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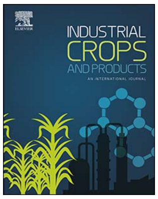

Research paper

Revealing the structure of bamboo lignin obtained by formic acid delignification at different pressure levels

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ABSTRACT

Bamboo was fractionated using formic acid based on a one-step organosolv process under high pressure (at 145 °C for 45 min, 0.3 MPa) and at atmospheric pressure (at 101 °C for 120 min), respectively. High-pressure formic acid lignin, atmospheric formic acid lignin and milled wood lignin of bamboo were subjected to comprehensive structural characterization using gel permeation chromatography (GPC), Fourier transform infrared (FTIR) and solution-state NMR techniques (^{1}H, ^{13}C, 2D-HSQC, and ^{31}P-NMR spectroscopies). The results indicated that the formic acid fractionation under high pressure presents a quick and efficient delignification method by enhancing the cleavage of interunitary bonds in lignin (β-O-4′, β-β and β-5′), and dissolved lignin also occurred condensation reaction. As compared to atmospheric formic acid lignin, high-pressure formic acid lignin obtained showed higher purity and yield, and had relatively higher contents of phenolic and carboxylic groups.

1. Introduction

Lignin is the second most abundant biopolymer right after cellulose present in lignocellulosic biomass. It is expected to play an important role in the foreseeable future as a renewable source for the production of high-value chemicals and new materials (Lora and Glasser, 2002), since the extensive use of fossil-based resources has caused significant environmental, human health, and socio-economic concerns. Enormous amount of lignin is produced as a by-product by the pulp and paper industry. In the conventional pulp mills, the Kraft process and the sulfite process produce 60–100 kton of Kraft lignin and 1 Mton of lignosulfonates per year, respectively (Bugg and Rahmanpour, 2015). However, the lignin structure is significantly altered during these pulping processes, and lacks high-added-value applications. The majority of the lignin produced is simply burnt to generate energy, and only approximately 2% by mass is available commercially (Mansouri and Salvadó, 2006). Therefore, establishment of an effective fractionation process is of great significance to the conversion and the utilization of lignin as the major component of lignocellulosic biomass. New lignocellulosic fractionation technologies using organic solvents, which can easily be recovered and reused, such as alcohols, organic acids, cresols and phenols, have recently been developed to obtain cellulose, hemicellulose, and lignin without serious degradation (Kleinert, 1931; Bucholz and Jordan, 1982; Schweers et al., 1972; Sano et al., 1989; McDonough, 1993). The organosolv fractionation process, one of the most promising fractionation techniques, allows the isolation of lignin as a potential renewable source together with cellulose pulp that is easier to be bleached, and the whole process is environment-friendly and requires low capital investment (Jahan et al., 2007a; Bozell et al., 2011). This process has opened the possibility of exploiting the three components of lignocellulose, especially high-quality lignin.

Among organic solvents, formic acid has attracted increasing attention recently for the use in fractionation processes, due to its ability to achieve selective delignification with simultaneous hemicellulose degradation and satisfying cellulose pulp yield (Li et al., 2012). The process has demonstrated high efficiency on different biomass materials such as non-woods (Li et al., 2012; Zhang et al., 2010a; Zhang et al., 2010b; Li et al., 2010), hardwoods (Dapía et al., 2000; Dapía et al., 2002; Abad et al., 2000), and softwoods (Obrocea and Cimpoesu, 1998). The cellulose pulp, lignin, and hemicellulose fractions obtained from formic acid fractionation can be further used for the conversion into value-added products, including a variety of chemicals and materials (Kupiainen et al., 2012). The lignin dissolved in the spent liquor during the formic acid fractionation process can be easily separated by

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adding water. It has been reported that acetic and formic acid organosolv fractionation (65/35 mass ratio, 85% in water) of wheat straw at 105 °C for 3 h resulted in that 96% of lignin was removed from wheat straw (Snelders et al., 2014). According to the study by Li et al. (2012), the Milox method achieved the highest delignification (88.9%) for bamboo, followed by aqueous formic acid with the addition of H_2O_2 (FP, 87.9%), aqueous formic acid (F, 80.4%), and aqueous formic acid with the addition of HCl (FH, 79.1%) at the same treatment temperature (100 °C) and reaction time (120 min). It has been reported that fractionation of rice straw in 90% formic acid-water solution at 100 °C for 60 min resulted in 85% lignin removal (Lam et al., 2001). In most of those works, fractionation of lignocellulose by formic acid was conducted at atmospheric pressure. The relatively mild conditions may hinder the improvement of reaction efficiency. In order to achieve more efficient delignification, the whole fractionation process requires a long reaction time or a higher proportion of solvent. However, research by Dapía et al. (2002) indicated that a single stage of formic acid fractionation of beech wood under high pressure level at 110–130 °C yielded higher degree of delignification than the treatment of the same raw material at atmospheric pressure. Haverty et al. (2012) investigated the autothermal, single-stage, performic acid pretreatment of *Miscanthus* × *giganteus* at pressures of 35 bar by adding 100 mg/L $Fe_2(SO_4)_3$ in 4.0 M NaOH to 7.5% H_2O_2 in aqueous formic acid, and achieved 89% and 88% removal of lignin and hemicelluloses, respectively, in 30 min. However, these studies were focused mainly on finding an efficient fractionation of lignocellulose with less attention to the mechanism of delignification and the possibility of using the second largest fraction, lignin. In order to use lignin obtained from formic acid fractionation under high pressure levels as a raw material for the production of high-value chemicals in a future biorefinery industry, its structure and properties should be revealed and studied in details.

