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Structural changes of bamboo-derived lignin in an integrated process of autohydrolysis and formic acid inducing rapid delignification

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ABSTRACT

Bamboo chips were efficiently fractionated using an integrated process of autohydrolysis and formic acid to induce rapid delignification. Autohydrolysis pretreatment facilitated oligosaccharide production, while the subsequent rapid-delignification using formic acid at a low liquid/solid ratio with a relatively short reaction time allowed obtaining cellulose fibers and lignin. The major inter-unit linkages of side-chain in lignin were cleaved during the combined fractionation process. The lignin fraction exhibited higher purity, more phenolic OH groups, less condensed phenolic OH groups, and higher syringyl/guaiacyl ratio (S/G) as compared to MWL and formic acid lignin from the direct formic acid delignification. These results indicate that the combined fractionation process presents a promising approach to the commercial utilization in the biorefinery industry.

1. Introduction

Lignin is one of the most abundant renewable natural resources on earth, and million tons of lignin are generated from the pulping industry every year (Abdelkafi et al., 2011). It isconsidered as a potential substitute of fossil fuels for the utilization in the field of synthesis of new materials, as well as fine chemicals production (Zakzeski et al., 2010; Blaser et al., 2001). Until now, only about 2% of the lignin produced from conventional pulping processes, such as sulphite pulping and kraft pulping, has been commercially used (Gosselink et al., 2004), and the majority of the lignin is usually burnt to generate energy (Li et al., 2012). Uncontrolled modification of lignin and the formation of complex structures during conventional pulping processes are the major drawbacks for its further development of commercial applications. Recently, a new integrated biorefinery technology based on organosolv fractionation has been developed to selectively separate the main components of lignocellulosic biomass, including cellulose, hemicellulose, and lignin, without extensive degradation and modification of these three products (Delmas, 2008).

Among organosolvents, formic acid shows a strong ability to fractionate different lignocellulosic biomasses, such as non-woods (Li et al., 2012; Zhang et al., 2010a,b; Li et al., 2010), hardwood (Dapía et al., 2000; Dapía et al., 2002; Abad et al., 2000), and softwood (Obrocea and Cimpoesu, 1998), into cellulose pulp, hemicelluloses, and lignin. It is reported that fractionating bamboo in 85% of formic acid solution with a liquid/solid ratio of 20:1 (mL/g) at 101 °C for 2 h can result in a removal of about 80.4% lignin (Li et al., 2012). Under the same operating conditions (i.e., raw material, temperature, reaction time, and a liquid/solid ratio), the typical Milox method achieved a degree of delignification of 88.9%, while 87.9% and 79.1% for the methods of aqueous formic acid with the addition of H_2O_2 or HCl, respectively (Li et al., 2012). However, most of these studies were conducted at atmospheric pressure under mild reaction condition, the degree of delignification is relatively low compared to conventional pulping processes, especially for birch, bamboo, and *Eucalyptus* species. Under a high pressure, one-step formic acid fractionation achieved a fast and efficient delignification for bamboo chips, while obtaining 42.2% cellulose fibers, 31.5% lignin, and 8.5% hemicellulose-rich fraction (Zhang et al., 2017a). This process reached a degree of delignification of 92.7% for bamboo and the lignin fraction obtained had a relatively high content of phenolic and carboxylic groups (Zhang et al., 2017b). However, under harsh conditions, most of the hemicelluloses would be seriously degraded into monosaccharides and new chemical compounds, such as acetic acid, furfural, and hydroxymethylfurfural, and these degradation products are difficult to be effectively collected.

As an environmentally friendly and economically feasible

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technology, autohydrolysis, in which lignocellulose material is pretreated with just hot water, has been used to selectively remove hemicelluloses prior to pulping processes (Ligero et al., 2011; Romaní et al., 2011; Wörmeyer et al., 2011). This process is catalyzed by hydronium ions generated by water and acetic acid produced from the cleavage of acetyl groups of hemicelluloses (Garrote et al., 2004; Ruiz et al., 2012), and leads to a liquid phase rich in hemicellulose-derived monosaccharides or oligosaccharides without causing a significant degradation of cellulose and lignin. Afterwards, sugars degraded from hemicelluloses can be recovered in a liquid phase (Garrote et al., 2001), whereas cellulose and lignin remained in solid phase can be used to further fractionation (Kim et al., 2009; Laser et al., 2002). Recently, it has been demonstrated that the autohydrolysis process facilitates the subsequent kraft pulping of hardwood by increasing the solubility of lignin (Lu et al., 2012). An integrated biorefinery technology combining autohydrolysis with ethanol organosolv fractionation has also been proposed (El Hage et al., 2010; Huijgen et al., 2012). However, the subsequent delignification in this process generally needs a higher temperature (over 170 °C) and acid catalyzing the process (e.g., H_2SO_4). Besides, Wen et al. (2013) developed a three-step fractionation process for bamboo powder. After autohydrolysis, the treated bamboo powder was further fractionated into lignin and pulp by the mixture of formic acid and acetic acid at 107 °C for 3 h with a liquid/solid ratio of 20:1 (mL/g), and the obtained pulp was finally conducted an extended delignification with alkaline hydrogen peroxide. There is no doubt that a higher liquid/solid ratio and a longer reaction time would increase the total project cost for the commercial application in the biorefinery industry.

