



Efficient separation of functional xylooligosaccharide, cellulose and lignin from poplar via thermal acetic acid/sodium acetate hydrolysis and subsequent kraft pulping

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ABSTRACT

Thermal acetic acid/sodium acetate hydrolysis (ASH) on poplar wood chips were carried out to obtain functional xylooligosaccharide, then the hydrolyzed wood chips were subjected to kraft pulping (KP) to fractionate cellulose and lignin. The separated three fractions were extensively characterized for further utilization in view of the integral biorefinery concept. The extraction efficiency of hemicelluloses by ASH strongly depends on the buffer ratio of the acetic acid/sodium acetate buffer solution. The ASH facilitated producing a high ratio of xylooligosaccharides with high molecular weight, while prevented further degradation of the saccharides, and simultaneously inhibited the condensation of lignin facilitating the subsequent kraft delignification. The obtained cellulose pulps had higher intrinsic viscosities as compared with the traditional autohydrolysis-KP process. Moreover, the ASH-KP process delivered a high purity of lignin with relatively high molecular weight. Therefore, the proposed integrated fractionation strategy is conducive to convert the lignocellulosic components into bio-based functional materials.

1. Introduction

The problem of greenhouse gas emissions and the emerging depletion of fossil reserves have led people to turn their attention to bio-renewable resources (Dong et al., 2020; Jahan et al., 2014; Kumar and Christopher, 2017). Lignocellulosic biomass, a renewable and abundant resource, is expected to become the major raw material for the production of chemicals, materials, and fuels following the biorefinery concept (Kleinert and Barth, 2008; Snelders et al., 2014; Wang et al., 2019). To utilize the available biomass as completely and efficiently as possible, the fractionation of raw material into their main macromolecular components, i.e. cellulose, hemicellulose and lignin, is prerequisite (Huijgen et al., 2012; Snelders et al., 2014). As cellulose is trapped in a hemicellulose-lignin matrix, it is of great significance to establish an effective, economical feasible and environmental fractionation process.

Traditionally, pulp and paper industry, the largest one to utilize the lignocellulosic biomass industrially on a large scale (Shi et al., 2019), mainly focused on the application of cellulose, while most of lignin and partial hemicelluloses (about 50 %) were dissolved into the waste liquor during pulping process (Chirat et al., 2012). Lignin fraction in the

waste liquor usually was employed in power generation, a route of low-added-value application. Hemicellulose degradation products, mainly a complex mixture of sugar acids, were difficult to separate and purify from the waste liquor (Mendes et al., 2011). Therefore, a more economical method for hemicelluloses utilization is to separate them prior to pulping process and convert them into high value-added products (Chen et al., 2010; López et al., 2014; Lu et al., 2012). Prehydrolysis can purposefully urge the conversion of hemicelluloses into xylooligosaccharides (XOS) which can be utilized in the field of pharmaceutical chemical, feed, and nutraceutical, achieving high value-added application (Wang et al., 2019). On the other hand, prehydrolysis can loosen the biomass structure, thus improving the accessibility of cooking agents to the lignocellulosic matrix during subsequent delignification process. The modification of the lignin structure and its rearrangement within the lignocellulosic matrix caused by prehydrolysis will affect the efficiency of subsequent delignification process (Vallejos et al., 2015). In addition, the removal of part of extractives and water-soluble ash minerals by prehydrolysis (Huijgen et al., 2012) can reduce the consumption of the cooking agents. Therefore, some integrated biorefinery technologies based on prehydrolysis and subsequent delignification have been proposed (Wen et al., 2013b; Zhu et al., 2015).

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Combination prehydrolysis with pulping is a promising protocol, in which the prehydrolysis aims to remove hemicelluloses while the subsequent pulping facilitates to obtain lignin and cellulose-rich residue (Wang et al., 2019; Zhang et al., 2018; Zhu et al., 2015). Wen et al. (2013b) successfully fractionated bamboo (*Phyllostachys pubescens*) into xylooligosaccharide, high-purity lignin and purified pulp using a three-step integrated process involving autohydrolysis, organic acids delignification, and alkaline hydrogen peroxide extended delignification. Wang et al. (2019) proposed an integrated process based on hydrothermal pretreatment and kraft delignification to deconstruct the lignocellulosic biomass. The hydrothermal pretreatment resulted in the partial cleavage of β -O-4 linkages in lignin and glycosidic bonds in hemicelluloses, facilitating the production of xylooligosaccharides, reducing the chemicals dosage of the following delignification, and benefiting the subsequent bleaching process. The investigation of López et al. (2014) revealed that autohydrolysis of eucalyptus wood facilitated carrying out soda-anthraquinone pulping under milder operating conditions. Thus, the properties of the soda-anthraquinone cellulose pulp and paper from the autohydrolyzed eucalyptus wood were good as or even better than those obtained from the unhydrolyzed wood (Loaiza et al., 2016; López et al., 2014). However, it was found that autohydrolysis reduced the lignin yield of organosolv delignification due to the formation of pseudo-lignin and lignin recondensation during autohydrolysis (Huijgen et al., 2012). Additionally, part of the hemicelluloses would be seriously degraded into monosaccharides and further degraded products such as formic acid, acetic acid, and furfural under harsh autohydrolysis conditions (Leschinsky et al., 2009; Liu et al., 2013), which were difficult to collect for application (Wang et al., 2019) and would complicate the downstream processes. Therefore, the ideal prehydrolysis process of the lignocellulosic biomass should provide high efficient extraction of hemicellulose, while avoiding or keeping minimum degradation of hemicelluloses and condensation of lignin.

It is the hydronium ion derived from water autoionization along with acetic acid came from splitting of acetyl group in hemicellulose that facilitates the breakage of glycosidic bonds in hemicellulose to produce mono- and oligosaccharides during prehydrolysis (Garrote et al., 1999). High level of hydrogen ions will accelerate the hydrolysis of hemicelluloses and secondary degradation of the dissolved sugars under severe conditions. Meanwhile, the depolymerization and recondensation of lignin as well as the formation of pseudo-lignin are also dependent on hydrogen ion concentration in the prehydrolysis system (Chen et al., 2010). Maintaining the hydrogen ion concentration within an appropriate range is an effective strategy to control the degradation reaction of hemicelluloses and reduce the recondensation of lignin (Weil et al., 1998). Li and Gellerstedt (2008) modified the autohydrolysis reaction and pH value by adding either 2-naphthol or NaOH. Compared to the plain hot-water extraction process, less acidolysis and fewer lignin-lignin condensation reactions took place for the modified autohydrolysis process. Weil et al. (1998) developed a base addition profile to help control the pH of the prehydrolysis system in order to reduce any acid-catalytic degradation and the formation of monosaccharides degradation products. Increasing the end pH of the extract system slightly by adding small amounts of NaHCO_3 could inhibit hydrolytic cleavage of both polysaccharide chains and acetyl groups, consequently obtaining more galactoglucomannans (GGMs) with higher molar mass (Song et al., 2011a). Buffer solution that possesses the pH buffering ability (Liu and Maroto-Valer, 2012) is a promising option to mitigate the degradation of carbohydrates and the recondensation of lignin. Control the pH of the hot-water extraction of spruce wood by phthalate buffer solutions, the yield of GGM was as high as the extraction with plain water, while much less lower-molar-mass compounds derived from hemicelluloses existed in the control system (Song et al., 2011b). Extraction with phthalate solution efficiently inhibited the hydrolysis of hemicelluloses and deacetylation of GGM.

