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Structure and thermal property of alkaline hemicelluloses from steam exploded *Phyllostachys pubescens*

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ABSTRACT

An environmentally friendly pretreatment process was developed to fractionate hemicelluloses from dried and water-immersed *Phyllostachys pubescens* chips by steam explosion followed with alkali and alkali/ethanol extractions. The detailed chemical and structural features of the isolated hemicellulosic fractions were comparatively investigated by HPAEC, GPC, FT-IR, ^{13}C NMR spectroscopies, and TGA analysis. It was found that the xylose/arabinose ratios of hemicelluloses obtained from alkali and alkali/ethanol extractions were 21.5–34.4 and 7.7–9.9, respectively, suggesting that hemicelluloses extracted with alkali had relatively lower degree of branches than those extracted with alkali/ethanol. Hemicellulosic fractions isolated from the water-immersed samples were obtained in high yields and exhibited similar compositions, which can be used as raw materials for production of value-added products. Furthermore, the hemicelluloses extracted with alkali had relatively higher molecular weight than those extracted with alkali/ethanol. In addition, an increment of incubation time resulted in a decreased thermal stability of hemicelluloses obtained from water-immersed sample.

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1. Introduction

Lignocellulosic biomass has complex structure and is mainly comprised of three components: cellulose, hemicelluloses, and lignin. This resource can serve as a source of carbon-neutral or carbon-negative feedback for the production of biofuels, chemicals, and polymers, generally referred to as the biorefinery (Ragauskas et al., 2006). The integration of biomass and biorefinery manufacturing technologies offers the potential for the development of sustainable biopower and biomaterials that will lead to a new manufacturing paradigm (Ragauskas et al., 2006).

As we known, the most promising strategy is to integrate biofuels production into a biorefinery scheme in which the major components of the lignocellulosic biomass can be converted into value-added products to offset the costs of the whole process (Pan et al., 2005). Most biorefinery processes currently focus on cellulose as the main active participant, while less attention has been paid to hemicelluloses and lignin. Consistent with the economic requirements of a biorefinery for biomass, the recovered hemicelluloses and lignin have physiochemical characteristics suitable for the development of valuable co-products (Pan et al., 2005). In this work, we attempt to develop a biorefinery process to effectively separate cellulose, hemicelluloses, and lignin.

Lignocellulosic biomass is resistant to microbial and enzymatic deconstruction, known as biomass recalcitrance (Himmel et al., 2007). Several natural factors are believed to contribute to the recalcitrance of biomass to chemicals and enzymes, including the degree of lignification, the structural heterogeneity and complexity of cell-wall constituents, the crystalline structure of cellulose, and the inhibitors to subsequent fermentations that exist naturally in cell walls or are generated during conversion processes (Himmel et al., 2007). Therefore, biomass recalcitrance must be overcome for high-value utilization of lignocellulosic biomass. Indeed, pretreatment is one of the key steps in biorefinery process (Stark, 2011). The objective of pretreatment is to effectively fractionate hemicelluloses and lignin, and is conducive to subsequent enzymatic digestibility of cellulose. A multitude of pretreatments have been developed, and can be classified into physical, chemical, physicochemical, and biological methods (FitzPatrick, Champagne, Cunningham, & Whitney, 2010; Galbe & Zacchi, 2007). Among various pretreatments, steam explosion is one of the most common physical methods. The advantages of steam explosion

