Degradation and Redeposition of the Chemical Components of Aspen Wood during Hot Water Extraction

Haiyan Chen,[a] Yingjuan Fu,[a,*] Zhaojiang Wang,[a] and Menghua Qin [a,b,*]

Hot water extraction (HWE) prior to pulping of wood is a promising method in constructing a platform for traditional pulping or for biorefinery processing. In this study, HWE of aspen wood at a maximum reaction temperature ($T_{reaction}$) between 140 and 180 ºC was investigated to obtain an optimal extraction condition for wood-derived products. The effect of extraction temperature and reaction time on the extraction performance of the chemical constituents was evaluated, and the degradation and redeposition of lignin and carbohydrates during the HWE process were assessed. Results showed that a minimum $T_{reaction}$ of 160 ºC was necessary for satisfactory carbohydrate removal. The dissolution and readsorption of sugars reached a balance, such that no more sugars in pre-extraction liquor (PEL) were adsorbed on the wood surface under more severe extraction conditions. The reduction of sugars dissolved in PEL should result from the formation of furfural or its derivatives. At the final extraction stage, the dissolved lignin in PEL could redeposit on the exothecium rather than the endothecium of the wood chips.

Keywords: Hot water extraction; Degradation; Carbohydrate; Lignin; Redeposition; Biorefinery

Contact information: a: Key Laboratory of Pulp & Paper Science and Technology of the Ministry of Education, Qilu University of Technology, Jinan 250353, Shandong, China; b: Organic Chemistry Laboratory, Taishan University, Taian 271021, Shandong, China;
** Corresponding authors: fyingjuan@163.com; qmh@qlu.edu.cn*

INTRODUCTION

Environmental and economic concerns have led to a great amount of research in renewable sources to replace fossil fuels. The use of lignocellulosic materials to produce valuable biofuels and biochemicals, the so-called biorefinery, is attracting increasing attention because of its strategic significance in recent years (Kamm *et al*. 2009). One of the biggest challenges of converting woody biomass into biofuels is to depolymerize its structural polysaccharides into fermentable monosaccharides (Chen *et al*. 2010). Steam explosion, dilute acid pretreatment, ammonia pretreatment, and hot water extraction are effective separation methods (Mosier *et al*. 2005). Hot water extraction is presently receiving considerable attention, since it does not use harmful compounds, and therefore it reduces the need for neutralization and expensive construction materials (Ormsby *et al*. 2012). However, the effectiveness of the hot water extraction between hardwood and softwood is different. The higher amount of acetyl groups bound to the hemicelluloses, better delignification efficiency, and lower tendency of lignin condensation make hardwood more suitable to hot water extraction than softwood (Sixta 2006).

The main constituents of hardwood are cellulose (40 to 55%), hemicellulose (24 to 40%), and lignin (18 to 25%) (Sun and Cheng 2002). Structurally, cellulose consists of glucose molecules ($C_6H_{12}O_6$) that are connected end to end linearly as a polymer through

1-O-4 β-glycosidic bonds (Liu 2010). Hemicelluloses are shorter than cellulose and have a low degree of polymerization, with 150 to 200 monomer units. Hemicellulose molecules contain branches and include a variety of monosaccharides (arabinose, galactose, glucose, xylose, mannose, *etc.*) (Kumar *et al.* 2009). Due to the presence of crystalline regions, a high degree of polymerization, and linear configuration, cellulose has a higher thermal stability than hemicellulose (Borrega *et al*. 2011a). Lignin, an amorphous polymer composed of monolignols, is a three-dimensional macromolecule with a carbon to oxygen atom ratio higher than 2:1. Therefore, lignin is a more energy-rich substance than sugars, of which the carbon to oxygen ratio is nearly 1:1 (Liu 2010).

Due to the structural dissimilarity, the extraction efficiency of lignin and carbohydrate is different under varied parameters. There have been many studies about the influence of hot water extraction on the degradation of carbohydrates. According to Chirat *et al.* (2012), it was possible to extract significant quantities of xylose and xylose oligomers from hardwood chips. Moreover, the tougher the conditions of pre-extraction, the higher the xylose proportion of monomers released. Borrega *et al.* (2011a) reported that the main carbohydrate in birch wood was degraded rapidly during the first stage of the extraction process, but thereafter its degradation was reduced when the temperature of the hot water extraction was between 180 ºC and 240 ºC.

Hot water extraction (HWE) is a weak acid extraction, and the formation of acidic conditions can promote the extraction of the carbohydrates (Borrega *et al.* 2011a; Vila *et al.* 2011). The acidic environment originates from the deacetylation of the hemicelluloses during HWE (Garrote *et al.* 2001). It was found that lignin condensation happened during HWE, and the possible reason of lignin condensation came from the acidic environment (Leschinsky *et al.* 2008). Moreover, the degradation of lignin increased along with the condensation reaction, and the degradation of lignin is much faster than its condensation at increasing extraction temperature and time (Borrega *et al*. 2011b). At the same time, sugar-degradation products such as furfural and hydroxymethyl furfural also have an influence on the condensation of lignin. Chua and Wayman (1979) observed an obvious condensation of lignin during HWE of the aspen wood, and they attributed this phenomenon to the reaction between lignin aromatic rings (with high charge density at C_6), furfural, and hydroxymethyl furfural. In addition, the redeposition of dissolved lignin occurred along with increasing the extraction conditions (Mašura 1987). Besides, research of aspen HWE showed that pseudo-lignin, broadly defined as aromatic material, was produced from dilute acid pretreated hemicellulose and cellulose (Hu *et al.* 2012). Because the HWE is an acidic extraction without addition of any external acid, it is possible that pseudo-lignin is generated during the HWE process. The pseudo-lignin may contribute to the lignin deposition, and partial lignin deposition may have a relationship with carbohydrates. The degradation and readsorption of the chemical constituents is very important to the subsequent pulping. However, information about the redeposition performance of lignin-derived phenolic compounds during the extraction process is quite limited. One research effort in sugar maple discovered that vanillin, syringaldehyde, *p*-hydroxybenzoic acid, and guaiacol did exist in the pre-extraction liquor (PEL) (Goundalkar *et al.* 2010). They are phenolic compounds of guaiacyl (G), syringyl (S), and *p*-hydroxy phenyl (H), and the change of their content reflects the redeposition of lignin. This degraded lignin in PEL can be separated, purified, and made into daily supplies. For example, vanillin (Rødsrud *et al.* 2012) can be processed into spices added to toilet soap, perfume, and food seasoning. *P*-hydroxybenzoic acid can be modified into fine chemical products such as corrosion

