	88.5 ± 0.2
P50Ba	44.3	15.5; 31.1; 32.7	1.7	14.8 ± 0.1	77.2 ± 0.2
$P50BaW_{05}$	43.8	15.1; 30.7; 32.3	1.7	15.0 ± 0.2	77.1 ± 0.1
P60t3Ba	37.6	4.6; 24.8; 26.1	ND	11.5 ± 0.4	88.9 ± 0.2
$P60t3BaW_1$	25.9	4.4; 17.9; 18.9	ND	14.8 ± 0.2	89.0 ± 0.3
P60t6Ba	40.9	2.4; 28.1; 29.5	ND	11.4 ± 0.3	89.6 ± 0.4
$P60t6BaW_1$	21.1	2.4; 12.0; 12.7	ND	14.7 ± 0.2	89.3 ± 0.2
KP1[a]	42.7(40.3)	21.3(19.1); 30.5(28.3); 33.0(30.7)	7.7 (6.4)	25.4 ± 0.3	61.2 ± 0.1
KP2[a]	36.7(33.4)	14.9(13.4); 26.9(24.6); 28.5(25.7)	3.5 (2.7)	26.5 ± 0.2	76.9 ± 0.2
KP3[a]	22.7(19.4)	6.3(3.2); 10.8(7.9); 11.3(8.2)	ND	37.3 ± 0.3	85.9 ± 0.3

[a] The numbers in parentheses are the KNs subtracted the HexA contribution to KN (= 0.084HexA (μMol/g pulp)) (Chai et al., 2001). HexA was not detected in the *p*-TsOH pulps and their bleached pulps. ND = pulp with lower lignin content and cannot be tested.

Illustrator CS6. Chemical structures were drawn using ChemDraw Pro 14.0.

3. Results and discussion

3.1. Chemical composition of fibers from AHF and kraft processes

The dissolved birch wood lignin can be repolymerized (condensed) throughout the AHF process, and then reprecipitated onto the fiber surface during filtration and washing. Therefore, fiber lignin includes the reprecipitated lignin as well as the insoluble residue lignin after AHF. Dilute NaOH solutions (0.00625 mol/L) at 0.5 or 1% charge on OD fibers were used to remove reprecipitated lignin from AHF pulp fibers. Decreases in KN were not observed after alkaline washing fiber samples P40FT (P40T80t20FT), P50FT (P50T90t20FT), P60FT (P60T90t20FT) and P50Ba (P50T90t20Ba), suggesting that the amounts of reprecipitated lignin were negligible in these samples (Table S1). P60t3Ba (P60T90t30Ba) and P60t6Ba (P60T90t60Ba) were also washed at 0.5% (W_{05}) NaOH and 1% (W_1) NaOH charges, and KNs of the washed fiber samples $P60t3BaW_{05}$ and $P60t3BaW_1$, and $P60t6BaW_{05}$ and $P60t6BaW_1$ were decreased from 37.6 to 29.3 and 25.9, and from 40.9 to 27.6 and 21.1, respectively (Table S1).

Fibers with varied KNs from AHF flow-through (FT), batch (Ba), batch with washing (BaW), and kraft pulping under different conditions were compared (Table 1). Notably, more cellulose was degraded by kraft pulping (KP) than by AHF using *p*-TsOH (Ba, BaW, and FT) at the same extent of delignification. For example, KP2 and $P60t3BaW_1$ had similar extent of delignification, i.e., 87% for KP2 vs 89% for $P60t3BaW_1$, but cellulose loss at 29.1% for KP2 was significantly higher than 16.5% for $P60t3BaW_1$ (Table 1). By contrast, less hemicellulose was degraded for KP than AHF (Ba, BaW, and FT) at the same extent of delignification. For example, KP1 and P50Ba had nearly the same extent of delignification, i.e., 82% for KP1 vs. 81% for P50Ba, but hemicellulose dissolution of 56.7% for KP1 was much lower than 78.0% for P50Ba (Table 1). In summary, alkaline kraft pulping dissolved more cellulose and retained more hemicelluloses than acidic AHF.

