Comparative Study of Water-soluble and Alkali-soluble Hemicelluloses Extracted by Hydrothermal Pretreatment

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Abstract: The purpose of this study was to explore the differences of the hemicelluloses extracted by hydrothermal pretreatment using water and alkaline solutions (NaOH or KOH). The physicochemical properties and structural characteristics of two water-soluble and four alkali-soluble hemicelluloses extracted from the triploid of *Populus tomentosa Carr*. through the hydrothermal pretreatment were comparatively studied. It was observed that the alkalis (NaOH and KOH) were more effective than distilled water as extractants. Sugar analysis showed that xylose (66.83%~86.49%) was the major constituent, followed by glucose (6.83%~18.49%). Mannose (1.40%~8.42%), galactose (2.17%~4.05%), and arabinose (0.21%~2.26%) were also detected in the hemicellulosic fractions. The results of gel-permeation chromatography (GPC) indicated that the hemicelluloses extracted using the alkaline solutions had relatively higher molecular weights than those solubilized in distilled water. Further, based on spectroscopic ^{1}H-nuclear magnetic resonance (^{1}H-NMR) and two-dimensional heteronuclear singular quantum correlation (2D-HSQC) analyses, it was confirmed that the hemicellulosic fractions had a major structure of (1→4)-β-*D*-xylan and a minor structure of (1→4)-α-*D*-glucan with small amounts of substituted sugars and glucuronic acid attached.

Keywords: water- and alkali-soluble hemicelluloses; hemicellulose structure; hydrothermal pretreatment



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1 Introduction

Hemicelluloses, which are one of the primary components of biomass, have attracted

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much attention owing to their high potential for use as fuels as well as versatile materials in the chemical and biomedical industries[1]. The physicochemical properties and structural characteristics of hemicelluloses depend largely on the feedstocks and pretreatment methods. Thus, several researchers have devoted significant efforts to the effective extraction and isolation of hemicelluloses. The strategies that have been explored successfully include alkali extraction[2-3], organic solvent extraction[4], the ultrasound-assisted method[5], microwave irradiation[6], the steam explosion method[7], column chromatography[8], and the hydrothermal method[9-10]. Hemicelluloses could be extracted from sweet sorghum stem in a yield of 76.3% using 60% ethanol containing 2.5% KOH at 75℃ for 3 h[2]. Sun et al[4] extracted hemicellulosic fractions from *Tamarix austromongolica* using organic solvents (dimethyl sulfoxide and triethylamine) and KOH solutions. They found that compared to the hemicellulosic fractions isolated using the KOH solutions, the organosolv-soluble hemicellulosic fractions contained higher amounts of glucose (6.5%~33.7%) and arabinose (5.6%~14.8%) and lower amounts of xylose (54.8%~62.2%). Janker-Obermeier et al[6] reported that more than 80% of the hemicelluloses could be removed from wheat straw without excessive saccharide degradation or solubilizing high amounts of cellulose through microwave-assisted alkali pretratment.

Compared to the conventional methods, the hydrothermal pretreatment is a promising one for the extraction and isolation of hemicelluloses and has the advantages of a short reaction time, high percentage conversion, and relatively low reaction temperature[10]. The hydrothermal pretreatment has been reported to be an effective method for obtaining a series of xylooligosaccharides from the major components (cellulose, hemicellulose, and lignin) of lignocelluloses[11-12]. Hemicelluloses with an 82.2% xylan could be separated from corncob using the continuous-flow-type hydrothermal method at 200℃ for 10 min[13]. More recently, carbohydrates and lignin were successfully extracted from triticale, wheat, barley, oats, canola, and mustard straws by a hydrothermal treatment at 165℃ for 20~30 min[14]. Guo et al[15] performed a hydrothermal pretreatment on lignocelluloses using both acids and alkalis. The lignocelluloses were treated with 0.73% H_2SO_4 at 150℃ for 6.1 min in the first stage and 0.024 g lime/g at 202℃ for 30 min in the second stage. This resulted in high glucose (>80%) and xylose (>70%) recovery yields. In a previous study, our group extracted hemicellulosic fractions from the triploid of *Populus tomentosa Carr*. by sequential organic solvent (dimethylformamide) extraction at 160℃ for 24 h using the hydrothermal method[10].