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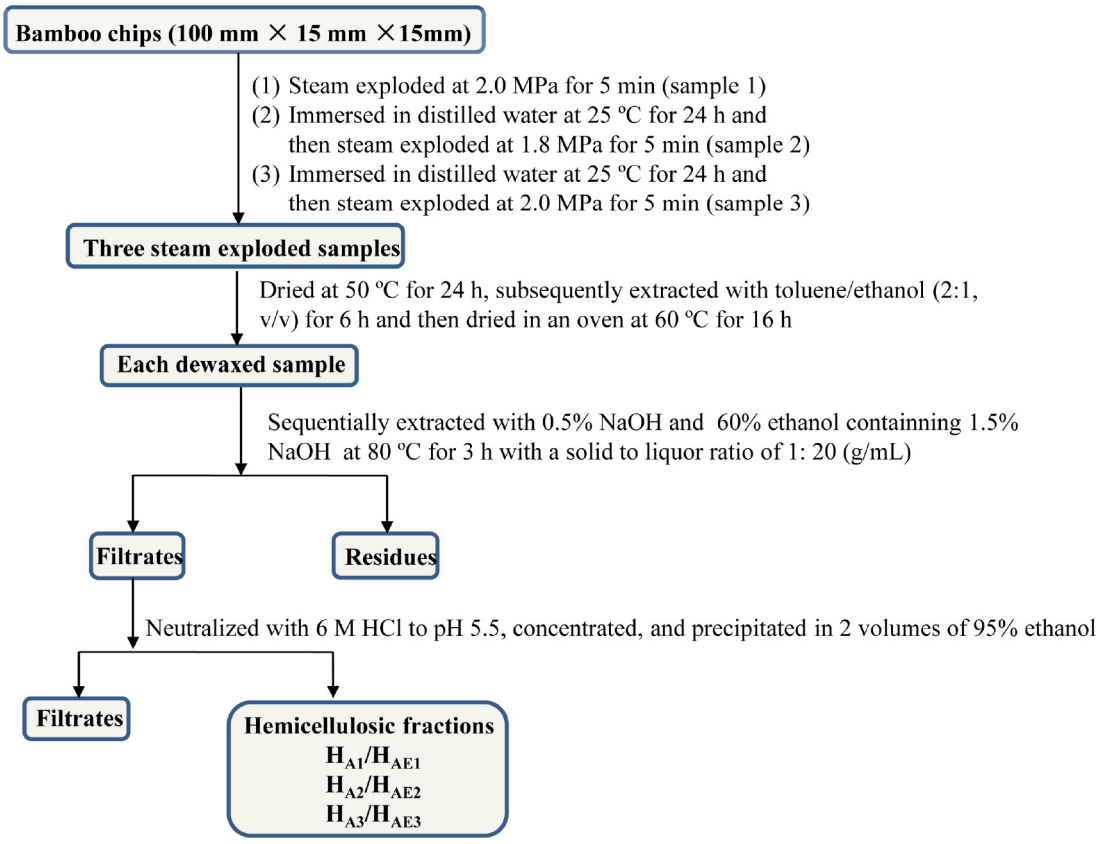

Fig. 1. Scheme of hemicelluloses fractionation.

include a significantly lower environmental impact, lower capital investment, and less hazardous process chemicals (Li, Lennholm, Henriksson, & Gellerstedt, 2001). This pretreatment has been shown to be effective in opening up biomass structure, increasing the susceptibility of cellulose fibres to enzymatic hydrolysis for the production of fermentable sugars (Ramos, Breuil, Kushner, & Saddler, 1992), and assisting the fractionation of biomass components (Heitz et al., 1991; Montané, Salvadó, & Farriol, 1997). However, steam explosion has some limitations, such as only partial destruction of hemicelluloses and incomplete disruption of the lignin-carbohydrate matrix (Sun & Cheng, 2002). Based on the above reasons, a two-stage approach by using steam explosion pretreatment followed by sequential alkali and alkali/ethanol extractions was developed to treat biomass in this study. In this approach, the main components (cellulose, hemicelluloses, and lignin) of bamboo (*Phyllostachys pubescens*) can be effectively fractionated and then used for subsequent high-valued conversion.

For comprehensive understanding of this fractionation process, the chemical structures and thermal properties of the hemicelluloses obtained were studied in detail, which will be very helpful for the further optimization of this process and the utilization of hemicelluloses.

2. Experimental

2.1. Materials

P. pubescens, which is a kind of popular bamboo in Jiangxi province (China), was air-dried and cut into an average size of 100 mm × 15 mm × 15 mm. The component analysis of the dewaxed *P. pubescens* has been determined by our group (Wen, Sun, Xue, & Sun, 2013). All chemicals purchased were of analytical or reagent grade and used without further purification.

2.2. Steam explosion pretreatment and fractionation process

Before the steam explosion pretreatment, bamboo chips were separated into three batches (300 g for each batch). To evaluate the effect of water impregnation on the subsequent steam explosion pretreatment, two batches were immersed in distilled water at 25 °C for 24 h, and the other batch was kept dry at room temperature (without water impregnation). The whole procedure for fractionating hemicelluloses is shown in Fig. 1. The steam explosion pretreatment was carried out in a 7.5 L stainless steel vessel designed especially for the processing of lignocellulosic biomass. The reactor was heated with saturated steam to reach the required pressure, at the end of the steaming, the pressure was instantaneously released to stop the reaction, and the exploded feedstock was collected. Specifically, the sample without water impregnation (sample 1) was treated at 2.0 MPa for 5 min, while the two water-immersed samples were treated at 1.8 MPa (sample 2) and 2.0 MPa (sample 3) for 5 min, respectively. Then the exploded samples were oven-dried at 50 °C for 24 h and dewaxed with methylbenzene/ethanol (2:1, v/v) in a Soxhlet apparatus for 6 h, and the samples were dried in an oven at 60 °C for 16 h. It should be noted that the components of the three dewaxed samples were determined by the standard analytical procedure of the National Renewable Energy Laboratory (NREL) (Sluiter et al., 2011). Afterwards, the three samples (10 g) were treated with 0.5% NaOH (NaOH/water = 0.5/100, w/v) (alkali treatment) under a solid-to-liquor ratio of 1:20 (g/mL) at 80 °C for 3 h to obtain hemicellulosic fractions H_{A1}, H_{A2}, and H_{A3}, respectively. Then the residuals were successively treated with 60%

