THE STRUCTURAL CHARACTERIZATION OF CORN STALKS HEMICELLULOSES DURING ACTIVE OXYGEN COOKING AS A PRETREATMENT FOR BIOMASS CONVERSION

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The structural characteristics of corn stalks hemicelluloses during the active oxygen cooking process as a pretreatment of biomass conversion were investigated in this work. The hemicelluloses obtained from the corn stalks, pulp, and yellow liquor were evaluated by high-performance anion-exchange chromatography (HPAEC), Fourier transform infrared spectroscopy (FT-IR), gel permeation chromatography (GPC), and ^{1}H-^{13}C 2D hetero-nuclear single quantum coherence (HSQC) spectroscopy. Based on the sugar and GPC analysis, FT-IR, and NMR spectroscopy, it could be concluded that the hemicelluloses were composed of backbones of (1→4)-β-D-xylopyranose substituted α-L-arabinofuranose and 4-*O*-methyl-α-D-glucuronic acid. During the cooking process, the hemicelluloses with more side chains were removed from raw material. The backbones were significantly damaged as well. Additionally, the ester linkages in the raw material were completely broken after the cooking.

Key words: Corn stalks; Hemicelluloses; Active oxygen; Solid alkali

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INTRODUCTION

Depletion of fossil fuels and increasing energy demands have prompted the search for alternative and sustainable energy resources (Rodríguez *et al.* 2011). Biomass is one of the most abundant and renewable resources in nature, storing solar energy through plant photosynthesis in the form of cell wall polymers (Wen *et al.* 2011). It can be transformed into environmentally friendly materials, clean fuels, and platform chemicals and is considered to be one of the most convenient and the least polluting energy, suitable for the replacement of fossil energy sources in many applications.

The three main components in the plant cell wall are cellulose, hemicelluloses, and lignin. In general, hemicelluloses combine with cellulose microfibrils by hydrogen bonds, and with lignin by covalent bonds (Peng *et al.* 2011; Sun *et al.* 2011). Hemicelluloses are the most abundant hetero-polysaccharide in the ligno-cellulose and are composed of various sugar units and uronic acids, such as D-xylose, L-arabinose, D-glucose, D-galactose, D-mannose, D-glucuronic acid, D-galacturonic acid, and 4-*O*-methyl-α-D-glucuronic acid (Peng *et al.* 2011; Zhang *et al.* 2011). The hemicelluloses of agricultural residues are composed of β-D-(1→4)-linked xylopyranosyl (Xyl*p*) backbone chains substituted with 4-*O*-methyl-α-D-glucuronic acid (Glc*p*A) and D-xylopyranosyl and L-arabinofuranosyl (Ara*f*) residues (Sun *et al.* 1998; Sárossy *et al.* 2012).

Corn stalks are a widely available and abundant agricultural residue in China and have a huge potential for biomass conversion. But most of the corn stalks are burnt directly in the field, which can cause serious environmental pollution. In addition, the complexity of the components results in a diversity of products. Therefore, it is necessary to employ pretreatment processes to isolate the agricultural residues into cellulose, hemicelluloses, and lignin before biomass conversion. Pulping is one of the effective ways. One of the current cooking processes include the soda and kraft process, in which strong alkali and/or sulfur compounds are used as cooking chemicals; this can efficiently remove the lignin from raw material. However, these processes can also lead to serious environmental pollution (Zhao *et al.* 2011). In recent years, many new or modified processes have been developed (Huang *et al.* 2008; González-García *et al.* 2010; Garcia *et al.* 2011; Loacutepez *et al.* 2011), but such approaches still cannot fundamentally solve the above problems.

In an effort to reduce pollution, a clean pulping process – active oxygen cooking – has been developed by using active oxygen (O_2 and H_2O_2) and solid alkali (MgO) as cooking chemicals. The O_2 and H_2O_2 have high activity to lignin and have been applied in a totally chlorine free (TCF) bleaching process for a long time (Salmela *et al.* 2008; Egüés *et al.* 2012). In the bleaching process, O_2 and H_2O_2 can form various ions and/or radicals in the alkali medium (usually add NaOH), which can break down the lignin structure in the pulp.

