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The structural changes of the bagasse hemicelluloses during the cooking process involving active oxygen and solid alkali

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ABSTRACT

This work describes the structural changes of bagasse hemicelluloses during the cooking process involving active oxygen (O_2 and H_2O_2) and solid alkali (MgO). The hemicelluloses obtained from the bagasse raw material, pulp, and yellow liquor were analyzed by high-performance anion-exchange chromatography (HPAEC), gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FT-IR), and ^{1}H–^{13}C 2D hetero-nuclear single quantum coherence spectroscopy (HSQC). The results revealed that the structure of the bagasse hemicelluloses was L-arabino-(4-*O*-methylglucurono)-D-xylan. Some sugar units in hemicelluloses were oxidized under the cooking conditions. Additionally, the backbones and the ester linkages of hemicelluloses were heavily cleaved during the cooking process.

1. Introduction

The lignocellulosic biomass is an abundant, low-cost, and renewable resource, which is composed of 20–50% cellulose, 20–40% hemicelluloses, and 10–30% lignin.[1–3] As the most abundant polysaccharide after cellulose in lignocellulosic materials, hemicelluloses are hetero-polysaccharides and consist of different kinds of sugar units, such as xylose, arabinose, galactose, mannose, glucose, glucuronic acid, 4-*O*-methyl-D-glucuronic acid, and galacturonic acid.[4] In most herbaceous plants, hemicelluloses are primarily composed of 1,4-linked β-D-xylopyranose (Xyl*p*) units, which serve as backbone and can be substituted by short side chains at C-2 and/or C-3.[2]

Bagasse is the residue in sugar and alcohol industries. It is estimated that 70–80 million tons of bagasse are produced annually in China.[5] However, half of bagasse is used as an energy source by direct burning, and only a small proportion is applied in producing high value-added products by biorefinery. The biorefinery has attracted more and more attention due to the energy crisis. But conventional biomass refining processes (pulping) are not only in high cost, but also cause environmental pollution. Therefore, it is vital to develop an efficient and environmentally friendly way to pretreat the agricultural residue for paper-making or biorefinery.

The peroxide and oxygen are clean oxidants and have been used in total chloride free (TCF) bleaching process for a long time.[6,7] Hydroperoxide anion (HOO^-), formed in the alkaline media (added sodium hydroxide), is the principal active species in peroxide bleaching system. In addition, peroxide can decompose into the hydroxyl radicals ($HO^{\cdot}$) and superoxide anion radicals ($O_2^{-\cdot}$) in alkaline conditions. The active species mentioned above can break the linkages between cellulose, hemicelluloses, and lignin, lead to the oxidation of lignin and the dissolution of lignin and hemicelluloses.[8] The oxygen can also form superoxide anion radicals ($O_2^{-\cdot}$), hydroperoxide anion (HOO^-), hydroxyl radicals ($HO^{\cdot}$), and superoxide anion (O_2^-) under the alkaline conditions. The derivative groups of oxygen are crucial for the degradation of lignin during the bleaching process. However, the oxygen and peroxide have not been used as the cooking chemicals until now.

A novel cooking process, active oxygen cooking involving solid alkali, was developed by our group, in which active oxygen species (O_2 and H_2O_2) and solid alkali (MgO) were added as cooking chemicals.[1] The addition of MgO can provide a weak alkali environment and protect the carbohydrate during the cooking process. Moreover, the solid alkali can be partially reused by simple treatment after recycling from cooking liquor (yellow liquor). More importantly, no noxious gas and effluent contained high consistency alkali are discharged to the environment after the cooking. In the cooking process, subtotal lignin (95.3%) and most of hemicelluloses (78.2%) were removed from bagasse. It is seen from the cooking chemicals and the cooking results that the active oxygen cooking process with solid alkali is an efficient and environmentally friendly pretreatment technology of biomass conversion. To clarify the effect of active oxygen on the hemicellulosic structure, the bagasse hemicelluloses obtained from raw material, pulp, and yellow liquor were studied via various methods in the present study.

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Table 1
The primary components of the bagasse and the pulp

	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ash (%)	Wax (%)	Yield
Bagasse	36.83	30.22	25.58	1.95	4.53	–
pulp	79.39	13.06	2.37	2.58	1.59	50.54

[a] The values on table are based on the oven dried weight.

2. Materials and methods

2.1. Materials and the active oxygen cooking process

The bagasse was obtained from Zhangzhou Biorany Bio-energy Co. Ltd, China. The active oxygen cooking process was described in our previous work.[1] The detailed operations were given as follows: 50 g bagasse (oven dried weight), 15% by weight dosage of MgO (based on the oven dry weight of bagasse) and 3% by weight dosage of hydrogen peroxide (based on the oven dry weight of bagasse) were placed in a 2 L stainless, rotating autoclave at a solid-to-liquor ratio of 1:6 (w/v). After being sealed, the autoclave was filled with oxygen of 1.0 MPa. Cooking was performed at 165 °C for 2 h with a heating rate of 1 °C/min. After cooking, the yellow liquor was extruded from the raw stock and stored in a refrigerator, and the resulting pulp was washed three times with deionized water and dried in air. The raw material and air-dried pulp were milled and their main components, ash and benzene/ethanol extraction were evaluated according to the literature[9] and Tappi standards T 204 cm-97, T 211-02 (Tappi 2002). The main components of the bagasse and pulp are shown in Table 1.