Alkali-based extraction has several advantages. For instance, it is easier to perform, more environmentally friendly, and more cost-effective compared to other pretreatment methods. This method has been used to separate cellulose, hemicellulose, and lignin and is highly suited for fully utilizing lignocelluloses[16]. The alkali extraction of hemicelluloses includes a treatment with a NaOH or KOH aqueous solution and an alkaline hydrogen peroxide solution[2,17-18]. Approximately 83.7% of the total hemicelluloses could be extracted from delignified *Populus gansuensis* using KOH solution at 25℃ for 10 h[17]. Xu et al[18] investigated the extraction of alkali-soluble hemicelluloses with higher molecular weights from perennial ryegrass leaves (*Lolium peree*) using NaOH or KOH at 22℃ for 2 h or 16 h.

The triploid of *Populus tomentosa Carr*., which is a fast-growing hardwood species and is widely planted in Northern China to prevent wind erosion and control desertification, is of considerable economic and ecological importance. Although the native structural features of hemicelluloses from *Populus tomentosa Carr*. have been investigated by many methods, such as the alkali extraction[3], ultrasound-assisted method[5], stepwise dilute sulfuric acid-catalyzed hydrothermal pretreatment[9], sequential organic solvent (dimethylformamide) extraction through hydrothermal method[10], and the sequential three-step extraction with different volume ratios of dioxane and water containing 1% NaOH[19]. However, to our knowledge, there is no comparative study on water-soluble and alkali-soluble

hemicelluloses extracted by hydrothermal pretreatment. In addition, determining the structure of extracted hemicelluloses prior to preparing hemicellulose-based materials is of prime importance.

With these facts in mind, two water-soluble and four alkali-soluble hemicelluloses were extracted from the triploid of *Populus tomentosa Carr*. through hydrothermal pretreatment at 160℃ for 12 h or 24 h using distilled water, 1 mol/L NaOH, and 1 mol/L KOH aqueous solutions, respectively, and the physicochemical properties and structural characteristics of hemicelluloses were investigated systematically. A series of characterizations were performed, which yielded interesting results. For example, xylose (66.83%~86.49%) was found to be the major constituent while glucose (6.83%~18.49%) and mannose (1.40%~8.42%) were the secondary components in these hemicelluloses. The hemicelluloses extracted using the alkaline solutions had relatively higher molecular weights than those solubilized in distilled water. Further, the hemicellulosic fractions had a major structure of (1→4)-β-*D*-xylan and a minor structure of (1→4)-α-*D*-glucan attached with small amounts of substituted sugars and glucuronic acid. It is hoped that the structural characterization of the isolated water-soluble and alkali-soluble hemicelluloses will result in these hemicelluloses being used as green and novel biomaterials through biorefinery processes.

2 Experimental

2.1 Materials

Timbers of the triploid of *Populus tomentosa Carr*. (3 years old) were obtained from Shandong Province, China. Chips of the wood were ground to pass through a mesh sieve whose pore size corresponded to 40~60 wires per inch. The waxes were removed from the wood powder with a Soxhlet apparatus under reflux (98℃) for 6 h using toluene/ethanol (2∶1, v/v). The dewaxed sample was dried in a cabinet oven with air circulation at 60℃ for 16 h. The delignification of the extractant-free sample was performed using the following method. First, the extractant-free sample (15 g) was mixed with 300 mL of aqueous solution which contained 15 g of $NaClO_2$ in a flask. Then, the mixture was acidified to a pH value of 3.8~4.0 using acetic acid, and the flask was heated in a water bath at 75℃ under continuous stirring for 1 h. Next, 7.5 g of $NaClO_2$ and half the volume of the acetic acid used before were added to the flask, which was kept for another hour under the same conditions. After the completion of the delignification process, the obtained holocellulose was dried at 60℃ for 16 h. All the chemicals used were of analytical grade and purchased from Sigma Chemical Company (Beijing, China).