The prehydrolysis-kraft process is currently regarded as the most environmentally friendly and industrially scalable route to produce dissolving pulp, the high-purity cellulose pulp (Borrega et al., 2013; Dong et al., 2020; Leschinsky et al., 2009). It is the most compatible and easily industrialized process for integrating a pulp mill into a forest biorefinery, where high value-added products derived from hemicellulose and lignin can be produced in addition to the cellulose pulp (Kumar and Christopher, 2017; Martín-Sampedro et al., 2014). Recently, many researches have been performed to develop the integrated fractionation processes for the conversion and utilization of all the components in the lignocellulosic biomass. However, these researches mainly focused on the quality of obtained cellulose pulps (Dong et al., 2020; Loaiza et al., 2016; López et al., 2014; Martín-Sampedro et al., 2014), the characteristics of the lignin and hemicellulose fractions were rarely discussed. Additionally, the way the chemical components remained in the prehydrolysis stage affecting the reaction behavior of the residual solids in the subsequent fractionation stage has not been completely understood. Acetic acid (HAc) came from the splitting of the labile acetyl groups in hemicellulose side is a main source of H^+ and the buffer solution of acetic acid/sodium acetate (HAc-NaAc) has buffering ability to maintain the solution pH within the range of 3.76–5.76. In this study, a thermal HAc-NaAc hydrolysis (ASH) process was proposed to replace the autohydrolysis step applied in the traditional kraft-based dissolving pulp process in order to maintain the hydrogen ion concentration within an appropriate range for controlling the degradation reaction of hemicelluloses and reducing the condensation of lignin. The separation efficiency of xylooligosaccharide, cellulose pulp and lignin by the proposed ASH-KP integrated fractionation process was evaluated and the influence of buffer ratio of the HAc-NaAc buffer solution on the reaction behavior of the main chemical components was investigated. Moreover, the obtained fractions were characterized thoroughly in order to determine further application potential of the different fractions.

2. Materials and methods

2.1. Materials

Poplar tree (*populus* \times *euramericana* cv. “Neva”) of six-year old was harvested from Shandong province, East China. The outer and inner layers of bark were peeled off and the stem was chopped into small pieces. The wood chips with 15 mm (thickness) \times 25 mm (width) \times 25 mm (length) were collected, air-dried and stored in a hermetic polypropylene bag before use. The chips was mainly composed of 44.94 % glucose, 13.88 % xylose, 0.49 % arabinose, 1.18 % galactose, 3.16 % mannose, 18.23 % Kalsol lignin, and 5.54 % acid soluble lignin, determined by a two-step acid hydrolysis and subsequent sugar and lignin analysis (Hong et al., 2013; Sluiter et al., 2012). The moisture and extractives of the chips were 4.53 % and 3.02 % determined by Tappi T264 om-88 and Tappi T204 cm-07, respectively. The standard sugars were purchased from Sinopharm Chemical Reagent Co., Ltd., China and Aladdin Inc., Shanghai, China. Other chemicals and reagents used in the experiments, such as acetic acid (HAc), sodium acetate (NaAc), sodium sulphide, and sodium hydroxide, were of analytical grade.

2.2. Methods

2.2.1. Thermal HAc-NaAc hydrolysis of poplar wood chips

Thermal HAc-NaAc hydrolysis (ASH) of the poplar wood chips was carried out in a level rotary digester (JL632-4, KKK, Tokyo, Japan) by varying buffer ratio (molar ratio of NaAc to HAc) of the buffer solution. According to previous experiments, the rest of the variables was fixed at: 400 g of dry wood chips, liquor/solid ratio of 6:1 (w/w), HAc-NaAc concentration of 0.15 mol/L, maximum temperature (T_{max}) of 170 °C, time up to T_{max} of 60 min, time at T_{max} of 60 min. After the hydrolysis were completed, the reactant was immediately cooled down to room

temperature by submerging the digester into water. Then the hydrolyzed wood chips and hydrolysate was separated and stored for later use or analysis.

2.2.2. Analysis of the hydrolysates

The hydrolysates were analyzed for their pH and the content of monosaccharides, oligosaccharides, sugar degradation products, and lignin. The total sugars in the hydrolysates were measured by ion chromatography based on the post-hydrolysis of the hydrolysates with 4 wt% H₂SO₄ at 121 °C for 1 h. The contents of the oligosaccharides were expressed as the increase of the monosaccharides in the hydrolysates before and after acid hydrolysis (Shi et al., 2019). The contents of monosaccharides were determined using a Dionex ICS-5000 ion chromatography system (Thermo Fisher Scientific, MA, USA) equipped with a CarboPac™PA20 column (150 × 3 mm), an ED40 electrochemical detector, and an AS50 autosampler. The column was maintained at 30 °C. 96 % pure water and 4% 50 mmol/L NaOH were used as the eluents at a flow rate of 0.4 mL/min.

The degradation products in the hydrolysates such as furfural, 5-HMF (5-Hydroxymethylfurfural), and *p*-hydroxybenzoic acid (PHBA), were determined using high performance liquid chromatography (HPLC) (Snelders et al., 2014). The HPLC system (LC-20A, Shimadzu Corp., Tokyo, Japan) was equipped with a UV-vis detector at 280 nm and an organic acid analysis column (300 × 7.8 mm). The column was maintained at 60 °C and 5 mmol/L H₂SO₄ was used as the eluent at a flow rate of 0.6 mL/min. All samples were analyzed repeatedly and recorded on average.

The molecular weight of oligosaccharides was analyzed by gel permeation chromatography (GPC) (Song et al., 2011b). The hydrolysate was centrifuged at 8000 r/min for 3 min and the supernatant was filtered by a 0.2 μm filter. Then the M_w , M_n and molecular weight distribution (M_w/M_n) of the oligosaccharides in the filtered supernatant was analyzed using a GPC system (LC-20AD, Shimadzu Corp., Tokyo, Japan) equipped with a RID-20A differential refractometer and a Phenomenex μm 500 Å LC column (300 × 7.8 mm) at 30 °C with pure water as eluent (1.0 mL/min).

Lignin and lignin-related substances in the hydrolysates were measured by UV absorption at 205 nm using deionized water as a reference, after dilution with the deionized water until the absorbance values were in the range of 0.2–0.7 (GB/T-10337-1989).

2.2.3. Kraft pulping of the hydrolyzed wood chips

The kraft pulping of the hydrolyzed and un-hydrolyzed poplar wood chips (comparison group) was carried out in a rotary six-pot digester (2201-6, Green Wood Instruments, LLC, Andover, Massachusetts USA) using a fixed process conditions: 50 g of dry wood chips, solid/liquid ratio of 1: 5 (w/w), 16–18 % active alkali (calculated as Na₂O) and 20 % sulfidity, heating rate of 1.25 °C/min, maximum temperature of 170 °C, 90 min to the maximum temperature and 90 min at the maximum temperature. Once the reaction completed, the residual solids were separated from the black liquors by filtration. The black liquors were filtered with a 200-mesh sieve and sealed in reagent bottles for later use. The densities of the black liquors were determined by measuring the weight of the black liquors in a known volume. Total dissolved solids (TDS) of the black liquors were determined by using the method TAPPI T264cm-97. The residual alkali content of the black liquors was determined by automatic titration according to SCAN-N 33:94.