remover and sterilizing agent. Syringaldehyde can be changed into an edible essence, and guaiacol is a fine chemical intermediate applied to medicine and the compound of dyestuff and spice. Therefore, it is meaningful to seek the optimal HWE condition in order to acquire the maximum of phenolic compounds in PEL.

This work concentrated on the investigation of the degradation of carbohydrates and lignin of the aspen wood during HWE under various conditions. The possible lignin deposition was also evaluated. Furthermore, by determination of degradation products from both lignin and carbohydrates, a detailed response profile was provided for a better understanding of the HWE process.

EXPERIMENTAL

Materials

Raw materials and chemicals

Aspen wood (a mixture of *Populus* × *euramericana* 'Guariento' and *Populus* × *euramericana* 'Neva') chips were obtained from Huatai Group Corp. Ltd., China. The wood chips were about 2.0 to 3.5 cm long, 1.2 to 2.0 cm wide, and 0.5 cm thick. After washing and drying, the clean aspen wood was kept in sealed bags in a freezer at -25 ºC. The contents of holocellulose, pentosan, ash, and wax in the aspen wood were analyzed according to the Chinese National Standards GB/T 2677.10 (1995), GB/T 12032 (1989) and GB/T 2677.9 (1994), GB/T 2677.3 (1993), and GB/T 2677.6 (1994), respectively. The content of lignin was measured according to the method described by Sluiter *et al.* (2007). Analysis of the acetyl content was performed as described by Chen *et al* (2010). The results are shown in Table 1.

Methanol (CH_3OH), phosphoric acid (H_3PO_4), and sodium hydroxide (NaOH) were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd., China. Standard samples of arabinose, galactose, glucose, xylose, mannose, acetic acid, and furfural were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Standard samples of the phenolic lignin such as vanillin, p-hydroxybenzoic acid, syringaldehyde, and guaiacol were purchased from Shanghai Zhanyun Chemical Co., Ltd., China.

Table 1. Composition of the Aspen Wood (mean ± standard deviation)

Component	Holo-cellulose	Pentosan	Acid Insoluble Lignin	Acid Soluble Lignin	Acetyl	Ash	Wax
Content (g kg^{-1} dry wood)	781.3±6.0	219.6±4.0	237.3±2.3	21.1±0.2	23.6±1.2	17.0±0.3	6.3±1.1

Methods

Hot water extraction

Hot water extraction was an acidic extraction without addition of any external acid. The pre-extraction step was performed in an electrically heated oil bath containing four bombs. The quantity of aspen wood chips used for each experiment was 30 g (as oven dried weight). The solid to liquor ratio (S:L) was set at 1:6. About 55 min of time was needed to reach the desired maximum temperature ($T_{reaction}$). The HWE were conducted at various

$T_{reaction}$ and reaction time to investigate the degradation of carbohydrate and lignin. The $T_{reaction}$ are 140 ºC, 150 ºC, 160 ºC, 170 ºC, and 180 ºC. At each value of $T_{reaction}$, the reaction times were 0 min, 30 min, 60 min, and 90 min, respectively. At the end of the treatment, When the HWE test was completed and extraction vessels cooled down to 75 ºC to 77 ºC, solids and liquids were separated and collected for further analysis.

Determination of residue composition in aspen wood

To analyze the composition of aspen wood residue after HWE, the wood residue was air-dried and milled using a Wiley Mill. Then the fractions with 40 to 60 mesh of aspen wood residue were collected, and the contents of holocellulose, pentosan, and lignin were determined, respectively. Determination of holocellulose was performed according to the standard method of GB/T 2677.10 (1995), and determination of pentosan was performed using the standard methods of GB/T 12032 (1989) and GB/T 2677.9 (1994). For lignin content measurement, the lignocellulose material was subjected to a two-step acid hydrolysis. The content of lignin was measured according to the method described by Sluiter *et al.* (2007).

HPLC analysis of the phenolic compounds

Phenolic compounds in the PEL were analyzed with a Shimadzu Prominence LC-20A HPLC system with a CTO-20A column oven and a LC-20AT pump, which was controlled by Shimadzu LC-solution software (Shimadzu International Trading (Shanghai) Co., China). High performance liquid chromatography (HPLC) was conducted using a Symmetry C18 column (5.0 μm, 4.6 mm × 250 mm) from Waters Corp. (Milford, MA, USA). The injector and column temperature was set at 35 ºC, and the injection volume was 20 μL. The mobile phases consisted of 40% CH_3OH (solvent A) and 60% H_3PO_4 (0.1% v/v, solvent B). The phenolic compounds were detected with a diode array detector at 210 nm and were identified and quantified by comparison with the retention times and the peaking area of standard samples.