2.2 Extraction of hemicelluloses

The scheme for the extraction of hemicelluloses from *Populus tomentosa Carr*. through the hydrothermal method using distilled water or alkaline solutions is shown in Fig.1. The hemicelluloses were separated from the holocellulose (1 g) through extraction using 30 mL of distilled water or a 1 mol/L KOH aqueous solution or a 1 mol/L NaOH aqueous solution at 160℃ for 12 h or 24 h. The resulting filtrates were concentrated under reduced pressure to approximately 50 mL. Anhydrous

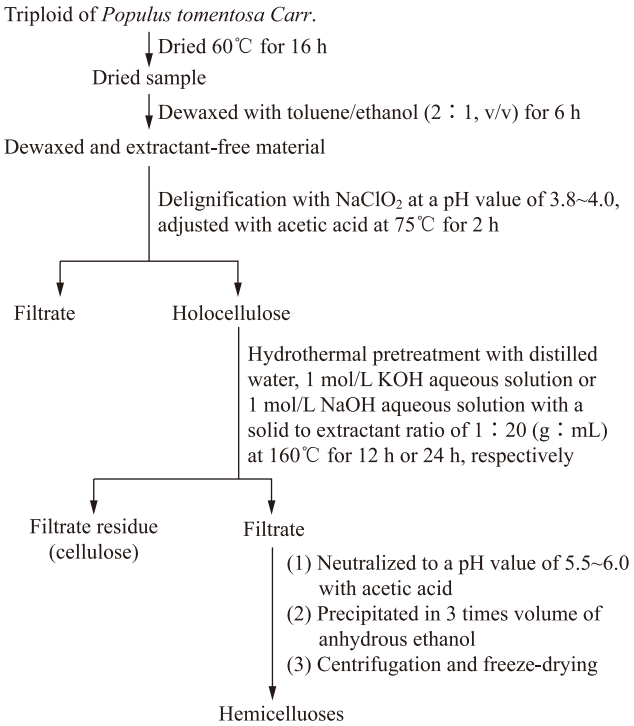


Fig.1 Scheme for extraction of hemicelluloses from triploid of *Populus tomentosa Carr*.

ethanol was added, and the resulting mixtures were kept still overnight. The precipitates were obtained by freeze-drying after centrifugation. The hemicelluloses obtained using distilled water, NaOH, or KOH for 12 h or 24 h were labeled as H1 and H2, H3 and H4, H5 and H6 (as shown in Table 1), respectively. All the weights and yields given were on a moisture-free basis.

Table 1 Yields of the six hemicelluloses extracted using different extractants at 160℃ for different durations

Hemicelluloses	Extractant	Time/h	Yield/%
H1	Distilled water	12	0.30±0.05
H2	Distilled water	24	0.24±0.03
H3	1 mol/L NaOH	12	3.87±0.22
H4	1 mol/L NaOH	24	3.27±0.17
H5	1 mol/L KOH	12	3.62±0.19
H6	1 mol/L KOH	24	3.06±0.29

2.3 Chemical characterization

Fourier-transform infrared (FT-IR) spectroscopy was performed on a Nicolet iN10 spectrophotometer with a mercury cadmium telluride detector. The spectra were recorded in the wave number of 675~4000 cm^{-1} at a resolution of 4 cm^{-1}. The solution-state ^{1}H-NMR spectrum was recorded on a Bruker AVIII 400 MHz spectrometer using a 20 mg sample in 1.0 mL of D_2O. Heteronuclear single quantum coherence (HSQC) experiment was also performed on a Bruker AVIII 400 MHz spectrometer using a 20 mg sample dissolved in 1.0 mL of D_2O. The spectral widths for ^{1}H-NMR and HSQC were 20 000 Hz and 5000 Hz, respectively. The concentrations of the neutral sugars and uronic acids in the six hemicelluloses were determined using a high-performance anion-exchange chromatography system (Dionex ICS3000, US) with an amperometric detector, an AS50 autosampler, a Carbopac™ PA-20 column (Dionex), and a guard PA-20 column (Dionex). The average molecular weights (*M*w) of the samples were estimated by gel-permeation chromatography (GPC) performed using a PL aquagel-OH 50 column (Polymer Laboratories Ltd.) calibrated with pullulan polysaccharide standards (peak average molecular weights of 738, 12 200, 100 000, and 1600 000, Polymer Laboratories Ltd.).