The residual solids, i.e. cellulose fractions, were named as cellulose pulps AH-CP, ASH₁-CP, ASH₂₁-CP, ASH₃-CP, ASH₄₁-CP, and ASH₅-CP, respectively, according to the corresponding hydrolysis conditions in Table 1. As a reference, the cellulose pulp obtained from the un-hydrolyzed poplar wood chips was named as CP₀. After being washed with distilled water to neutral, the cellulose pulps were placed in sealed bags for later analysis. The pulp yields were determined gravimetrically after oven drying to constant weight.

Table 1

Main chemical compositions and their contents in the hydrolysates after thermal HAC-NaAc hydrolysis (ASH) or autohydrolysis (AH) of poplar at 170 °C for 60 min.

Samples	AH	ASH ₁	ASH ₂₁	ASH ₃	ASH ₄₁	ASH ₅
Buffer ratio	–	0.03	0.1	0.3	1.0	3.0
HAC-NaAc mol/L	0	0.15	0.15	0.15	0.15	0.15
Initial pH	6.35	3.2	3.8	4.2	4.76	5.2
Terminal pH	3.51	3.57	3.53	3.67	3.89	4.58
Residue chip yield %	83.90	85.30	83.66	84.32	86.83	89.52
Monosaccharide g/L	5.60	5.95	3.25	1.77	0.54	0.15
Arabinose	0.33	0.25	0.20	0.10	0.04	0.01
Galactose	0.52	0.61	0.34	0.22	0.09	0.03
Glucose	1.10	1.12	0.80	0.44	0.18	0.07
Xylose	3.42	3.72	1.80	0.93	0.19	0.02
Mannan	0.23	0.25	0.11	0.08	0.04	0.02
Oligosaccharide g/L	10.84	8.16	9.08	8.73	7.94	5.45
Arabinan	–	–	–	0.02	0.09	0.01
Galactan	0.49	0.25	0.46	0.40	0.46	0.35
Glucan	1.73	1.52	1.45	1.37	1.10	0.79
Xylan	7.95	6.18	6.90	6.75	6.19	4.13
Mannan	0.67	0.21	0.27	0.21	0.19	0.18
M_w g/mol	1327	1362	2106	3011	5042	6869
Furfural g/L	0.77	0.82	0.61	0.59	0.44	0.37
5-HMF g/L	0.21	0.23	0.19	0.16	0.10	0.06
Acid soluble lignin g/L	3.78	4.20	3.92	4.31	4.71	4.26

2.2.4. Analysis of the cellulose pulps

Kappa numbers, ISO whiteness and intrinsic viscosities of the cellulose pulps were measured according to Tappi T236, Tappi T525, and SCAN15:62 method, respectively. The main components of the cellulose pulps were determined according to NREL's Laboratory Analytical Procedure (Sluiter et al., 2012).

2.2.5. Separation, purification and characterisation of lignin

The black liquors, 25 mL of each one, were first submitted to lignin precipitation by adding 72 % H₂SO₄ to pH = 2 and subsequent water addition (water/liquor = 9:1, v/v). Then the mixture were centrifuged, and the sediments (kraft lignins) were separated from the liquid phases. After being centrifugation washed with water to pH = 7.0, the obtained kraft lignins were dried and quantified gravimetrically. The results were expressed as gram of precipitate in liter of black liquor [g/L] (Alekhina et al., 2015). The obtained kraft lignins were named as AH-KL, ASH₁-KL, ASH₂₁-KL, ASH₃-KL, ASH₄₁-KL, ASH₅-KL, and KL₀, respectively, corresponding to the cellulose pulps.

The FT IR spectra of the recovered KLS were obtained on a spectrophotometer (ALPHA-T, Bruker Co., Ltd., Karlsruhe, Germany) using the KBr pellet technique (Wang et al., 2016). Each spectrum was recorded over 16 scans, in the frequency range from 4000 to 500 cm⁻¹, with a resolution of 0.4 cm⁻¹.

For two-dimensional ¹H-¹³C NMR (2D HSQC) analysis, 60 mg of KLS was placed into a 5-mm NMR tube and dissolved in 0.5 mL of DMSO-d₆ (Wen et al., 2013a). The 2D HSQC NMR spectra of the KLS were recorded on an AVANCE II 400 spectrometer (Bruker, Karlsruhe, Germany) using a standard Bruker HSQC pulse sequence, "hsqcetpsi2". Relative inter-unit linkage levels in the KLS were estimated semi-quantitatively using volume integration of contours in the 2D HSQC NMR spectra, and the well-resolved α-carbon contours were used for volume integration for β-O-4, resinol (β-β), and phenylcoumarane (β-5) linkages (Wang et al., 2016).

The lignin was first acetylated with acetic anhydride (Wang et al., 2016). Molecular weight distribution and average molecular weight of the acetylated lignin were determined by GPC analysis carried out on a GPC waters system (Waters e2695, USA), using a 2489UV-Vis detector (280 nm), three 300 mm × 7.8 mm Phenol 5U columns (10000, 500, and 50 Å, respectively), and a 50 mm × 7.8 mm Phenogel 5U guard column (Phenomenex, Torrance, CA) coupled in series with THF as following phase (1.0 mL/min) at 30 °C.