ethanol containing 1.5% NaOH (ethanol/water/NaOH = 60/40/1.5, v/v/w) (alkali/ethanol treatment) under a solid-to-liquor ratio of 1:20 (g/mL) at 80 °C for 3 h to obtain another three hemicelluloses fractions H_{AE1}, H_{AE2}, and H_{AE3}, respectively. The hemicelluloses obtained with alkali and alkali/ethanol extractions were categorized as Hemi-A and Hemi-AE, respectively. The purification procedure of all hemicellulosic fractions obtained was performed according to a previous literature procedure (Sun et al., 2012).

2.3. Chemical characterization

The composition of neutral sugars and uronic acids of all hemicellulosic fractions were determined by high performance anion exchange chromatography (HPAEC). The neutral sugars and uronic acids in the fractions were liberated by hydrolyzing 10 mg hemicelluloses with 4 ml 6% sulphuric acid at 105 °C for 2.5 h. After hydrolysis, the samples were diluted 50-fold with ultrapure water and injected into a HPAEC system (Dionex ICS 3000, USA) with an amperometric detector, a Carbopac TMPA-20 column (4 × 250 mm, Dionex), and a guard PA-20 column (3 × 30 mm, Dionex). Neutral sugars and uronic acids were separated in carbonate free 18 mM NaOH under N_2 atmosphere with post-column addition of 0.3 M NaOH at a rate of 0.5 mL/min. Running time was 45 min, followed by 10 min elution with 0.2 M NaOH to wash the column and then another 15 min elution with 18 mM NaOH to re-equilibrate the column. Calibration was performed with standard solutions of L-rhamnose, L-arabinose, D-glucose, D-xylose, D-mannose, D-galactose, glucuronic acid and galacturonic acid. Results of the yields and sugar compositions of the samples were presented as mean values of three parallels, and the relative standard deviation was below 0.5%.

The molecular weights and molecular weight distributions of all hemicellulosic fractions were examined by gel permeation chromatograph (GPC), using a PL aquagel-OH 50 column (300 mm × 7.7 mm, Polymer Laboratories Ltd.). The column oven was controlled at 30 °C. The system was calibrated with PL pullulan polysaccharide standards (peak average molecular weights of 783, 12,200, 100,000, 1,600,000, Polymer Laboratories Ltd.). The detector was a differential refractive index detector (RID). The eluent was 0.02 M NaCl in 0.005 M sodium phosphate buffer (pH 7.5) and the flow rate was 0.5 mL/min. All fractions were prepared at a concentration of 0.1% before measurement. The measurement was conducted with three parallels and the relative standard deviation was below 5%.

Thermogravimetric analysis (TGA) was investigated by a simultaneous thermal analyzer (TGA Q200, TA, USA). Samples weighted 8–10 mg were heated in a platinum crucible from room temperature to 600 °C at a heating rate of 15 °C/min under N_2 atmosphere.

2.4. Spectroscopic characterization

The FT-IR spectra of all hemicellulosic fractions were recorded on a Bruker spectrophotometer in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. A KBr disc containing 1% finely ground sample was used for measurement.

The soluble-state ^{13}C-NMR spectrum was recorded on a Bruker AV III 400 MHz spectrometer operating in the FT mode at 100.6 MHz. Hemicelluloses (80 mg/mL in D_2O) were placed in the sample probe and the resonance spectra were obtained. The spectra were recorded at 25 °C after 30,000 scans. A 30° pulse flipping angle, a 9.2 μs pulse width, a 1.36 s acquisition time, and a 1.89 s relaxation delay time were used. The spectral width was 15,400 Hz for the ^{13}C-NMR.

Table 1
Chemical compositions (wt%) of the dry dewaxed *Phyllostachys pubescens*.

Sample[a]	Cellulose	Hemicelluloses	TL[b]	Total component
1	56.0	6.8	17.8	80.6
2	48.4	18.1	21.2	87.7
3	50.1	16.1	21.3	87.5

All the numbers are based on an absolute percentage of the steam-exploded dewaxed sample.

[a] Samples 1 (without water impregnation), 2 (with water impregnation at room temperature for 24 h) and 3 (with water impregnation at room temperature for 24 h) were steam exploded at 2.0, 1.8, and 2.0 MPa for 5 min, respectively.

[b] TL, total lignin (acid insoluble lignin + acid soluble lignin).

