



# Isolation of hemicelluloses from sugarcane bagasse at different temperatures: Structure and properties

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## ABSTRACT

Seven hemicellulosic fractions were extracted with 10% KOH from delignified sugarcane bagasse for 10 h at 20, 25, 30, 35, 40, 45, and 50 °C, respectively. Chemical composition and structural features of all the fractions were investigated by a combination of HPAEC, GPC, FT-IR, 1D (<sup>1</sup>H, <sup>13</sup>C) and 2D (HSQC) NMR spectra, and TGA-DTA. Notable differences in the molecular weights were observed that the fractions extracted at 20 °C, 25 °C, and 30 °C showed relatively lower molecular weights (68, 400–76, 900 g mol<sup>−1</sup>) and the extraction at elevated temperatures from 35 to 50 °C yielded the hemicellulosic populations of somewhat higher *M<sub>w</sub>* (80, 400–93, 300 g mol<sup>−1</sup>). However, the differences in the yield, chemical composition, structural features and thermal stability were much less pronounced in this study. The results also suggested that all the hemicellulosic polymers had a backbone of (1 → 4)-β-D-xylan and mainly substituted with (1 → 2) and (1 → 3)-linked arabinofuranosyl residues, and also with 4-O-methyl-D-glucuronic acid linked to O-2 of the backbone.

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## 1. Introduction

Among various agricultural residues, sugarcane bagasse is one of the most abundant lignocellulosic materials produced in the process of sugar extraction (Cardona, Quintero, & Paz, 2010). In general,  $5.4 \times 10^8$  dry tons of sugarcane is processed annually throughout the world and 1 ton of sugarcane generates 280 kg of bagasse (Cerqueira, Rodrigues, & Meireles, 2007). About 50% of this residue is used to generate heat and power to run the sugar, ethanol and distillery plants and the remaining is usually stockpiled, constituting an environmental problem due to the risk of spontaneous combustion of the stored bagasse (Lavarack, Griffin, & Rodman, 2000; Pandey, Soccol, Nigam, & Soccol, 2000). Therefore, it is necessary to develop methods for the production of fuel and chemicals which offer economic, environmental, and strategic advantages (Adsul et al., 2004). Sugarcane bagasse has a complex structure, and is primarily composed of cellulose (40–50%), hemicelluloses (25–35%), and lignin (15–35%) (Gnansounou, 2010; Hailing & Simms-Borre,

2008; Mohamed, Mohammadi, & Darzi, 2010). Among the components, hemicelluloses have emerged as an immense renewable biopolymer resource. They have the potential to be integrated in a wide variety of applications, such as film-former substances, thickeners, emulsifiers, stabilizers and binders in the food, pharmaceutical and cosmetic industries (Spiridon & Popa, 2008). In addition, hemicelluloses are precursor chemicals for the synthesis of a large number of substances via established chemical methods (furfural, 5-hydroxymethylfurfural, and levulinic acid) or via biotechnological methods (lactic acid and succinic acid production) (Neureiter et al., 2004; Wedig, Jaster, & Moore, 1987).

Hemicellulosic polymers are complex components in the cell wall of different plants. They form hydrogen bonds with cellulose, covalent bonds (mainly α-benzyl ether linkages) with lignin, and ester linkages with acetyl units and hydroxycinnamic acids, which restrict the liberation of hemicellulosic polymers from the cell wall matrix. Hence, it is necessary to isolate pure and high yield hemicelluloses and then study their structural features before converting them into value-added products through economically viable processes. So far, a number of methods have been used to isolate hemicellulosic polymers from plant sources, including extraction with alkali, alkaline peroxide, organic solvent, or ultrasonication and twin-screw extrusion treatments, as well as steam or microwave treatment. Among these methods, alkaline extractions have been widely accepted since the alkaline agents hydrolyze

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ester linkages between the hemicelluloses and the other parietal components, liberating hemicelluloses in the aqueous media. In previous studies, aqueous solutions of potassium, sodium, barium, calcium, and lithium hydroxide have been widely used to isolate hemicelluloses at different temperatures. Fazilah, Mohd Azemi, Karim, and Norakma (2009) extracted hemicelluloses using potassium hydroxide at 40 °C from oil palm frond. Xylans were isolated using aqueous potassium hydroxide at 20 °C from *Eucalyptus globules* pulps (Lisboa, Evtuguin, Pascoal Neto, & Goodfellow, 2005). Some other studies were done at 4 °C (Fares, Renard, Crepeau, & Thibault, 2004), 30 °C (Xiao, Sun, & Sun, 2001), room temperature etc. (Cyran & Saulnier, 2007; Komiyama, Kato, Aimi, Ogiyama, & Shimizu 2008; Pitkänen, Tuomainen, Virkki, Aseyev, & Tenkanen, 2008). However, to the best of our knowledge, relatively little is known about the precise nature of hemicelluloses extracted at different temperatures. The use of high temperatures increases processing costs. Therefore, the objective of this study was to extract sugarcane baggage hemicellulosic polymers at different temperatures and examine the detailed information about the structural features of all these hemicellulose samples. The hemicellulosic polymers were characterized by high-performance anion-exchange chromatography (HPAEC), gel permeation chromatography (GPC), Fourier transform infrared (FT-IR), 1D and 2D NMR spectroscopy, and thermogravimetric analysis.