Inspired by the mechanism mentioned above, the active oxygen cooking process involving solid alkali from corn stalks was studied. After cooking, 73.1 % hemicelluloses and 85.4 % lignin were removed from the raw material under the cooking conditions (data shown in Table 1). Meanwhile, 502 kg of polysaccharide-rich pulp could be obtained from 1 ton corn stalks, which is good feedstock for biomass conversion (data shown in Table 1). In comparison with traditional cooking process, the pollution caused by the cooking chemicals could be completely eliminated in the active oxygen cooking process. In practice, no noxious gas or effluent containing high consistency alkali are discarded to the environment after cooking. Moreover, the solid alkali, hemicelluloses, and lignin in weakly alkaline (pH *ca*. 8.0) yellow liquor can be recycled. The above facts showed that the active oxygen cooking was an efficient and clean pretreatment process of biomass conversion. To clarify the effect of active oxygen on the hemicellulosic structure during the cooking process and further understand the cooking mechanism, the hemicelluloses were extracted from the raw material, pulp, and the yellow liquor and analyzed via various methods.

MATERIAL AND METHODS

Material and Cooking Process

Corn stalks were supplied by China BBCA Group Corp., Anhui, China. The cooking process was described in our previous work (Pang *et al.* 2012). The detailed operations were given as follow: 50 g corn stalks (oven dried weight), 7.5 g MgO, and 3 % wt dosage of H_2O_2 (based on the oven dried weight of corn stalks) were placed in a 2 L stainless, rotating autoclave at a solid-to-liquor ratio of 1:6 (g/mL). After being sealed, the autoclave was filled with O_2 of 1.0 MPa. Cooking was performed at 165 °C for 2 hours.

After cooking, the yellow liquor was extruded from the raw stock and stored in a refrigerator, and the resulting pulp was washed with deionized water and dried in air. The primary components of the corn stalks and pulp are shown in Table 1.

Table 1. The Primary Components of the Corn Stalks and Pulp

	Cellulose/%	Hemicelluloses/%	Lignin/%	Ash/%	Wax/%	Yield/%
Corn stalk	39.12*	23.96	21.73	7.95	4.22	-
Pulp	68.96	12.72	6.27	9.02	1.09	50.20

* The values in the table were based on the oven dried weight.