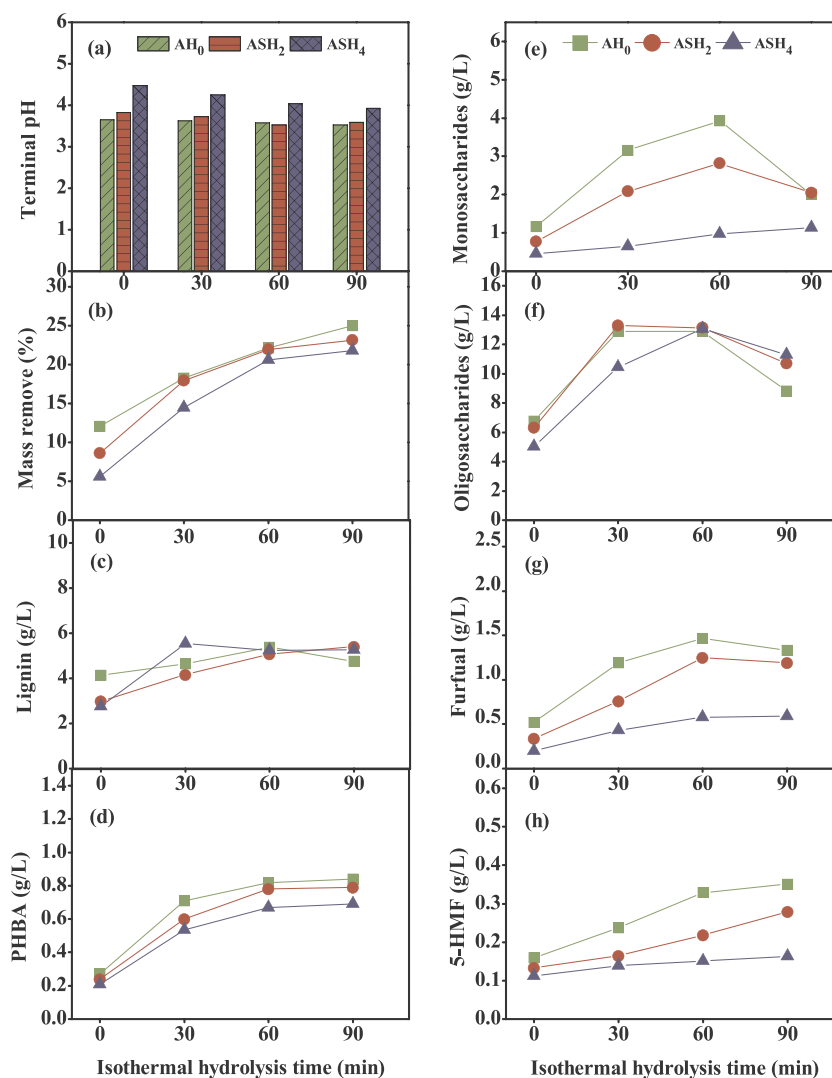


Fig. 1. Variation of mass removal and main substances in the hydrolysates with duration during the thermal HAC-NaAc hydrolysis (ASH₂, buffer ratio = 0.1; ASH₄, buffer ratio = 1.0) and autohydrolysis (AH₀) at 175 °C.

3. Results and discussion

The thermal HAC-NaAc hydrolysis (ASH) section of the integrated fractionation process expects to remove the hemicelluloses from the poplar wood chips, which is similar to the prehydrolysis step applied in the traditional kraft-based dissolving pulp process. The hemicellulose-depleted wood chips are then subjected to kraft pulping (KP) for separating cellulose and lignin. Special attention is paid to the influence of buffer ratio of the HAC-NaAc buffer solution on fractionation efficiency of the integrated process.

3.1. Extraction efficiency of xylooligosaccharide by ASH process

The change trend of solution pH during hydrolysis of poplar wood chips is shown in Fig. 1(a). For the autohydrolysis (AH₀) system, i.e. thermal hydrolysis with plain water, the pH value dropped rapidly from 6.35 to 3.65 in the process of heating up to $T_{max} = 175$ °C. Then the solution pH slowly decreased to 3.53 during the isothermal hydrolysis stage. The hydronium ions generated via water autoionization along with the HAC subsequently generated from the cleavage of the acetyl groups in hemicelluloses side were responsible for the pH decrease (Lu et al., 2012; Song et al., 2011b). In addition, some of uronic acids liberated into the solution by hydrolytic depolymerisation of hemicelluloses and pectins also contributed to the generation of hydronium

ions (Dong et al., 2020; Garrote et al., 1999). For the HAC-NaAc buffer solution system, the solution pH decreased gradually during the ASH process. The terminal pH of the ASH hydrolysates was higher than that of the AH₀ process. As the conjugate base of HAC, the NaAc can accept the protons of carboxylic acid, mainly HAC, maintaining the hydrogen ion concentration within a certain range. Moreover, the buffering ability of the HAC-NaAc buffer solution to resist pH change depends on the buffer ratio. Therefore, the solution pH of the ASH system with buffer ratio of 1.0 (ASH₄) was higher than that with buffer ratio of 0.1 (ASH₂).

The tendency of mass removal along with extending isothermal hydrolysis time is shown in Fig. 1(b). A more rapid release of wood components into the hydrolysate occurred at the heating up stage for AH₀ than ASH, which was consistent with the change of solution pH. The ASH resulted in a slightly lower mass removal compared to the AH₀ process at the same isothermal hydrolysis time. When the poplar wood chips was hydrolyzed by HAC-NaAc buffer solution at 175 °C for 90 min, about 22.5 % of the total mass was removed. Table 1 showed that the main substances released into the hydrolysates were hemicellulose-derived sugars that existed in the form of both monosaccharides (mainly xylose) and oligosaccharides (mainly xylan). During the ASH process of poplar wood chips, the H⁺ generated by the dissociation of HAC combines with water to form hydronium ion H₃O⁺. The H₃O⁺ can rapidly protonize the oxygen atom of glycosidic bond in carbohydrates,

weakening the bond energy and causing the glycosidic bond broken and depolymerizing the carbohydrates into oligomers or monomers. Fig. 1(e–h) showed that the oligosaccharides in the hydrolysates rapidly generated during the first stage of both the ASH and AH₀ process. The contents of mono- and oligosaccharides as well as furfural, the acid-catalyzed dehydration products of pentoses, reached maximum at isothermal hydrolysis time of 60 min, and thereafter decreased. The decline of the mono- and oligosaccharides content at isothermal hydrolysis time of 90 min was due to the further hydrolytic depolymerisation of these sugars (Song et al., 2011b). In addition, the content of 5-hydroxymethylfurfural (5-HMF), the dehydration products of hexoses, increased gradually with the isothermal hydrolysis time. Compared with the AH₀, the generation rate of monosaccharides and sugar-decomposition products in the ASH system was significantly low, indicated that the pH level was a key parameter governing the overall proton-catalyzed hydrolysis process of wood components and then influences the main characteristics of extracted substances (Song et al., 2011a).

Table 1 showed that after autohydrolysis of the poplar wood chips at 170 °C for 60 min (AH), the content of xylan in the hydrolysates was 7.95 g/L, which proportion in total sugars was 48.36 %. For the ASH process, the extraction efficiency of hemicelluloses strongly depends on the buffer ratio of HAc-NaAc buffer solution. Increasing the proportion of NaAc in the buffer solution decreased the yields of both total sugars as well as xylan. The xylan yields of the ASH processes were slightly lower than that of the AH system. However, when the initial pH were controlled at 3.8, 4.2, 4.76, and 5.2 by the HAc-NaAc buffer solutions, the proportion of xylan in total sugars was 55.96 %, 64.29 %, 73.0 %, and 73.75 %, respectively, much higher than that of the AH system. Meanwhile, the amounts of sugar-decomposition products (furfural and 5-HMF) in the ASH hydrolysates were less than that in the AH system, which was due to the lower degradation level of monosaccharides under higher pH condition. Furthermore, a clear effect of hydrogen ion concentration on the molecular weight of oligosaccharides was observed in Table 1. Compared with the AH, the molecular weights of oligosaccharides released from the ASH process were significantly high, and conducting the ASH at high buffer ratio favored the production of high-molecular weight oligosaccharides as well as less monosaccharides and sugar-decomposition products. The gradual increase of molecular weight of oligosaccharides along with the increase of pH was consistent with the increase in proportion of xylan in total sugars. Additionally, increasing buffer ratio from 0.03 to 3.0 resulted in reducing significantly the degradation of cellulose as suggested by the low content of glucan and 5-HMF in the hydrolysates. Hydrolysis of glycosidic bonds in carbohydrates involve hydronium-catalyzed reactions (Borrega et al., 2011). All of the above results indicated that HAc-NaAc buffer solution could stabilize the concentration of hydrogen ions in the hydrolysis system, regulating the intensity of hydrolysis and ensuring the released hemicelluloses mainly in the form of xylooligosaccharide (XOS).