## 2. Experimental

### 2.1. Materials

The raw material used in the experiment was sugarcane bagasse collected in a sugar factory (Guangzhou, China). The sugarcane bagasse was first air dried, then in an oven at 55 °C. The dried sugarcane bagasse was ground using a laboratory mill, and screened to select the fraction of particles with a size between 0.18 and 0.45 mm. After that, the powder was stored in desiccator until needed. All standard chemicals were analytical grade, purchased from Sigma Chemical Company (Beijing).

### 2.2. Isolation of hemicelluloses

The dried powder was first delignified with sodium chlorite in acidic solution (pH 3.8–4.0, adjusted by acetic acid) at 75 °C for 2 h. After the treatment, the residue (holocellulose) was filtered off and washed thoroughly with distilled water, and further dried in a cabinet oven with air circulation for 16 h at 50 °C. Subsequently, the holocellulose was extracted with 10% KOH with a solid to liquor ratio of 1:20 (g ml<sup>-1</sup>) for 10 h at 20, 25, 30, 35, 40, 45, and 50 °C, respectively. All the filtrates were acidified with glacial acetic acid until the pH reached 5.8. Then the filtrates were mixed with 2 volumes ethanol. The precipitates formed were recovered by filtration and freeze-drying and these hemicellulosic fractions were considered to be H20, H25, H30, H35, H40, H45, and H50 respectively. The scheme for the isolation of hemicellulosic polymers is illustrated in Fig. 1. All weights and yields are given on a moisture-free basis.

### 2.3. Structural and physiochemical characterization of hemicellulosic polymers

Neutral sugar composition, uronic acids, molecular weights, and thermal stability of the hemicellulosic fractions were determined as described previously (Bian, Peng, Peng, Xu, & Sun, 2010). FT-IR spectra were recorded using a Nicolet iN10 FT-IR Microscope (Thermo Nicolet Corporation, Madison, WI) equipped with a liquid nitrogen cooled MCT detector. Each sample was placed onto a micro-compression cell made of diamond and pressed in order to squeeze it. The squeezed hemicellulosic samples can be analyzed

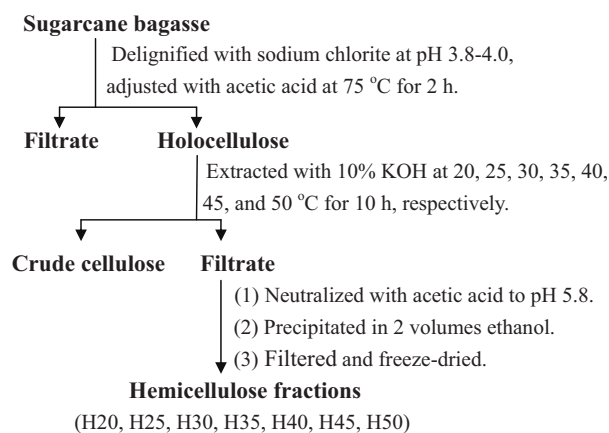


Fig. 1. Scheme for isolation of hemicellulosic polymers with different temperatures from sugarcane bagasse.

with the diamond anvil cell, placing directly on the stage of FT-IR microscope. The spectra were the average of 64 scans recorded at a resolution of 8 cm<sup>-1</sup> in the range from 4000 to 750 cm<sup>-1</sup>. The solution-state <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded based on the previously reported method by Peng, Peng, Bian, Xu, and Sun (2011). The proton-detected heteronuclear single quantum (HSQC) spectra were acquired by HSQCETGP experiment mode, over a t1 spectral width of 10,000 Hz and a t2 width of 1800 Hz and the acquired time (AQ) is 0.1278 s. The scanning time (NS) is 64. The delay between transients was 1.5 s and the delay for polarization transfer was correspond to an estimated average <sup>1</sup>H–<sup>13</sup>C coupling constant of 145 Hz. Data processing was performed using standard Bruker Topspin-NMR software.

## 3. Results and discussion

### 3.1. Yield and neutral sugar composition of hemicellulosic fractions

Strong interactions between hemicelluloses and lignin within the plant cell wall hamper their extraction from materials (Moine et al., 2007). Delignification can be considered on the basis of two observations. On the one hand, it was performed to remove lignin and also starch and protein. On the other hand, it rendered hemicelluloses more accessible to extraction (Jacobs & Dahlman, 2001). Hence preliminary delignification in this study helped considerably in the extraction of cell-wall hemicellulosic polymers from sugarcane bagasse. Since the preferred alkali is potassium hydroxide because the potassium acetate formed during the neutralization of the alkali extract is more soluble in alcohol used for precipitation than other acetate (Lawther, Sun, & Banks, 1996). In this study the delignified materials were extracted with 10% KOH at different temperatures. The yields and monosaccharide compositions of seven hemicellulosic fractions at elevated extraction temperatures are presented in Table 1. The seven hemicelluloses yielded 41.4–42.7% of the dry initial delignified materials. As can be seen from Table 1, xylose was the predominant neutral sugar component, comprising 83.1–84.6% of the total neutral sugars. A small amount of arabinose (11.0–12.1%) and minor quantities of glucose (2.1–3.1%), uronic acids (1.4–2.6%), and galactose (0.5–0.7%) were also verified in the seven hemicellulosic preparations. These results also suggested that the hemicellulosic polymers from the sugarcane bagasse were mainly composed of arabinoxylan. Apparently, all the hemicellulosic fractions extracted at elevated temperatures have a similar composition and all the sugar contents were almost equal. The molar ratios of arabinose to xylose were

