Polymer Degradation and Stability 98 (2013) 550–556

Contents lists available at SciVerse ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Structural features and thermal characterization of bagasse hemicelluloses obtained from the yellow liquor of active oxygen cooking process

Jian-Bin Shi [a,*], Qiu-Lin Yang [a], Lu Lin [b,*]

[a] State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, Guangdong Province, China
[b] School of Energy Research, Xiamen University, Xiamen 361005, Fujian Province, China

ARTICLE INFO

Article history:
Received 7 October 2012
Received in revised form
24 November 2012
Accepted 29 November 2012
Available online 12 December 2012

Keywords:
Hemicelluloses
Bagasse
Yellow liquor
Active oxygen

ABSTRACT

The bagasse hemicelluloses from the yellow liquor of active oxygen cooking process were successively precipitated by ethanol. The chemical component and structure of five hemicellulosic fractions and final residue were elucidated by a combination of destructive and nondestructive methods. Results showed that xylose was the main sugar residue in the hemicellulosic fractions, whereas final residue contained high content of uronic acids (30.47%), and lignin. The hemicellulosic fractions were composed of (1 → 4)-linked-β-D-xylopyranosyl backbones, but the degree of branching of hemicelluloses fractions depended on the precipitation process. Only 1.84% of hemicelluloses in the yellow liquor showed high molecular weight (24,078 g/mol), the remainder of hemicellulosic fractions was significantly degraded under cooking conditions. In addition, some branched sugar residues fell off the backbone and dissolved in the yellow liquor during the cooking process. And the thermal stability may relate to the ash content, component, molecular weight, and degree of branching of hemicellulosic fraction.

1. Introduction

Declining petroleum resources, combined with increased demand for petroleum by emerging economies, and political and environmental concerns about fossil fuels, it is imperative to utilize biomass as feedstock for the production of organic chemicals because of its abundance, renewability and world-wide distribution [1,2]. Throughout 20th century, lignocellulosic biomass has been used as raw material for the energy, building materials, pulp and paper. While lignocellulosic biomass have been studied intensively as alternative feedstock for bio-fuels, chemicals, pharmaceutical and material industry in recent years [3]. Bagasse is a waste by-product from the sugar and alcohol industry and composed of 40–50% cellulose, 20–30% lignin, and 30–35% hemicelluloses [3,4]. It is estimated that about 54 million tons of bagasse are generated annually throughout the world [5]. At least 50% of bagasse is burnt to generate heat to run the sugar milling process, but the remainder is stockpiled [6,7]. Due to the amount of bagasse as an industrial waste, there is great interest in converting the bagasse into fuels and chemicals that offer economic, environmental, and strategic advantage [8].

To efficiently and cleanly utilize the bagasse, a novel cooking process involving active oxygen and solid alkali was developed by our group as a pretreatment of biomass conversion [9–11]. In this process, active oxygen (O_2 and H_2O_2) and solid alkali (MgO) were added as cooking chemicals. To reduce the effect of adsorbable organic halides (AOX), biochemical oxygen demand (BOD), and chemical oxygen demand (COD), both O_2 and H_2O_2 have been applied in the total chlorine free (TCF) bleaching process, namely oxygen delignification and hydrogen peroxide bleaching process [12,13]. During this bleaching process, various magnesium ion compounds including $MgSO_4$, MgO, and $MgCO_3$ behave for prevent carbohydrate from hydrolyzing initiated by some oxidation reactions of carbohydrate [12–14]. However, there is few published paper on using O_2 and H_2O_2 with MgO in the cooking process as a pretreatment of biomass conversion except our group. In the conventional industrialized cooking process, such as, soda, kraft, and sulfite cooking process, NaOH, Na_2S, SO_2, and sulfite are applied as the cooking chemicals. As a result, abundant HO^-, S^{2-}, HS^-, SO_3^{2-}, HSO_3^-, Na^+, and H^+ are introduced to the cooking system. During active oxygen cooking study, it was found that H_2O_2 was completely depleted and/or decomposed under the cooking conditions. Therefore, the Mg^{2+} is the only ion brought into the cooking system. Furthermore, no noxious gas and effluent

Abbreviations: Xyl/Ara, the molar ratio of xylose to arabinose; Xyl/Ura, the molar ratio of xylose to uronic acids; o.d., oven dry weight.

* Corresponding authors. Tel./fax: +86 (0)20 22236719.
E-mail addresses: shijianbin1022@126.com (J.-B. Shi), lulin@xmu.edu.cn (L. Lin).

0141-3910/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymdegradstab.2012.11.020

contained high concentration alkali were discharged to environment and the cooking liquor (called yellow liquor) presented weak alkalinity (c.a. pH 8.0) after cooking. In other words, the pollution caused by the cooking chemicals can be completely eliminated during the active oxygen cooking process. In the cooking process, 95.3% lignin and 78.2% hemicelluloses were removed from bagasse, and the yield of bagasse pulp was calculated as 50.54% [11], which indicated the active oxygen cooking process is an efficient pretreatment process of biomass conversion. After cooking, the rich-polysaccharides pulp and the hemicelluloses recovered from the yellow liquor can be used for producing different chemicals, such as, transformation fuel, furfural, and 5-hydroxymethylfurfural [1,15–18].

Active oxygen cooking process is a new pretreatment process for the agricultural residue, and most of hemicelluloses were dissolved in the yellow liquor during the cooking process. Therefore, it is crucial to clarify the structural characterizations of bagasse hemicelluloses in yellow liquor for further utilizing the hemicelluloses in the yellow liquor and understanding the cooking mechanism. In the present study, the hemicelluloses in the yellow liquor were successively precipitated by the ethanol. And the structural characteristics, physicochemical, and thermal properties of the hemicellulosic fractions were investigated.