The increased proportion of xylan in total sugars was exceptional when the buffer ratio was 0.03 (initial pH = 3.2, sample ASH₁), in which the yield of xylan as well as total oligosaccharides decreased while the furfural and 5-HMF increased. Moreover, the molecular weight of oligosaccharide obtained at pH = 3.2 was much lower than those obtained from other ASH system. When the initial pH of ASH system is beyond the buffer range of pH = 3.76–5.76, there is not enough NaAc to accept the protons of HAc. The HAc-NaAc buffer solution lost its buffering ability to resist pH change. The severe acidic conditions (higher hydrogen ion concentration) enhanced the hydrolysis of hemicelluloses and promoted the further degradation of dissolved mono- and oligosaccharides, reducing xylan yield as well as the molecular weight of oligosaccharides. Meanwhile, the severe acidic conditions promoted the recondensation of dissolved lignin and the formation of pseudo-lignin which redeposited onto the surface of wood chips (Leschinsky et al., 2008), leading to a higher residue chip yield of ASH₁ than ASH₂₁ (Table 1). It is well accepted that the potentiality of isolated

XOS for industrial applications mostly requires the XOS being extracted in high yield along with high molecular weight (Borrega et al., 2011). However, when the poplar wood chips was hydrolyzed by ASH at buffer ratio of 3.0 (sample ASH₅, pH = 5.2), the xylan content in the hydrolysate reduced dramatically to 4.13 g/L, although the oligosaccharides had the highest molecular weight. This was due to the high concentration of NaAc keeping the hydrogen ion concentration at a lower level, slowing down the hydrolysis rate of glycosidic bonds in hemicelluloses. Moreover, the content of furfural and 5-HMF in the hydrolysate declined significantly, suggesting that the further conversion of sugars into furfural or 5-HMF was inhibited. Therefore, ASH conducted at buffer ratio of 0.1–1.0 (initial pH = 3.8–4.76) is recommended for producing high proportion of XOS with appropriate molecular weight and less secondary degradation products.

The ASH is an efficient process to extract most hemicelluloses from the wood chips obtaining XOS, meanwhile a partial lignin and volatile extractives are released from the lignocellulosic matrix. Fig. 1(c) and Table 1 showed that approximately 3 % of original lignin (based on the wood chips) was removed from the wood chips matrix during the ASH process. Ester and ether bonds in the lignin structure are easy to be attacked by hydrogen ions to form hydroxyl group or carbonyl group (Li and Gellerstedt, 2008), enhancing the removal of lignin from the lignocellulosic matrix. In addition, lignin which crosslinked with hemicelluloses by ester bonds is easily removed from the polysaccharide matrix by breaking these bonds (Garrote et al., 1999), causing the lignin fragments released into the hydrolysate. Compared with the AH system, the lignin contents in the hydrolysates of the ASH systems were slightly high, whereas the contents of p-hydroxybenzoic acid (PHBA) were low. And that the release of lignin into the hydrolysates slightly increased as the buffer ratio increased. This may be the fact that more NaAc increased the amount of lignin in the form of soluble sodium phenolates, which enhanced the hydrophilicity of lignin and made it easier to dissolve into the hydrolysate. As shown in Fig. 1(c, d), the amounts of both the lignin and PHBA released into the hydrolysate increased with extending the isothermal hydrolysis time. However, the lignin content in the hydrolysate decreased after the isothermal hydrolysis time exceeded 60 min particularly for the AH system, which was due to the further degradation of dissolved lignin as well as the redeposition of lignin on the wood chips surface (Leschinsky et al., 2008).

3.2. Separation cellulose from hydrolyzed chips by kraft pulping

After ASH, the hydrolyzed poplar wood chips were fractionated into cellulose pulps and black liquors containing lignin, sugars and degradation products by subsequent kraft pulping process. Table 2 gives the kraft pulping conditions of the hemicelluloses-depleted chips together with the yields, Kappa numbers and brightness of the cellulose fractions. The kraft pulping produced an extensive delignification of all of the wood chips due to the cleavage of the α - and β -aryl ether bonds in the lignin structure, followed by its fragmentation and dissolution (Alekhina et al., 2015), liberating lignin from the cellulose fraction. At the same time, most of hemicelluloses were effectively removed during the pulping process (Wang et al., 2019), giving a yield of approximately 48 % to the resulting cellulose pulps. When compared the hydrolyzed wood chips (by both ASH and AH) with un-hydrolyzed one, the active alkali needed to obtain a similar target Kappa number was much low. Removing hemicelluloses early by ASH or AH decreased the consumption of cooking reagents. (Martín-Sampedro et al., 2014). Moreover, the partially removal of lignin and cleavage of lignin-carbohydrate bonds (LCC) during hydrolysis process also contributed to the reduction in reagent consumption. Additionally, the formation of new phenolic hydroxyl groups in the residual lignin during hydrolysis process (Wang et al., 2016) was beneficial to the fragmentation and removal of lignin, because the phenolic α -ether linkage in the lignin can be broken, whereas the non-phenolic α -ether linkage cannot cleave

Table 2

Data obtained from the kraft pulping of the hydrolyzed and un-hydrolyzed poplar wood chips: the conditions of cooking, yields, impurity contents, and characteristics of the resulting cellulose pulps (CPs).

Cellulose pulps	AH-CP	ASH ₁ -CP	ASH ₂₁ -CP	ASH ₃ -CP	ASH ₄₁ -CP	ASH ₅ -CP	CP ₀
Active alkali %	15.10	15.35	15.06	15.18	15.63	16.12	18.0
Sulfidity %	20	20	20	20	20	20	20
Residual alkali %	1.61	1.21	1.24	1.80	2.78	3.18	5.61
Yield %	47.0	47.3	48.5	46.6	48.4	47.8	49.0
Kappa number	8.77	10.0	8.74	8.01	10.59	9.47	10.58
Brightness % ISO	32.7	30.6	32.4	33.5	31.7	32.0	32.4
Intrinsic viscosity cm ³ /g	873	919	942	974	1101	1156	1030
Glucan %	87.08	79.19	79.49	80.09	77.47	76.30	56.15
Xylan %	0.37	2.11	2.79	2.78	5.31	7.72	17.19
Mannan %	–	1.15	0.91	0.99	1.22	1.24	1.24
Acid soluble lignin %	1.87	1.63	1.65	1.43	1.84	2.00	3.02
Acid insoluble lignin %	3.49	5.18	4.33	4.78	4.51	4.92	5.89

during the kraft pulping. The enhanced delignification probably also attributed to higher available of lignin to the attack of the cooking reagents. As the mass transport of cooking chemicals into the wood chips may influence the overall kinetics in the initial part of the cooking and the delignification is governed by solubility and/or mass transport of lignin molecules occurring at the cell wall level (Mattsson et al., 2017), it is reasonable to assume that the increased porosities of wood chips caused by ASH or AH is conducive to the dissolution of lignin. Thus, ASH prior to kraft pulping demonstrated favorable effect on delignification. However, it should be noted that ASH of the poplar wood chips at pH = 3.2 (buffer ratio of 0.03) caused the cellulose pulp to have a higher residual lignin content (6.81 g/L). Condensation reactions of lignin extensively conducted at severe acidic conditions of hydrolysis, partially leading to the lower delignification and higher Kappa numbers of the cellulose pulps. The results was consistent with the brightness of the ASH₁-CP which was low compared with other cellulose pulps. As shown in Table 2, the yields of kraft pulping resulting from the hydrolyzed wood chips were slightly lower than that obtained from the un-hydrolyzed one. Apparently, this is mainly because most of hemicelluloses and some of lignin in the wood chips have been extracted by ASH or AH prior to the kraft pulping (Lu et al., 2012).