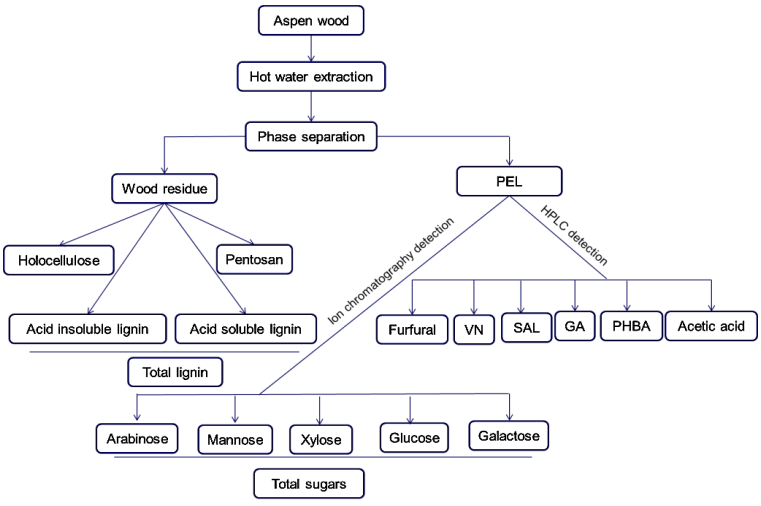

Fig. 1. The scheme of the main experimental procedure. HWE conditions: $T_{reaction}$ was from 140 ºC to 180 ºC, heat-up time to $T_{reaction}$ is 55 min, total reaction time after 55 min heat-up time at $T_{reaction}$ was from 0 min to 90 min, liquor to wood ratio is 6:1; VN, vanillin; SAL, syringaldehyde; GA, guaiacol ; PHBA, *p*-hydroxybenzoic acid

Analysis of the sugars in PEL

Oligo-saccharides in the PEL were converted to mono-saccharides by acid hydrolysis with 4% (g/g) H_2SO_4 at 121 ºC for 1.0 h. The mono-saccharide was then determined by an ion chromatography ICS-5000 system (Thermo Fisher Scientific, MA, USA) with a pulsed amperometric detector (PAD), which was controlled by Chromeleon 7.0 SR1 software. A CarboPac^{TM} PA20 (3 × 150 mm) coupled with a guard column (Dionex, CA, USA) was used. The column temperature was 30 ºC, and the detector temperature was 25 ºC. The injection volume was 20 µL, and the operating pressure was about 2600 to 3000 psi. The mobile phases consisted of 20% 10 mmol/L NaOH and 80% ultrapure water, and the flow velocity was 0.5 mL/min. Sugars were identified and quantified by comparison with the retention times and the peaking area of the standard samples. Each sample was analyzed at least twice.

Surface SEM analysis of the aspen wood chips

The surface of the aspen wood chip without HWE, and both the exothecium and the endothecium of the wood residue extracted at 170 ºC for 90 min were analyzed by scanning electron microscopy, environmental mode (ESEM; Quanta 200, FEI, Netherlands) at an accelerating voltage of 20 kV. The wood chips were cut into about 0.5 to 0.6 cm long, 0.5 cm wide and 0.2 cm thick. After freeze drying for 48 h, the specimens were fixed on the base plate and then sprayed gold coating.

RESULTS AND DISCUSSION

The Change of the Constituents in Aspen Wood Chips

The chemical compositions of the solid fractions and PEL after HWE were analyzed according to the experimental procedure shown in Fig. 1. The $T_{reaction}$ applied to the HWE experiments ranged from 140 ºC to 180 ºC, and the reaction time at $T_{reaction}$ was from 0 min to 90 min. The component yields were compared in order to evaluate the influence of pre-extraction conditions on the composition of the wood residue. As shown in Fig. 2, the yield of the lignocellulose as well as the contents of pentosan and holocellulose in the aspen wood residue decreased along with increasing $T_{reaction}$. When $T_{reaction}$ was higher than 160 ºC, the removal of these components had a rapid tendency. Therefore, a minimum $T_{reaction}$ of 160 ºC was necessary for a satisfactory hemicelluloses removal (Fig. 2b). Moreover, prolonging the reaction time at $T_{reaction}$ (≥30 min) could also further reduce the contents of hemicelluloses in the wood residue.

As shown in Fig. 3, the lignin contents of the aspen wood residue generally decreased with increasing $T_{reaction}$ and reaction time during HWE. A $T_{reaction}$ lower than 150 ºC could hardly extract lignin components from the wood. Increasing $T_{reaction}$ to 170 ºC, the HWE could extract about 20% of lignin from the wood in 60 min. Higher temperature could not obtain more lignin extracted. In contrast, more lignin was found to be present in the wood residue, probably due to the readsorption and redeposition of the dissolved lignin on the wood fiber surface at higher temperature and longer extraction time.

It could be seen clearly from Figs. 2 and 3 that the extracted lignin and carbohydrates had a different behavior in readsorption and redeposition during the final extraction stage. Despite probable readsorption of the dissolved carbohydrates (Mašura 1987), the rate of the readsorption and dissolution of carbohydrates should almost be equal.