3. Results and discussion

3.1. Effects of steam explosion pretreatment on chemical components and yields of hemicelluloses

The component analysis of the raw material (without steam explosion) has been determined by our group (Wen et al., 2013). Meanwhile, the chemical compositions of the dry material (sample 1, without water impregnation) treated at 2.0 MPa and two water-immersed samples treated at 1.8 MPa (sample 2) and 2.0 MPa (sample 3) for 5 min, are given in Table 1. As compared with the raw material, the contents of hemicelluloses and lignin in steam-exploded samples decreased, which is due to the fact that steam explosion pretreatment promotes hemicellulose hydrolysis, dissolves small amounts of lignin, and opens up the plant cell wall structure (Carvalheiro, Duarte, & Gírio, 2008; Negro, Manzanares, Oliva, Ballesteros, & Ballesteros, 2003). As can be seen from Table 1, the cellulose percentage of sample 1 was higher (56.0%) than those of sample 2 (48.4%) and sample 3 (50.1%), while the hemicelluloses and lignin percentages of sample 1 (6.8 and 17.8%) were lower than those of sample 2 (18.1 and 21.2%) and sample 3 (16.1 and 21.3%).

To reduce the influence of wax on the yield and purity of hemicelluloses, 6 h methylbenzene/ethanol extraction was used. The yields of all hemicellulosic fractions are given in Table 2. In the present study, sequential extractions of dewaxed samples 1, 2, and 3 with alkali and alkali/ethanol at 80 °C for 3 h released 4.9, 9.9, and 10.4% (alkali treatment) and 3.7, 2.8, and 2.5% (alkali/ethanol treatment) hemicelluloses of the initial amounts of the dry dewaxed samples, respectively. Obviously, hemicelluloses obtained from the two-step extraction procedure accounted for 8.6, 12.7, and 12.9% of the steam exploded dewaxed samples, corresponding to 76.4, 70.3, and 70.3% of the original hemicelluloses in cell walls, respectively, indicating that most of hemicelluloses can be extracted under the given conditions. It is well known that the alkali and alkali/ethanol

Table 2
Yields of hemicelluloses and contents of neutral sugars and uronic acids (wt%) of the hemicellulosic fractions obtained from *Phyllostachys pubescens*.

	Hemicellulosic fractions[a]					
	H_{A1}	H_{A2}	H_{A3}	H_{AE1}	H_{AE2}	H_{AE3}
Yields[b]	4.9	9.9	10.4	3.7	2.8	2.5
Arabinose	3.2	2.5	2.9	10.9	9.6	8.1
Galactose	6.5	4.3	4.6	2.6	3.0	4.5
Glucose	18.0	3.9	4.6	1.3	1.6	5.4
Xylose	69.3	86.6	85.1	84.4	83.9	80.3
Glucuronic acid	2.2	2.4	2.4	0.6	1.6	1.0
Galacturonic acid	0.8	0.3	0.4	0.2	0.3	0.7
Xyl/Ara[c]	21.7	34.6	29.3	7.7	8.7	9.9

[a] H_{A1}, H_{A2}, and H_{A3} represent the hemicellulosic fractions fractionated with 0.5% NaOH at 80 °C for 3 h from samples 1–3, respectively, while H_{AE1}, H_{AE2}, and H_{AE3} represent the hemicellulosic fractions subsequently fractionated with 60% ethanol containing 1.5% NaOH at 80 °C for 3 h from the corresponding residues.

[b] Yields of the hemicellulosic fractions (% dry dewaxed sample, w/w).

[c] Xylose to arabinose ratio.

Table 3
Weight-average (M_w) and number-average (M_n) molecular weights and polydispersities (M_w/M_n) of the hemicellulosic fractions isolated from *Phyllostachys pubescens*.

	Hemicellulosic fractions[a]					
	H_{A1}	H_{A2}	H_{A3}	H_{AE1}	H_{AE2}	H_{AE3}
M_w	7410	10,080	9350	14,050	9630	4700
M_n	6380	8070	7620	10,840	8090	3960
M_w/M_n	1.16	1.25	1.23	1.30	1.19	1.19

[a] Corresponding to the hemicellulosic fractions in Table 2.

treatments may break some linkages between lignin and/or carbohydrates and hydroxycinnamic acids, such as *p*-coumaric and ferulic acids. Acidic moieties (i.e. carboxylic and phenolic groups) ionized in alkaline solutions might promote the dissolution of hemicelluloses (Scalbert, Monties, Guittet, & Lallemand, 1986). As can be seen from Tables 1 and 2, increasing the incubation pressure from 1.8 to 2.0 MPa did not significantly improve the total yield of hemicelluloses. In addition, it could be concluded that water impregnation is an effective pretreatment method to increase the yield of hemicelluloses.

