



One-step process based on the order of hydrothermal and alkaline treatment for producing lignin with high yield and antioxidant activity



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ABSTRACT

Three one-step processes based on the order of hydrothermal (170 °C, 30 min) and alkaline treatment (2% NaOH, 90 °C, 120 min) have been proposed for the production of lignin from wheat straw. The yield, purity, dissociation mechanism, structural transformation, and antioxidant activity of the lignins obtained from the various processes were systematically investigated. It was found that the order of hydrothermal and alkaline treatments had significant effects on the structural features and antioxidant activities of lignins. Hydrothermal process facilitated the subsequent alkaline delignification, releasing lignins with the highest yield (90.3%) and purity (97.4%). The β -O-4 linkages were obviously cleaved during the hydrothermal treatment, which resulted in an increase content of phenolic OH groups. The types and content of phenolic OH groups in lignins were closely related to its antioxidant properties. The lignins released during the one-step process based on successive hydrothermal and alkaline treatment had a high yield and antioxidant activity and the process would be very beneficial to the industrial production of potential antioxidant for food oils and fats, as well as food preservative that prevent the loss of food flavour.

1. Introduction

Abundant agricultural and forest biomass provide a vast renewable resource for the biorefinery industry. The biochemical conversion of biomass to biofuels and biochemicals typically involves pretreatment, enzymatic saccharification, and microbial fermentation. The nature of plant cell wall recalcitrance has made biomass highly resistant to enzymatic saccharification (Mosier et al., 2005). Among the components of biomass, lignin plays a negative role in the biochemical process for producing bioethanol (Zeng et al., 2014). Lignin can physically impede the access of cellulases to cellulose and/or reversibly or irreversibly adsorb cellulases during enzymatic saccharification of biomass, and thus impairs their activities (Li and Zheng, 2017). Various biorefinery processes for biomass including hydrothermal, alkaline, organic, ionic liquid, and steam explosion treatments have been applied to reduce recalcitrance and enhance the enzymatic saccharification ratio of biomass (Saha et al., 2013; Zhao et al., 2008; Park et al., 2010; Brandt et al., 2011; Rocha et al., 2012; Huang et al., 2015).

On the basis of previous investigations, a combination of hydrothermal and alkaline treatment was considered to be a promising integrated technology that could improve sugar release performance for various biomass types. For instance, the effect of hydrothermal and alkaline treatment conditions on enzymatic saccharification of oat

straw and corn stover had been investigated (Chen et al., 2017; Romani et al., 2016). Among the treatment processing, hydrothermal treatment mainly caused solubilization of hemicelluloses as well as structural variations of lignins, whereas alkaline treatment removed large amounts of lignins and hemicelluloses, which in turn contributes to the reduction of biomass recalcitrance for enzymatic saccharification. However, the aforementioned combined process based on a two-step process with hydrothermal and alkaline treatment required a large amount of water and a long operation time. This means that pure economic profit was reduced for producing bioethanol, since water consumption as well as operating and environmental costs increased. Based on the above considerations and previous research results, three one-step processes based on the order of hydrothermal (170 °C, 30 min) and alkaline treatment (2% NaOH, 90 °C, 120 min) have been proposed for enhancing enzymatic saccharification of wheat straw. However, as a biorefinery process, lignin was received due to its potential value in developing biobased materials and chemicals. Lignin, the second most abundant natural polymer, is a phenolic constituent derived primarily from three different phenylpropanoid units, such as syringyl, guaiacyl, and *p*-hydroxyphenol units (Ralph et al., 2004). In addition, there are approximately 12 different substructures with different intermonomeric linkages. The lignin content, composition, and structure varies widely among various plant species, among individuals, and even in different

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tissues of the same individual plant (Chakar and Ragauskas, 2004). Compounds with phenolic hydroxyl groups exhibit a certain degree of antioxidant activity. However, most of the antioxidants currently used are chemically synthesized resulting in high cost and greater side effects (Chen et al., 1992). Thus, lignin containing a large amount of phenolic hydroxyl groups can act as a natural product for antioxidants in the food industry, preventing the loss of food flavour (Dong et al., 2011; Sun et al., 2014).

In the present study, the structural features and chemical reactivity of the lignin fractions obtained from three one-step process based on the order of hydrothermal and alkaline treatment were thoroughly investigated by high performance anion exchange chromatography (HPAEC), gel permeation chromatography (GPC), quantitative two-dimensional heteronuclear single quantum coherence (2D-HSQC) and ^{31}P NMR spectroscopy. In addition, the antioxidant ability of the lignin was also detected by in vitro DPPH radical scavenging test. These results will offer some valuable information in the potential application of wheat straw for the production of lignin-based antioxidant in biorefinery industries.

2. Materials and methods

2.1. Materials

Wheat straw (WS) was harvested from the farm of Qishan County (Shaanxi, China). The dried WS was cut into small pieces and then ground and the fractions passing 20–40 mesh were collected. The powders were extracted with toluene/ethanol (2:1, v/v) in a Soxhlet instrument for 6 h. The composition of WS was 42.8% glucan, 24.4% xylan, and 21.1% lignin (20.1% Klason lignin and 1.0% acid-soluble lignin), which was determined by National Renewable Energy Laboratory (NREL) standard analytical procedure (Sluiter et al., 2008). All chemicals were analytical grade and purchased from Sigma-Aldrich and Megazyme.