However, more severe conditions, especially at the final extraction stage, could lead to the readsorption or redeposition of more lignin. Moreover, the increment of the total lignin in wood residues under the violent HWE conditions mainly came from the acid-insoluble lignin rather than the acid-soluble portion. One reason could be that the water-soluble phenolic compounds, mainly acid insoluble lignin, were condensed to undissolvable material under the severe conditions (Kemppainen *et al.* 2012).

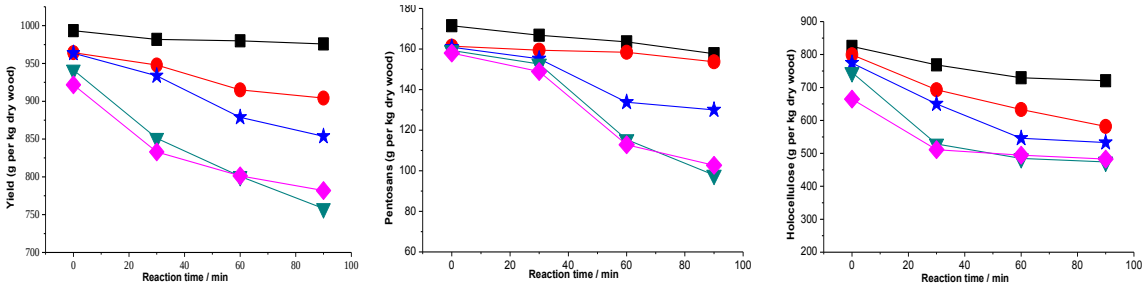

Fig. 2. Effect of the $T_{reaction}$/reaction time of the HWE on the (a) lignocellulose yield, (b) pentosan contents, and (c) holocellulose contents of the aspen wood residue (-■- 140 ºC, -●- 150 ºC, -★- 160 ºC, -▼- 170 ºC, -◆- 180 ºC)

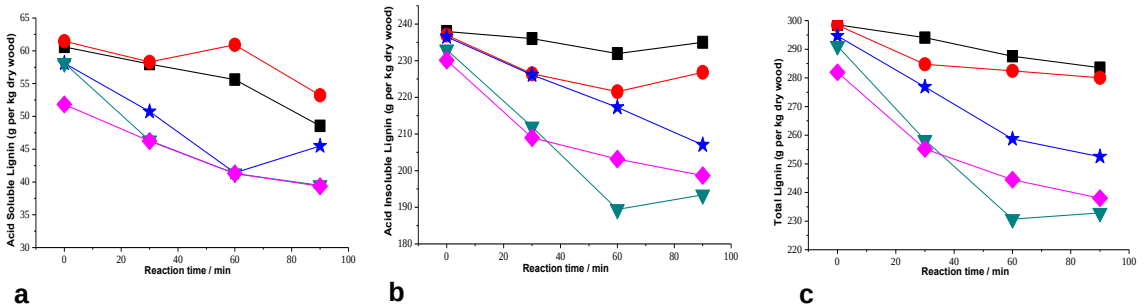

Fig. 3. Effect of the $T_{reaction}$/reaction time of the HWE on the (a) acid soluble lignin content, (b) acid insoluble lignin content, and (c) total lignin content of the aspen wood residue (-■- 140 ºC, -●- 150 ºC, -★- 160 ºC, -▼- 170 ºC, -◆- 180 ºC)

Degradation and Conversion of Carbohydrates

The content of dissolved carbohydrates in PEL

The hemicelluloses in hardwood are composed mainly of xylose and a small quantity of glucose, arabinose, galactose, and mannose (Kumar *et al.* 2009). The initial degradation rates of all kinds of sugar were different during HWE. Figure 4 shows that a certain amount of arabinose, galactose, and glucose degraded and dissolved into the PEL at 140 ºC, whereas the degradation of xylose and mannose did not occur until 150 ºC. In addition, regarding the amount of the five sugars in the PEL, the order of the maximum extraction value was: xylose>mannose>glucose>galactose>arabinose.

When the reaction time was prolonged at $T_{reaction}$ conditions lower than 160 ºC, a greater concentration of total sugars was dissolved. However, when the $T_{reaction}$ exceeded 170 ºC, a longer reaction time (more than 60 min) could result in the reduction of dissolved sugar. Besides the glucose, the other sugars such as xylose, mannose, arabinose, and galactose exhibited a similar extraction trend. In order to get more sugars dissolved, $T_{reaction}$ more than 160 ºC was necessary. A considerable amount of sugars could be extracted at 160 ºC for 90 min, or at higher temperature (170 ºC) for a shorter time (≤ 60 min).

From Fig. 2 and Fig. 4, one interesting question should receive attention. Figure 2 shows that the amount of carbohydrates in wood residues was almost consistent with increasing the severity of extraction condition, indicating that the dissolution and readsorption of sugars reached a balance and that no more sugars in PEL were adsorbed on the wood surface. On the other hand, the more severe conditions could indeed reduce the concentration of sugars dissolved. These two results seem contradictory.

