Effects of Alkaline Hydrogen Peroxide Pre-Extraction on Bamboo Lignin Chemistry and Other Bamboo Chemical Components

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This paper aimed to investigate the reasons for improved properties of bamboo alkaline peroxide mechanical pulp (APMP), such as relatively high brightness and low post-colour number, by alkali hydrogen peroxide pre-extraction (AHPP) treatment. It was found that AHPP could affect the dissolution of 1% sodium hydroxide extractives, benzene-ethanol extractives, and acid-soluble lignin. The results of Fourier transform infrared (FTIR) and ^{13}C-nuclear magnetic resonance spectroscopy (^{13}C-NMR) illustrated that carboxyl, syringyl, guaiacyl, acetyl, and methoxyl groups of the milled wood lignin (MWL) in bamboo were degraded slightly after AHPP treatment. However, some lignin-like structures, the links of α-O-4, β-O-4, and some carbohydrates such as xylan, α-glucose, β-glucose, α-mannose, and β-mannose in lignin-carbohydrate complexes (LCCs) were degraded noticeably. The analysis of UV spectrophotometry indicated that AHPP treatment was conductive to the degradation of some chromophores in MWL. The degradation of MWL and LCC under simulated AHPP conditions showed consistency with the above results.

Keywords: AHPP; Bamboo APMP; LCC; MWL; Chemical components

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INTRODUCTION

Currently, more and more attention is being given to the utilization of renewable feedstocks. Bamboo is viewed as one of the most promising non-wood resources, especially in consideration of its abundance, wide distribution, rapid growth, and long fibers. Alkaline peroxide mechanical pulp (APMP) process has many advantages, such as higher yield, better pulp strength, lower energy consumption, and less pollution than other chemical-mechanical processes (CMP) (Xu and Sabourin 1999). The production of APMP with different materials has been popularly applied in the pulp and paper industry (Richardson 2001; Xu 2001). However, there are some major problems hindering the development of bamboo high-yield pulp (HYP), such as high refining energy consumption, low brightness, and high post-color number (PC). These issues occur because bamboo has some special chemical-physical properties, including the tight and compact structure, the high content of hemicellulose, the high content of chromophoric groups, and their distribution in bamboo fiber cell layers. Moreover, it is difficult to obtain relatively high brightness in consideration of the low bleachability of bamboo APMP (Liang 2011). Therefore, the commercialization of bamboo APMP has not been realized so far.

It has been reported that pre-extracting wood chips prior to the CMP can reduce chemical and energy consumption, improve some pulp properties, and produce added-value biofuels and biochemicals with extracted hemicellulose (Sun and Cheng 2002; Liu *et al*. 2012; Song *et al*. 2011). The pre-extracting methods primarily include steam explosion (Martin-Sampedro *et al*. 2014), hot water pre-extraction (Saukkonen *et al*. 2012), acid hydrolysis (Liu *et al.* 2012), and alkali extraction (Zhou *et al*. 2013). Moreover, every pretreatment processes has its own particular advantages and limitations (Cetinkol *et al.* 2010). It is reported that hydrogen peroxide in alkaline media could serve as a mild agent for solubilizing macromolecular hemicelluloses, in addition to its dual role in delignifying and bleaching (Sun *et al.* 2000). Also, alkaline hydrogen peroxide pre-extraction (AHPP) is an effective method for extracting hemicellulose and comparatively beneficial to subsequent pulping and bleaching, according to our previous study (Song *et al.* 2011). AHPP could reduce energy consumption and improve APMP brightness. For a given freeness, the refining energy consumption with a refiner and the beating energy consumption with PFI-stuff grinder were reduced by 18.8% and 60.0%, respectively. The brightness of APMP was increased by 7.0% ISO, and the yellowing was reduced by 58.2%.

Moreover, the extraction of hemicelluloses from biomass is restricted by the physical and covalent interactions with other cell-wall constituents, such as the presence of lignin networks, lignin-hemicellulose linkages, and the physical intermixing between hemicelluloses and cellulose. Generally, the presence of and changes to lignin chromophoric structures are mostly responsible for the brightness and susceptibility to light-induced yellowing. Also, the content of phenolic hydroxyl groups in bamboo lignin is high and it is generally defined as “guaiacyl-syringyl” lignin, which has high reactivity in pulping (Tai *et al.* 1990; Chen *et al.* 1993). Additionally, it is reported that lignin-carbohydrate complexes (LCCs) may act to prevent the chemical reagents from attacking cellulose (Taherzadeh 1999; Sassner *et al.* 2005). These chromophores and chemical molecules are responsible for the physical and chemical behaviors of pulps in papermaking and affect some chemical reactions during technological operations (*e.g.* pulping, high-temperature refining of wood chips, and extraction). This offers a good justification for the importance of acknowledging the structural changes of chromophores in raw materials or pulp after pre-extraction. Therefore, aiming to illustrate the improvement in APMP brightness and low PC after AHPP, the effects of AHPP on the lignin chemistry and on other chemical components of bamboo were investigated in this study. The influences of various extractive conditions on chemical components were studied. The structural changes of bamboo milled wood lignin (MWL) and LCCs, before and after AHPP treatment, were characterized by ^{13}C-NMR and FTIR analysis. Also, the contents of conjugated carbonyl, catechol, and *o*-benzoquinone were determined by UV spectrophotometry. To further investigate the effects of AHPP on the properties of bamboo APMP, MWL and LCCs were directly degraded under simulated AHPP conditions, and the structural changes of MWL and LCCs were analyzed by ^{13}C-NMR.

