



Extraction of hemicellulose by hot water to reduce adsorbable organic halogen formation in chlorine dioxide bleaching of bagasse pulp



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ABSTRACT

To study the influence of the content of hemicellulose on the adsorbable organic halogen (AOX) formation in chlorine dioxide bleaching, a pH pre-corrected hot water pretreatment was developed. The influence of lignin on AOX formation was eliminated by the control of hot water extraction time, AOX formation was decreased by 33.27% under optimal hot water extraction conditions. The chemical composition of bleaching effluent was analyzed by GC–MS, and the formation of chlorobenzene and chlorophenol was inhibited by removal of hemicellulose, the ring structures of which were degraded into chain macromolecules and small molecules. The hemicellulose structure of raw material and bleached pulp was characterized by ATR-FTIR and NMR. This finding revealed differences in the structures of the bagasse hemicelluloses and the solid residual hemicelluloses. AOX formation was affected by the structure of hemicellulose. A new process combining biorefinery and clean pulp and paper was developed through these experiments.

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1. Introduction

The conversion of biomass to chemicals and energy is imperative to sustaining our current way of life (Liu, 2010). Research and development are required to improve the energy conversion efficiency of forest biomass to meet industrial and residential energy requirements (Amidon and Liu, 2009; Martin-Sampedro et al., 2014). The primary focus of recent research is making full use of hemicellulose in lignocellulosic biomass, by developing biomass refining technology (Feria et al., 2012; Liu et al., 2012). Hemicelluloses have increasingly been the focus of recent studies as feedstock for bioethanol, biopolymers, emulsion stabilizers, and for possible health applications (Gilani and Stuart, 2015; Krogell et al., 2013; Persson et al., 2009). A pretreatment step is important in biomass processing for breaking up the plant cell walls, dissolving the hemicelluloses and lignin, and decreasing the cellulose crystallinity in biomass. Pretreatment of biomass is also crucial for the biofuel production process (Ma et al., 2013; Peng et al., 2012). Over the last several decades, a variety of physical, chemical, thermochemical and biological methods for pretreating

hemicelluloses have been suggested for technical and/or economical effectiveness (Alvira et al., 2010; Zhao et al., 2016) including: dilute acid pretreatment (Gaur et al., 2016; Wang et al., 2012), hot water pretreatment (Krogell et al., 2013; Li et al., 2014; Yao et al., 2015), alkaline pretreatment (Sabiha-Hanim et al., 2015; Sun et al., 2013; Yuan et al., 2010), steam explosion versus steam pretreatment (Martin-Sampedro et al., 2014), enzymatic pretreatment (Krawczyk et al., 2013; Nie et al., 2016), etc. Hot water extraction, is an environmentally benign process, that has been widely used for lignocellulosic biomass pretreatment (Ma et al., 2013) and which has been essential for improving the competitiveness of the pulp and paper industry (Feria et al., 2012). Materials in the hot water pretreatment process can be divided into two parts, a solid phase and a liquid phase. For the liquid phase, the hot water extraction-based biorefinery strategy includes five production pathways (Huijgen et al., 2012). Extraction of hemicellulose is used to produce (i) biogas, (ii) hemicellulose for C5-sugars, (iii) C5-sugars, (iv) furfural and (v) hemicellulose for animal feed. The solid phase, includes three production pathways (i) a biorefinery process for the production of paper from lignocellulosic residue with hot water pretreatment (Feria et al., 2012), (ii) biodegradable polymers from lignocellulosic residues (Ruiz et al., 2013), (iii) glucose and aromatics are produced after separation/hydrolysis.

As the main chemical in elemental chlorine free (ECF) bleaching technology, chlorine dioxide has a good selectivity in delignification

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(Nie et al., 2015). The production of absorbable organic halogen (AOX) is greatly reduced when the elemental chlorine free (ECF) process is employed for pulp bleaching (Nie et al., 2014; Sharma et al., 2014; Singh et al., 2008). Because the papermaking industry discharges a large amount of wastewater annually, the total AOX which are released into the environment have been increasing. AOX are a persistent organic pollutant (POPs) (Jaacks and Staimez, 2014), which pose an enormous environmental threat.

Many researchers have focused on the lignin oxidation mechanism of ECF bleaching (Nie et al., 2014; Zhu et al., 2003). Research has shown that the residual lignin in unbleached pulp is the main source of AOX formed. However, hemicellulose pretreatment and enzyme pretreatment have become the focus of current research (Nie et al., 2015; Sharma et al., 2014), these studies indirectly demonstrated that hemicellulose has an effect on the formation of AOX. This paper mainly focuses on the effects of hot water extraction of hemicellulose on AOX formation during chlorine dioxide bleaching of bagasse pulp. To reduce the degradation of cellulose or lignin and obtain high molecular weight hemicellulose from extracts, the hot water extraction process was optimized. The change in AOX formation with or without hemicellulose extraction was compared, after the same cooking and bleaching processes.