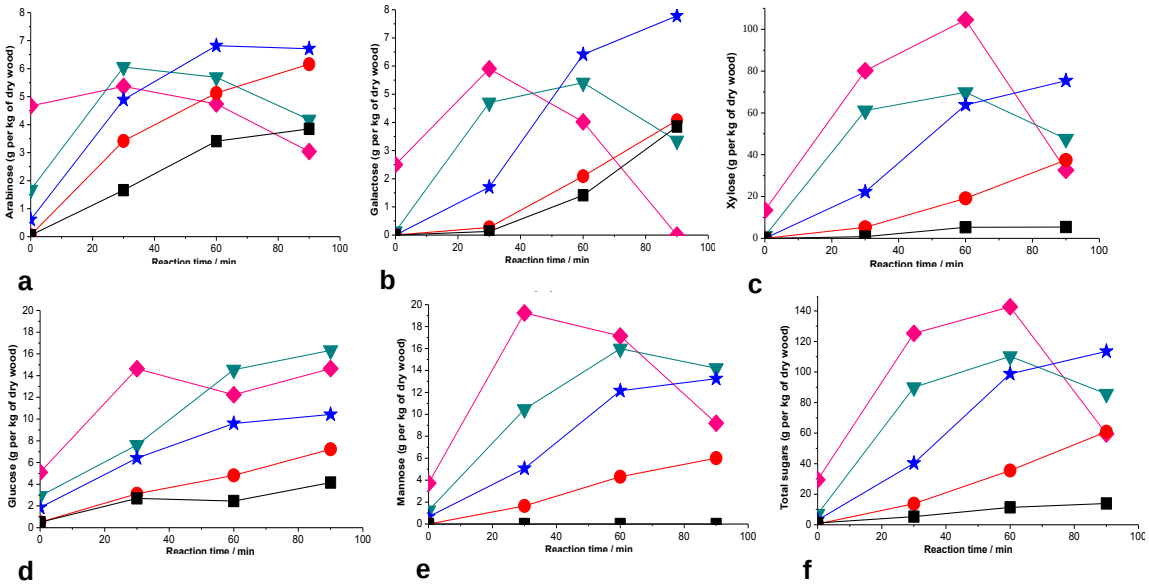

Fig. 4. Effect of the $T_{reaction}$/reaction time of the HWE on the content of (a) arabinose, (b) galactose, (c) xylose, (d) glucose, (e) mannose, and (f) total sugars in the PEL (-■- 140 ºC, -●- 150 ºC, -★- 160 ºC, -▼- 170 ºC, -◆- 180 ºC)

The content of acid and furfural in PEL

The acetyl groups that are bound to hemicellulose can be cleaved under the hot water extraction conditions (Garrote *et al.* 2001; Mittal *et al.* 2009). As shown in Fig. 5, the concentration of the acetic acid released from the wood chips into the PEL during HWE increased with increasing the $T_{reaction}$ or reaction time. At the same time, the acidity of the PEL became stronger. Previous studies (Chirat *et al.* 2012; Borrega *et al*. 2011a) found that the formation of acidic conditions promoted the extraction of wood components, especially the extraction of carbohydrates.

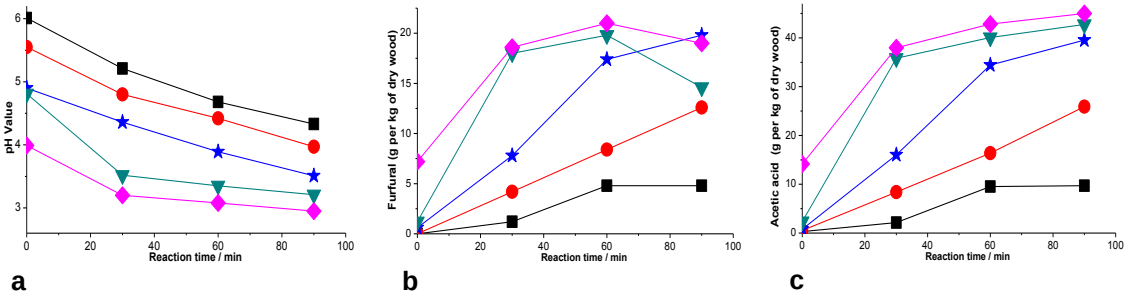

Fig. 5. Effect of the $T_{reaction}$/reaction time of the HWE on (a) the pH value, (b) the amount of furfural, and (c) the amount of acetic acid in the PEL (-■- 140 ºC, -●- 150 ºC, -★- 160 ºC, -▼- 170 ºC, -◆- 180 ºC)

It is well known that furfural or its derivatives are formed under the HWE conditions. The effect of HWE condition on the furfural concentration in PEL is shown in Fig. 5b. The concentration of furfural increased when the $T_{reaction}$ or reaction time was increased, meaning that the sugars in the PEL further degraded into furfural. A maximum content of furfural was obtained when the HWE was carried out at 180 ºC for 60 min. Previous studies (Conner and Lorenz 1986; Garrote and Parajó 2002; Mittal *et al.* 2009; Liu 2010) also showed that the decrease of sugars in PEL attributed to the second degradation of the monomers (such as hydroxymethyl furfural or furfural).

Figure 5b also shows that the content of furfural in the PEL decreased under severe HWE conditions ($T_{reaction} \geq 170$ ºC and reaction time ≥ 60 min). This may be due to the condensation of aromatic rings of lignin with furfural (Chua and Wayman 1979). Therefore, the reduction of sugars dissolved in PEL under severe extraction conditions should result from the formation of furfural or its derivatives.