2. Materials and methods

2.1. Materials

The bagasse was obtained from Zhangzhou, Fujian Province, China. The composition (*w*/*w*) of bagasse was celluloses 39.12%, hemicelluloses 23.96%, lignin 21.73%, ash 7.95% and benzene/ethanol extraction 4.22% based on oven dry weight (o.d.), and the methods and the data also showed in our previous paper [11].

2.2. Methods

2.2.1. The active oxygen cooking operations

The active oxygen cooking operations were described in our previous study [10,11]. The detailed operations are given as follow: 50 g bagasse (o.d.), 15% wt. dosage of MgO and 3% wt. dosage of H_2O_2 (based on the o.d. of bagasse) were placed in a 2 L stainless, rotating autoclave at a solid-to-water 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 h. At the end of cooking, the yellow liquor was collected and stored in a refrigerator.

2.2.2. Fractional isolation of the hemicelluloses in the yellow liquor

In order to study the structural characteristics of bagasse hemicelluloses in the yellow liquor, the hemicellulosic fractions were isolated by sequential precipitation with ethanol and the detailed operations are given as follow. The yellow liquor (200 mL) was adjusted to 1.5–2.0 with HCl in a beaker and centrifuged at 5000 rpm for 10 min to remove the lignin. The supernatant was neutralized to pH 5.5 with NaOH and poured into one volume of 95% ethanol. The precipitated hemicelluloses were centrifuged at 5000 rpm for 10 min and freeze-dried. Then, the supernatant was concentrated to 100, 50, 70, 30 mL at a reduced pressure, and poured into two, three, five, and seven volumes of 95% ethanol, respectively, according to the same method mentioned above, but did not adjust the pH. The supernatant precipitated with seven volumes of ethanol was concentrated to 20 mL and directly freeze-dried. The hemicellulosic fractions precipitated with one, two, three, five, and seven volumes of ethanol were labeled B_1, B_2, B_3, B_5, B_7, respectively; the final residue was named R_B.

2.2.3. Physiochemical characterization of the hemicellulosic fractions

2.2.3.1. Chemical characterization. The ash content of hemicellulosic fractions was determined by calcinating sample under 700 °C in Muffle furnace. Fractions B_1 and B_7 were not tested for running of the sample. The neutral sugars and the uronic acids in the hemicellulosic fractions and final residue were obtained by hydrolysis with 5.5 mL of 6.5% H_2SO_4 at 105 °C for 2.5 h. After hydrolysis, the hydrolyzate was diluted to 50 mL (after adjusted the pH value to 7.0) and analyzed by high-performance anion-exchange chromatography (HPAEC) (Dionex ICS-3000, USA) with pulsed amperometric detection, a CarboPac™ PA 20 column (3 × 150 mm) and a CarboPac™ Guard column (3 × 30 mm). The eluent was 0.002 M sodium NaOH when eluted the monosaccharide, however, the eluent was 0.1 M NaAc and 0.002 M NaOH when eluted the uronic acid due to the weak eluting power of the NaOH. The operations were run at 30 °C for 30 min, and the flow rate was 0.5 mL/min.

The molecular weights of the hemicellulosic fractions were determined by gel permeation chromatography (GPC). The GPC system comprises 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), and eluted with 0.02 M KH_2PO_4 pH 6.0 at a flow rate of 0.6 mL/min. The calibration of the GPC columns was made with glucan reference material.

2.2.3.2. Spectroscopic and thermal characterization. Fourier transform infrared spectra (FT-IR) of the hemicelluloses samples were obtained on an FT-IR spectrophotometer (Bruker Tensor 27, Germany) using the KBr disk method. Thirty-two cans were taken of each hemicellulosic fraction recorded from the range 4000–400 cm^{-1} in the transmission mode.

The ^1H and ^{13}C NMR spectra of the hemicelluloses (80 mg in 1 mL D_2O) were obtained on Bruker AV 600 instrument. For the solution-state ^1H NMR spectrum, the proton spectrum was recorded at 25 °C after 16 scans at 600 MHz. The acquisition time (AQ) was 2.6477 s, the relaxation delay time was 1.00 s, and pulse width was 12.1 μs. And ^{13}C NMR spectrum was recorded at 150.90 MHz after 10, 000 scans at 25 °C. A 8.100 μs pulse width, 2.0 s delay time between scans, and 0.9110 s AQ were used.

The thermogravimetric analysis (TGA) of the hemicellulosic fractions was performed on the TGA Q500 (TA, USA) thermal analysis instrument. Approximately 10 mg hemicelluloses was evenly distributed in the platinum crucible and heated form the room temperature to 700 °C at a heating rate of 10 °C/min under high purity nitrogen gas flow at 60 mL/min.

3. Results and discussions

3.1. Yield and sugar composition of hemicellulosic fractions

During the active oxygen cooking process, 78.2% of hemicelluloses were removed from raw material [11]. The hemicellulosic polymers in the yellow liquor were a mixture of a number of polysaccharides with different degree of polymerization (DP) and side chains. The different precipitation process can affect the yield and sugar component of hemicellulosic fraction. As shown in Table 1, 1.84%, 14.66%, and 24.82% of hemicelluloses were precipitated from the yellow liquor with one, two, and three volumes ethanol, respectively. However, only 16.58% and 2.52% of hemicelluloses were obtained when the supernatant was precipitated with five and seven volumes of ethanol. Obviously, the yield of