2. Materials and methods

2.1. Raw material

Bagasse was provided by a local sugar refinery (Guangxi, China). The chemical composition of bagasse was analyzed (Ruiz et al., 2011). Approximately, 2 g bagasse was treated with 10 mL of 72% (w/w) H_2SO_4 , 7 min at 45 °C. The reaction was interrupted by adding 50 mL distilled water and then diluted to 275 mL. The mixture was autoclaved for 30 min at 121 °C for complete hydrolysis of oligomers. The mixture was filtered and the hydrolysate adjusted to 500 mL. The hydrolysate was analyzed by HPLC in a Waters e2695 (USA) chromatograph equipped with a refractive index detector and symmetry shield TM RP18 column. Chromatographic separation was performed with the mobile phase of 0.02 mol/L ammonium acetate and acetonitrile (82%/18%). The samples were analyzed for glucan, xylan, arabinan and acetyl groups. The solid obtained in the filtration after hydrolysis was oven-dried and weighed. The mass obtained corresponded to the residual lignin (Klason lignin) and the soluble lignin was determined by spectroscopy at 280 nm.

3.9 mol L⁻¹ of sodium hydroxide was used for controlling the pH of the solution. Activated carbon and ceramic wool were purchased from Analytik-Jena instrument company (Germany), other chemicals were purchased from Alladdin (Shanghai, China). All assay reagents were obtained from Sigma (USA). All of the chemicals used were analytical grade.

2.2. Hot water extraction

The hot water extraction was carried out in a rotary digester with six 1000 mL stainless steel cylindrical reactors (Greenwood, USA). Bagasse was treated with pure water, at a ratio of 5:1. To control hydrolysate pH at the highest temperature (170 °C) and holding time (60 min), 4% sodium hydroxide was added. Alcohol precipitation was used for the separation and purification of hemicellulose (Yao et al., 2015).

2.3. Cooking and chlorine dioxide bleaching

The cooking was performed in a continuous digester (Greenwood, USA) with six 1000 mL stainless steel cylindrical reactors. The basic method was as follows: 150 g bagasse was treated with

pure water, at a ratio of 5:1, 10% sodium hydroxide was added, the mixture was heated to a temperature of 160 °C over a 90 min period and the temperature was held for 60 min. The bleaching reaction was carried out in a sealed polyethylene bag. 10 g of unbleached bone dry pulp was mixed with bleaching fluid, and the pulp concentration was adjusted to 10% in the sealed bag during the bleaching process. Mixing was allowed to take place for 5 min, after which the sealed bag was placed in a constant temperature water bath. Next, sulfuric acid was added to adjust the initial pH to 3.5–4. 120 kg tp⁻¹ (2.0%) chlorine dioxide was added to the pulp slurry when the reaction temperature reached 65 °C. The pulps were kneaded every 5 min and were washed after the bleaching. Waste liquid was collected when the reaction time achieved the set point; 5 mL of the effluent was pipetted out to dilute it 200 times and adjust the pH value (Nie et al., 2014; Nie et al., 2015).

2.4. Chemical composition analysis and structure identification

The Multi AOX analyzer was employed to determine AOX formation in the bleaching effluent. The chemical composition of the bleaching effluent was analyzed by GC–MS (Gas Chromatography–Mass Spectrometry). The hemicellulose structure was characterized in raw material and bleached pulp using ATR–FTIR and NMR. These experiments resulted in a new process combining biorefinery and clean pulp and paper.

2.4.1. AOX content analysis

The Multi X2500 AOX analyzer (Germany) was employed to identify AOX in the bleaching effluent. The basic method and process are described in our previous studies (Nie et al., 2015): bleaching effluent was passed first through the activated carbon column, where the organic chloride of the bleaching effluent was adsorbed by the activated carbon column. Sodium nitrate was then used to wash the adsorbed inorganic chloride out of the activated carbon column, and the activated carbon column was burned in a combustion furnace, while the content of AOX was calculated using the micro coulomb titration method (Yuan et al., 2012).

2.4.2. Chemical composition analysis of bleaching effluent

The chemical composition of the bleaching effluent was quantified by GC–MS (Agilent 6890–5973, USA) (Kukkola et al., 2006; Singh et al., 2008). The basic method and process were described previously (Yao et al., 2016).

2.4.3. Characterization of hemicelluloses

The chemical structure of the native hemicelluloses and their derivatives were evaluated by ATR–FTIR, and ¹H and ¹³C NMR spectroscopies. ATR–FTIR spectra of HE with or without bleaching were measured on a ZnSe crystal ATR (USA) and Nexus 470 spectrometer (Canada) using 16 scans with frequencies ranging between 500 and 4000 cm⁻¹. The solution-state ¹H and ¹³C NMR spectra were obtained on a Bruker MSL-300 spectrometer at 300 and 74.5 MHz. ¹H NMR spectra were recorded at 25 °C from 20 mg of sample dissolved in 1.0 mL D₂O for hemicelluloses. Sampling conditions are as follows: the sampling time 3.98 s, relaxation time 1.0 s, and cumulative number of sampling is 128 scans. Calibration curves used a solvent peak of 4.7 ppm. The basic method and process for ¹³C NMR are described in Duchesne (Duchesne et al., 2001).

3. Results and discussion

3.1. Raw material composition analysis

The chemical composition of bagasse was previously analyzed by Moretti, Qiu and Rocha et al. (Moretti et al., 2016; Qiu et al., 2012; Rocha et al., 2015). The bagasse contains 45.03% cellulose,

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