EXPERIMENTAL

Materials

Fresh bamboo was kindly provided by Gaofeng farm (Nanning, China). The bamboo was chipped and screened manually. The chip size was 15 to 25 mm in length, 3 to 5 mm in thickness, and 10 to 20 mm in width. The composition of the chemical components in the raw materials was as follows (based on the results after different solvents dissolution): ash - 2.20%, 1% sodium hydroxide solubility - 23.90%, benzene-ethanol extractives - 3.17%, holocellulose - 78.21%, pentosan - 18.26%, acid-insoluble lignin - 23.20%, and acid-soluble lignin - 1.13%.

Methods

Hemicellulose pre-extraction

The bamboo chips were pre-extracted in a stainless steel digester with a built-in temperature sensor. The operating conditions of alkaline hydrogen peroxide pre-extraction (AHPP) were as follows: solid-to-liquid ratio 1:8, 1.5% hydrogen peroxide (on bamboo chips), temperature 90 °C, 4 h, initial pH 12.6 (adjusted with sodium hydroxide) (Song *et al.* 2011).

Determinations of chemical components in bamboo

Determinations of chemical components in bamboo chips (before and after pre-extraction) were carried out as follows: ash (TAPPI T211 om-02), ethanol-benzene extractive (TAPPI T204 cm-97), 1% sodium hydroxide solubility (TAPPI T212 om-02), pentosan (TAPPI T223 cm-01), acid-soluble lignin (TAPPI T250 cm-85), acid-insoluble lignin (TAPPI T222 om-02), and holocellulose (Zobel and McElwee 1966).

Preparation and analysis of MWL and LCC

The samples of bamboo chips before and after AHPP treatment were milled to particles in the range of 40 to 100 mesh with a Wiley mill (Thomas Scientific, USA). The particles were then extracted by benzyl alcohol and hot water, and the extracted particles were dried over phosphorus pentoxide. After that, the samples were subjected to a 72-h ball-milling with the mill, then were extracted by dioxane/water [1:1 (v:v)] for 12 h. The fractionation was performed according to the improved method of Björkman (1957).

The structures of MWL and LCCs before and after AHPP treatment were analyzed by ^{13}C-NMR and FTIR. The NMR spectra were recorded on a Bruker DRX-400 spectrometer (Bruker, Germany). DMSO-d$_6$ was used as the solvent. Chemical shifts were referenced to TMS (0.0 ppm). The ^{13}C-NMR spectra were recorded at 100.59 MHz using 5-mm-diameter tubes with the following parameters: 90° pulse angle; 3-s relaxation delay, and 12,000 scans. The MWL/LCC was dissolved in DMSO-d$_6$. FTIR spectra of MWL and LCCs were obtained using a Perkin Elmer BXII spectrometer (Perkin Elmer, USA) in the 4000 to 400 cm^{-1} range with eight scans at a resolution of 4.0 cm^{-1}. For this purpose, dried samples were ground and pelletized with spectroscopic grade KBr. The contents of chromophoric groups in MWL samples were determined using an ultraviolet-visible (UV-vis) spectrophotometer (Agilent, USA) in the wavelength of 200 to 1000 nm. MWL sample (5 mg) was dissolved in 0.1 mol/L NaOH solution (10 mL). A 1 mL aliquot was diluted to 10 mL with deionized water. In addition, the content of carbonyl groups was determined with the method of Lundquist (1977). The contents of catechol and *o*-quinone in lignin samples were determined using Imsgard's method (Imsgard 1971).

Degradation experiment of MWL and LCC

In order to investigate the effects of AHPP on the structures of bamboo MWL and LCC, the samples of MWL or LCC (500 mg) were treated in a stainless steel reactor under simulated AHPP conditions as follows: 1.5% hydrogen peroxide (on MWL or LCC), temperature 90 °C, 4 h, initial pH 12.6 (adjusted with sodium hydroxide). The samples were immediately freeze-dried after the treatment.

RESULTS AND DISCUSSION

Effects of Pre-Extracting Conditions on Bamboo Chemical Components

Effects of hydrogen peroxide dosage on bamboo chemical components

The results of hydrogen peroxide dosage effects on bamboo chemical components are shown in Table 1. The data indicated that the contents of some chemical components in residual bamboo chips, such as holocellulose, pentosan, and lignin, did not noticeably change with increasing hydrogen peroxide dosage during the AHPP process. However, the contents of ash, 1% sodium hydroxide solubility, and benzene-ethanol extractives were reduced by 20.91%, 17.20%, and 77.60%, respectively. These results suggest that the increase of hydrogen peroxide dosage had many advantages on removing ash, 1% sodium hydroxide solubility, and benzene-ethanol extractive of bamboo chips. The reason for the removal of ash might be that the extracted raw materials had a more open structure because of the removal of hemicelluloses and lignin (Jahan *et al.* 2012), and hence the ash was more directly exposed to the environment of chemical agents. The pentosan content of residual bamboo chips was the least when hydrogen peroxide dosage was 1.5%, similar to the results of our previous study (Song *et al.* 2011). Hydrogen peroxide dosage had little influence on the content of residual holocellulose in pre-extracted bamboo chips, which would benefit the subsequent pulp yield and properties (Santiago and Neto 2007). Attention should be paid to the fact that the increase in hydrogen peroxide dosage was not a prerequisite for good delignification, according to the results.