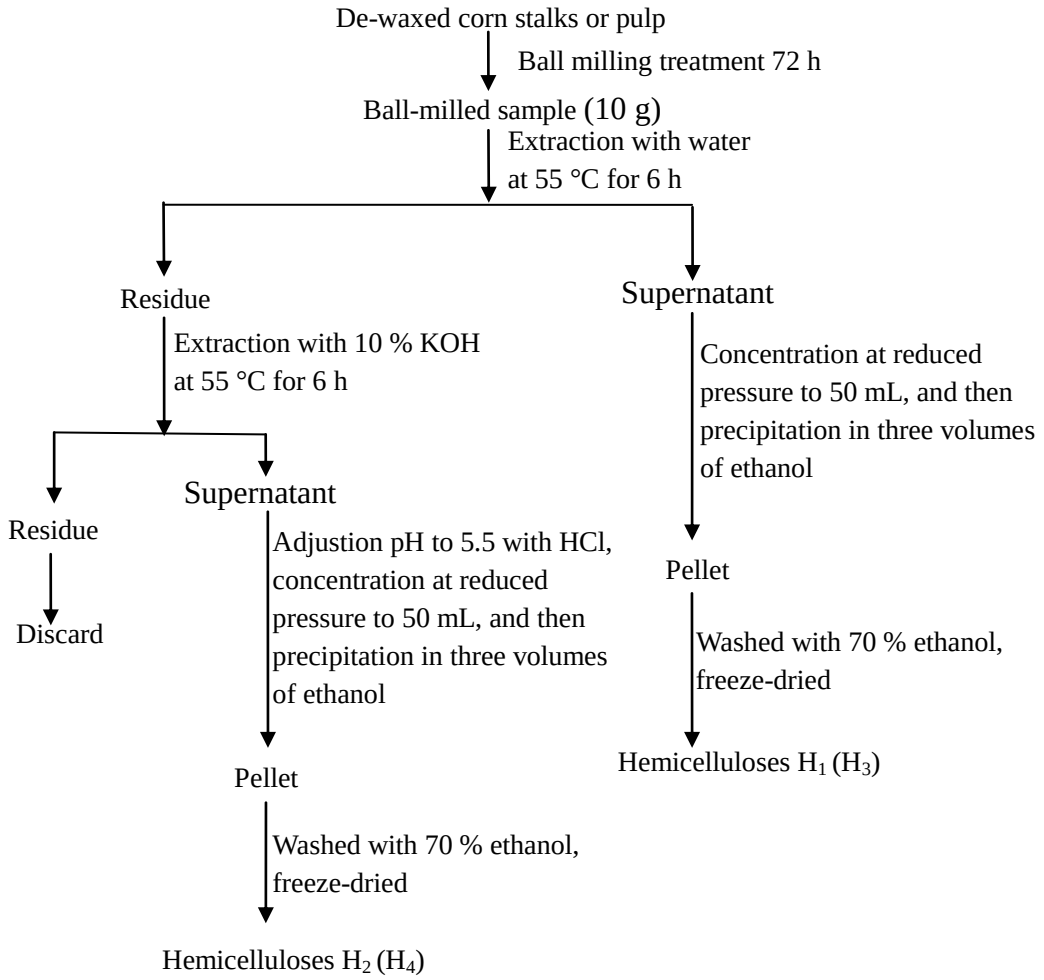

Fig. 1. The scheme of the corn stalks hemicelluloses extraction process

The Extraction of the Hemicelluloses

A scheme for extraction of hemicelluloses from corn stalks and pulp is illustrated in Fig. 1. The de-waxed sample was ball-milled with a vibratory milling apparatus at room temperature for 72 hours. Then, the ball-milled sample (10 g) was suspended in water with a solid-to-liquid ratio (g/mL) of 1:20 at 55 °C for 6 hours. The resulting mixture was centrifuged at 5000 rpm for 10 minutes. The supernatant was concentrated to 50 mL at a reduced pressure and poured into three volumes of 95% ethanol. The precipitated hemicelluloses were centrifuged, washed with 70% ethanol, and freeze-dried. The residue was extracted at 50 °C for 6 hours using 10% KOH with a solid-to-liquid ratio (g/mL) of 1:20. The resulting mixture was centrifuged at 5000 rpm for 10 minutes, and the pH of the supernatant was adjusted to approximately 5.5 with HCl. The rest of process occurred as described above. The hemicelluloses in the yellow liquor could be precipitated directly by the ethanol. The processes were described as follows: 50 mL yellow liquor was poured into three volumes of 95% ethanol; after centrifugation, the precipitated hemicelluloses were washed with 70% ethanol and freeze-dried. The

hemicelluloses extracted with water and alkali from corn stalks were named H_1 and H_2, respectively; the hemicelluloses extracted with water and alkali from pulp were called as H_3 and H_4, respectively; the hemicelluloses in the yellow liquor were labeled as H_5.

Sugar Composition Analysis

The monosaccharides and the uronic acids in the hemicelluloses were liberated by hydrolyzing approximate 10 mg sample using 5.5 mL of 6.5 % H_2SO_4 for 2.5 hours at 105 °C. After acid hydrolysis, the hydrolyzates were diluted to 50-fold (after adjusting the pH value to 7.0) and injected into the HPAEC system (Dionex ICS-3000, USA) with pulsed amperometric detection, a CarboPac^{TM} PA1 column (4×250 mm), and a CarboPac^{TM} Guard column (4×50 mm). The total running time was 30 min, and the flow rate was 0.5 mL/min during the analysis process. The eluent was 0.002 M NaOH when eluting the monosaccharide; however, the eluent was 0.1 M NaAc and 0.002 M NaOH when eluting the uronic acids.

Molecular Weight Analysis

The molecular weights of the hemicelluloses were determined by GPC. The GPC system comprised a Waters 1525 binary HPLC pump, a Waters 717 plus Auto-sampler, a Waters 2414 refractive index detector, and a Breeze (V3.3) GPC work station (Waters, USA). The samples were dissolved in the eluent and injected into the TSk-GELG-5000PW xL column (7.8×300 mm) and TSk-GELG-3000 PW xL column (7.8×300 mm) (TOSOH, Japan) in a series. The eluent flow (0.02 M pH 6.0 KH_2PO_4) was 0.6 mL/min. The GPC column and injection system were maintained at 35 °C during the analysis. Glucan was applied as a reference substance.