3.2. Contents of neutral sugars and uronic acids

It is well known that the hemicellulosic components differ with respect to their location in plant cell wall and extraction process. The main sugars of gramineous plants are xylose, arabinose, glucose, galactose, mannose, rhamnose, and uronic acids. In this study, to analyze the difference among these hemicelluloses, the contents of neutral sugars and uronic acids of the six obtained hemicellulosic fractions, are given in Table 3. Obviously, the main sugar was xylose (69.3–86.6%), followed by glucose (1.3–18.0%), arabinose (2.5–10.9%), and galactose (2.6–6.5%). 4-*O*-methyl-D-glucuronic acid (4-*O*-Me-α-D-Glc*p*A, 0.6–2.4%) and galacturonic acid (GalA, 0.2–0.8%) were observed as minor constituents. Meanwhile, no rhamnose and mannose were detected. These data indicated that the dominant hemicelluloses in *Phyllostachys pubescen* were arabinoxylans (AXs). In AXs, linear β-(1,4)-D-xylopyranose backbone is substituted by α-L-arabinofuranosyl units in the positions 2-*O* and/or 3-*O* and by 4-*O*-Me-α-D-Glc*p*A or GalA in the position 2-*O* (Brillouet, Joseleau, Utille & Lelievre, 1982; Shibuya & Iwasaki, 1985). It is worth mentioning that a noticeable amount of glucose was observed in H_{A1} extracted with alkali from sample 1. However, less than 5.0% glucose was detected in all of the hemicelluloses obtained from water-immersed samples, which is in contrast with about 36.6% glucose isolated by combination steam explosion and alkali extraction (Wang, Xu, Sun, & Jones, 2010). On the basis of the above results, it could be concluded that hemicelluloses with relatively high purity can be obtained from the water-immersed biomass by steam explosion followed with alkaline post-treatment. Moreover, as a result of the steam explosion pretreatment, the xylose content of Hemi-A fractions treated with 0.5% NaOH was 69.3% in H_{A1} and then increased to 86.6% in H_{A2} and 85.1% in H_{A3}.

Additionally, the xylose/arabinose (Xyl/Ara) ratio linearly decreased from 21.7–34.6 for Hemi-A to 7.7–9.9 for Hemi-AE fractions, suggesting that hemicelluloses extracted with alkali had relatively lower degree of branching than those extracted with alkali/ethanol. On the other hand, as compared with H_{A1}, H_{A3} presented a higher Xyl/Ara ratio, and the similar trend was also found in fractions H_{AE1} and H_{AE3}. The results indicated that hemicelluloses extracted from the water-immersed sample had relatively lower degree of branching than those extracted from the dry sample. The results indicated that long-chain hemicelluloses having small amounts of branches were more easily obtained from the water-immersed sample than dry sample (without water-immersed).

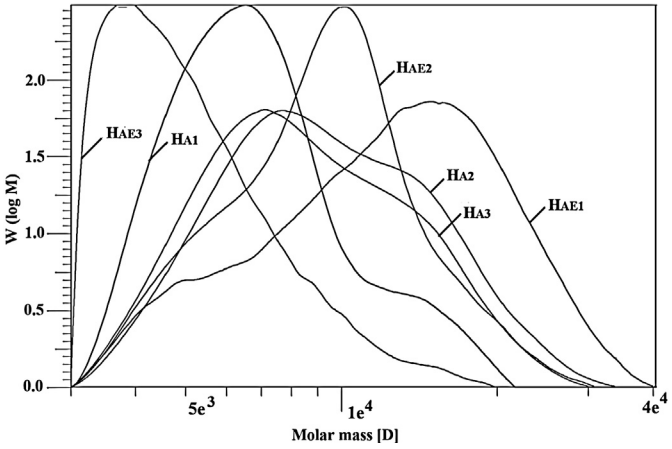

Fig. 2. Molecular weight distributions of the six hemicellulosic fractions.

3.3. Molar mass

The weight-average (M_w) and number-average (M_n) molecular weights and the polydispersity (M_w/M_n) are given in Table 3. In order to intuitively illustrate the degradation extent of hemicelluloses during steam explosion pretreatment and the following alkali and alkali/ethanol extractions, the molecular weight distribution curves of all hemicellulosic fractions are shown in Fig. 2. Obviously, for sample 1, H_{A1} exhibited a relatively lower M_w as compared with H_{AE1}, which was probably due to its low content of xylose in total sugars. For samples 2 and 3, hemicellulosic fractions H_{A2} (M_w = 10,080 g/mol; M_w/M_n = 1.25) and H_{A3} (M_w = 9350 g/mol; M_w/M_n = 1.23) showed relatively higher M_w and M_w/M_n than H_{AE2} (M_w = 9630 g/mol; M_w/M_n = 1.19) and H_{AE3} (M_w = 4700 g/mol; M_w/M_n = 1.19), respectively. This difference was probably due to the different pretreatment and extraction methods. Based on this result and Xyl/Ara ratios (Table 3), it was found that the alkali-extractable hemicelluloses obtained from water-immersed samples had high Xyl/Ara ratios, M_w and M_w/M_n, and the same result also was observed in their alkali/ethanol hemicelluloses. This is in agreement with the findings observed by Peng et al. (2012).