Table 1. Effects of Hydrogen Peroxide Dosage on Bamboo Chemical Components

	Hydrogen peroxide dosage (%)	Ash (%)	1% sodium hydroxide solubility (%)	Benzene-ethanol extractive (%)	Holo-cellulose (%)	Pentosan (%)	Acid-insoluble lignin (%)	Acid-soluble lignin (%)
Bamboo without AHPP		2.20	23.90	3.17	78.21	18.26	23.20	1.13
	1.0	1.96	20.90	2.01	77.97	18.06	22.87	1.03
	1.5	1.92	20.62	1.93	76.80	17.13	22.65	1.02
	2.0	1.87	20.47	1.80	76.54	17.50	22.40	1.09
	2.5	1.79	19.88	1.16	76.53	17.83	22.13	1.10
	3.0	1.74	19.79	0.71	76.30	18.20	22.00	1.05
Max-Change rate		20.91	17.20	77.60	2.44	6.19	5.17	9.73

Effects of reaction temperature on bamboo chemical components

As shown in Table 2, compared with those of the raw materials, the contents of ash, holocellulose, pentosan, and acid-soluble lignin in residual bamboo chips after AHPP did not obviously decrease, but there was a remarkable decline in the contents of 1% sodium hydroxide solubility, benzene-ethanol extractives, and acid-soluble lignin with increasing temperature, these values decreased by 17.57%, 61.20%, and 19.47% when the temperature was raised to 90 °C. Additionally, when bamboo chips were pre-extracted at 90 °C, the content of residual pentosan was less than that at other temperatures, which supported our previous conclusion that the yield of pre-extracting pentosan was a maximum at 90 °C (Song *et al.* 2011). Generally, the formulas of hemicellulose are $(C_5H_8O_4)_n$ and $(C_6H_{10}O_5)_n$ and they are called, respectively, pentosans and hexosans. Therefore, the decreasing content of pentosan in bamboo indicated that AHPP was responsible for the solubilization of hemicelluloses. Therefore, 90 °C is a good reaction temperature for the removal of 1% sodium hydroxide solubility, benzene-ethanol extractives, and acid-soluble lignin, as well as the extraction yield of pentosan.

Table 2. Effects of Reaction Temperature on Bamboo Chemical Components

	Reaction temperature (°C)	Ash (%)	1% sodium hydroxide solubility (%)	Benzene-ethanol extractive (%)	Holo-cellulose (%)	Pentosan (%)	Acid-insoluble lignin (%)	Acid-soluble lignin (%)
Bamboo without AHPP		2.20	23.90	3.17	78.21	18.26	23.20	1.13
	50	2.18	23.75	2.51	76.02	17.80	22.45	1.12
	60	2.15	23.60	2.37	75.78	17.67	22.40	1.01
	70	2.11	23.50	1.73	75.51	17.65	22.34	0.92
	90	2.08	19.89	1.50	74.91	17.50	22.04	0.91
	95	2.03	19.70	1.23	74.90	17.55	21.93	0.92
Max-change rate		7.73	17.57	61.20	4.23	4.16	5.47	19.47

Effects of holding time on bamboo chemical components

The data given in Table 3 suggest that holding time had a marked influence on the contents of bamboo chemical components such as 1% sodium hydroxide solubility, benzene-ethanol extractives, and acid-soluble lignin, which maximally decreased by 16.32%, 57.73%, and 30.09%, respectively. Moreover, the acid-soluble lignin, which is mostly represented by syringyl units (Sun *et al.* 2003), and the higher removal rate of syringyl units were associated with the higher delignification rate. Hence, the extension of holding time would be conducive to a higher brightness of bamboo chips and APMP.

In addition, some components, including lignin and pentosan, significantly decreased when the holding time was extended from 2 to 4 h. The content of holocellulose only decreased by 8.04% when the holding time reached 8 h, indicating that cellulose was degraded at a low level with the extension of holding time during the AHPP process.

Table 3. Effects of Holding Time on Bamboo Chemical Components

	Holding time (h)	Ash (%)	1% sodium hydroxide solubility (%)	Benzene-ethanol extractive (%)	Holo-cellulose (%)	Pentosan (%)	Acid-insoluble lignin (%)	Acid-soluble lignin (%)
Bamboo without AHPP		2.20	23.90	3.17	78.21	18.26	23.20	1.13
	1	2.16	21.49	2.14	74.20	18.23	22.35	1.10
	2	2.13	21.10	1.80	73.83	18.13	22.28	1.00
	4	2.09	20.49	1.61	73.55	17.88	21.91	0.79
	6	2.04	20.10	1.52	73.18	17.73	21.65	0.80
	8	1.95	20.00	1.34	71.92	17.65	21.45	0.93
Max-change rate		11.36	16.32	57,73	8.04	3.34	7.54	30.09

Effects of solid-to-liquid ratio on bamboo chemical components

Table 4 shows that the contents of 1% sodium hydroxide solubility, benzene-ethanol extractives, and acid-soluble lignin remarkably decreased as the solid-to-liquid ratio increased.