**Table 1**

Yield (% dry initial delignified material) and sugar composition of hemicellulosic fractions.

Fraction <sup>a</sup>	Molar composition						
	Yield <sup>b</sup>	Ara <sup>c</sup>	Gal <sup>c</sup>	Glc <sup>c</sup>	Xyl <sup>c</sup>	UA <sup>c</sup>	Ara/Xyl
H20	41.8	11.0	0.5	2.5	83.4	2.6	0.13
H25	42.6	11.2	0.5	3.0	83.1	2.1	0.13
H30	41.4	11.3	0.5	3.1	83.8	1.4	0.13
H35	42.7	12.1	0.6	2.8	83.2	1.4	0.15
H40	42.1	11.9	0.5	2.8	83.4	1.4	0.14
H45	41.9	11.9	0.7	2.4	83.3	1.6	0.14
H50	42.4	11.3	0.5	2.1	84.6	1.5	0.13

<sup>a</sup> H20, H25, H30, H35, H40, H45 and H50 represent the hemicellulosic fractions extracted with 10% KOH with a solid to liquor ratio of 1:20 (g ml<sup>-1</sup>) for 10 h at 20, 25, 30, 35, 40, 45, and 50 °C, respectively.

<sup>b</sup> % Dry initial delignified material.

<sup>c</sup> Abbreviation: Ara, arabinose; Gal, galactose; Glc, glucose; Xyl, xylose; UA, uronic acid.

approximately 0.13–0.15. It is noteworthy that the hemicellulosic polymers extracted with aqueous potassium hydroxide at elevated temperatures from 20 °C to 50 °C had nearly equal arabinose to xylose ratios, indicating the same degree of branching. From the yields and the analysis of monosaccharide compositions, it can be concluded that the temperatures from 20 °C to 50 °C under the conditions used appears to be less important on the yield and monosaccharide composition of sugarcane bagasse hemicelluloses.

### 3.2. Distribution of molecular weight

The weight-average ( $M_w$ ) and number average ( $M_n$ ) molecular weights of the seven hemicellulosic fractions were determined by gel permeation chromatography. The values of average molecular mass and polydispersity ( $M_w/M_n$ ) of the hemicellulosic polymers are presented in Table 1, and the GPC profiles of all the fractions are shown in Fig. 2. All the alkali-soluble hemicelluloses exhibited weight-average molecular weights varying between 68,400 and 93,300 g mol<sup>-1</sup>. It is clear that the hemicellulosic fractions H20, H25, H30 extracted with 10% KOH at 20 °C, 25 °C, and 30 °C showed relatively lower molecular weights, with a  $M_w$  ranging from 68,400 to 76,900 g mol<sup>-1</sup>. When the treatment temperature increased to 35 °C, the  $M_w$  reached the highest of the seven fractions with a value of 93,300 g mol<sup>-1</sup>. However, a further increase of temperature from 40 °C to 50 °C led to a slight decrease in  $M_w$  from 82,700 to 80,400 g mol<sup>-1</sup>. This indicated that alkaline extraction with 10% KOH at 35 °C resulted in the highest molecular weight among the seven hemicellulosic fractions and the extraction at elevated temperatures (35–50 °C) yielded hemicelluloses with somewhat higher  $M_w$ . Besides, these relatively higher molecular weights may also suggest that alkaline treatment at 40–50 °C did not degrade the macromolecular structure of sugarcane bagasse hemicelluloses to a noticeable extent. Overall, an increase of temperatures from 20 to 35 °C during the alkaline extraction facilitated the dissolution of hemicelluloses with higher  $M_w$  from H20 to H25, to H30, and H35, whereas a further increase of the temperatures from 40 to 50 °C could result in a slight degradation of the dissolved hemicelluloses. The minor degradation of the hemicellulosic fraction was mainly due to the fact that the linkages between the glycosyl units were prone to be cleaved at relatively higher temperatures, which resulted in a decrease of the molecular weights of the hemicellulosic fractions from H40 to H45, and to H50. It should be noted that the molecular weights of polysaccharides vary depending on the variable factors, such as the isolation methods, solvents, calibration methods, and their estimation combinations (Fazilah, Mohd Azemi, Karim, & Norakma, 2009). In addition, the polydispersity indices of the hemicellulose fractions were 2.70–3.58, showing a broadening of the molecular weight distribution with increasing

average molecular weights. In particular, the polydispersity of H35 with 3.58 was broader compared to other fractions, which was consistent with the distribution curves (Table 2).