3 Results and discussion

3.1 Yields of hemicelluloses

The yields of the extracted hemicelluloses were listed in Table 1. It could be seen that the yields of H1, H2, H3, H4, H5, and H6 were 0.30%, 0.24%, 3.87%, 3.27%, 3.62%, and 3.06%, based on the dewaxed material, 1.32%, 1.09%, 17.26%, 14.61%, 16.17%, and 13.66%, based on the hemicelluloses in the raw material, respectively. The highest extraction yield (3.87%) was obtained using 1 mol/L NaOH aqueous solution at 160℃ for 12 h. As expected, the results indicated that the yields of hemicelluloses obtained using the NaOH aqueous solution and KOH aqueous solutions were similar and the alkaline extractants were more effective than distilled water. It is believed that the hydroxyl ions liberated from the alkaline solutions cause the cellulose to swell, leading to the breakage of the intermolecular hydrogen bonds between the cellulose and the hemicellulose. The hydrolysis of the ester bonds, which played an important role in connecting the polysaccharides of the cell wall, resulted in the liberation of substantial amounts of hemicelluloses from the cell wall[20]. It could be seen from Table 1 that the yields of both the water-soluble and the alkali-soluble hemicellulosic fractions decreased with an increase in the extraction time from 12 h to 24 h. This might be because of the thermal instability of hemicelluloses; with an increase in the extraction time, the high temperature (160℃) probably induced the degradation of the hemicelluloses, resulting in a decrease in the yields. In a previous study[21], we had observed a weight loss of 10.53% at 160℃, which had confirmed the thermal instability of hemicelluloses; this loss was attributable to the fracturing of the side chains (such as uronic acids).

3.2 Contents of neutral sugars and uronic acids

The constituents of carbohydrate polymers are determined not only by their location in the cell wall but also by the extraction method used[22]. For this reason, the six hemicellulosic fractions were subjected

to a sugar analysis. The results were listed in Table 2. The data indicated that xylose (66.83%~86.49%) was the primary unit in all the hemicellulosic fractions, followed by glucose (6.83%~18.49%). Mannose (1.40%~8.42%), galactose (2.17%~4.05%), and arabinose (0.21%~2.26%) were also present as minor components. Uronic acid was only detected in H6, and it was probably 4-*O*-methyl-α-*D*-glucuronic acid, along with minor amounts of *D*-galacturonic acid or *D*-glucuronic acid. These results suggested that the hemicellulosic fractions of triploid of *Populus tomentosa Carr*. probably mainly contained the glucomannan and galactose side chains.

Table 2 Contents of neutral sugars and uronic acids of the six hemicellulosic fractions %

Hemicelluloses	Arabinose	Galactose	Glucose	Xylose	Mannose	Uronic acid
H1	2.26±0.13	4.01±0.74	18.49±0.87	66.83±0.58	8.42±0.29	ND
H2	2.19±0.17	3.88±0.81	17.51±0.86	68.62±0.93	7.81±0.16	ND
H3	0.36±0.04	2.17±0.18	10.79±0.72	82.82±0.79	3.86±0.22	ND
H4	0.21±0.07	2.19±0.43	12.91±0.10	80.45±0.52	4.23±0.34	ND
H5	1.11±0.01	4.05±0.54	6.83±0.59	86.49±0.82	1.51±0.04	ND
H6	0.71±0.04	3.71±0.47	7.63±0.19	84.99±0.98	1.40±0.03	1.55±0.03

*ND, not detectable.