Table 4. Effects of Solid-to-Liquid Ratio on Bamboo Chemical Components

	Solid-to-liquid ratio	Ash (%)	1% sodium hydroxide solubility (%)	Benzene-ethanol extractive (%)	Holo-cellulose (%)	Pentosan (%)	Acid-insoluble lignin (%)	Acid-soluble lignin (%)
Bamboo without AHPP		2.20	23.90	3.17	78.21	18.26	23.20	1.13
	1:6	2.13	23.22	2.52	76.92	18.04	23.15	0.97
	1:8	2.11	23.01	2.51	75.05	17.85	22.84	0.90
	1:10	2.07	22.80	2.50	74.83	17.83	22.62	1.01
	1:12	2.00	19.27	2.37	74.71	17.80	22.34	1.12
	1:15	1.91	17.41	0.68	74.53	17.79	22.26	1.11
Max-change rate		13.18	27.15	78.55	4.71	2.57	4.05	20.35

It is well known that 1% sodium hydroxide solubility contain components such as lignin, pentosans, hexosan, and resin acid, the decreasing contents of which are generally a result of the delignification and solubilization of hemicelluloses. Furthermore, hydroxyl radicals generated by the dissociation of hydrogen peroxide are capable of attacking practically all the ether linkages between lignin and hemicelluloses, which subsequently resulted in a release of these components. The decreasing content of benzene-ethanol extractives denoted that the pigments and aliphatic acid, which were associated with bound lignin and linked to hemicellulose through ether bonds, were partly degraded or released because of the oxidizing and degrading effect of hydrogen peroxide, thus leaving a cellulose-enriched residue for paper making (Sun *et al.* 2000). Nevertheless, the contents of residual holocellulose, pentosan, and acid-soluble lignin showed a rapid decrease when the solid-to-liquid ratio was raised from 0 to 1:8, then the downtrend of these components decelerated with the increase of solid-to-liquid ratio.

In conclusion, AHPP had a substantial effect on the dissolution of 1% sodium hydroxide solubility, benzene-ethanol extractives, and acid-soluble lignin under various pre-extracting conditions. Beyond that, compared with other parameters, the hydrogen peroxide dosage seemed to have a more obvious effect on the removal of ash and pentosans. The solid-to-liquid ratio affected the contents of 1% sodium hydroxide solubility and benzene-ethanol extractives mostly remarkably. Moreover, the holding time had the most obvious effect on the dissolution of acid-soluble lignin compared to other pretreatment conditions. Moreover, the increase of pretreatment conditions did not lead to very remarkable removal of pentosans, holocellulose, and lignin. The evident dissolution was favorable to the improvement of APMP brightness. Also, the dissolution of tested components enhanced more channels for the fiber to be in contact with the chemicals. Therefore, fiber was fully softened and swelled prior to refining and easily separated in the following refining stage, which can lead to a marked decrease of refining energy consumption (Hou *et al*. 2014). Additionally, the slight decrease in holocellulose content would benefit the subsequent pulp yields. The results powerfully confirmed our previous pulping conclusions that PC, yield, and refining energy consumption of the APMP after AHPP treatment are decreased and the brightness is increased (Song *et al.* 2011). However, the dissolution of some components could not fully explain the reasons for the improved pulp properties after AHPP treatment, especially the brightness improvement. Therefore, the effects of AHPP on the structures of MWL and LCC were further studied with FTIR, ^{13}C-NMR, and UV-Vis spectroscopy.

Effects of AHPP on the Structures of MWL and LCCs in Raw Materials

FTIR analysis of MWL and LCC structures

The FTIR spectra of MWL and LCCs in bamboo before and after AHPP treatment are shown in Figs. 1 and 2, respectively. As can be seen in Fig. 1, there were few differences in spectra (a) and (b), indicating that the chemical structure of bamboo MWL was only degraded slightly during the AHPP process. However, some bands, such as those at 2974, 1085, 1044, 879 cm^{-1}, corresponding to C-H stretching vibration, stretching vibration of C-O-C, guaiacol vibration, and guaiacol lignin (Fang *et al.* 1999), were weakened compared with those of the MWL without AHPP. These results provided proof that AHPP had some effects on oxidative degradation of MWL, primarily because hydroperoxyl and hydroxyl radicals generated by the decomposition of hydrogen peroxide were responsible for the delignification. In addition, the intensity of other bands was mostly constant, which indicated that the delignification effect of the AHPP method was not distinct.