FT-IR Analysis

FT-IR spectra of the hemicelluloses samples were obtained on a FT-IR spectrophotometer (Bruker Tensor 27, Germany). The samples were combined with KBr in slices containing 1% finely ground hemicelluloses. The scanning range was 4000 to 400 cm^{-1} in transmission mode.

Nuclear Magnetic Resonance (NMR) Analysis

The ^{1}H-^{13}C 2D hetero-nuclear single quantum coherence (HSQC) spectra of the hemicelluloses (80 mg in 1 mL D_2O) were obtained on a Bruker AV 600 instrument in the HSQC experiment mode at 25 °C. The spectral widths were 6000 and 25000 Hz for the ^{1}H- and ^{I3}C-dimensions, respectively. The acquired time per scan was 0.0984 s, the relaxation delay time was 1.5 s, and the pulse width was 12.1 Hz.

RESULTS AND DISCUSSIONS

Content of Neutral Sugars and Uronic Acids

The neutral sugars and the uronic acids in the hemicellulosic fractions were identified and qualified by analysis of the sugars obtained via sulfuric acid hydrolysis method, and the results are shown in Table 2. Obviously, xylose was the predominant sugar constituent (53.46 to 76.18 %) in the five hemicellulosic preparations. Moreover, it was shown that considerable amounts of the arabinose (4.54 to 13.81 %), galactose (1.27 to 11.31 %), and glucose (6.18 to 17.82 %) were present. However, small amounts of uronic acids (1.46 to 5.14 %), mainly 4-*O*-methl-glucuronic acid or glucuronic acid, were also identified. The content of the xylose in H_1 was the lowest among the five hemicellulosic preparations, and the other sugar residues, especially the glucose, showed a relatively high level. The H_1 has been usually called the "hair regions" of pectic

polysaccharides, suggesting that more branched hemicelluloses are easily extracted by hot water; and the glucose in the H_1 perhaps came from α-glucan and pectic polysaccharides (Peng *et al.* 2009). After the cooking, most of the arabinose and galactose were dissolved in the yellow liquor, leading to the results that the content of the above two sugars in H_3 and H_4 was much lower than in H_1, H_2, and H_5. Nevertheless, the amount of glucose in the H_5 was the lowest among the five hemicellulosic fractions, which indicated the cellulose was slightly degraded during the active oxygen cooking process.

Moreover, the molar ratios of xylose to arabinose and uronic acids were indicative of the degree of linearity of hemicelluloses. High molar ratio shows that the hemicelluloses possess more side chains. The molar ratios of arabinose to xylose and arabinose to uronic acids in the raw material and yellow liquor were higher than that in the pulp, respectively. This suggested that hemicelluloses with more side chain were removed from the raw material during the cooking process.

Table 2. Monosaccharide Composition and Uronic Acids Content of the Hemicelluloses from the Corn Stalks, Pulp, and Yellow Liquor (%, w/w)

Hemicelluloses	Sugar Composition				Uronic acids	Molar Ratio	
	Ara	Gal	Glu	Xyl		Ara/Xyl[a]	Ura/Xyl[b]
H_1	12.64	10.94	17.82	53.46	5.14	0.237	0.068
H_2	12.26	5.17	16.09	62.89	3.60	0.195	0.040
H_3	5.66	3.54	12.79	75.07	2.94	0.075	0.027
H_4	4.54	1.27	16.54	76.18	1.46	0.060	0.013
H_5	13.81	11.31	6.18	65.46	3.23	0.211	0.034

[a]Ara/Xyl, the molar ratio of arabinose to xylose.
[b]Ura/Xyl, the molar ratio of uronic acids to xylose.

Average Molecular Weight

To investigate the degradation extent of hemicelluloses during the cooking process, the weight-average (M_W) and number-average (M_N) molecular weights, as well as the polydispesity (M_W/ M_N) of five hemicellulosic preparations were analysed by GPC. The GPC results are listed in Table 3, where it is shown that all of the hemicellulosic fractions exhibited lower weight-average (M_W) molecular weights (6931 to 11505 g/mol) than what has been reported (Sun *et al.* 2010). Evidently, the M_W of alkali-soluble hemicelluloses (H_2 and H_4) (9644 to 11505 g/mol) were subequal to those of the water-soluble polysaccharides (H_1 and H_3) in the range of 10165 to 11191 g/mol, which indicated that the hemicelluloses in the raw material pulp possessed similar degree of polymerization.