Interestingly, the xylose content was higher and the glucose content was lower in the alkali-soluble hemicellulosic fractions (H3~H6), as compared to the case for the water-soluble hemicellulosic fractions (H1 and H2). It could be seen from Table 2 that the xylose contents increased from 66.83% (H1) and 68.62% (H2) to 82.82% (H3) and 80.45% (H4), respectively, while the glucose contents decreased from 18.49% (H1) and 17.51% (H2) to 10.79% (H3) and 12.91% (H4), respectively. When the 1 mol/L KOH solution was used instead of the 1 mol/L NaOH solution, the xylose contents increased further to 86.49% and 84.99% in H5 and H6, respectively, while the glucose contents decreased to 6.83% and 7.63%. A similar decreasing trend was also observed in the case of the mannose content. These results indicated that glucose and mannose were probably present as side chains in the hemicelluloses of *Populus tomentosa Carr*. and that they were partially cleaved or degraded in the alkaline solutions and subsequently readily solubilized during the extraction process. In contrast to the case for the four alkali-soluble hemicelluloses, the contents of glucose (18.49% and 17.51%) and mannose (8.42% and 7.81%) were relatively higher and those of xylose (66.83% and 68.62%) were lower in the water-soluble hemicelluloses (H1 and H2). The water-soluble hemicelluloses exhibited a more complex structure with a greater number of side chains. It was possible that α-glucosans or pectin polysaccharide were also exited[23]. However, uronic acid, in particular, 4-*O*-methyl-α-*D*-glucuronic acid, as well as galacturonic acid, was not detected in any of the hemicellulosic fractions; the exception was H6.

The xylose/arabinose molar ratios in H1, H2, H3, H4, H5, and H6 were found to be 29.6∶1, 31.3∶1, 230.1∶1, 383.1∶1, 77.2∶1, and 119.7∶1, respectively. The xylose/arabinose molar ratio indicated the degree of linearity or branching of hemicelluloses[24]. That is to say, a high molar ratio indicates a high degree of polymerization and a small degree of bonding with the other monosaccharide constituents[5]. The xylose/arabinose molar ratios for the four alkali-soluble hemicelluloses higher than those for the two water-soluble hemicelluloses indicated that less-branched hemicellulosic fractions were obtained using the alkaline solutions. Moreover, the xylose/arabinose molar ratios for the hemicellulosic fractions extracted using a shorter period (12 h) were lover than those for the hemicellulosic fractions obtained after 24 h, demonstrating that fractions with a greater number of branches could be obtained within a relatively short period.

3.3 Molecular weight distribution

The molecular weights of the six hemicelluloses were analyzed by GPC. The weight-average (*M*w) and number-average (*M*n) molecular weights as well as the polydispersity (*M*w/*M*n) values of the hemicelluloses were listed in Table 3. One could see that the four

Table 3 *M*w, *M*n and *M*w/*M*n of the six hemicelluloses

Hemicellulose	*M*w	*M*n	*M*w/*M*n
H1	8545	7219	1.18
H2	5566	5008	1.11
H3	9869	7951	1.24
H4	10582	8500	1.24
H5	11036	8650	1.28
H6	10686	8547	1.25

alkali-soluble hemicelluloses showed relatively higher molecular weights (9869~11036 g/mol) than did the water-soluble hemicelluloses. However, all six hemicelluloses had molecular weights lower than those reported in the literature[3]; this might be the result of the degradation of the hemicelluloses during the hydrothermal pretreatment and the cleavage of the glycosidic ether linkages present between the sugar units in the macromolecular structure of the hemicelluloses, owing to the high alkalinity of the NaOH and KOH solutions. In addition, the fact that the molecular weights of the two water-soluble hemicellulosic fractions (8545 and 5566) were lower may be explained by the presence of considerable amounts of glucomannan, which is a low-molecular-weight polysaccharide. Furthermore, the data in Fig.2 indicated that the hemicelluloses extracted using distilled water for 12 h or 24 h yielded lower-molecular-weight polymers and that these polymers exhibited narrower molar mass distributions, with the polydispersity values being 1.18 and 1.11, respectively. However, the fractions H3, H4, H5, and H6 yielded relatively large macromolecules with broader molecular weight distributions, with the polydispersity values being 1.24, 1.24, 1.28, and 1.25, respectively.