Generally, it is important to get hemicelluloses with narrow polydispersity because of their more homogeneous physicochemical properties. As shown by the data in Table 3, all hemicellulosic fractions showed a relatively low polydispersity index (M_w/M_n, 1.16–1.30), implying a chemical and structural homogeneity.

3.4. Structural analyses

FT-IR spectroscopy is used to identify polysaccharides, check their purity, carry out semiquantitative analyze, determine structural feature, and investigate complex and intermolecular interactions. Fig. 3 shows the FT-IR spectra of the six hemicellulosic fractions. Most of the absorption bands can be assigned according to literatures (Kačuráková, Belton, Wilson, Hirsch, & Ebringerová, 1998; Kačuráková, Ebringerova, Hirsch, & Hromadkova, 1994; Sun, Wen, Ma, & Sun, 2013). Obviously, there is no significant difference among these fractions, suggesting that these hemicelluloses had a similar structure. The signals at 3431 and 2943/2841 cm^{-1} are assigned to the stretching —OH and —CH, respectively. The absorption at 1637 cm^{-1} is attributed to the absorbed water, since hemicellulosic polymers usually have a strong affinity for water. Characteristic peaks of hemicelluloses at 1462, 1385, 1329, 1265, 1223, 1153, 1043, 983, and 898 cm^{-1} were observed, in which the signals at 1153 (the C—O—C vibration)/983 and 1043 cm^{-1} (the C—O, C—C stretching or C—OH bending) are typical signals of arabinosyl and xylopyranosyl units, respectively. The absorption bands

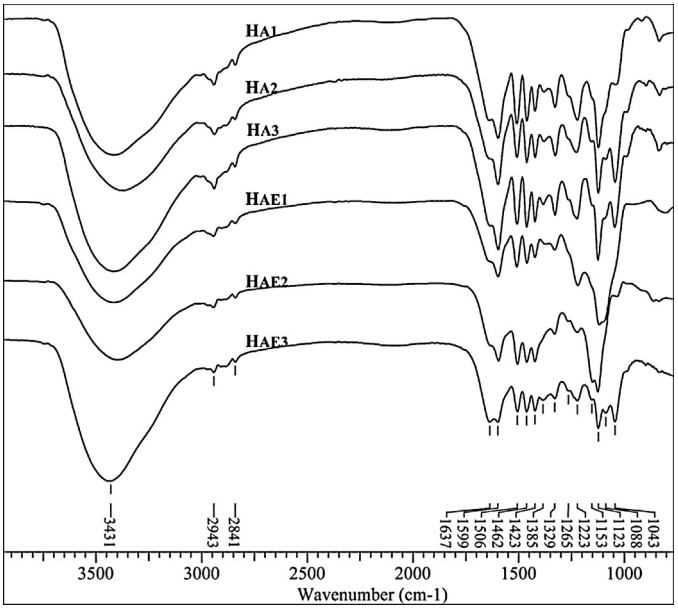

Fig. 3. FT-IR spectra of the hemicellulosic fractions.

at 1462, 1385, 1329, 1265, and 1123 cm^{-1} represent —CH_2 symmetric bending, methyl C—H wagging and —OH, —CH_2, and C—H bending, respectively. Furthermore, the occurrence of the signal at 1506 cm^{-1} in all hemicellulosic fractions is originated from the phenolic ring absorbance of lignin. Previous researches had reported that AXs isolated from gramineous plants were usually contaminated with small amounts of phenolic acid and lignins (Ebringerova, Hromadkova, Alföldi, & Berth, 1992; Hromádková & Ebringerová, 1995; Kačuráková et al., 1999). The band at 1599 cm^{-1} is attributed to uronic acid carboxylate, and the signal at 1423 cm^{-1} is from the symmetric stretching vibration of glucuronic acid groups as side chains. The intensity of the latter signal in Hemi-AE is smaller than that in Hemi-A for each sample, which was supported by the data obtained from sugar analysis. As expected, the disappearance of the ester band at about 1730 cm^{-1} in all hemicellulosic fractions revealed that the steam explosion pretreatment followed with alkaline extractions completely saponified the ester bands of hemicelluloses, such as acetyl and uronic ester groups (Wang et al., 2010). Besides, the signal at 1123 cm^{-1} in all hemicellulosic fractions is assigned to the in-plane ring stretching, which commonly presents in the FT-IR spectra of cellulosic materials, implying that a little part of cellulose was degraded into oligosaccharides and monosaccharide during the autohydrolysis process and alkaline post-treatments (Wang et al., 2010).