In the present study, bamboo chips were selected and fractionated into cellulose fibers, hemicellulosic sugars, and lignin using a combined fractionation process based on autohydrolysis and subsequent formic acid rapid-delignification at a low liquid/solid ratio (7:1) under a low pressure (0.15 MPa). The structural features of the lignin fractions obtained in the integrated process are thoroughly investigated and characterized by Fourier transform infrared spectroscopy (FT-IR), gel permeation chromatography (GPC), thermogravimetry (TG), ^{13}C, 2D heteronuclear single quantum coherence (2D-HSQC), and quantitative ^{31}P-nuclear magnetic resonance (NMR) spectroscopy. It is believed that the enhancing understanding of structural features of lignin polymers would facilitate the integrated utilization of lignocellulosic biomass.

2. Materials and methods

2.1. Material

Bamboo (*Neosinocalamus affinis*) chips (20–30 mm long, 10–20 mm wide, and 3–4 mm thick) were obtained from Sichuan Province in China and selected as the raw materials in this study. According to the NREL LAP method (Zhang et al., 2010b), the moisture content of the selected bamboo chips used in this study was 9.43% based on an oven dried weight. The primary chemical compositions of the bamboo chips were as follows: Klason lignin 25.56%, acid-soluble lignin 1.87%, xylan 21.96%, glucan 39.63%, ethanol-toluene extractives 2.10%, and ash 2.2%.

2.2. Autohydrolysis and formic acid rapid-delignification process

The autohydrolysis was carried out in a 15-l electrically heated and thermostatically controlled rotary digester (Xianyang Tongda Light Industrial Equipment Co. Ltd., China). Two hundred grams of dry bamboo chips and distilled water with a solid-to-liquid-ratio of 1: 6 were added in the digester. The mixture was heated to 170 °C in 30 min, and then this temperature was kept for 60 min (based on the optimum condition in the preliminary experiment). After the autohydrolysis treatment was completed, the mixture of autohydrolyzed bamboo chips and the spent autohydrolysis liquor was rapidly cooled down to about 80 °C. After filtration with a 120-mesh nylon screen, the autohydrolysis residue (AH-residue) was thoroughly washed with distilled water and oven-dried at 50 °C overnight for later use.

100 g of the dry AH-residue was further treated at a temperature of 135 °C for 45 min using 85% (v/v) formic acid at a liquid/solid ratio of 7:1 (mL/g) in a self-designed reactor, which includes a 3 L Hastelloy alloy sealed container and an outer jacket containing electrical wires and intelligent temperature control system. After the delignification, the obtained brown pulp (mainly cellulose fibers) was filtered and washed with 85% (v/v) formic acid (85 °C, 3 × 500 mL) and distilled water (85 °C, 3 × 500 mL). The filtrate and the washing liquids weremixed together as black liquor, and then evaporated in a rotary evaporator to recover formic acid. Then 10 volumes of distilled water were poured into the concentrated black liquor to precipitate the lignin dissolved in the delignification process. The crude lignin was obtained by centrifugation at a speed of 3000 rpm for 10 min and then washing with distilled water twice at room temperature. After conducting the further lignin purification process according to the literature method (Abdelkafi et al., 2011), the autohydrolysis-pretreated formic acid lignin (AHFL) was obtained. For comparison, the non-autohydrolysis bamboo chips were also treated with the same delignification and lignin (i.e., formic acid lignin, FL) purification experiments as the autohydrolyzed ones.

2.3. Milled wood lignin (MWL) extraction

To investigate the structure changes of lignin during autohydrolysis and formic acid rapid-delignification process, MWL as a representative of native lignin was isolated for comparison. The bamboo MWL and AH-residue milled wood lignin (AHMWL) were extracted, respectively, according to the method of Björkman (1954).

2.4. Determination and structural characterization

The degradation by-products of carbohydrates, such as acetic acid and furfural, in the spent autohydrolysis liquor were analyzed by a high-performance liquid chromatography (HPLC) system according to the literature (Wang et al., 2014). Sugar analysis was conducted using an ion chromatography ICS-5000 system (Thermo Fisher Scientific, MA, USA) with a pulsed amperometric detector. The test samples were first acid hydrolyzed based on a literature method (Hong et al., 2013). Then the reducing sugars were analyzed on a CarboPacTMPA20 (3 × 150 mm) coupled with a guard column (Dionex, CA, USA) according to the published method (Wang et al., 2013). The sugar contents of the samples before acid hydrolysis represented the monomeric form of the sugars. The content of oligomeric sugars was calculated by considering the difference between the sugar contents of samples before and after the acid hydrolysis.

The obtained lignin samples were acetylated with acetic anhydride according to the literature (Zheng et al., 2016). Molar-mass characteristics and dispersity index of the acetylated lignin were determined using GPC with a LT-ELSD detector (Shimadzu, Japan) based on a literature method (Zhang et al., 2017b). Thermogravimetric (TG) and differential thermogravimetric (DTG) analysis were conducted by using a thermal gravimetric analyzer (TGA Q50, TA instruments, USA). The test samples of 4–6 mg, which were vacuum dried at 40 °C for 48 h before measurement, were heated in an aluminum crucible from ambient temperature up to 1000 °C at a heating rate of 10 °C/min, while using a constant nitrogen flow as an inert atmosphere during the experiment. FT-IR spectra of the lignin samples were recorded on a FT-IR spectrophotometer (IRPrestige-21, Shimadzu, Japan) in the range of 4000–400 cm^{-1} using a KBr disc containing finely ground samples (1%). NMR spectra (^{13}C NMR and 2D HSQC spectra) were obtained on a 500 MHz Bruker Avance instrument at 25 °C. 80 mg of the lignin sample was dissolved in 0.75 mL of deuterated dimethyl sulfoxide (DMSO-d_6). The ^{13}C NMR spectra were acquired with a minimum of 20,000 scans, a