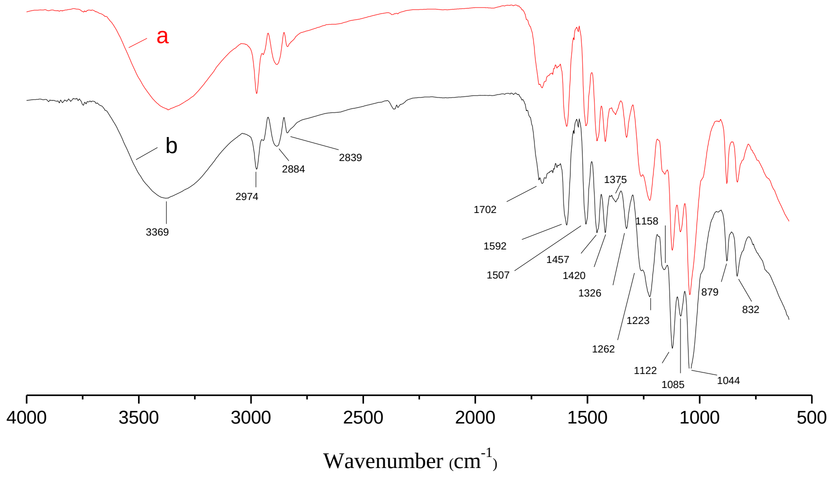

Fig. 1. FTIR spectra of MWL of bamboo (a) before and (b) after AHPP

As shown in Fig. 2, the intensity of LCC characteristic signals exhibited a declining tendency after AHPP treatment. The characteristic absorptions at 3369, 2976, 1716, 1458, 1236, 1158, 1041, and 879 cm^{-1} can be assigned to the LCC structure (Sun and Tomkinson 2002; Peng *et al.* 2010). The bands at 3369 and 2976 cm^{-1} can be assigned to the hydroxyl bond (O-H) stretching vibration and the C-H of aliphatic stretching vibration, which decreased dramatically after AHPP treatment. These facts suggest that some carbohydrates were hydrolyzed and dissolved out of the LCC after AHPP treatment. Also, a noticeable decrease was observed at 1716 cm^{-1} in the spectrum of Fig. 2(b), which can be assigned to the unconjugated carbonyl group stretching vibration. The constant shoulders ranging from 1327 to 833 cm^{-1} in Fig. 2(b) were weakened, which were associated with some chromophore structures such as syringyl and condensed guaiacol vibration, methoxy group of guaiacol vibration, stretching vibration of C-C, C-O, C=O, ester carbonyl, and HGS (hydroxybenzene-guaiacol-syringyl) lignin, stretching vibration of C-O-C, guaiacol vibration, and guaiacol lignin (Fang *et al.* 1999).

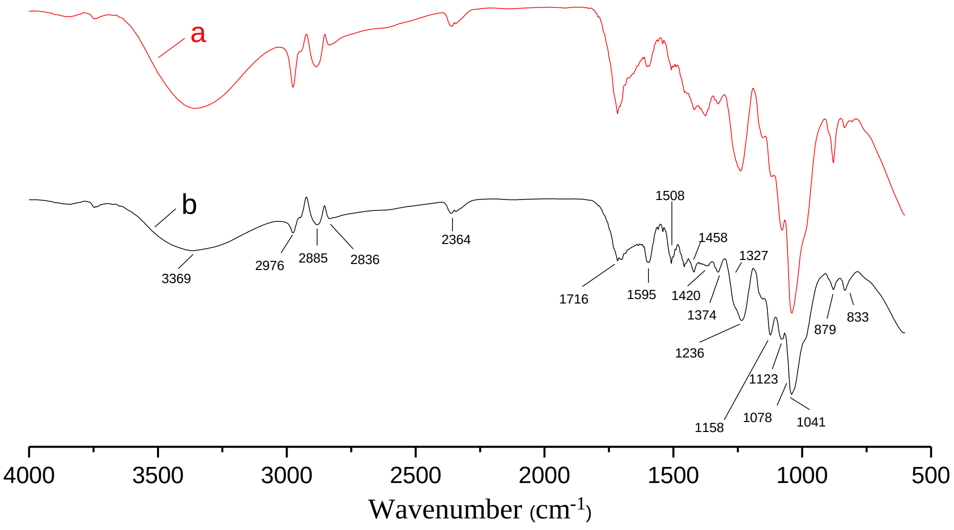

Fig. 2. FTIR spectra of LCC of bamboo (a) before and (b) after AHPP

These weakened groups confirmed the degradation of abundant chromophores and the cleavage of the chemical bonds between lignin and carbohydrates after AHPP treatment. Additionally, these observations were also in good agreement with those obtained by Fang *et al.* (1999). The information obtained from the results was due to the formation of hydroperoxide anions (HOO-) in alkaline media during the AHPP process, which were the principal active species and led to the degradation of LCC. Also, HOO^- anions are strong nucleophiles that preferentially attack the ethylenic and carbonyl groups presented in hemicellulose-lignin complex, and subsequently converted some chromophores such as quinones, cinnamaldehyde, and ring-conjugated ketones into non-chromophoric species (Fang *et al.* 1999). These findings also upheld the results obtained in the bleaching experiment, in which the brightness and PC of APMP were improved compared with those of the APMP without pre-extraction.

^{13}C-NMR analysis of MWL and LCC structures

The ^{13}C-NMR spectra of MWL and LCC in bamboo before and after AHPP treatment are shown in Figs. 3 and 4, respectively. Almost all signals of the MWL after AHPP treatment were weakened compared with those of the untreated bamboo MWL. Signals at 172.5, 152.7, 130.7, and 115.4 ppm can be assigned to the -COO of acyl, cinnamic acid, benzoic acid, and styrene, the C_3/C_4 of syringyl, the C_1 of guaiacyl, and the C_5 of etherified guaiacyl, respectively (Capanema *et al.* 2004). These signals were weakened in comparison to those of bamboo MWL. Signals at 72.6, 60.4, and 21.4 ppm, attributed to the methyl of pinoresinol, syringyl, and the methyl of acetyl, were noticeably weakened, which further confirmed that some chromophoric groups existing in MWL structures were partly degraded after AHPP treatment, leading to the improvement of APMP brightness. Also, the degradation of MWL would result in a decrease in PC.