To assess the potential of the delignified, cellulose rich solid residue for valuable applications in view of the integral biorefinery concept, detailed properties of the cellulose pulps such as chemical composition and intrinsic viscosity were analysed. Table 2 showed that the resulting cellulose pulps were enriched in glucan compared to the raw material (56.15–87.08 % vs 44.94 %) due to most of hemicelluloses and lignin were effectively removed by the hydrolysis and subsequent kraft pulping process (Wang et al., 2019). However, some of hemicelluloses and lignin were still present in the cellulose pulps. The residual xylan, mannan, and lignin in the cellulose pulp CP₀ were 17.19 %, 1.24 %, and 8.91 %, respectively, indicating that they were hard to degrade and remove completely by the kraft pulping. The xylan contents of the cellulose pulps obtained from the hydrolyzed wood chips were much lower than that of the CP₀, indicating that the overall hemicellulose removal was obviously higher when ASH or AH was included. This was main due to most of hemicelluloses have been removed during the ASH or AH process. Another reason was that the remaining hemicelluloses in the hydrolyzed wood chips might be more susceptible to alkaline peeling (Chirat et al., 2012), thus decreasing the content of hemicelluloses in the obtained cellulose pulps. Moreover, the amount of xylan and mannan in the ASH-CPs decreased with decreasing the buffer ratio of the HAc-NaAc hydrolysis system, which was consistent with the hemicelluloses removal in Table 1. The high content of glucan and low contents of hemicelluloses and residual lignin in the obtained cellulose pulps will be beneficial to produce cellulose-based functional materials.

The AH had adverse effect on the intrinsic viscosity of cellulose pulp (873 for AH-CP vs 1030 for CP₀). Cellulose depolymerization occurred in the AH process (Table 1) in turn led to its significant degradation

during subsequent kraft pulping owing to peeling reactions. On the other hand, the removal of hemicelluloses and other components by hydrolysis may improve the accessibility of cellulose to the cooking reagents, resulting in the degradation of cellulose. However, in comparison with the AH-CP, the ASH-CPs showed higher intrinsic viscosities. In fact, the intrinsic viscosities of the cellulose pulps increased with increasing the buffer ratio of the HAc-NaAc buffer solution. This result agreed with the change trends of glucan and HMF found in Table 1.

3.3. Recovery of lignin and its properties

After the kraft pulping process, the black liquors resulting from the ASH- and AH-hydrolyzed poplar wood chips exhibited lower total dissolved solids (TDS) compared to that from the un-hydrolyzed ones (Table 3). For the hydrolyzed wood chips, most of hemicelluloses have been already extracted by the ASH or AH process, so their further degradation and dissolution into the black liquors was limited. As shown in Table 3, approximately 30–38 % of the dissolved substances in the black liquors could be recovered as lignin fractions by selective acid precipitation. The yields of the isolated lignins from the ASH- and AH-hydrolyzed wood chips were higher than that from the un-hydrolyzed ones. Furthermore, slightly lower yields of lignins were obtained from the ASH-hydrolyzed wood chips than from the AH-hydrolyzed ones, in spite of the TDS of the corresponding black liquors showed no obvious difference. Additionally, the lignin yield slightly decreased with increasing the buffer ratio of the ASH system, which was consistent with the gradually reduced delignification as suggested by the Kappa number and residual lignin content of the corresponding cellulose pulp (Table 2). It should be pointed out that the ASH₁-KL had the highest recovery yield, which might attribute to its highest molecular weight (2995 g/mol), because larger lignin molecule had a lower degree of solubility (Mattsson et al., 2017).

Table 3 showed that only minor amount of carbohydrate impurities (mostly hemicelluloses) was found in the fractionated KLs, indicating that the recovered lignins had relatively high purity. The main sugar bonded to the KLs was xylan. Other sugars were also present in the lignins, where glucose, galactose and arabinan were in minor amount, while mannose was in trace amount. This could be explained by the fact that hemicelluloses could precipitate together with the lignin due to their lower solubility in acidic conditions (Martín-Sampedro et al., 2019). In addition, the presence of the lignin-carbohydrate covalent associations (LCC) in the KLs was another source of the carbohydrate impurities. As expected, an increase in sugar content with increasing buffer ratio of the ASH systems was observed. Performing ASH at lower buffer ratio resulted in more intensive hydrolysis of lignin-carbohydrate bonds led to low carbohydrate impurities in the isolated lignin after kraft pulping.

The weight-average molecular weights (M_w) and the polydispersity

Table 3

Yields, sugar contents and structural properties of the kraft lignins (KLs) recovered from the black liquors (BLs) of the kraft pulping.

Lignins	MWL	AH-KL	ASH ₁ -KL	ASH ₂₁ -KL	ASH ₃ -KL	ASH ₄₁ -KL	ASH ₅ -KL	KL ₀
TDS of BL %		14.96	14.63	14.79	14.61	14.37	14.81	15.49
Yield g/L		54.60	58.99	52.54	47.08	45.18	42.97	40.38
Arabinose ‰		0.035	0.033	0.019	0.018	0.022	0.030	0.018
Galactose ‰		0.065	0.054	0.063	0.125	0.123	0.193	0.235
Glucose ‰		0.195	0.084	0.111	0.211	0.254	0.154	0.419
Xylose ‰		0.600	0.317	0.616	1.087	1.060	1.833	1.987
Mannan ‰		0.038	–	–	–	–	–	–
<i>M_w</i> g/mol	5854	2052	2995	2486	2454	2448	2346	1342
<i>M_w</i> / <i>M_n</i>	1.55	2.37	2.13	2.55	2.40	2.47	2.31	2.19
β-O-4 ^a	40.20	6.25	6.32	7.55	5.26	6.33	6.42	5.41
β-β ^a	3.67	2.50	2.53	3.14	2.63	2.53	3.16	3.38
β-5 ^a	4.91	1.25	1.26	1.16	1.31	1.27	1.38	0.68
-OCH ₃ ^b	62	36	29	31	30	34	34	32
CD ^c	0.77	1.79	1.81	1.62	1.45	1.38	1.36	1.56

^a Results expressed per 100 Ar based on quantitative 2D HSQC NMR.^b Quantification is based on the assumption that the aromatic region of the ¹³C NMR spectra (δ 101.5 to 162 ppm) contains 600 aromatic carbon atoms; results expressed per 100 Ar.^c Degree of condensation (CD) = (C-substituted aromatic C + O-substituted aromatic C) / H-substituted aromatic C.