Effect of HWE on Phenolic Compounds in PEL

Table 2. Effect of the $T_{reaction}$/Reaction Time of the HWE on the Content of Phenolic Lignin in the PEL

Extraction conditions		mg L^{-1} PEL					G/S	G/H
		VN	GA	SAL	*p*-HBA	Total		
140 ºC	0 min	ND	ND	10.54	26.01	36.55	0	0
	30 min	5.20	ND	205.41	116.76	327.37	0.025	0.045
	60 min	9.98	0.01	48.15	175.20	233.34	0.208	0.057
	90 min	11.07	0.02	49.17	180.88	241.14	0.226	0.061
150 ºC	0 min	ND	ND	38.95	51.31	90.26	0	0
	30 min	7.65	2.32	268.93	209.87	488.77	0.037	0.048
	60 min	12.27	6.71	157.47	250.96	427.41	0.121	0.076
	90 min	19.98	11.74	115.95	367.06	514.73	0.273	0.086
160 ºC	0min	ND	ND	130.90	90.65	221.55	0	0
	30 min	7.88	4.62	188.36	260.92	461.78	0.066	0.048
	60 min	30.74	21.27	114.79	525.75	692.55	0.453	0.099
	90 min	38.93	30.08	131.44	620.36	820.81	0.525	0.111
170 ºC	0 min	ND	ND	273.52	148.30	421.82	0	0
	30 min	27.10	16.07	133.74	452.74	629.65	0.323	0.095
	60 min	55.90	49.41	173.94	794.64	1073.89	0.606	0.132
	90 min	51.83	66.04	55.63	813.53	987.03	2.119	0.145
180 ºC	0 min	10.12	3.42	266.04	265.01	544.59	0.051	0.051
	30 min	51.56	52.27	152.39	707.92	964.14	0.681	0.147
	60 min	43.29	69.98	34.49	816.76	1024.52	1.199	0.139
	90 min	39.10	94.85	69.59	844.71	1001.25	4.290	0.150

ND: No Detected; VN, vanillin; SAL, syringaldehyde; *p*-HBA, *p*-hydroxybenzoic acid; GA, guaiacol; S/G, mass ratio of S to G lignin unit; H/G, mass ratio of H to G lignin unit

Table 2 shows the effect of HWE conditions on the phenolic compounds in PEL. The monomeric compositions are given in terms of vanillin (VN), guaiacol (GA), syringaldehyde (SAL), and *p*-hydroxybenzoic acid (*p*-HBA). Vanillin and syringaldehyde resulted from the degradation of no-condensed guaiacyl and syringyl units, respectively

(Sun *et al.* 1996). Moreover, for all the pre-extraction liquor, the dominant phenolic compound was *p*-hydroxybenzoic acid, which came from the non-condensed *p*-hydroxyphenyl unit (Sun *et al.* 1996).

The results in Table 2 exhibited that all of the PEL had lower phenolic contents. However, the content of total phenolic compounds increased with increasing reaction time, but thereafter it decreased. The highest content of total phenolic compounds was acquired at 170 ºC for 60 min (1073.89 mg L^{-1} PEL). Table 2 shows that the yields of guaiacol and p-hydroxybenzoic acid increased along with increasing HWE conditions in PEL. *P*-hydroxybenzoic and guaiacol displayed the highest yields (844.71 mg L^{-1} PEL and 94.85 mg L^{-1} PEL, respectively) at 180 ºC for 90 min. In addition, vanillin and syringaldehyde reached a maximum (55.90 mg L^{-1} PEL and 273.52 mg L^{-1} PEL, respectively) with increasing reaction time or $T_{reaction}$, but thereafter their concentrations decreased. These results suggested that the aspen wood could be reconsidered as a feedstock for the lignin biorefineries, which could be extracted, modified, and used as daily products.

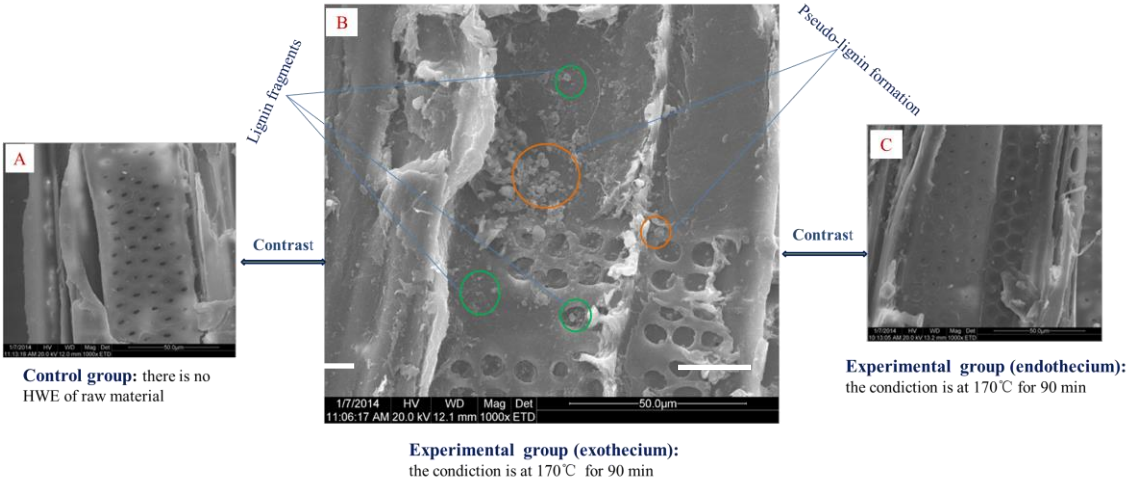

Fig. 6. Scanning electron micrographs showing the redeposition of the lignin on the wood residue: (a) surface of the aspen wood without HWE; (b) exothecium; and (c) endothecium of the aspen wood extracted at 170 ºC for 90 min. Scale bar is 25 μm.