Generally speaking, alkali has a higher permeability than water and can extract high-molecular-weight hemicelluloses. Accordingly, the above results indicated that the hemicelluloses might be seriously degraded during the extraction process of strong alkali. After the cooking, the M_W of H_5 was much lower than that of the hemicellulosic fractions extracted from the raw material and pulp, which suggested that the glycosidic bonds of hemicelluloses in yellow liquor were significantly cleaved under the cooking conditions. In addition, the relatively low polydispersity (1.23 to 2.17) showed that all of the hemicelluloses fractions had a narrow distribution of molecular sizes.

Table 3. Weight-average (M_w) Molecular Weights, Number-average (M_N) Molecular Weights (g/mol), and Polydispersity (M_W/M_N) of the Hemicelluloses from the Corn Stalks, Pulp, and Yellow Liquor

	Hemicelluloses				
	H_1	H_2	H_3	H_4	H_5
M_N	9101	8675	6721	5473	3188
M_W	11191	11505	10165	9644	6931
M_W/M_N	1.23	1.33	1.51	1.76	2.17

Table 4. The Main Functional Groups of Corn Stalks Hemicelluloses

Wave Numbers (cm^{-1})	Functional Groups	Compounds
3800-3000	O-H stretch	Hydroxyl groups
2980-2840	C-H stretch	Alkyl
1730	C=O stretch	Carboxylic ether
1642	-	Absorbed water
1514	Aromatic skeleton vibration	Lignin
1463,1250	CH_2 bend	Alkyl
1170-1000	-	Arabinoxylan
1044	C-O, C-C stretch, or C-OH bend	Xylan
896	C_1-H bend	β-D-Xylose
788-400	C-C stretch	The ring of the sugar

FT-IR Spectra

The spectra of all the hemicelluloses are shown in Fig. 2, and the typical functional groups and the FT-IR signals with the possible compounds are listed in Table 4. The absorption at 3429 cm^{-1} was attributed to the O-H stretching vibrations of -OH groups and hydrogen bonding. The C-H stretching vibration gave signals at 2981 and 2924 cm^{-1}. The band at 1642 cm^{-1} was due to the banding mode of absorbed water in the hemicellulosic fractions. The prominent band at 1044 cm^{-1} was assigned to C-O, C-C stretching, or C-OH bending in xylan, indicating a dominant xylan of the hemicelluloses (Peng *et al.* 2010). The weak band at 1161 and 987 cm^{-1} showed the presence of the arabinosyl constituents, which were attached to xylopyranosyl constituents as side chains. The band at 1082 cm^{-1} was related to the C-OH bending. The sharp band at 896 cm^{-1} corresponds to the C_1 group frequency, and this signal was characteristic of *β*-glycosidic linkage between the sugar units. However, the intensity of *β*-glycosidic bonds in H_5 was very weak. This phenomenon resulted from the degradation of the hemicelluloses during the cooking process, which corresponded to the conclusion obtained from GPC results. In addition, the intensities of *β*-glycosidic linkages in the alkaline-soluble hemicelluloses (H_2 and H_4) were higher than the water-soluble hemicelluloses (H_1 and H_3), which suggested that the process extracted with alkali could get higher purity hemicelluloses. The signals at 1463, 1419 (1423), 1387, and 1250 cm^{-1} represented C-H, OH, or CH_2 bending vibrations, and the very low absorbance at 1323 cm^{-1} arose from the C-C and C-O skeletal vibrations. In addition, the occurrence of very small bands at 1514 cm^{-1} in all spectra was attributed to aromatic skeletal vibration of associated lignin in the hemicelluloses. The presence of a shoulder peak at 1730 cm^{-1} in spectrum H_1 implied that the hemicellulosic fraction extracted by water contained small amounts of the ester bonds of carboxylic groups of ferulic and/ or *p*-coumaric acids (Peng *et al.* 2009). However, the band at 1730 cm^{-1} disappeared in the rest of the hemicellulosic fractions, which indicated that the ester bonds were completely cleaved under the cooking conditions.