3.2. Effect of fiber consistency on oxygen bleaching

AHF and kraft fibers were bleached using elemental chlorine free (ECF) sequence of O-D-P and results are shown in Table 2. P40FT, P50FT, and P60FT fiber samples with KNs of 81.1, 38.5, and 23.0 were O bleached to KNs of 48.0, 25.8, and 4.1, and then further sequence bleached to KNs of 26.0, 1.7, and 0 (undetectable). At the same time, their ISO brightness reached 46%, 80%, and 89% respectively after the bleaching (Table 2 and Fig. 1). The washed fibers from batch AHF ($P50BaW_{05}$, $P60Ba3W_1$, and $P60Ba6W_1$) with KNs of 43.8, 25.9, and 21.1 were O bleached to KNs of 15.1, 4.4, and 2.4, and then further sequence bleached to KNs of below 2 with ISO brightness of 77.1%, 89.0%, and 89.3% respectively (Table 2 and Fig. 1)

The effect of reprecipitated lignin on bleaching was studied by comparing bleachabilities of water-washed and NaOH-washed pulps.

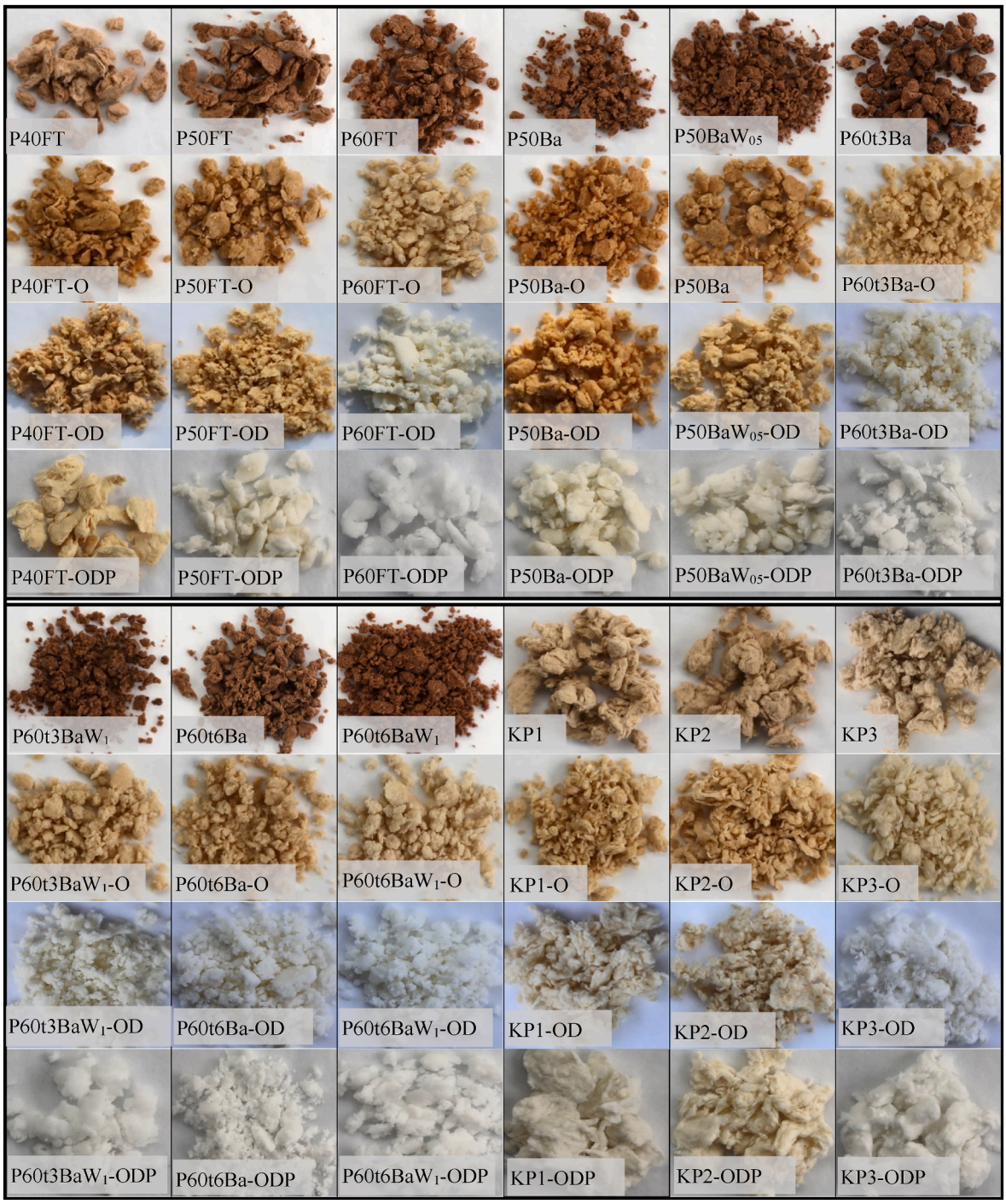

Fig. 1. The images of flow-through, batch, batch washed, and kraft pulps along with their bleached counterparts.

P60t3Ba with KN 37.6 was very thoroughly washed using 1.0% NaOH which brought it to KN 25.9; this means that the amount of reprecipitated lignin in P60t3Ba was equivalent to KN 11.7. Interestingly, however, P60t3Ba and P60t3BaW$_1$ showed almost identical KN after O bleaching (i.e., 4.63 and 4.41) and nearly the same ISO brightness of 89.0% after sequence bleaching (Table 2 and Fig. 1). Similarly, P60t6Ba (with the amount of reprecipitated lignin equivalent to KN 19.8) and P60t6BaW$_1$ (without reprecipitated lignin) showed the same bleachability after O bleaching at 20% solids with the same KN 2.4 and similar ISO brightness around 89% (Table 2 and Fig. 1). These results strongly suggest that the NaOH washing step is not necessary when O bleaching AHF pulps.

Our previous study showed that *p*-TsOH fractionated fibers containing reprecipitated lignin had lower bleachability than a thoroughly washed sample under O bleaching (at 110 °C and 6% NaOH and 10% consistency for 60 min), suggesting that the reprecipitated lignin is highly condensed and difficult to react with the bleaching chemicals (Ma et al., 2020); this appears to contradict results reported here (at 110 °C and 3% NaOH and 20% consistency for 60 min). However, compared with our previous O bleaching, NaOH dosage in the present study was decreased from 6% to 3% and fiber consistency was increased from 10% to 20%. Because a decrease in NaOH dosage is known to have a negative effect on lignin removal, the comparison suggests that the higher bleaching consistency at 20% in the present study not only compensated