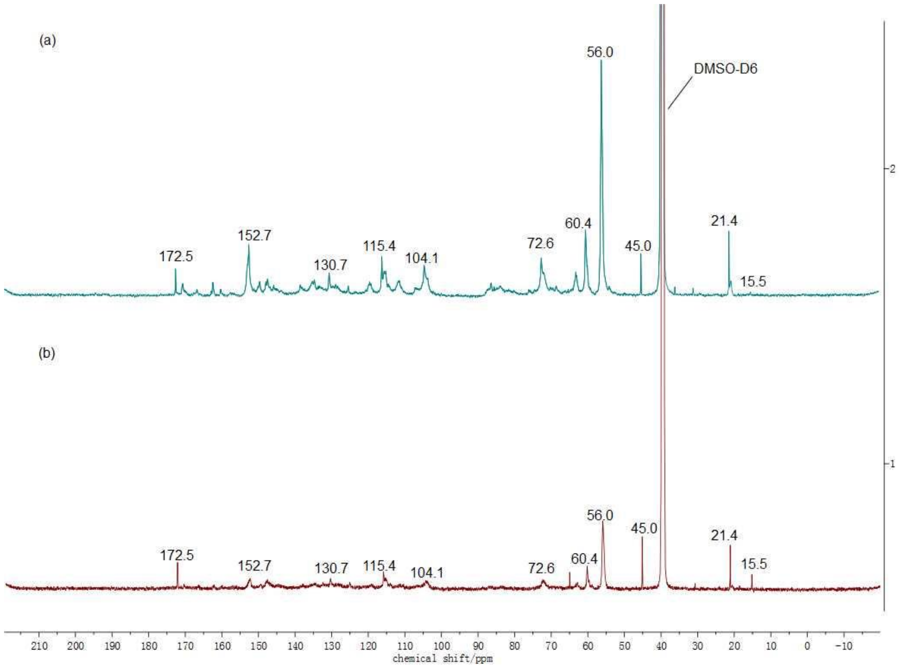

Fig. 3. ^{13}C-NMR spectra of MWL of bamboo (a) before and (b) after AHPP

The decrease in intensity of the signals was extraordinary in Fig. 4(b) compared with Fig. 4(a), which indicated that AHPP was conducive to the degradation of LCC. Signals of groups such as acetyl and cinnamic acid at 172.1 and 159.9 ppm were weakened after AHPP treatment. The signals of aromatic hydrocarbons in the range of 152.9 to 100.1 ppm were also weakened. Moreover, the signals at 152.9, 130.6, 115.4, 103.7, and 21.4 ppm, corresponded to the C_5/C_3 of etherified syringyl, the C_1 and C_5 of etherified syringyl and guaiacol, the C_2 or C_6 of etherified syringyl and guaiacol, the phenol acetylated syringyl, and methoxy group, respectively (Xie *et al*. 2000). These results indicated that there were many structures of etherified syringyl and guaiacol and acetylated syringyl and guaiacol in bamboo LCC (Fig. 4(a)), and some of them were observably decomposed during the AHPP process.

Signals in the range of 80.1 to 56.2 ppm, which were weakened remarkably after AHPP treatment, were assigned to structures such as the C_α, C_β, and C_γ of β-O-4, the C_3/C_4, C_2 of xylan, the C_γ of pinoresinol, the C_3, C_4, and C_5 of β-glucose, the C_3 and C_5 of β-xylose, the C_γ of α-O-4, the C_6 of α-mannose and β-mannose, and the C_6 of α-glucose and β-glucose (Peng *et al.* 2010). These weakened signals indicated that the links of α-O-4, β-O-4, and part of carbohydrates such as xylan α- and β-glucose, α- and β-mannose were hydrolyzed or dissolved out of LCC during pre-extraction. These results were similar to those of our previous study, in which the extracts of AHPP bamboo contained sugar components including xylan, glucose, mannose, and galactose (Song *et al.* 2012). Furthermore, the degradation of these sugar components in carbohydrates proved the effects of AHPP on the dissolution of pentosan and holocellulose in Tables 1 to 4. One other thing to note was that β-O-4 was generally the main coupling bond between guaiacyl and syringyl in lignin (You *et al*. 2015), which demonstrated that the structures of guaiacyl and syringyl in LCC had been degraded in some way.