(*M_w*/*M_n*) of the isolated KLs was analyzed by GPC. The cleavage of α-O-4 and β-O-4 linkages led to formation of lower molecular weight lignins that dissolved into the black liquors (Alekhina et al., 2015). As compared with the KL₀, the *M_w* and polydispersities of both the ASH-KLs and AH-KL were obviously high due to the condensation reactions of lignin occurred under acidic hydrolysis conditions. In spite of this, the formation of condensed structures during the hydrolysis had no significant effect on the delignification, which confirmed that the hydrolysis facilitated subsequent kraft pulping of hardwood by increasing the cleavage of the phenolic α-ether linkage, the solubility of lignin and the mass transport of lignin molecules (Lu et al., 2012; Mattsson et al., 2017). Nevertheless, the significantly higher *M_w* of the ASH₁-KL and the higher Kappa number of the ASH₁-KP indicated that the stable covalent C–C bonds formed by severe condensation of lignin could not depolymerize during the kraft pulping process.

For a better understanding of the structural features of the isolated lignins, FT IR and 2D HSQC NMR spectroscopy analysis were performed and the inter-unit linkages in the lignins were estimated. Fig. 2 shows the FT IR spectra (fingerprint regions) of the KLs. The vibration bands of functional groups associated with the lignin structure were found in the FT IR spectra as follows, which displayed typical hardwood lignin patterns: 1714 cm⁻¹, unconjugated β-ketone carbonyl groups resulted from the breakage of the β-O-4 linkages or conjugated/unconjugated carboxyl acid (Martín-Sampedro et al., 2019; Wang et al., 2016); 1615, 1514, and 1423 cm⁻¹, aromatic ring vibrations of the phenylpropane skeleton; 1461 cm⁻¹, C–H deformation and bending of methoxyl;

1326 cm⁻¹, aromatic ring breathing vibration of S units; 1273 and 1216 cm⁻¹, aromatic ring breathing vibration of G units; 1116 cm⁻¹ and 1054 cm⁻¹, aromatic in-plane bending (C–H bond deformation) of S and G units, respectively (Martín-Sampedro et al., 2019); 913 cm⁻¹ and 832 cm⁻¹, C–H out of plane bending in positions 2, 5 and 6 of G units and in positions 2 and 6 of S units, respectively. The similar absorption bands observed in the FT IR spectra of the ASH-KLs, AH-KL and KL₀ demonstrated that pre-extraction hemicelluloses from the lignocellulosic matrix by thermal HAc-NaAc hydrolysis had no effect on the structures of the kraft lignins.

2D HSQC NMR spectra of the poplar MWL, KL₀, AH-KL and ASH₂₁-KL were compared in Fig. 3, displaying two regions corresponding to the side-chain region and aromatic region of the lignin structures (Martín-Sampedro et al., 2019; Yuan et al., 2011). In the aromatic region, the HSQC spectra showed the aromatic rings of the different lignin units: C_{2,6}-H_{2,6} correlation of S units at δ_C/δ_H 103.9/6.58 ppm (S_{2,6}); C_{2,6}-H_{2,6} correlation of C_α oxidized S units at δ_C/δ_H 106.1/7.21 ppm (S_{2,6}′); C₂-H₂ correlation of G units at δ_C/δ_H 110.7/6.97 ppm (G₂); C₅-H₅ correlation of G units at δ_C/δ_H 114.8/6.73 ppm (G₅); C₆-H₆ correlation of G units at δ_C/δ_H 119.0/6.79 ppm (G₆); C_{2,6}-H_{2,6} correlation of hydroxybenzoate substructures at δ_C/δ_H 131.4/7.62 ppm (PB_{2,6}). The intensified signals at δ_C/δ_H 106.1/7.21 ppm (S_{2,6}′) together with the newly appeared signals at δ_C/δ_H 111.3/7.48 ppm, δ_C/δ_H 115.5/7.43 ppm and δ_C/δ_H 119.6/7.55 ppm (C_α oxidized G units, G′) in the HSQC spectra of KL₀, AH-KL and ASH₂₁-KL confirmed the cleavage of the alkyl-aryl ether linkages and the formation C_α ketone in the KLs. Additionally, the signals of PB_{2,6} still existed in the KLs, implying that the *p*-hydroxybenzoate substructures were relatively stable during the kraft pulping process.

The aliphatic side-chain region exhibited the cross-signals of methoxyl groups (-OCH₃, δ_C/δ_H 55.7/3.24 ppm) and the different inter-unit linkages of lignins: β-O-4 (A), C_α-H_α at δ_C/δ_H 71.9/4.81 ppm, C_β-H_β at δ_C/δ_H 83.8/4.32 and 86.2/4.03 ppm, C_γ-H_γ at δ_C/δ_H 59.7/3.44 ppm; β-β (B), C_α-H_α at δ_C/δ_H 84.8/4.67 ppm, C_β-H_β at δ_C/δ_H 53.3/3.02 ppm, C_γ-H_γ at δ_C/δ_H 70.7/3.80 and 71.4/4.16 ppm; β-5 (C), C_α-H_α at δ_C/δ_H 86.5/5.43 ppm, C_β-H_β at δ_C/δ_H 52.8/3.45 ppm, C_γ-H_γ at δ_C/δ_H 62.4/3.71 ppm; β-1 (D), C_β-H_β at δ_C/δ_H 59.7/2.77 ppm, and I (*p*-hydroxycinnamyl alcohol end groups), C_γ-H_γ at δ_C/δ_H 61.8/4.3 ppm. Signals corresponding to carbohydrate impurities were found at δ_C/δ_H 63.2/3.30 ppm (C₅-H₅) in the spectra, being particularly noticeable for the poplar MWL, which also showed cross-signals at δ_C/δ_H 72.9/2.89 ppm (C₂-H₂), δ_C/δ_H 73.5/3.14 ppm (C₃-H₃) and δ_C/δ_H 76.1/3.52 ppm (C₄-H₄). The weakness of these signals attributed to the C₂-H₂, C₃-H₃ and C₄-H₄ of xylose (Yuan et al., 2011) in the spectra of the ASH₂₁-KL and AH-KL was in accord with their lower sugar contents

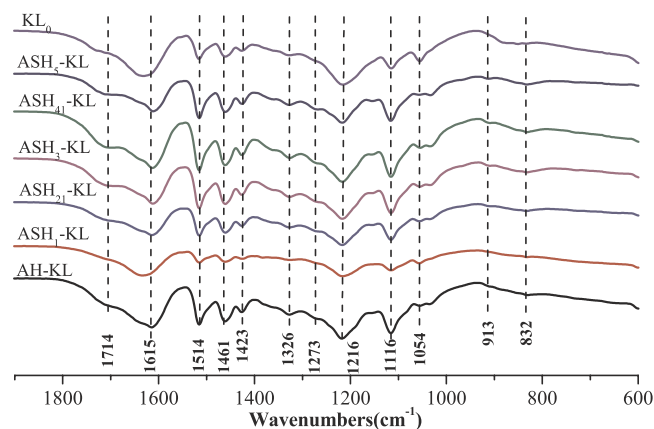


Fig. 2. The FT IR spectra (1800–600 cm⁻¹) of the kraft lignins (KLs) recovered from the black liquors of the kraft pulping.