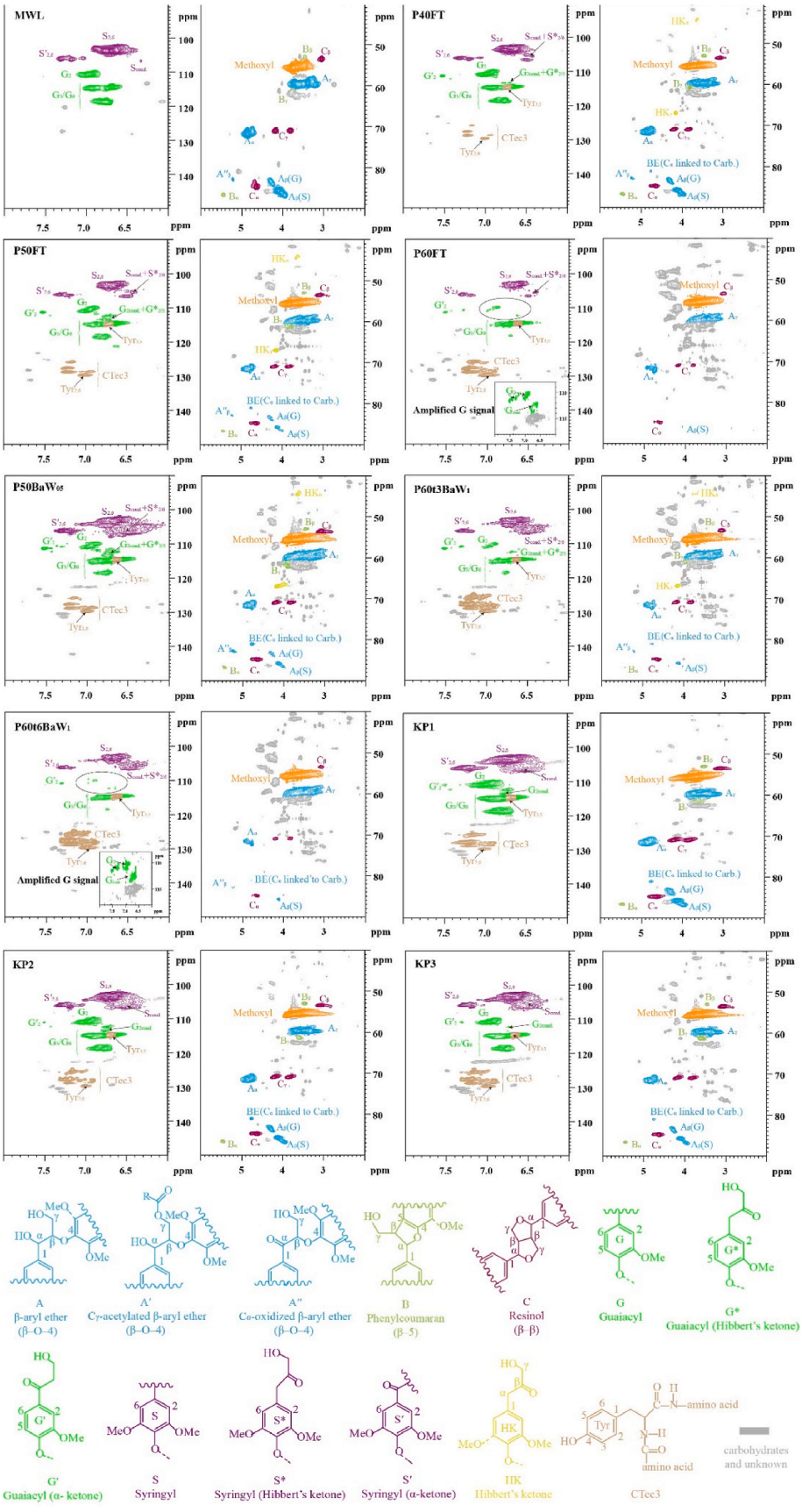

Fig. 2. The aromatic and aliphatic regions of CEL in 2D NMR spectra along with the structures.

Table 3
Semi-quantitative chemical structural data of CEL from 2D-HSQC spectra.

Sample	MWL	P40FT	P50FT	P60FT	P50BaW$_{0.5}$	P60t3BaW$_1$	P60t6BaW$_1$	KP1	KP2	KP3
Lignin content (%)		14.8	7.0	4.2	8.0	4.7	3.8	7.3	6.1	3.5
Units										
G	21.1	26.4	30.5	21.9	16.3	17.3	11.4	26.4	25.2	22.8
S	78.9	73.6	69.5	78.1	83.7	82.7	88.6	73.6	74.8	77.2
S/G	3.75	2.79	2.28	3.57	5.13	4.78	7.79	2.78	2.97	3.38
$G_{cond.}$/G	0	4.34	21.4	28.6	36.1	37.3	49.1	12.5	12.9	8.42
$S_{cond.}$/S	1.0	11.3	22.8	28.1	50.4	52.0	51.8	25.5	27.5	26.4
HK	0	1.07	2.52	0	1.07	2.16	0	0	0	0
Linkages										
β-O-4 (A)	64.4	48.1	32.1	20.4	14.4	9.60	8.64	33.6	31.6	27.7
β-5 (B)	7.03	3.06	2.19	0	0.99	0.83	0.00	2.21	2.31	1.64
β-β (C)	2.11	5.72	7.86	5.92	3.44	3.94	3.76	6.31	5.89	5.27
LCC										
BE	1.30	0.87	1.42	1.30	1.43	1.24	0.67	0.92	1.27	1.08
PhGlc	0.08	0.14	0.15	1.36	0.03	0.11	0	0	0	0
Est	0.10	0	0	1.12	0.22	0.10	0.18	0.18	0.23	0.34
Sum	1.48	1.01	1.57	3.77	1.68	1.46	0.85	1.10	1.50	1.42