2.2. Extraction of hemicelluloses

The procedures for extraction of hemicelluloses in bagasse and pulp using hot water and KOH are illustrated in Figure 1. The ball-milled sample was extracted with water at 55 °C for 6 h with a solid-to-liquid ratio of 1:20 (g/mL). The resulting mixture was centrifuged at 5000 rpm for 10 min. The supernatant was concentrated to 50 mL under vacuum and poured into three volumes of 95% ethanol. After centrifugation at 5000 rpm for 10 min, the precipitated hemicelluloses was washed with 70% ethanol and freeze-dried. The residue extracted by hot water was extracted with 10% KOH at 50 °C for 6 h with a solid-to-liquid ratio of 1:20 (g/mL). The resulting mixture was centrifuged at 5000 rpm for 10 min and the pH of the filtrate was adjusted to approximately 5.5 with HCl, the remaining process occurred as described above. The hemicelluloses in the yellow liquor were directly precipitated by ethanol. A 50 mL aliquot of 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 by water and alkali from the bagasse were named H-1 and H-2, respectively; the hemicelluloses of the bagasse pulp that were extracted with water and alkali were labeled as H-3 and H-4, respectively; the hemicelluloses in the yellow liquor were called H-5.

2.3. Physiochemical characterization of the hemicelluloses

To determine the composition of hemicelluloses, the neutral sugars and uronic acids in the isolated hemicellulosic fractions were determined by high-performance anion-exchange chromatography (HPAEC). The monosaccharides and the uronic acids in the hemicelluloses were liberated by into hydrolyzing approximate 10 mg sample using 5.5 mL of 6.5% H_2SO_4 for 2.5 h at 105 °C. The hydrolyzates were diluted to 50 mL after adjusting the pH value to 7.0 and injected into HPAEC system (Dionex ICS-3000, USA) with pulsed amperometric detection, a Carbo Pac™ PA1 column (4 × 250 mm), and a Carbo Pac™ Guard column (4 × 50 mm). When eluting the monosaccharide, the eluent was 2 mM NaOH. However, due to the weak eluting power of the NaOH, the eluent was replaced with 100 mM NaAc and 2 mM NaOH when eluting the uronic acids. The molecular weights of the hemicelluloses were determined by GPC. The GPC system was comprised of a Waters 1525 binary HPLC pump, a Waters 717 plus Auto-sampler, a Waters 2414 refractive index detector, and a Breeze (V 3.3) GPC work station (Waters, USA). The samples were dissolved in the eluent and injected into the TSk-GELG-5000 PW xL column (7.8×300 mm) and TSk-GELG-3000 PW xL column (7.8 × 300 mm) (TOSOH, Japan), as well as eluted with 20 mmol/L KH_2PO_4 at a flow rate of 0.6 mL/min and constant temperature of 35 °C. Glucan was served as a reference substance. 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 4000–400 cm^{-1} in the transmission mode. The ^1H–^{13}C 2D hetero-nuclear single quantum coherence (HSQC) spectra were obtained on a Bruker AV 600 spectrometer in the HSQC experiment mode at 25 °C. The spectral widths were 6009 and 25,000 Hz for the ^1H- and ^{13}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.

3. Results and discussions

3.1. Content of neutral sugars and uronic acids

To characterize the hemicellulosic fractions, the samples were analyzed by HPAEC and the results are presented in Table 2. As shown in Table 2, xylose (57.43–79.92%) was the predominant sugar component in five hemicellulosic fractions. However, uronic acids (1.44–3.54%), primarily glucuronic acid or 4-*O*-methyl-glucuronic acid, and galactose (0.88–6.36%) were in small amounts. Moreover, considerable amounts of glucose (9.47–28.52%) and arabinose (5.50–10.49) were observed in hemicellulosic fractions. The results showed that there was not a great difference in the sugar component of hemicelluloses and the hemicelluloses fractions were mainly composed of arabinoxylan. It can be found in Table 2 that the amount of glucose in the yellow liquor was the lowest, which indicated the cellulose had lower degradation extent during the cooking process. The increase of the uronic acids after cooking indicated that the active oxygen can not only efficiently remove the lignin, but also oxidize the hemicelluloses during the cooking process. The molar ratios of arabinose to xylose (Ara/Xyl) (0.069–0.164) and uronic acids to xylose (UA/Xyl) (0.015–0.037) showed that most of the side chain came from the arabinose.

3.2. Average molecular weight

The weight-average (M_w), number-average (M_N) molecular weights, and the polydispersity (M_w/M_N) of the hemicelluloses from the bagasse, pulp, and yellow liquor are listed in Table 3. The M_w (4164–9264 g/mol) and M_N (4540–14,470 g/mol) of the five hemicellulosic fractions were relatively lower than those reported