3.4 FT-IR spectra

Fig.3 showed the FT-IR spectra of the hemicelluloses. One could see that there was no significant difference in the intensity of the main absorption peak among the six hemicelluloses. In Fig.3(a), the absorption peak at 3398 cm^{-1} could be attributed to the stretching vibrations of the hydroxyl groups, and the absorption band at 2908 cm^{-1} was related to the C—H stretching vibration of the methyl and methylene groups. The high-intensity absorption band at 1632 cm^{-1} corresponded to the bending mode of the absorbed water, since hemicelluloses had a strong affinity for water, owing to its disordered structure in the solid state[25]. The bands at 1424, 1408, and 1316 cm^{-1} represented the bending and stretching vibrations of C—H and C—O. The absorbance peak at 1050 cm^{-1} was attributable to the stretching vibration of the glycosidic bond (C—O—C), which was a typical characteristic of xylans[26]. The

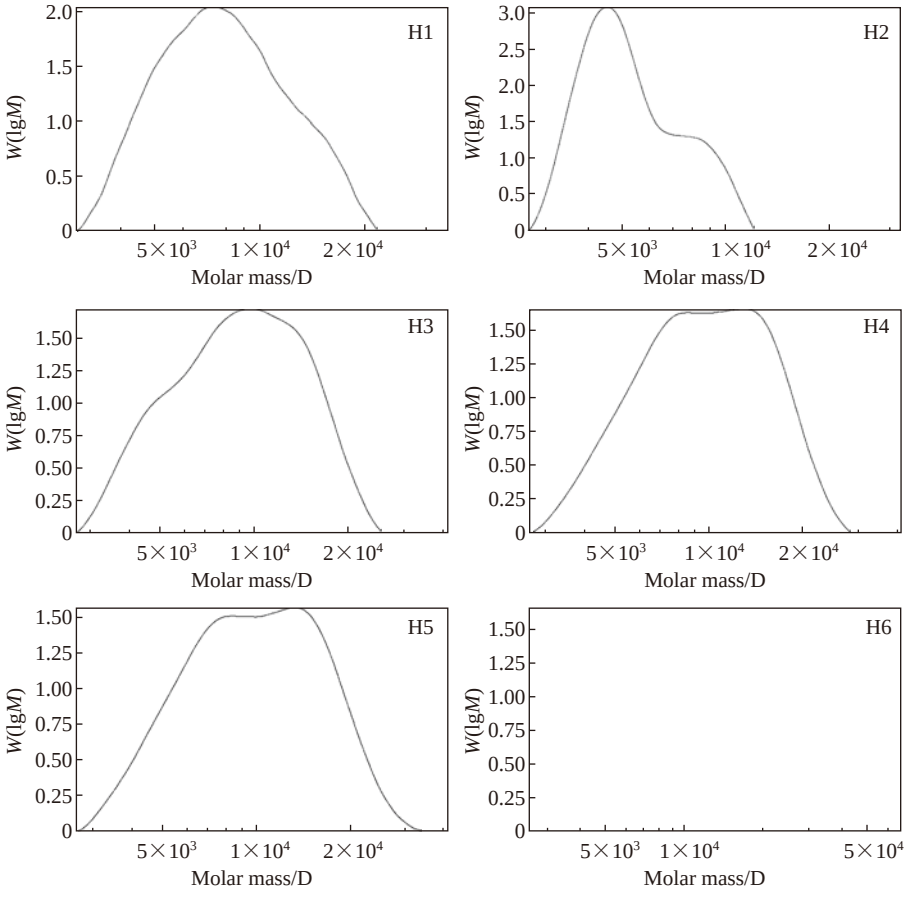


Fig.2 Molecular weight distributions of the six hemicelluloses

small band at 896 cm^{-1} was characteristic of the β-glycosidic linkages between the sugar units.