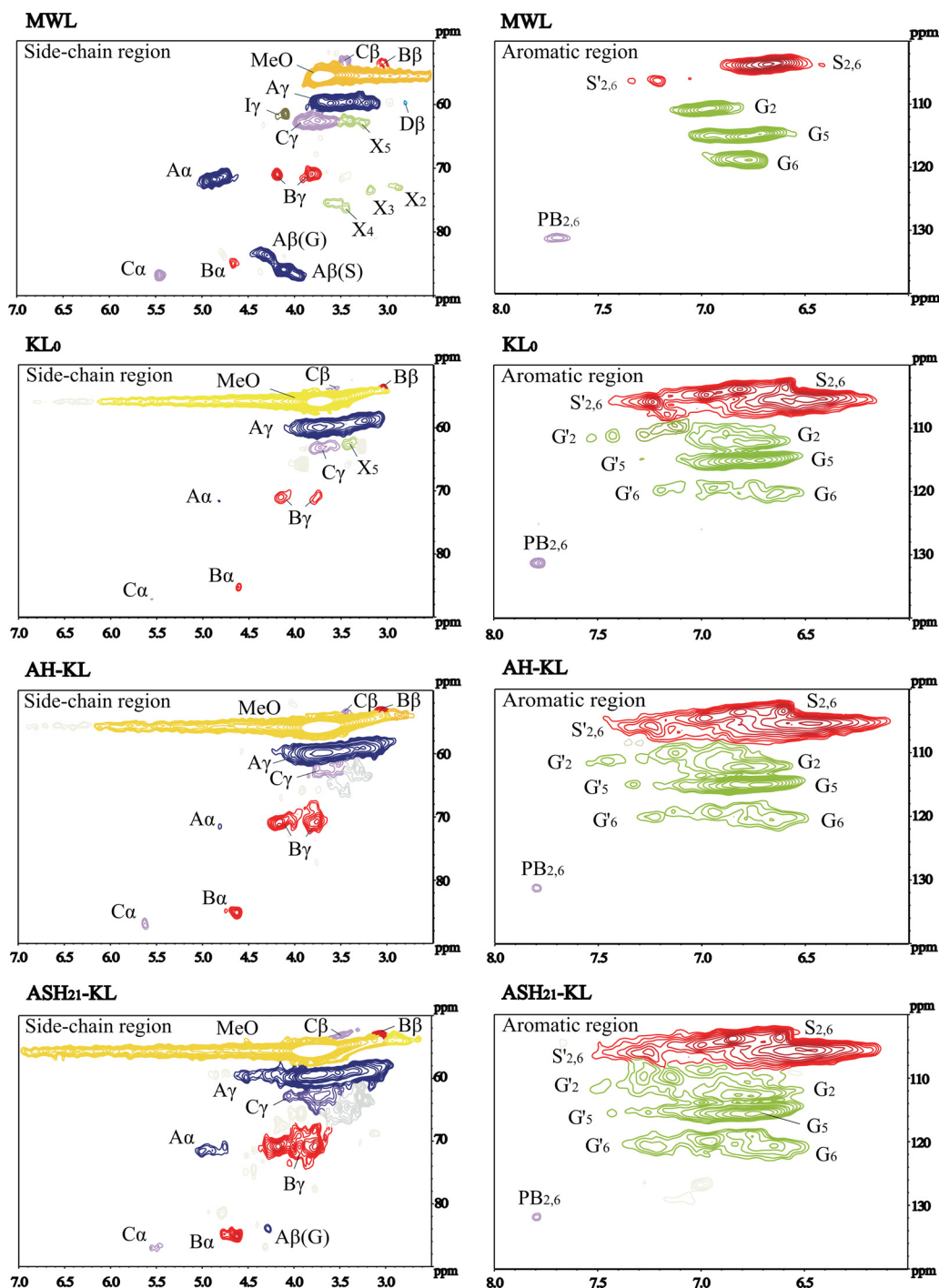


Fig. 3. 2D HSQC NMR spectra, δ_C/δ_H 50.0-90.0/2.5-7.0 ppm side-chain region (left column) and δ_C/δ_H 100.0-140.0/6.0-8.0 ppm aromatic region (right column) of the poplar MWL (Milled Wood Lignin) and kraft lignins (KLs) (A, β -O-4 aryl ether linkages; B, resinol substructures formed by β - β , α -O- γ , and γ -O- α linkages; C, phenylcoumarane substructures formed by β -5 and α -O-4 linkages; D, spirodienone substructures formed by β -1 and α -O- α linkages; I, *p*-hydroxycinnamyl alcohol end groups; S, syringyl units; S', oxidized syringyl units with a C α ketone; G, guaiacyl units; G' oxidized guaiacyl units with a C α -ketone; PB, *p*-hydroxybenzoate substructures.

showed in Table 3.

Compared to the poplar MWL, the contents of β -O-4 substructures in the KL₀, ASH-KLs and AH-KL were rather low, revealing an extensive cleavage of β -O-4 linkages during the kraft pulping process (Martín-Sampedro et al., 2019). The β -5 linkages in the poplar lignin was also significantly disrupted during the pulping process. However, the $-\text{OCH}_3$ groups and β - β linkages were still relatively abundant in all of the recovered lignins, revealing that $-\text{OCH}_3$ groups and C-C bonds were more resistant to the kraft pulping. It should be noted that the contents of β -5 linkages were slightly higher in both the ASH-KLs and AH-KL than that in the KL₀. This phenomenon may attributed to the formation of new β -5 linkages accompanying with the cleavage of β -O-4 linkages during the ASH-and AH- hydrolysis process (Wang et al.,

2016, 2019). Even so, all of the recovered kraft lignins exhibited similar structural features. Table 3 also showed that the condensation degrees of the recovered lignins were significantly higher than that of the poplar MWL. And the condensation degrees of the ASH-KLs slightly decreased with increasing the buffer ratio of ASH system, implying that HAC-NaAc buffered solution could inhibit the condensation reaction of lignin occurred under severe hydrolysis conditions.

4. Conclusions

Two-step consecutive treatment, ASH and KP, is an effectively integrated strategy to fractionate the main lignocellulosic components for further utilization. Performing ASH at buffer ratio of 0.1-1.0 extracts

satisfied amount of xylooligosaccharide with relatively high molecular weight, while results in less secondary degradation byproducts. The ASH facilitates the kraft delignification by inhibiting the condensation of lignin as well as improving its phenolic hydroxyl group and solubility. The separated cellulose pulp has high intrinsic viscosity, high glucan content and low contents of hemicellulose and lignin, which is beneficial to producing cellulose-based functional material. The recovered lignin ASH-KL exhibits similar purity and molecular structure but higher molecular weight compared with the AH-KL.

CRedit authorship contribution statement

Xiaohui Guo: Investigation, Writing - original draft. **Yingjuan Fu:** Conceptualization, Methodology, Validation, Supervision. **Fawei Miao:** Formal analysis, Data curation. **Quanshui Yu:** Visualization. **Na Liu:** Writing - review & editing. **Fengshan Zhang:** Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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