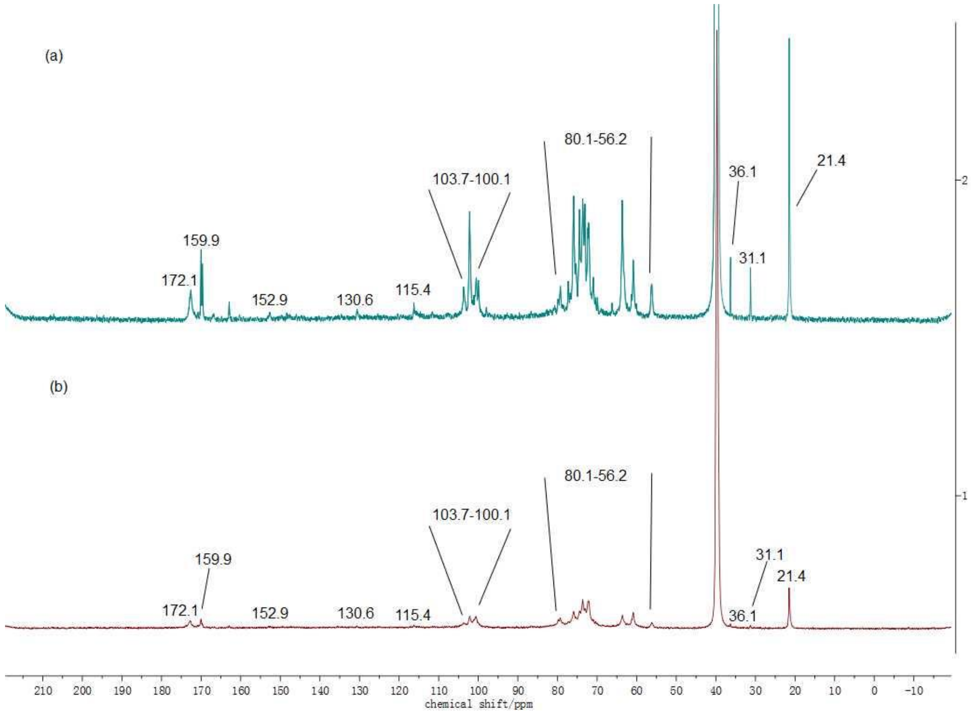

Fig. 4. ^{13}C-NMR spectra of LCC of bamboo (a) before and (b) after AHPP

It should be pointed out that the signals of Fig. 4(b) at 75.9 ppm related to the C_3/C_4 and C_2 of xylan units were weaker than those of Fig. 4(a). Gomes *et al.* (2013) found that a decrease in xylan content significantly decreased the chemical demand during the pulp bleaching process and increased the drainability of pulp. Therefore, these results suggested that APMP after AHPP treatment would obtain higher brightness than that with no pre-extraction with the same bleaching chemicals. These observations are consistent with the bleaching results from our previous study (Song *et al.* 2011).

UV spectrophotometry analysis of chromophores in bamboo MWL

Generally, the increased contents of conjugated carbonyl, catechol, and *o*-benzoquinone groups were found to contribute to the decrease in pulp brightness and increase in PC value. Furthermore, these kinds of chromophores contribute to most of the colors in pulp (Agarwal and McSweeny 1997; Agarwal 1998; Keating *et al.* 2006; Chen *et al.* 2010). Therefore, it was necessary to investigate the variations of these chromophores before and after pre-extraction, which would be advantageous to obtain a convincing explanation for the effects of AHPP on APMP brightness. The contents of conjugated carbonyl, catechol, and *o*-benzoquinone in bamboo MWL before and after AHPP treatment are shown in Table 5.

The results from Table 5 indicate that the amount of etherified carbonyl was three to four times more than that of phenolic carbonyl. Compared with the MWL without pre-extraction, different conjugated carbonyl groups in MWL after AHPP treatment decreased by different degrees and the total content of conjugated carbonyl considerably decreased, by 10.34%.

These decreases would be advantageous to the improvement of APMP brightness. On the other hand, there was more catechol than *o*-benzoquinone in bamboo MWL. It was also observed that AHPP had a comparatively evident effect on the degradation of catechol and o-benzoquinone, the contents of which decreased by 10.84% and 12.24%, respectively. These conclusions were powerfully in favor of the effects of AHPP on the brightness improvement reported in our previous work (Song *et al.* 2011).

Table 5. Contents of Conjugated Carbonyl, Catechol, and *o*-Benzoquinone in MWL Before and After AHPP

Sample	Conjugated carbonyl (%)					Catechol (%)	*o*-Benzoquinone (%)
	Etherified α-carbonyl	Etherified γ-carbonyl	Phenolic α-carbonyl	Phenolic γ-carbonyl	Total conjugated carbonyl		
Non-extracted	4.14	2.07	0.99	0.63	7.83	1.66	0.98
AHPP	3.87	1.80	0.81	0.54	7.02	1.48	0.86

Degradation of MWL and LCC

According to the previous results, it was evident that AHPP had an obvious influence on the chemical structures of MWL and LCC and that it affected the properties of APMP. To further illustrate the effects of AHPP on the variations of MWL (and LCC) chemical structures, MWL and LCC were directly degraded under simulated AHPP conditions. The ^{13}C-NMR spectra of MWL and LCC before and after degradation are shown in Figs. 5 and 6, respectively. As shown in Fig. 5(b), the signals of MWL at 172.5, 152.5, 130.7, and 116.5 ppm were slightly weakened compared with those without degradation, which illustrated that some structures of MWL, such as the -COO of acyl, cinnamic acid, benzoic acid, styrene, syringyl, guaiacyl, and etherified guaiacyl had been slightly decomposed. Also, these observations were consistent with those of Fig. 3. Signals at 45.5 and 15.5 ppm can be assigned to the methoxyl and the methoxyl of acetyl (Capanema *et al.* 2004), which were remarkably weakened after degradation. The degradation of these chromophoric groups can lead to the improvement of bamboo APMP brightness.