Bamboo, one of the most abundant biomass feed stocks in the world, has received increasing attention as a biomass source for numerous applications within the emerging field of biorefinery. Approximately 6–7 million tons of bamboo is produced annually in Asia (Li et al., 2010). According to Li et al. (2012), the major components of bamboo (*Phyllostachys acuta*) have been fractioned using formic acid at atmospheric pressure. However, to the best of our knowledge, relatively little research has been focused on the investigation of the fate and structural characterization of lignin obtained from formic acid fractionation of bamboo under high pressure level. In this paper, we extracted three different lignin fractions from bamboo: lignin from bamboo in native form (Milled Wood Lignin, MWL), two different forms of formic acid lignin obtained using formic acid fractionation at atmosphere pressure (atmospheric formic acid lignin, AFL) and at a higher pressure (high-pressure formic acid lignin, HPFL), respectively. The structure features of the various forms of lignin were thoroughly investigated by chromatographic and spectroscopic techniques including Fourier transform infrared (FTIR), gel permeation chromatography (GPC), ^1H, ^{13}C, 2D heteronuclear single quantum coherence (2D-HSQC), and ^{31}P nuclear magnetic resonance spectroscopies.

2. Materials and methods

2.1. Raw material

Bamboo (*Neosinocalamus affinis*) chips, which were obtained from Sichuan Province in China, were selected as the raw material in this study. The chips were screened to select a fraction of particles with size smaller than 3 mm. According to the NREL LAP method (Zhang et al., 2010), the moisture content of the screened bamboo used directly in formic acid fractionation studies was 9.43% based on an oven dried weight. Basic chemical analysis gave the following results: 25.56% Klason lignin, 1.87% acid-soluble lignin, 21.96% xylan, 39.63% glucan, 2.10% ethanol-toluene extractives, and 2.2% ash on a dry weight basis.

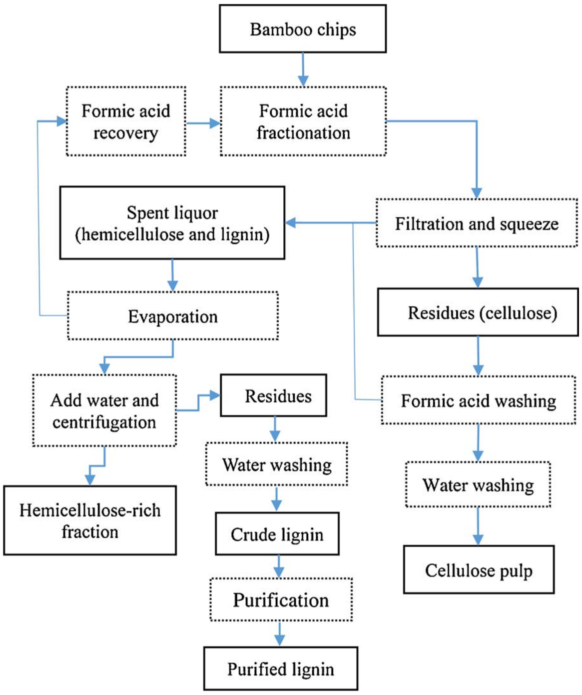

Fig. 1. Overview of the formic acid fractionation process of bamboo.

2.2. One step formic acid fractionation process

One-step fractionation of bamboo by formic acid was carried out in a 3 L Hastelloy alloy laboratory type reactor. The reactor was heated by an outer jacket containing electrical wires and intelligent temperature control system. Formic acid with concentration of 85% was used as the cooking agent. For a high pressure fractionation, bamboo (100 g) was delignified by the given cooking agent at 145 °C for 45 min with a liquid to solid ratio of 7:1(mL/g). For comparison, the fractionation of bamboo by the atmospheric formic acid process was conducted at boiling point (101 °C) for 120 min with a liquid to solid ratio of 20:1 according to a previous paper (Li et al., 2010).

As depicted in Fig. 1, when the reactions are finished, crude pulp (fibers, mainly cellulose) was separated from pulping liquor by filtration and pressed in order to eliminate as much lignin as possible. The crude pulp was afterwards washed with 85% formic acid and deionized water (85 °C) three times. The filtrate and the washing liquids were combined as black liquor and evaporated to near dryness (concentrated black liquor) using a rotary evaporator to recover formic acid. Then 10 vols of water were poured into the concentrated black liquor to precipitate the dissolved lignin. The crude lignin was separated by centrifugation at 3000 rpm for 10 min and washed with water twice at room temperature. The lignin purification process was conducted according to the method proposed by Abdelkafi et al. (2011). Then high-pressure formic acid lignin (HPFL) and atmospheric formic acid lignin (AFL) were obtained from the formic acid fractionation processes above, respectively.

2.3. Milled wood lignin (MWL) extraction

The milled wood lignin of bamboo was extracted according to the method of Björkman (1954). Briefly, the ball-milled bamboo (20 g) was extracted twice with dioxane/water (200 mL; 96:4, v/v) for 24 h. After the suspension was removed by centrifugation, the obtained solution was concentrated under reduced pressure. After freeze-drying, the crude milled wood lignin obtained was dissolved in acetic acid/water (20 mL; 9:1, v/v) and precipitated into water (400 mL). The precipitated lignin was filtered and then freeze-dried, dissolved in 1,2-

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