Overall, according to the results above, the HWE at 170 ºC for 60 min was an effective pretreatment for the aspen wood, as it showed not only a high hydrolysis yield of carbohydrates but also a certain amount of hydrolysis yield of phenolic lignin. However, when the reaction time was increased from 60 min to 90 min at 170 ºC, the total phenolic lignin in the PEL decreased more rapidly. The reduction of the lignin-derived products may be attributed to the redeposition of the lignin fragments and pseudo-lignin. This was confirmed by Fig. 6, which compared the surface of the raw material and the extracted wood residue at 170 ºC for 90 min. As can be seen from the micrographs of scanning electron microscope (SEM), many lignin fragments and flocculent pseudo-lignin became redeposited on the material surface after HWE (Fig. 6b) compared with the control sample (Fig. 6a). Based on the results of previous studies (Sannigrahi *et al.* 2011; Hu *et al.* 2012; Cao *et al.* 2014), the spherical particles appearing in these micrographs were regarded as evidence of re-deposited lignin. The redeposition mainly occurred in the exothecium of the extracted wood residue rather than the endothecium (compared Fig. 6b with Fig. 6c). As the pseudo-lignin was composed of the combination of carbohydrates and lignin

degradation products (Sannigrahi *et al.* 2011), the readsorption of carbohydrates may have a linkage with the lignin. Cao *et al.* (2014) also determined that the microspheres on the surface of wood chips were pseudo-lignin, which corresponded with Fig. 6b.

Table 2 also shows that the G/S and G/H ratios increased with increasing the $T_{reaction}$ or reaction time in a way. The relatively high G/S ratio might mean that the guaiacyl lignin units were easier to extract than the syringyl lignin units (Ross and Mazza 2010). The high G/H ratio in the PEL was also due to the easier extraction of guaiacyl lignin units than the hydroxyphenyl lignin units.

CONCLUSIONS

1. A minimum $T_{reaction}$ of 160 ºC was necessary for a satisfactory removal of carbohydrates, and prolonging the reaction time at $T_{reaction}$ ($\geq$ 30 min) could further extract carbohydrates from wood residues. The carbohydrates level in wood residues was almost at a stable state with increasing the severe extraction conditions, indicating that the dissolution and readsorption of sugars reached a balance and that no more sugars in PEL were adsorbed on the wood surface. The resistance of mass transfer may also limit the further dissolution of carbohydrate. On the other hand, the more severe conditions could indeed reduce the concentration of sugars dissolved. The decrease of sugars dissolved in PEL under severe extraction conditions should result from the formation of furfural or its derivatives.
2. By increasing $T_{reaction}$ to 170 ºC, the HWE could extract about 20% of lignin from wood in 60 min. Higher temperature could not cause more lignin to become extracted. Alternatively, more lignin was found to exist in wood residue, probably due to the redeposition of the dissolved lignin on the wood fiber surface under severe extraction conditions. Redeposition of the lignin might occur in the exothecium rather than the endothecium of the wood chips.

ACKNOWLEDGEMENTS

The authors would like to acknowledge financial support from the National Natural Science Foundation of China (31370581) and the Yellow River Mouth Scholar Program (DYRC20120105). The authors also thank Lucian Lucia at North Carolina State University for providing much useful advice for the manuscript.

REFERENCES CITED

Borrega, M., Nieminen, K., and Sixta, H. (2011a). "Degradation kinetics of the main carbohydrates in birch wood during hot water extraction in a batch reactor at elevated temperatures," *Bioresource Technology* 102(22), 10724-10732. DOI: 10.1016/j.biortech.2011.09.027

Borrega, M., Nieminen, K., and Sixta, H. (2011b). "Effects of hot water extraction in a batch reactor on the delignification of birch wood," *BioResources* 6(2), 1890-1903. DOI: 10.15376/biores.6.2.1890-1903

Cao, S. L., Ma, X. J., Lin, L., Huang, L. L., and Chen, L. H. (2014).“Lignin removal law during bamboo prehydrolysis with oxalic acid,” *Transaction of the Chinese Society of Agricultural Engineering* 30(5), 277-284(8).

Chen, X. W., Lawoko, M., and Heiningen, A. V. (2010). “Kinetics and mechanism of autohydrolysis of hardwoods,” *Bioresource Technology* 101(20), 7812-7819. DOI: 10.1016/j.biortech.2010.05.006

Chirat, C., Lachenal, D., and Sanglard, M. (2012). “Extraction of xylans from hardwood chips prior to kraft cooking,” *Process Biochemistry* 47(3), 381-385. DOI: 10.1016/j.procbio.2011.12.024

Chua, M. G. S., and Wayman, M. (1979). “Characterization of autohydrolysis aspen (*Populus tremuloides*) lignins: 3. Infrared and ultraviolet studies of extracted autohydrolysis lignin,” *Canadian Journal of Chemistry-revue Canadienne De Chime* 57(19), 2603-2611. DOI: 10.1139/v79-421

Conner, A. H., and Lorenz, L. F. (1986). “Kinetic modeling of hardwood prehydrolysis. Part III. Water and dilute acetic acid prehydrolysis of southern red oak,” *Wood and Fiber Science* 18(2), 248-263.

GB/T 2677.3. (1993). “Fibrous raw material-Determination of ash,” Chinese National Standardization Management Committee, China.

GB/T 2677.6. (1994). “Fibrous raw material-Determination of organic solvent extract,” Chinese National Standardization Management Committee, China.

GB/T 2677.9. (1994). “Fibrous raw material-Determination of pentosan,” Chinese National Standardization Management Committee, China.

GB/T 2677.10. (1995). “Fibrous raw material-Determination of holocellulose,” Chinese National Standardization Management Committee, China.