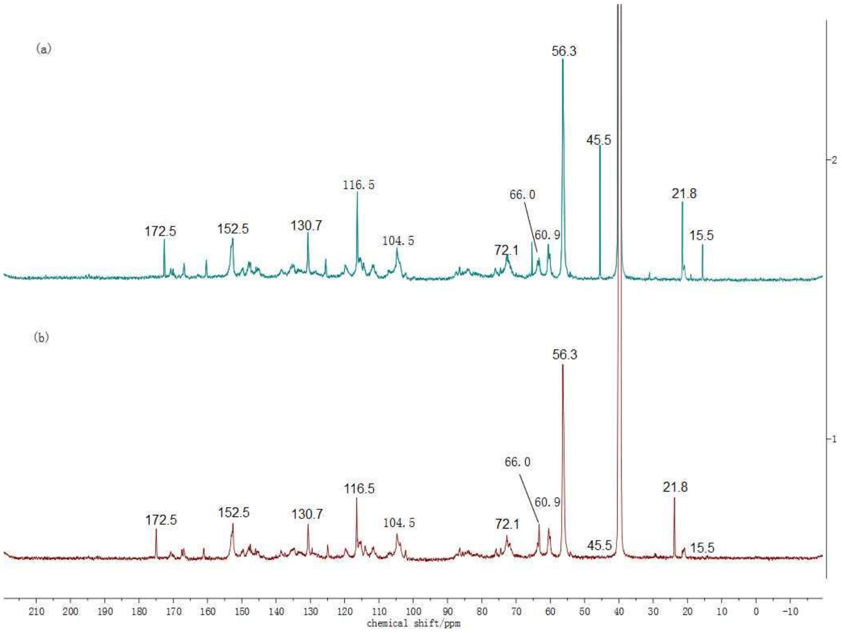

Fig. 5. ^{13}C-NMR spectra of MWL (a) before and (b) after degradation

Apparently, all the signals in Fig. 6(b) were weakened or even disappeared in comparison with those of Fig. 6(a), which indicated the degradation of LCC. Signals at 172.7, 169.6, 162.7, 116.3, and 103.3 to 99.9 ppm showed the same declining tendency with those of Fig. 4, which indicated that the amount of chromophoric groups decreased during AHPP process.

The weakened signals in the range from 79.7 to 56.0 ppm suggested that part of the carbohydrates were hydrolyzed and dissolved out of LCC. The results above were mostly in good agreement with the observations in Fig. 4. It is demonstrated that the information obtained from the study was convictive, moreover, would be instructional for the research of the effects of AHPP on APMP properties.

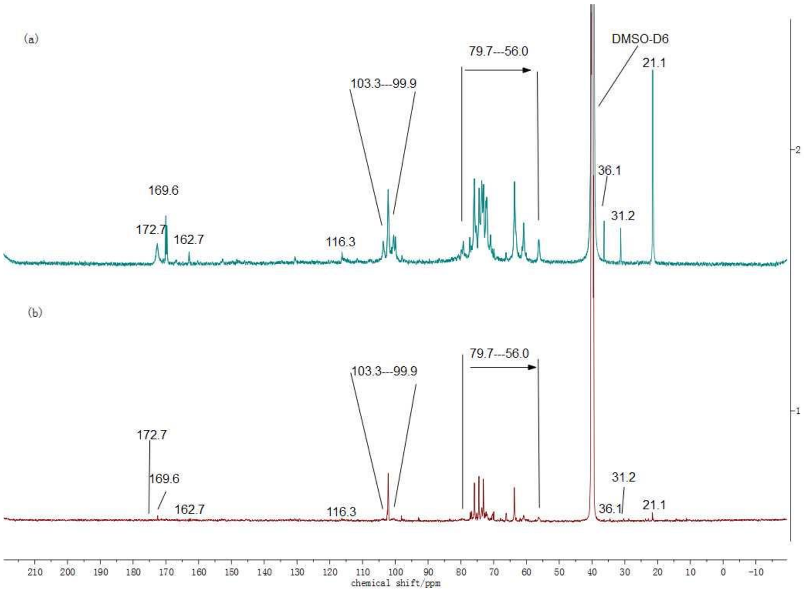

Fig. 6. ^{13}C-NMR spectra of LCC (a) before and (b) after degradation

CONCLUSIONS

1. The effects of AHPP treatment on bamboo chemical components indicated that most of the chemical components were decreased under various pre-extracting conditions. However, the pre-extracting conditions such as hydrogen peroxide dosage, reaction temperature, holding time, and solid-to-liquid ratio had noticeable effects on the dissolution of 1% sodium hydroxide extractives, benzene-ethanol extractives, and acid-soluble lignin. The increase of pre-extracting conditions did not remove pentosans efficiently.
2. The carboxyl, syringyl, guaiacyl, acetyl, and methoxyl groups of bamboo MWL were slightly degraded during AHPP treatment. However, the links between carbohydrate and lignin, and some carbohydrates such as xylan, α-glucose, β-glucose, α-mannose, β-mannose, and lignin-like structures in LCC were effectively degraded during AHPP treatment. Moreover, the contents of conjugated carbonyl, catechol, and o-benzoquinone in MWL decreased during AHPP treatment. These results validly explained the reasons of bamboo APMP relatively high brightness and low post-color number, by AHPP treatment. Moreover, the present research showed the importance of AHPP to improve bamboo APMP brightness and would further promote the possibility of bamboo APMP commercial applications.

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