### 3.3. FT-IR spectroscopy

The FT-IR spectra of the hemicellulosic fractions H20, H35, and H50 are shown in Fig. 3. As can be seen, the spectral profiles and relative intensities of most bands appeared to be rather similar, indicating a similar structure of the three hemicellulosic samples. The intensive band at 1038 cm<sup>-1</sup> is assigned to C–O, C–C stretching and the glycosidic (C–O–C) contributions, indicating a dominant xylan of the alkali-soluble hemicelluloses, which corresponded to the results obtained by sugar analysis. The sharp band at 895 cm<sup>-1</sup> is indicative of the  $\beta$ -configuration of the 1  $\rightarrow$  4 glycosidic bond between xylopyranose (Xylp) units of the main xylan chains. The peaks at 1165 and 980 cm<sup>-1</sup> are suggested as an index of arabinofuranosyl (Araf) contribution (Kačuráková, Ebringerová, Hirsch, & Hromádková, 1994). The signal at 1608 cm<sup>-1</sup> is assigned to uronic acid carboxylate and the residual water was observed at 1644 cm<sup>-1</sup>. The glucuronic acid group also leaves a characteristic imprint on the small symmetric stretching vibration at 1412 cm<sup>-1</sup> (Buslov et al., 2009). Band due to carbonyl (C=O) stretching were not observed. It is verified that the alkali treatment under the condition used completely cleaved the ester bond of hemicelluloses. Although extraction with alkaline solutions is widely used for isolating hemicelluloses, the procedure suffers from the drawbacks that the acetyl groups originally present in certain hemicelluloses are removed and also may cause a certain amount of degradation of the polysaccharides (so-called alkaline peeling) (Jacobs & Dahlman, 2001). In addition, the –CH<sub>2</sub> symmetric bending exhibits a signal at 1458 cm<sup>-1</sup> and the bands at 1381, 1323 and 1246 cm<sup>-1</sup> represent C–H stretching, OH or C–O bending vibration in hemicelluloses. All these indicated that it is possible to obtain information about the chemical composition and structure of hemicelluloses by analysis of the fingerprint region between 1800 and 800 cm<sup>-1</sup>. Meanwhile, the higher frequency band of OH stretching with a maximum at 3394 cm<sup>-1</sup> and the symmetric C–H vibration band appeared at 2888 cm<sup>-1</sup>.

### 3.4. 1D and 2D NMR spectra

From a structural point of view, NMR spectroscopic analysis can provide the information such as the nature, configuration, and relative content of monosaccharide required to establish the structure of the hemicellulosic fractions. To further elucidate the structural features of the hemicellulosic polymers extracted with different temperatures, the hemicellulosic fractions H20, H35 and H50 were investigated using 1D (<sup>13</sup>C and <sup>1</sup>H) and 2D (HSQC) NMR spectroscopy. The signals for <sup>1</sup>H and <sup>13</sup>C were assigned based on the HSQC spectra following the previously reported NMR data (Bendahou, Dufresne, Kaddami, & Habibi, 2007; Habibi, Mahrouz, & Vignon, 2002; Rao & Muralikrishna, 2007).

As can be seen from Fig. 4a, three hemicellulosic preparations showed analogous <sup>1</sup>H NMR spectra, indicating a similar structure of these hemicelluloses. Examination of the data revealed three important groups of protons: major signals at 4.34 (H-1), 3.96 (H-5eq), 3.66 (H-4), 3.40 (H-3), 3.25 (H-5ax), and 3.18 (H-2) ppm, assigned to D-xylopyranosyl units (Habibi et al., 2002). Other two groups of less intense signals, with the first corresponding to arabinofuranosyl units and the second attributed to 4-O-methyl-D-glucuronic acid residues.

The <sup>13</sup>C NMR spectra (Fig. 4b) contained five major signals corresponding to (1  $\rightarrow$  4)-linked- $\beta$ -xylan. The signal at 102.32 ppm corresponded to the anomeric region in a  $\beta$ -configuration, as confirmed by the <sup>1</sup>H NMR spectra, while the signals at 75.89, 74.91,