Generally, the shape of xylan infrared spectra strongly depends on the degree of substitution and the presence of arabinose or glucuronic units on O-2 or O-3 (Kačuráková et al., 1994, 1999). In the case of AXs highly substituted with arabinose on O-3, the intensity of the band assigned to the glycosidic bond at about 1153 cm^{-1} decreased. The decrease at 1153 cm^{-1} is accompanied with a decrease of the absorption band at about 983 cm^{-1}. It can be seen from Fig. 3 that the intensities of the two signals become weaker in the spectra of all Hemi-AE fractions than those of Hemi-A fractions, which revealed more arabinosyl units attached on O-3 of xylopyranosyl constituents. However, arabinose or Glc*p*A substitution on O-2 does not significantly affect the infrared spectra.

To further elucidate the structural features of the hemicelluloses fractionated from *P. pubescens*, hemicellulosic fraction H_{A3} was investigated by ^{13}C NMR spectroscopy (Fig. 4) and its signal assignments were made according to previous studies (Chaikumpollert, Methacanon, & Suchiva, 2004; Teleman, Lundqvist, Tjerneld, Stålbrand, & Dahlman, 2000). Obviously, the main 1,4-linked xylopyranosyl units are characterized by the five dominant peaks at 102.2, 76.1, 74.6, 73.1, and 63.3 ppm, which are assigned to C1, C4, C3, C2, and C5 of the β-D-Xyl*p* units, respectively. The signals of 4-*O*-Me-α-D-Glc*p*A with less intensity are detected at 82.6 and 59.7 ppm corresponded to C4 and OCH_3, respectively. Based on sugar compositions, FT-IR and ^{13}C spectroscopies, it could be concluded that the alkali-soluble hemicelluloses from the cell wall of *P. pubescens* were composed of 1, 4-linked β-D-Xyl*p* backbone, with Ara*f* linked to O-2 and O-3 and 4-*O*-Me-α-D-Glc*p*A linked to O-2 of the Xyl*p* residues, namely L-arabino-4-*O*-methyl-D-glucurono-D-xylan (L-Ara-4-*O*-Me-D-GlcpA-D-Xylan).

3.5. Thermal analyses

Temperatures and rates of pyrolysis, the endothermic or exothermic nature of the reactions, and the percentage of the residue at the final temperature were investigated to evaluate the thermal properties especially the thermal decomposition of hemicelluloses. In the pyrolysis reactions of hemicelluloses, acetic acid comes from the elimination of acetyl groups originally linked to xylose unit, furfural is formed by dehydration of xylose unit, formic acid proceeds to form carboxylic groups of uronic acid, and methanol arises from methoxyl groups of uronic acid (Demirbas

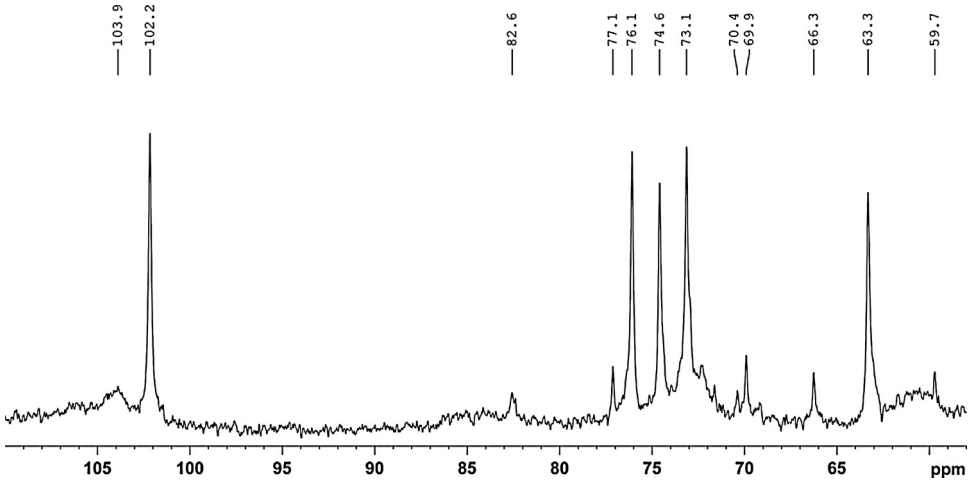

Fig. 4. ^{13}C-NMR spectrum of hemicellulosic fraction H_{A3}.