The small band at 1704 cm^{-1} (spectrum H2, Fig.3(b)) could be assigned to the acetyl and uronic ester groups of the hemicelluloses. This signal was not present in the spectra of samples H4 and H6 (Fig.3(b)), indicating that the ester bonds in the hemicelluloses were completely cleaved in the alkaline solutions. The adsorption peaks at 1596 cm^{-1} in the spectra of H3, H5, and H6 were related to the symmetric stretching of —COO in uronic acid, indicating that the uronic acid presented in these three samples. However, Table 2 showed that only H6 contained small amounts of uronic acid (1.55%), suggesting that the contents of uronic acid in H3 and H5 were very low which were out of the detection limit of the instrument. The adsorption peak located at 1050 cm^{-1} (Fig.3(a)) was related to the stretching vibration of C—O—C glycosidic bonds, which were mainly caused by the xylose in the products. The increase in the intensity of this peak suggested that the content of xylose increased in these samples, which were fit well with the results of sugar analysis (Table 2). The stretching vibration of C—O—C glycosidic bonds were located at 1044 cm^{-1} in Fig.3(b), and with increase in the xylose content (H2, H4, and H6 in Table 2), the intensity of this peak strengthened.

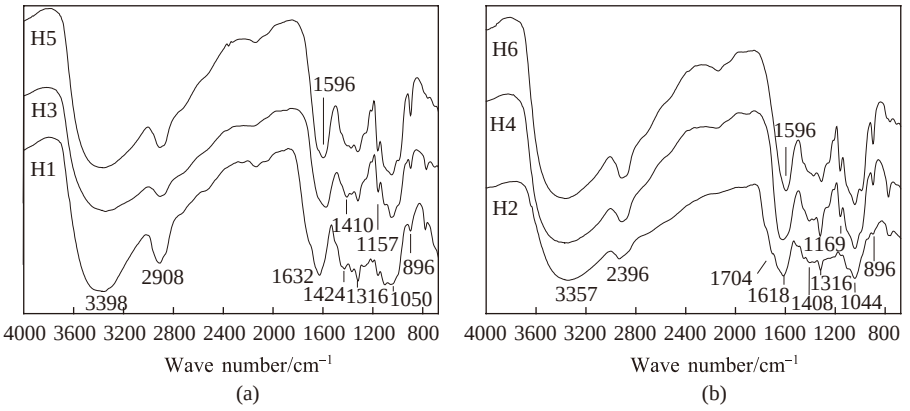


Fig.3 FT-IR spectra of the hemicelluloses extracted using the hydrothermal method at 160℃ for 12 h (a) and 24 h (b)

3.5 NMR spectra

Hemicellulosic fraction H4 was analyzed by ^{1}H-NMR spectroscopy, in order to characterize its structural features, as shown in Fig.4. The strong signal at 4.7 ppm is attributable to the residual solvent (HDO). Further, the main signals at 4.26 (H-1), 3.90 (H-5eq), 3.59 (H-4), 3.31 (H-3), 3.20 (H-5ax), and 3.10 ppm (H-2) could be assigned to the (1→4)-β-*D*-xylan residues, while the minor signals at 4.18 (H-5), 3.46 (H-2), and 3.33 ppm (OCH_3) corresponded to the 4-*O*-methyl-α-*D*-glucuronic acid residues. The signal at 8.28 ppm was attributable to the proton of the carboxy group of 4-*O*-methyl-α-*D*-glucuronic acid. The resonance at 1.28 ppm was due to the methyl protons of the ethanol remaining from the ethanol precipitation of the hemicelluloses. The very weak signal at 6.34 ppm corresponded to the C-β of the residual coumaric acid[27]. It could be seen from Fig.5 that the predominant five signals resulted in HSQC ^{13}C/^{1}H cross-peaks at 102.10/4.26, 73.02/3.10, 74.80/3.31, 75.98/3.59, 63.02/3.20, and 63.02/3.90 ppm (Table 4); these could be assigned to C-1, C-2, C-3, C-4, and C-5 of the (1→4)-β-*D*-xylan residues, respectively. In addition, the cross-peaks at 70.12/3.42, 73.28/3.48, 77.14/3.19, 71.89/3.90, and 56.48/3.64 ppm corresponded to C-2,