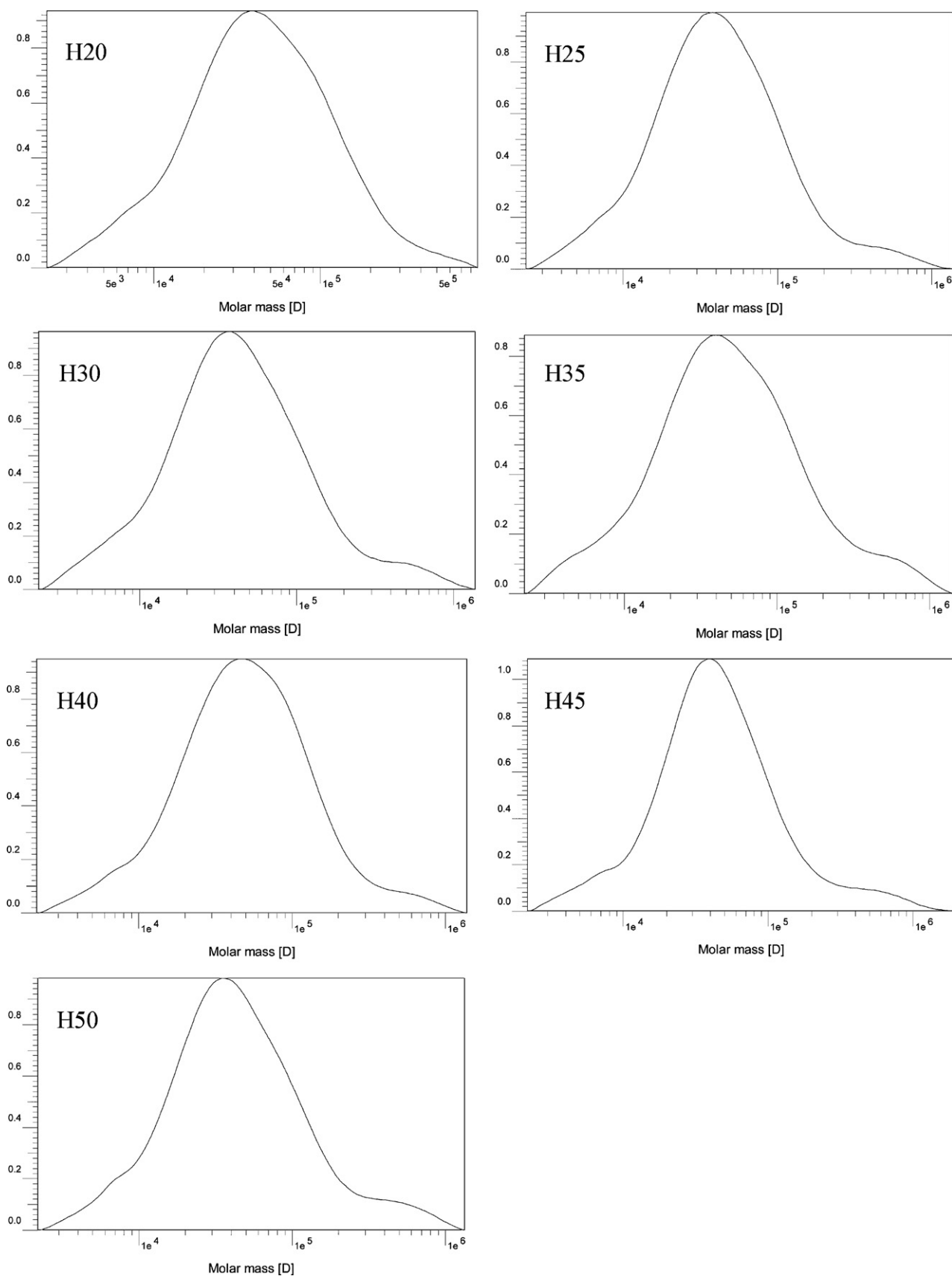


Fig. 2. Molecular weight distribution of hemicellulosic fractions.

**Table 2**Weight-average ( $M_w$ ) and number-average ( $M_n$ ) molecular weights and polydispersity ( $M_w/M_n$ ) of the hemicellulosic fractions.

	Hemicellulosic fraction <sup>a</sup>						
	H20	H25	H30	H35	H40	H45	H50
$M_w$	68,400	71,200	76,900	93,300	82,700	80,900	80,400
$M_n$	25,400	25,500	24,700	26,000	28,800	26,700	25,900
$M_w/M_n$	2.70	2.79	3.11	3.59	2.87	3.03	3.10

<sup>a</sup> Corresponding to the hemicellulosic fractions in Table 1.