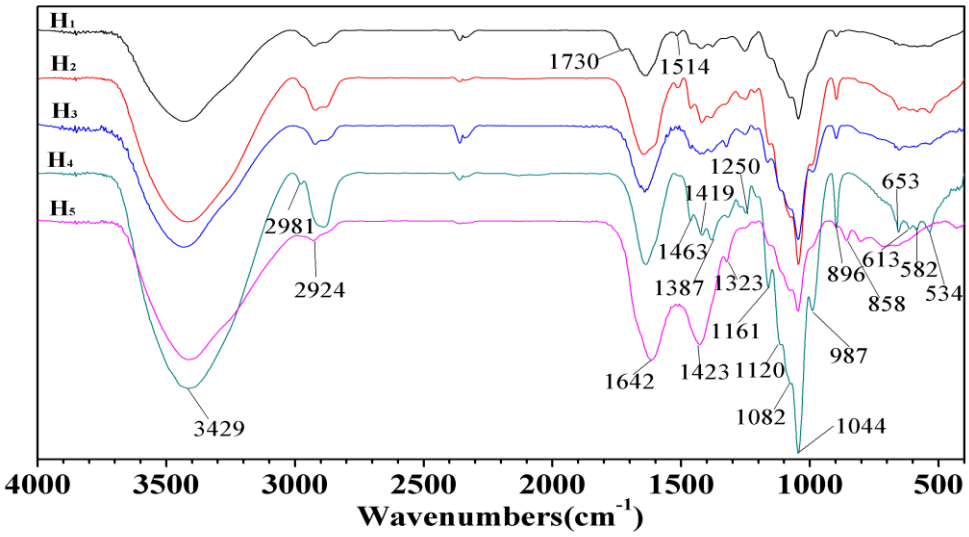

Fig. 2. FT-IR spectra of the hemicelluloses from the corn stalks, pulp, and yellow liquor

1D and 2D NMR spectra

To further study the structural features of the polymers, NMR spectroscopy was employed in this work. The ^{1}H and ^{13}C NMR spectra of H_1 are given in Fig. 3. The relevant ^{1}H NMR signals occurred in two regions: the anomeric region (δ 5.6 to 4.9 for the α-anomers and δ 4.9 to 4.3 for the β-anomers) and the ring proton region (δ 4.5 to 3.0) (Peng *et al.* 2009). The ^{1}H NMR spectra of H_1 showed the resonances of the three anomeric protons to be well isolated at 4.39, 5.22, and 5.31 ppm, which were assigned to (1→4)-*β*-D-Xyl*p*, 4-*O*-Me-α-D-Glc*p*A and α-L-Ara*f*, respectively (Peng *et al.* 2012). So the xylopyranose was in β-conformation, which is in agreement with the small sharp peak at 896 cm^{-1} in all the FT-IR spectra. The signal at 6.18 ppm was related to the small amount of associated lignin in the hemicelluloses. The methyl group of 4-*O*-Me-α-D-Glc*p*A was demonstrated by the corresponding singlet at 3.37 ppm. The ^{13}C NMR spectrum of H_1 showed five main signals at 62.97, 76.33, 73.64, 72.70, and 101.66 ppm, which were attributed to the C-5, C-4, C-3, C-2, and C-1 of (1→4)-*β*-D-Xyl*p*, respectively. However, the signals of other sugar units in the hemicelluloses were not detected.