the negative effect of lower NaOH dosage, but also improved the removal of reprecipitated lignin.

Oxygen delignification is controlled by three processes: (1) oxygen diffusion to the liquid/fiber interface, (2) oxygen mass transfer through the liquid film at the liquid/fiber interface on the fiber surface and within the fibers, and (3) oxygen reactivity with lignin (Sixta, 2006; Suess, 2010). Process (1) is rapid as gas diffusion is always fast. Process (3) is determined primarily by the extent of delignification and the reactivity of the residual lignin and hence, is substrate property dependent. Therefore, for a given fiber sample, process (2) is the rate controlling process restricted by oxygen solubility and film thickness. An increase in pulp fiber consistency decreases the thickness of the liquid boundary layer on fiber surface, allowing for accelerated oxygen transfer to the fiber. This effect of fiber solids loading on AHF and kraft pulp bleachability was directly verified, as can be noted from the KNs listed in Table 2. For example, when fiber consistency was increased from 10% to 12% and 20%, the KN of P60FT pulp decreased to 15.6, 14.8, and 4.1, respectively, after O bleaching from 23.0. Similarly, KN of KP3 pulp decreased to 8.2, 7.9, and 3.2, respectively, from 19.4. Today, industry oxygen delignification is predominantly conducted at medium consistency of 10–14% mainly due to difficulties in pumping pulp slurry (Sixta, 2006; Suess, 2010). This study demonstrated that a consistency of 20% in oxygen delignification is more efficient to overcome some substrate barriers to oxygen bleaching (such as reprecipitated lignin as discussed above and data in Table 2) (McDonough, 1983). The observed improvements at 20% consistency - lower NaOH dosage, improved removal of reprecipitated lignin and enhanced bleaching - would need to be balanced with the additional costs at the higher consistency.

3.3. Bleachability of residual lignin

To illustrate the effect of fiber substrate properties on oxidative delignification, results from bleaching kraft and AHF fibers of similar lignin content were compared. Greater bleachability of AHF fibers was observed with O and sequence bleaching. For example, kraft fiber sample KP1, with equivalent delignification (KN = 40) to AHF fiber samples P50Ba and P50BaW$_{05}$, showed a higher KN of 19 than approximately 15 for the two AHF samples after O bleaching, and a lower ISO brightness of 61.2% than 77.2% and 77.1% after sequence bleaching (Table 2). Similarly, kraft fibers KP3 with KN 20 also showed higher KN after O bleaching and lower ISO brightness after sequence bleaching than the AHF fiber sample P60t6BaW$_1$ (Table 2). Furthermore, kraft fiber sample KP2 starting with a slightly lower KN of 33 (discounted for HexA contribution) and a higher brightness of 27% than P50FT with KN of 39 and brightness of 16% showed lower brightness of 77% than 80% for P50FT after sequence bleaching (Table 2)

Because these observed differences in bleaching were from fiber samples with similar lignin content, we analyzed the chemical structure of lignin in the kraft and AHF fibers to seek possible explanation of the observed difference. It is generally understood that lignin chemical structure, or reactivity, in addition to lignin content is an important factor affecting bleaching (Gellerstedt and Al-Dajani, 2000; Gellerstedt et al., 1994).