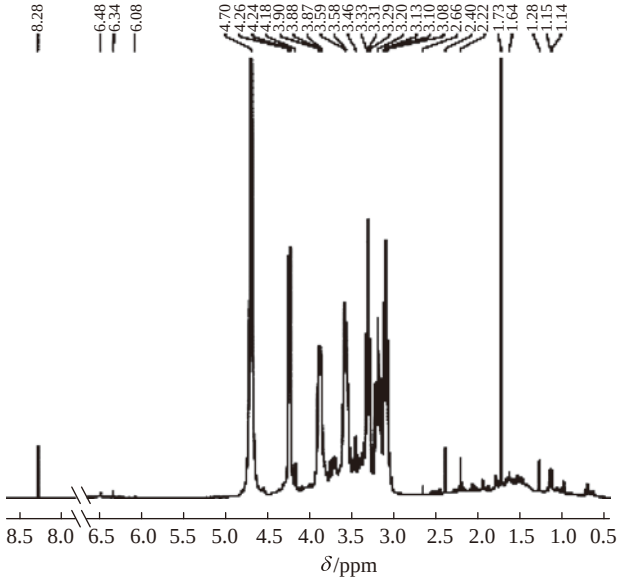
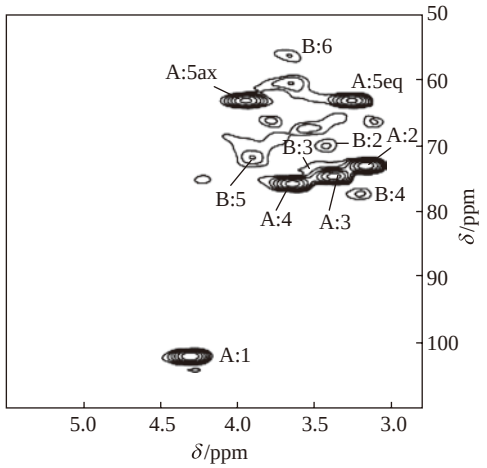


Fig.4 ^{1}H-NMR spectrum of hemicellulose H4



∗ A, (1→4)-*β*-*D*-xylan; B, (1→4)-*α*-*D*-glucan; ax, axial; eqe qa torial.

Fig.5 HSQC spectrum of hemicellulosic fraction H4

Table 4 Chemical shifts in ^{1}H-NMR and HSQC spectra of H4

Sugar residues	Chemical shift (H/C)/ppm						
	1	2	3	4	5ax[c]	5eq[d]	6
A	4.26	3.10	3.31	3.59	3.20	3.90	
	102.10	73.02	74.80	75.98	63.02	63.02	
B		3.42	3.48	3.19	3.90		3.64
		70.12	73.28	77.14	71.89		56.48

C-3, C-4, C-5, and C-6 of a (1→4)-*α*-*D*-glucan residue, namely, amylose[28-29]. On combining the results of the NMR, IR, and sugar analysis, one could conclude that the hemicellulosic fraction (H4) had a primary structure of (1→4)-*β*-*D*-xylan and a minor structure of (1→4)-*α*-*D*-glucan attached with minor amounts of substituted sugars and glucuronic acid.

4 Conclusions

In summary, in this study, two water-soluble and four alkali-soluble hemicellulosic fractions were extracted from the triploid of *Populus tomentosa Carr*. via a hydrothermal pretreatment. The effects of the solvents used and the extraction time on the structural and properties of the hemicellulosic fractions were investigated systematically. The results indicated that the hydrothermal pretreatment favored the extraction of xylose in a high yield and that the alkaline extractions were more effective than distilled water extraction. Thus, the alkalis used (NaOH and KOH) were more effective than distilled water. The results of the sugar analysis suggested that xylose (66.83%~86.49%) was the major unit of all the hemicellulosic fractions, followed by glucose (6.83%~18.49%); mannose (1.40%~8.42%), galactose (2.17%~4.05%), and arabinose (0.21%~2.26%) were also present as minor components. Hemicellulosic fraction H4 could be structurally defined as (4-*O*-methyl-*α*-*D*-glucurono)-*β*-*D*-xylan. Thus, the water- and alkali-based extraction of hemicelluloses from poplar through the hydrothermal method should result in the improved industrial utilization of these isolated hemicellulosic polymers.

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