The 2D-NMR spectra are shown in Fig. 3, and the chemical shifts of sugar units of H_1 are listed in Table 5 according to the literature (Sun *et al.* 1996; Hromadkova and Ebringerova 2003; Sun *et al.* 2004; Peng *et al.* 2009; Yuan *et al.* 2010; Wen *et al.* 2011; Zhang *et al.* 2011). The anomeric carbons and protons of the (1→4)-*β*-D-Xyl*p*, (1→4)-*β*-D-Xyl*p*-2-*O*-(4-*O*-Me-α-D-Glc*p*A), 4-*O*-Me-α-D-Glc*p*A, α-L-Ara*f*, and (1→4)-*β*-D-gluc*p* were characterized by the signals at 101.61/5.29, 103.17/4.56, 97.68/5.19, 107.41/5.29, and 96.40/4.48 ppm in the HSQC NMR spectrum of H_1 in the anomeric area (δC 110-90 and δH 5.6-4.3 ppm), respectively. In addition, the (1→4)-*β*-D-Xyl*p* units in H_1 were also detected by major signals at δ C/H 72.73/3.19 (C2-H), 73.61/3.46 (C3-H), 76.29/3.69 (C4-H), 62.87/4.00 ($C5\text{-}H_{eq}$), and 62.89/3.28 ($C5\text{-}H_{ax}$) ppm in the ring carbon resonate regions (90 to 60 ppm), and the intensities of the signals indicated that the content of xylose in H_1 was the highest, which was in good agreement with the sugar analysis. Furthermore, the other signals of α-L-Ara*f* residues were also detected by the presence of cross-peaks at δ 77.30/3.87 (C2-H), 80.86/4.06 (C3-H), 85.07/4.18 (C4-H), 61.11/3.73 ($C5\text{-}H_{eq}$), and 61.07/3.64 ($C5\text{-}H_{ax}$).