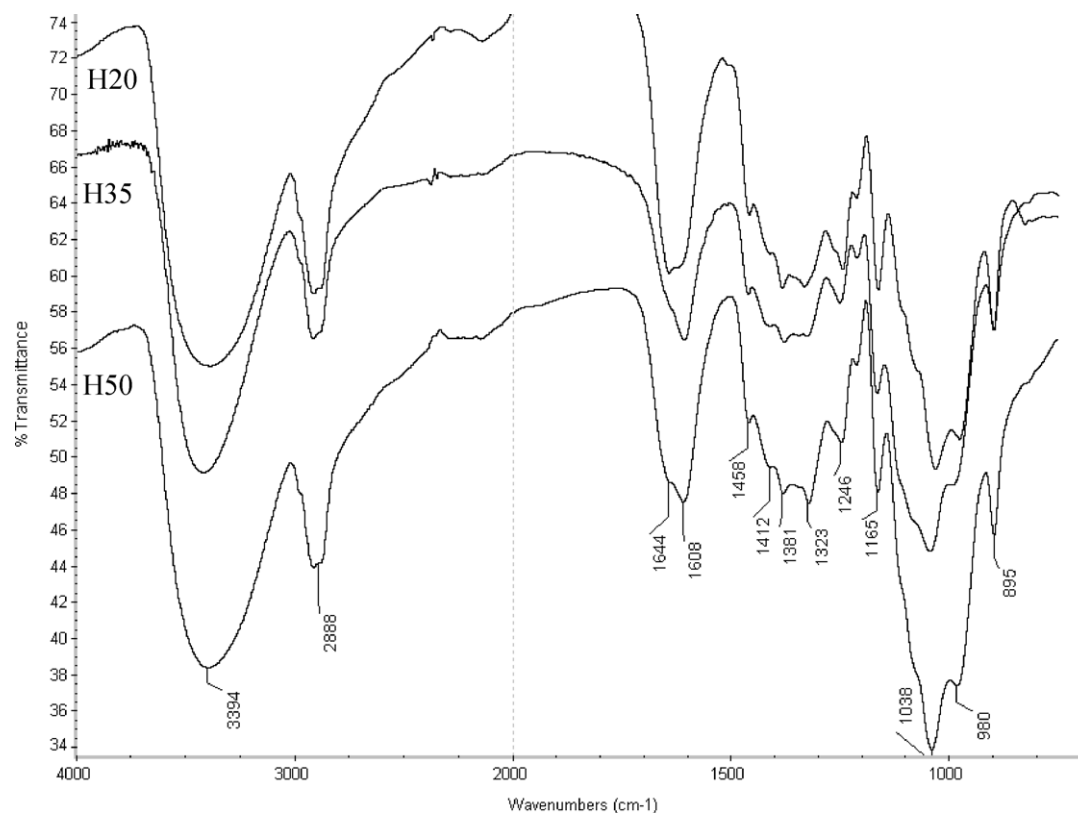
73.28, and 63.27 ppm corresponded to C-4, C-3, C-2, and C-5 of D-Xylp, respectively (Bendahou et al., 2007). Concerning the Araf units, the signals of C-1, C-4, C-2, C-3, and C-5 appeared at 109.50, 86.46, 80.23, 78.37, and 61.72 ppm, respectively. Moreover, small signals at  $\delta$  177.01, 97.46, 72.12, 73.86, 79.26, and 59.53 ppm, are characteristic respectively of COOH, C-2, C-3, C-4 and OCH<sub>3</sub>-4 of 4-O-methyl- $\alpha$ -D-glucuronic acid residues.

More specific information about the hemicellulosic fractions was obtained by 2D HSQC spectra. Fig. 5 shows the detailed NMR information of hemicellulose fraction H20. From this figure, it can be seen that the resonances of the anomeric protons of the arabinofuranosyl and 4-O-methyl- $\alpha$ -D-glucuronic acid residues overlapped at 5.18 ppm. The two peaks at  $\delta$  5.36 and 5.18 ppm are indicative of arabinosyl residues linked to O-2 and O-3 of the same xylose residue (Rao & Muralikrishna, 2007). Besides, the <sup>1</sup>H/<sup>13</sup>C cross peaks in HSQC spectra at  $\delta$  102.32/4.34 confirmed the (1  $\rightarrow$  4)- $\beta$ -glycosidic linkages of the xylan backbone. In spite of the occurrence of a low content of 4-O-methyl-D-glucuronic acid and higher contour levels of HSQC spectrum, only the OCH<sub>3</sub> at 59.53/4.34 ppm was detected in the spectrum corresponding to 4-O-methyl-D-GlcA residues. The results suggested that different temperatures did not cause diversity of structural features of hemicellulosic fractions in this study

and their structure was very similar with a linear (1  $\rightarrow$  4)- $\beta$ -D-xylan backbone decorated with branches at O-2 and O-3 of arabinofuranosyl or at O-2 of 4-O-methylglucuronic acid unit.

### 3.5. Thermal analysis

In evaluation of the thermal properties especially the thermal decomposition of different macromolecules, information of three parameters including the temperatures and rates of pyrolysis, the endothermic or exothermic nature of the reactions, and the percentage of the residue at the final temperature should be investigated. Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) curves of the hemicellulosic fractions H20, H35 and H50 are shown in Fig. 6. As can be seen, the TGA curves of the pyrolysis process appear to be divided into three weight loss phases. At the first stage, the samples just lost water, which was physical change (Peng & Wu, 2010). The endothermic peaks appear on the DTA curves at  $\sim$ 150 °C corroborate the moisture absorbed by hemicelluloses evaporate during heating up. At the second stage, the TGA curves showed similar behavior with one main stage of weight loss at temperatures between 220 and 320 °C for all three hemicellulosic fractions. This step can be ascribed