GB/T 12032. (1989). “Paper and board-Preparation of an offset print for test gloss,” Chinese National Standardization Management Committee, China.

Garrote, G., Domínguez, H., and Parajó, J. C. (2001). “Study on the deacetylation of hemicelluloses during the hydrothermal processing of eucalyptus wood,” *Holz als Roh- und Werkstoff* 59(1-2), 53-59. DOI: 10.1007/s001070050473

Garrote, G., and Parajó, J. C. (2002). “Non-isothermal autohydrolysis of eucalyptus wood,” *Wood Science and Technology* 36(2), 111-123. DOI: 10.1007/s00226-001-0132-2

Goundalkar, M. J., Bujanovic, B., and Amidon, T. E. (2010). “Analysis of non-carbo-hydrate based low-molecular weight organic compounds dissolved during hot water extraction of sugar maple,” *Cellulose Chemistry and Technology* 44(1-3), 27-33.

Hu, F., Jung, S., and Ragauskas, A. (2012). “Pseudo-lignin formation and its impact on enzymatic hydrolysis,” *Bioresource Technology* 117, 7-12. DOI: 10.1016/j.biortech.2012.04.037

Kamm, B., Schönicke, P., and Kamm, M. (2009). “Biorefining of green biomass-technical and energetic considerations,” *Clean* 37(1), 27-30.

Kemppainen, K., Inkinen, J., Uusitalo, J., Nakari-Setälä, T., and Siika-aho, M. (2012). “Hot water extraction and steam explosion as pretreatment for ethanol production from spruce bark,” *Bioresource Technology* 117, 131-139. DOI: 10.1016/j.biortech.2012.04.080

Kumar, P., Barrett, D. M., Delwiche, M. J., and Stroeve, P. (2009). “Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production,” *Industrial and Engineering Chemistry Research* 48(8), 3713-3729. DOI:

10.1021/ie801542g

Leschinsky, M., Zuckerstatter, G., Weber, H. K., Patt, R., and Sixta, H. (2008). "Effect of autohydrolysis of eucalyptus globules wood on lignin structure: Part 1: Comparison of different lignin fractions formed during water prehydrolysis," *Holzforschung* 62(6), 645-652. DOI: 10.1515/HF.2008.117

Liu, S. J. (2010). "Woody biomass: Niche position as a source of sustainable renewable chemicals and energy and kinetics of hot-water extraction/hydrolysis," *Biotechnology Advances* 28(5), 563-582. DOI: 10.1016/j.biotechadv.2010.05.006

Mašura, M. (1987). "Prehydrolysis of beech wood-highly purified dissolving pulp produced by sulphur free pulping," *Wood Science and Technology* 21(1), 89-100.

Mittal, A., Chatterjee, S. G., Scott, G. M., and Amidon, T. E. (2009). "Modeling xylan solubilization during autohydrolysis of sugar maple wood meal: Reaction kinetics," *Holzforschung* 63(3), 307-314. DOI: 10.1515/HF.2009.054

Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y. Y., Holtzapple, M., and Ladisch, M. (2005). "Features of promising technologies for pretreatment of lignocellulosic biomass," *Bioresource Technology* 96(6), 673-686. DOI: 10.1016/j.biortech.2004.06.025

Ormsby, R., Kastner, J. R., and Miller, J. (2012). "Hemicellulose hydrolysis using solid acid catalysts generated from biochar," *Catalysis Today* 190(1), 89-97. DOI: 10.1016/j.cattod.2012.02.050

Rødsrud, G., Lersch, M., and Sjöde, A. (2012). "History and future of world's most advanced biorefinery in operation," *Biomass and Bioenergy* 46, 46-59.

Ross, K., and Mazza, G. (2010). "Characteristics of lignin from flax shives as affected by extraction conditions," *International Journal of Molecular Sciences* 11(10), 4035-4050. DOI: 10.3390/ijms11104035

Sannigrahi, P., Kim, D. H., Jung, S., and Ragauskas, A. (2011). "Pseudo-lignin and pretreatment chemistry," *Energy and Environmental Science* 4(4), 1306-1310. DOI: 10.1039/c0ee00378f

Sixta, H. (2006). "Multistage kraft pulping," in: *Handbook of Pulp,* 1st Ed, H. Sixta, (ed.), Wiley-VCH, Weinheim, pp. 708-720.

Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., and Crocker, D. (2007). "Determination of structural carbohydrates and lignin in biomass," *Technical Report for Laboratory Analytical Procedure (LAP),* NREL, Golden, CO, USA.

Sun, R., Lawther, J. M., and Banks, W. B. (1996). "Effects of extraction time and different alkalis on the composition of alkali soluble wheat straw lignins," *Journal of Agricultural and Food Chemistry* 44(12), 3965-3970. DOI: 10.1021/jf9600566

Sun, Y., and Cheng, J. Y. (2002). "Hydrolysis of lignocellulosic materials for ethanol production: A review," *Bioresource Technology* 83(1), 1-11. DOI: 10.1016/S0960-8524(01)00212-7

Vila, C., Romero, J., Francisco, J. L., Garrote, G., and Parajó, J. C. (2011). "Extracting value from eucalyptus wood before kraft pulping: Effects of hemicelluloses solubilization on pulp properties," *Bioresource Technology* 102(8), 5251-5254. DOI: 10.1016/j.biortech.2011.02.002

Article submitted: December 15, 2014; Peer review completed: February 16, 2015; Revised version received and accepted: March 26, 2015; Published: April 1, 2015.
DOI: 10.15376/biores.10.2.3005-3016