Cellulosic enzymatic lignin (CELs) from AHF and kraft fiber samples (representing residual lignin in these fibers) and MWL of birch wood were analyzed by 2D NMR as shown in Fig. 2. Semi-quantitative results for predominant lignin substructures are listed in Table 3. Because native lignin contains abundant (up to 70% per 100 Ar units) and easy to cleave aryl ether β-O-4 linkages (β-O-4), this linkage content is considered a good indication of lignin reactivity (Galkin and Samec, 2016; Li et al., 2015; Rinaldi et al., 2016). Birch MWL was 64.4% β-O-4; CELs from kraft (KP1, KP2, and KP3), flow-through (P60FT), and batch (P50BaW$_{05}$, P60t3BaW$_1$, and P60t6BaW$_1$) fibers had 27.7–33.6%, 20.4% and 8.64–14.4% (Table 3) β-O-4, respectively, indicating that the residual lignin in the three kraft fiber samples was more reactive than the residual lignin in the AHF fibers. i.e., More of the reactive lignin was removed (solubilized) by AHF than by the kraft process.

Furthermore, condensed diphenylmethane structure of CELs formed during *p*-TsOH and kraft process were also calculated. Despite higher temperatures used in kraft pulping (160–165 °C) as compared to the AHF runs (90 °C), CELs from kraft fibers showed lower apparent condensed G and S ratios, $G_{cond.}/G$ = 8.42–12.9% and $S_{cond.}/S$ = 25.5–30.6%, than the corresponding CEL from P60FT fibers, 28.6% and 28.1%, and CELs from batch AHF fibers, 36.1–49.1% and 50.4–51.8% (Table 3). (Apparent because NMR HSQC will exhibit loss of signal assigned to G_{cond} & S_{cond} under severe conditions due to loss of C-H signal upon formation of new C-C bonds.) The condensed G and S ratios ($G_{cond.}/G$ and $S_{cond.}/S$) (Ma et al., 2021; Shimada et al., 1997) of MWL were only 0% and 1.0%, respectively (Table 3). It is known that lignin with a greater extent of condensation and less β-O-4 is more difficult to bleach (Froass et al., 1996b; Gellerstedt and Al-Dajani, 2000; Ma et al., 2020), however the residual lignin in AHF pulp (represented by CEL) had less β-O-4 and apparently a higher degree of condensation than CEL of a kraft pulp with the same KN, yet it was easier to bleach which suggests there are factors other than lignin content and lignin reactivity as represented by β-O-4 aryl ether linkages that significantly contributed to the observed differences in the bleachabilities of AHF and kraft fibers (Table 2).

LCCs can play an important role in limiting the efficiency of oxygen delignification (Sixta, 2006). However, the measured total LCCs (including benzyl ether (BE), phenyl glycoside (PhGlc) and γ-ester (Est) type LCCs) between AHF and the corresponding kraft fiber samples with

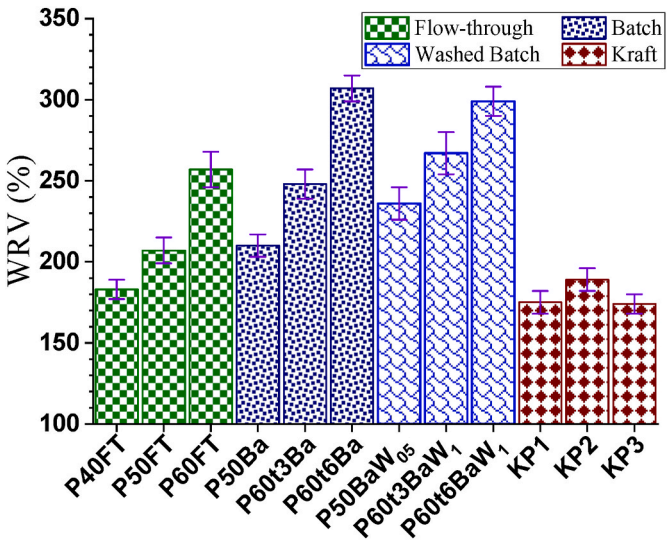

Fig. 3. Water retention values (WRVs) of AHF and kraft pulps.

similar KN (Table 3, Fig. S1) were indifferent, suggesting that the greater bleachability of AHF fibers was not due to a difference in total LCCs of CELs among batch, flow-through and kraft fiber samples (Table 3, Fig. S1).