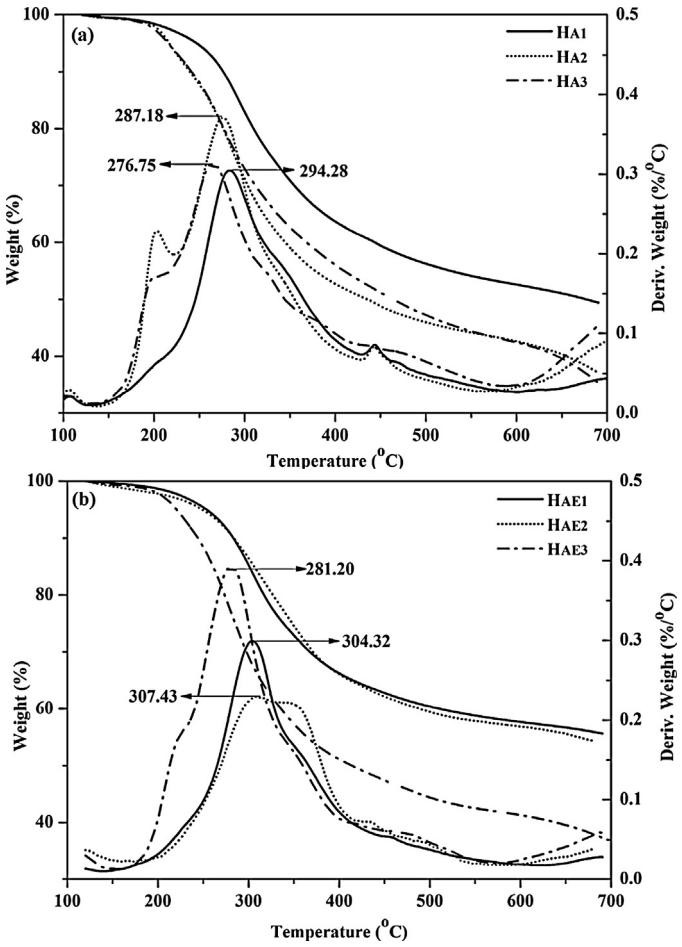

Fig. 5. Thermal gravimetric and differential thermal curves of Hemi-A (a) and Hemi-AE (b).

& Gullu, 1998). Thermal degradation (thermal gravimetric analysis TGA and differential thermal analysis DTA) curves of Hemi-A and Hemi-AE fractions are shown in Fig. 5.

The maximum decomposition temperature (TM) is defined as the temperature of the maximum decomposition rate (VM) of substrate (Hodgson et al., 2011). As shown in Fig. 5a and b, TM increased in the order $H_{A3} < H_{A2} < H_{A1}$ and $H_{AE3} < H_{AE1} < H_{AE2}$ at the main decomposition stage of 200–400 °C. A rapid decline of weight in this stage was attributed to the fragmentation of the main and side chains of hemicellulosic polymers. In this stage most of hemicelluloses (about 50–70%) decomposed and the volatiles (i.e. CO, CO_2, CH_4, CH_3COOH, and HCOOH) were released from the residual char but there was still some slight mass loss that could be seen as further scission reaction of the C—C and C—O bands (Maschio, Koufopanos, & Lucchesi, 1992; Peng & Wu, 2010). The release of CO_2 was mainly due to the cracking and reforming of functional groups of carboxyl and COOH (Yang, Yan, Chen, Lee, & Zheng, 2007). It was found that the char residues at 690 °C were 49.4% for H_{A1}, 35.4% for H_{A3}, 55.7% for H_{AE1}, and 37.3% for H_{AE3}, implying that hemicelluloses obtained from dry sample showed relatively higher residual weights than the corresponding hemicelluloses extracted from water-immersed samples.

As shown in Fig. 5a, compared with H_{A2}, H_{A3} showed lower thermal stability, probably due to more degradation in the pyrolysis process. Similar observation was also shown in H_{AE2} and H_{AE3}. Besides, hemicelluloses extracted from sample 1 presented relatively higher thermal stability as compared with those extracted from sample 3, which was due to the changes of chemical composition and structure during the steam explosion process. Furthermore, the exothermic peaks at around 700 °C in the DTA curves of all hemicellulosic fractions were presented. Yang et al. (2007) reported that the cracking of methoxy groups released methane at around 400–600 °C and a slight shift of the exothermic peak towards a high-temperature region was also observed by Wang et al. (2010). Generally, the exothermic peaks of hemicelluloses appear at lower temperatures than those of lignin, and their thermal decomposition occurs at a lower temperature. Therefore, it can be concluded that the condensation products mainly derived from lignin and hemicelluloses or their degradation products, which was also revealed by Wang et al. (2010).

4. Conclusion

In this study, *P. pubescens* chips with or without water impregnation were pretreated by steam explosion followed with alkali and alkali/ethanol extractions to fractionate hemicelluloses. Hemicelluloses fractionated from the water-immersed materials were obtained in high yields and exhibited similar compositions. The alkali-extracted hemicelluloses had relatively higher molecular weights and xylose/arabinose ratios than the alkali/ethanol-extracted hemicelluloses. This study suggests that the two-stage approach is effective to fractionate hemicelluloses from water-immersed bamboo. In this biorefinery process, all major components of the biomass can be converted into value-added products. Further work is ongoing to investigate the structures and antioxidant activity of lignin, which was also simultaneously fractionated by the two-stage approach.

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