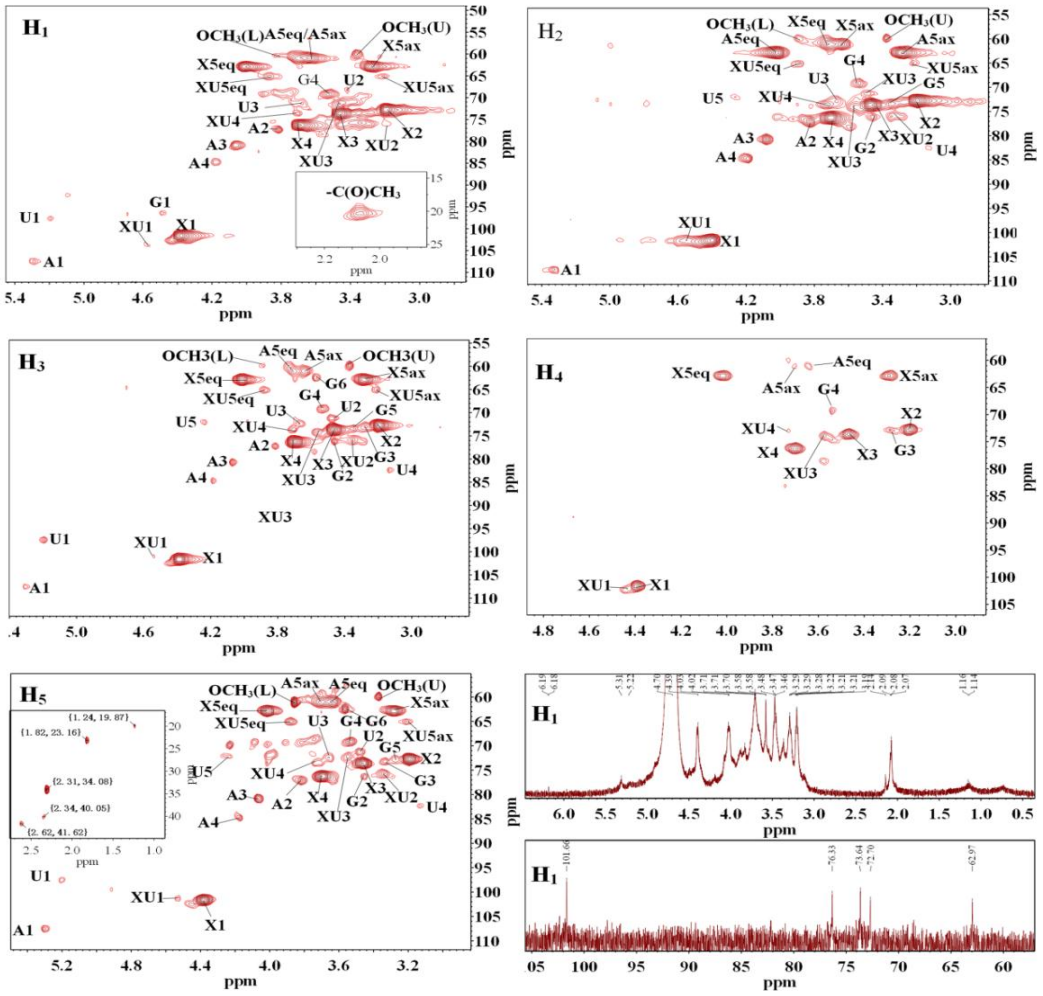

Fig. 3. The HSQC spectra of the hemicellulose from the corn stalks, pulp, and yellow liquor and the ^{1}H and ^{13}C NMR spectra of H_1. The designations are as follows: X, (1→4)-*β*-D-Xyl*p*; XU, (1→4)-*β*-D-Xyl*p*-2-*O*-(4-*O*-Me-α-D-Glc*p*A); U, 4-*O*-Me-α-D-Glc*p*A; A, α-L-Ara*f*; G, (1→4)-*β*-D-gluc*p*; L, lignin; ax, axial; eq, equatorial.

Table 5. ^{1}H and ^{13}C Chemical Shift (ppm) Assignments for H_1

Sugar Residues	Chemical Shift (ppm) H/C							
	1	2	3	4	5ax	5eq	6	-OCH3
X	101.61	72.73	73.61	76.29	62.87[a]	62.89	-	-
	4.37	3.19	3.46	3.69	4.00	3.28	-	-
A	107.41	77.30	80.86	85.07	61.11	61.07	-	-
	5.29	3.87	4.06	4.18	3.73	3.64	-	-
XU	103.17	76.12	71.39	73.68	65.15	65.16	-	-
	4.56	3.20	3.46	3.71	3.22	3.22	-	-
U	97.68	68.19	71.30	82.57	72.01	-		60.07
	5.19	3.42	3.68	3.13	4.27	-		3.37
G	96.40	75.76		69.09	73.63	-		-
	4.48	3.52		3.52	3.46	-		-

The designations are as follows: X, (1→4)-*β*-D-Xyl*p*; XU, (1→4)-*β*-D-Xyl*p*-2-*O*-(4-*O*-Me-α-D-Glc*p*A); U, 4-*O*-Me-α-D-Glc*p*A; A, α-L-Ara*f*; G, (1→4)-*β*-D-gluc*p*; ax, axial; eq, equatorial.

[a] The underlined values were from the spectrum of H_2.

The signals at 68.19/3.42, 71.30/3.68, and 60.07/3.37 ppm were attributed to the C-2, C-3, and the methyl of the 4-*O*-Me-α-D-Glc*p*A, respectively. The weak signal at 60.36/3.83 ppm was assigned to the associated lignin, which was consistent with the results of FT-IR analysis. Signals of glucose from the cellulose were also shown in the spectrum of H_1. Based on the above analysis, it could be concluded that the hemicellulosic H_1 were composed of (1→4)-*β*-D-Xyl*p* backbones substituted with α-L-Ara*f* and 4-*O*-Me-α-D-Glc*p*A.

For other 2D NMR spectra, the main sugar units of hemicelluloses were detected except H_4, which might be caused by the unique characteristic of H_4. H_4 was extracted by the KOH and was characterized as alkali-soluble hemicelluloses. The molar ratios of xylose to arabinose and uronic acids in the Table 2 showed that there were few branched chains in the H_4, which could also affect its dissolubility in D_2O. But sugar analysis showed that H_4 contained the same sugar units as other hemicellulosic fractions. This suggests that there was not a large difference in structure to all of the fractions. The cross-signals at 61.11/3.86 ppm observed in most of the HSQC spectra were assigned to methoxyl groups of lignin, indicating the associated lignin in the five hemicellulosic fractions, which was consistent with the FT-IR analysis. The acetyl group could only be found in the H_1 and H_5 fractions, which indicated that the ester linkages were completely cleaved during the cooking process. In the H_5 spectrum, many unknown signals were detected in comparison with other spectra, which can be attributed to the degradation products of corn stalks during the cooking process.

CONCLUSION

1. The hemicelluloses obtained from raw material, pulp, and yellow liquor from the active oxygen cooking process were composed of (1→4)-*β*-D-Xyl*p* backbones substituted with α-L-Ara*f* and 4-*O*-Me-α-D-Glc*p*A.
2. The backbones of hemicelluloses were heavily broken under cooking conditions. In addition, the acetyl groups in the raw material were completely cleaved after cooking.
3. Hemicelluloses with more side chains were removed during the cooking process.

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