3.4. Effect of hemicellulose removal and fiber porosity on bleachability

It is well known that hemicellulose removal can improve cellulose accessibility to cellulase to improve enzymatic digestibility of a lignocellulosic substrate (Grohmann et al., 1985; Leu and Zhu, 2013; Yang and Wyman, 2004; Zhu et al., 2012). It is, therefore, conceivable that the greater amount of xylan removal by AHF may provide improved accessibility of fiber's residual lignin to bleaching chemicals, which would explain why AHF fibers have better bleachability than kraft fibers with similar lignin content despite the kraft fiber lignin being more reactive (more β-O-4) and, apparently, less condensed. This is consistent with the known fact that fibers from sulfite pulping (typically have lower hemicellulose content) are easier to bleach than equivalent kraft fibers (Sixta, 2006). As shown in Table 1, AHF pulps have a much lower hemicellulose content (8.0–9.5%) than kraft pulp (17.2–18.4%).

Water retention value (WRV) measures a pulp fiber's accessibility to water and can be used as a measure of fiber porosity (pores greater than water molecule) or accessibility of fibers (or lignin) to bleaching chemicals (Gu et al., 2018; Luo and Zhu, 2011; Luo et al., 2011). As shown in Fig. 3 and Table S2, except for P40FT from a low severity AHF fractionation, AHF fibers had greater WRVs of 207–307% than kraft fibers of 165–205%. For example, using fibers of earlier comparisons between AHF and kraft fibers, WRVs of P50Ba and P50BaW$_{05}$ were 210% and 236%, respectively, significantly greater than 175% for KP1. In other words, the accessibility of both AHF fiber samples is greater than that of the kraft fiber and resulted in their better bleachability. Similarly, the same applies to the other two sets of comparison samples discussed earlier.

The effect of hemicellulose removal or fiber accessibility on bleaching can also be seen by comparing the two AHF fiber samples P50FT and P60t6Ba. As shown in Table 1, P50FT had a lower lignin content of 7.0% (KN = 38.5) and a greater hemicellulose content of 10.7% than 7.4% (KN = 40.9) and 8.0%, respectively, of P60t6Ba. After oxygen delignification at 20% consistency, P50FT had KN = 15.8, significantly higher than KN = 2.4 of P60t6Ba. After ODP sequence bleaching, P50FT had fiber brightness of 80% as compared to 90% for P60t6Ba (Table 2). That is, P60t6Ba had lower hemicellulose content (or greater hemicellulose removal during AHF) which improved fiber accessibility despite it having higher lignin content before oxygen delignification. The greater accessibility of P60t6Ba can be clearly seen from the WRVs of these two samples (Fig. 3), i.e., WRV = 307% for P60t6Ba compared with 207% for P50FT.

For producing fibers, other properties such as cellulose degree of polymerization (DP), fine content, fiber length, etc. are also important. Viscosities of the oxygen and sequence bleached AHF fibers were between 203 and 286 mL/g, significantly lower than kraft fibers 691–944 mL/g (Fig. 4A and Table S3), suggesting that the strong acid *p*-TsOH at high concentrations substantially depolymerized cellulose, as viscosity is an indirect measure of the degree of polymerization of cellulose chains in fibers. In addition to lower viscosity (lower DP), AHF fibers also had substantially shorter fiber length and greater fine content than the kraft fibers (Fig. 4B and C and Table S4), all of which improves lignin accessibility to bleaching chemicals.