**Fig. 3.** FT-IR spectra of hemicellulosic fractions H20, H35, and H50.



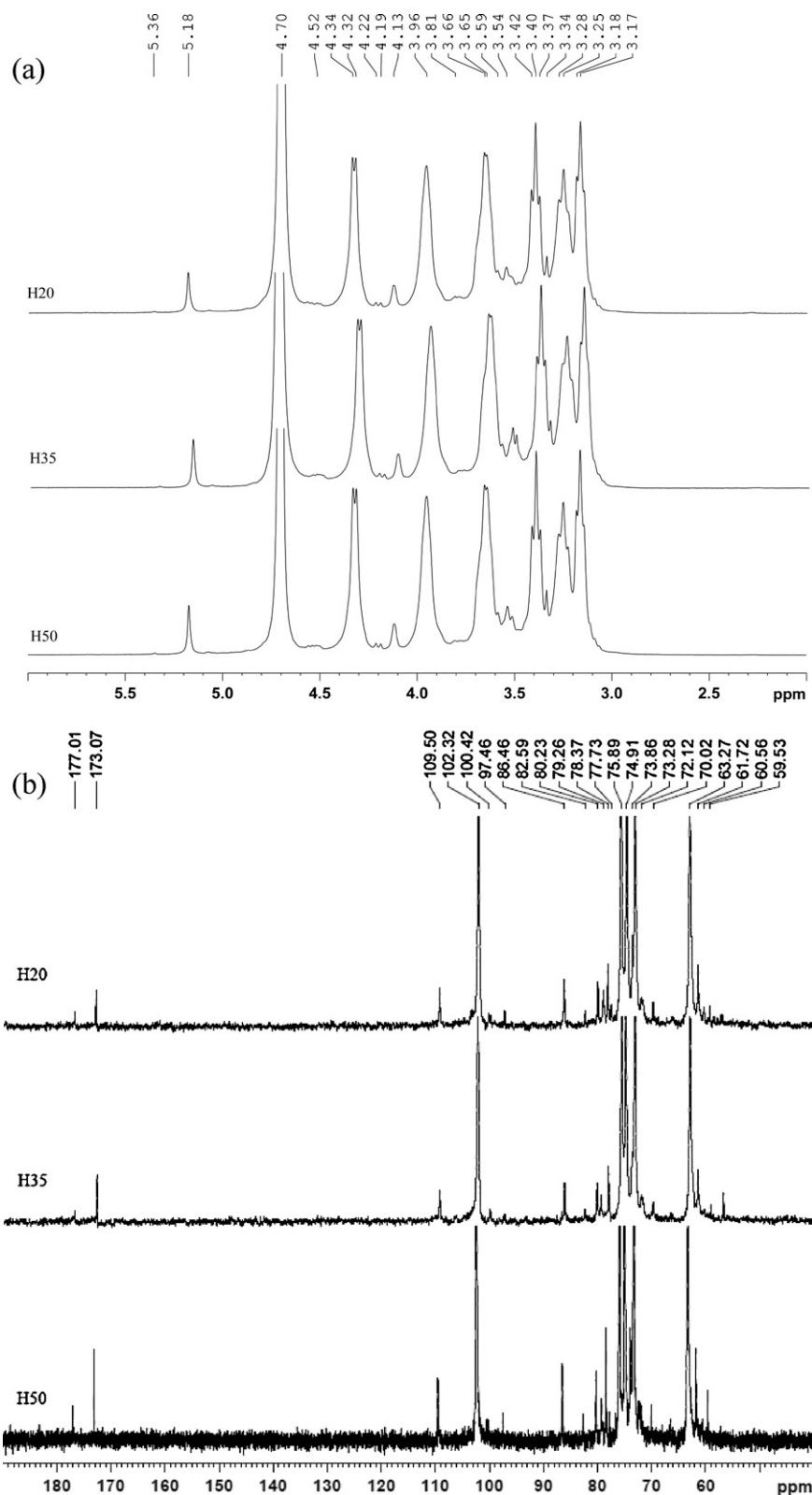


Fig. 4.  $^1\text{H}$  NMR (a) and  $^{13}\text{C}$  NMR (b) spectra of hemicellulosic fractions H20, H35 and H50.

to pyrolysis phase and the hemicelluloses began to pyrolyze and dehydration and fragmentation of side chains may take place. Moreover, the decarboxylation and decarbonylation may also take place in this stage and hemicellulosic polymers decompose into  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{CH}_3\text{COOH}$ , and  $\text{HCOOH}$  etc. (Hu, Zhou, & Qu, 2000;

Maschio, Koufopoulos, & Lucchesi, 1992). At the point about  $310^\circ\text{C}$ , exothermal peaks appear in this stage on the DTA curve. The last stage, the weight loss was not very evident. The exothermal peaks change into relatively smooth ones, this means that the rates of heat released slow down. However, it should be noted that there were

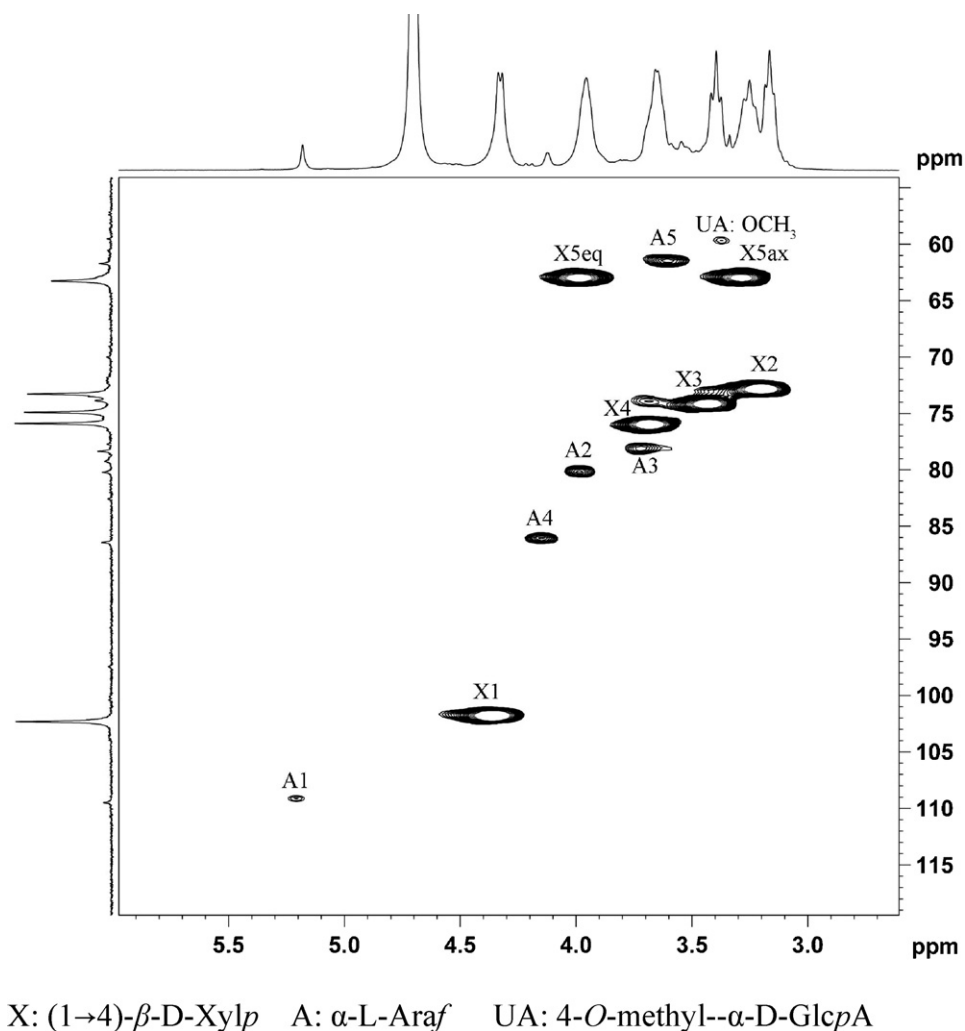


Fig. 5.  $^1\text{H}/^{13}\text{C}$  NMR (HSQC) spectrum of hemicellulosic fraction H20.

still ~20% solid residues left at 600 °C for all hemicellulose samples. This is probably due to the salts formed during the extraction processes and end-products of the decomposition of hemicelluloses. Taken together, there was no clear difference of thermal stability among these fractions.

#### 4. Conclusion

There were no significant differences in the yields of the seven hemicellulosic fractions isolated at the temperatures of 20–50 °C (41.4–42.7%), and all these hemicelluloses have similar compositions which were composed of large quantities of xylose (83.1–84.6%) and small amounts of other sugar components. However, the alkaline extraction with 10% KOH at 35 °C resulted in the highest molecular weight and the extraction at elevated temperatures (35–50 °C) yielded hemicelluloses of somewhat higher  $M_w$  than those extracted at 20–30 °C. The alkaline treatments at 40–50 °C did not degrade the macromolecular structure of sugarcane bagasse hemicellulosic polymers to a noticeable extent. In addition, all the seven fractions had a similar structure and they all were 4-O-methyl-glucuronoarabinoxylans consisting of a linear (1→4)- $\beta$ -D-xylopyranosyl backbone decorated with branches at O-2 and O-3 of arabinofuranosyl or at O-2 of 4-O-methylglucuronic acid unit.

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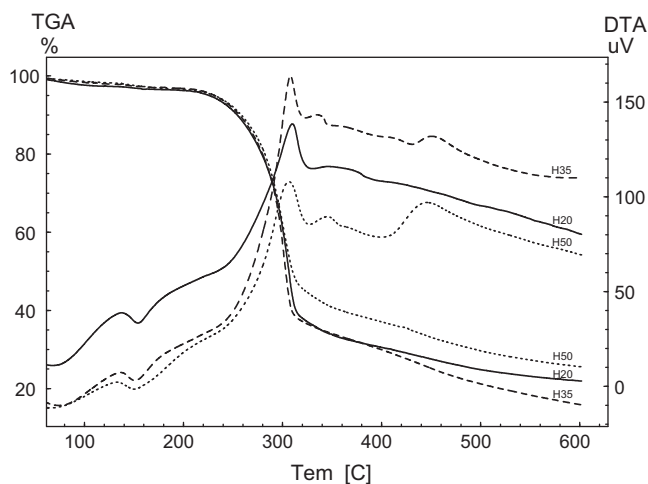


Fig. 6. Thermogram of hemicellulosic fractions H20, H35 and H50.

Technology (973, 2010CB732204), and China Ministry of Education (No. 111).

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