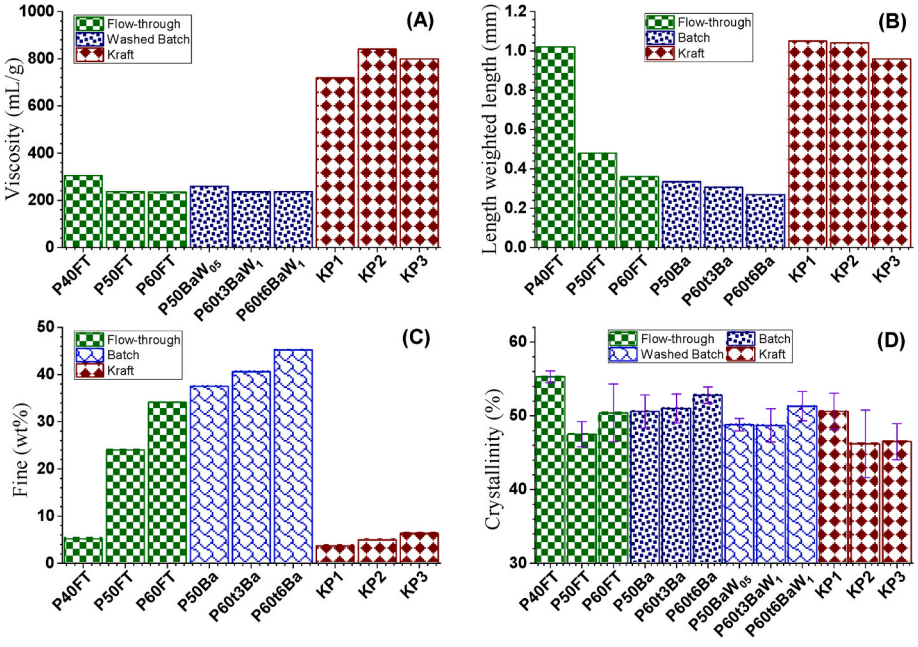

Fig. 4. Cellulose properties of *p*-TsOH and Kraft pulp, (A) viscosity, (B) length in weight, (C) fines in weight, and (D) crystallinity by Raman intensity at 380 cm^{-1}..

The mean fiber length of AHF sample P40FT from a low severity run of P40T90t20 was similar to those of the kraft fiber samples; increasing AHF severity to improve delignification resulted in significant reduction in fiber length, however no significant variation in crystallinity among the sequence bleached fibers was observed (Fig. 4D and Table S5) using Raman intensity at 380 cm^{-1} (Agarwal et al., 2010, 2018). This suggests that *p*-TsOH AHF does not as readily degrade cellulose - including its disordered regions - into simple sugars, despite its shorter fibers and lower DP. That is, *p*-TsOH as an hydrotrope is significantly different from mineral acids, which produce more crystalline fibers.

4. Conclusions

Wood fibers from acid hydrotropic fractionation (AHF) using toluenesulfonic (*p*-TsOH) showed greater bleachability than fibers from kraft pulping at the same kappa number under oxygen delignification at fiber consistency of 20%. The improved fiber accessibility through removal of hemicelluloses in AHF and the minimization of barriers for oxygen mass transfer in the water film on fiber surface by using high fiber consistency can overcome the decreased lignin reactivity, which is characterized by β-O-4 aryl ether linkages of the residual lignin, to improve oxidative delignification (bleaching). For oxidative delignification using gaseous chemicals, such as oxygen, mass transfer or lignin accessibility is more important than lignin reactivity for the extent of delignification studied in chemical pulping. The results from this study also have significance for biomass utilization through biorefinery using oxidative delignification.

CRediT authorship contribution statement

Qingzhi Ma: conducted all the fractionation bleaching experiments and drafted the manuscript, Writing – original draft. **Kolby Hirth:** conducted 2D NMR experiments along with data analyses, Data curation, Formal analysis, contributed to manuscript writing and revision, Writing – original draft. **Umesh P. Agarwal:** conducted Raman crystallinity measurements and data analyses, Data curation, Formal analysis. **J.Y. Zhu:** worked with Ma designed the research project and made major rewriting of the manuscript, Writing – original draft.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Zhu is a co-inventor of the *p*-TsOH 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.jclepro.2022.132351.

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