2.2. One-step process based on hydrothermal and alkaline treatment

To investigate various processes based on order of hydrothermal and alkaline treatment on the effects of yield, purity, dissociation mechanism, structural transformation, and antioxidant activity of lignin, corresponding lignin should be collected from the processes (Scheme 1). Three processes were performed in a batch reactor (100 mL internal volume, Sen Long Instruments Company, Beijing, China). Specific processes were as follows: (1) 7.0 g dewaxed powders were treated with 2% NaOH aqueous solution at 90 °C for 120 min under a solid-to-liquor ratio of 1:10 (g/mL). At the end of pretreatment, the mixtures were cooled to room temperature. The collected liquid fractions were neutralized with 6 M HCl, and were further concentrated to 30 mL under vacuum; (2) 7.0 g dewaxed powders were treated under the same alkaline treatment condition stated above. At the end of the reaction, the reaction system was neutralized with 6 M HCl, followed by heating to 170 °C for 30 min. Subsequently, the liquid fractions were neutralized with 6 M NaOH, and were further concentrated to 30 mL under vacuum; (3) 7.0 g dewaxed powders were treated under the same hydrothermal treatment condition stated above. At the end of the reaction, the reaction system was neutralized with 6 M NaOH, followed by a further treatment in 2% NaOH at 90 °C for a further 120 min. Subsequently, the liquid fractions were neutralized with 6 M HCl, and were further concentrated to 30 mL under vacuum.

The aforementioned three processes based on hydrothermal and alkaline treatments were defined as AP, AHP, and HAP, respectively. In addition, the three concentrated solutions were respectively poured into 95% ethanol (90 mL) with vigorous stirring to remove polysaccharides. The supernatants were concentrated to 30 mL and poured into 150 mL acidic water (pH = 2.0, adjusted by HCl) to precipitate the lignins. The precipitates obtained by centrifugation and freeze-drying,

were named as alkaline lignin (AL), alkaline/hydrothermally lignin (AHL), and hydrothermally/alkaline lignin (HAL) according to the AP, AHP, and HAP, respectively.

2.3. Analysis procedures

The associated polysaccharides in the lignins were calculated by using HPAEC as reported previously (Sun et al., 2014). Molecular weights of the acetylated lignins were determined by GPC with an ultraviolet detector (UV) at 240 nm. The acetylation of lignin was done according to Pan et al. (2006). The column used was a PL-gel 10 mm mixed-B 7.5 mm i.d. column, which was calibrated with PL polystyrene standards. 4 mg of the lignin was dissolved in 2 mL of tetrahydrofuran (THF), and 20 μL lignin solutions were injected. The column was operated at ambient temperature and eluted with THF at a flow rate of 1.0 mL/min. The solution-state NMR spectra of the lignins were acquired on a Bruker AVIII 400 MHz spectrometer at 25 °C. For 2D HSQC spectroscopic experiments, the data were acquired in HSQC experiment mode using 60 mg lignin in 0.5 mL DMSO- d_6 (Sun et al., 2016). Functional groups (phenolic hydroxyl, aliphatic hydroxyl and carboxyl groups) of the lignins were determined by ^{31}P NMR spectra according to the recent publications (Sun et al., 2016). Meanwhile, the antioxidant activities of the lignins were also estimated using 2, 2-diphenyl-1-picryl-hydrazyl (DPPH) free radical in methanol solution (Dizhbite et al., 2004; Pan et al., 2006). All the measurements were conducted in duplicate, and the relative standard deviation was found to be below 5.0%. All the data represented are the averages of the results obtained from the duplicated experiments.

3. Results and discussion

3.1. Yields and associated polysaccharides of the lignins

The yields of the lignins were calculated based on the Klason lignin in WS and the results were shown in Table 1. Particularly, AP could obtain 48.2% of the lignin from the WS, while only 10.6% of the lignin was extracted from the WS by the AHP, implying that the subsequent hydrothermal treatment inhibited the dissociation and release of alkaline lignin during the AHP. By contrast, up to 90.3% of the HAL was obtained from the WS by the HAP, indicating that hydrothermal treatment facilitated the subsequent alkaline delignification. In other words, the HAP was a promising technology for efficiently loosening the tight cell wall structure, and then facilitating the release of lignin from the plant cell wall with the assistance of alkaline treatment. To verify the purity of the collected lignins, the associated polysaccharides of the lignins were detected by HPAEC (Table 1). As can be seen, all the lignins fractions contained a rather low amount of associated polysaccharides (< 4.7%), implying that all lignins had relatively high purity. In detail, xylose was the major monosaccharide in the lignins, suggesting that the associated polysaccharides in the lignins were derived from hemicelluloses.

3.2. Molecular weight determination

Changes in molecular weights of the lignins indirectly provided valuable insights into fragmentation and recondensation reactions of lignins during the different processes. To determine the effects of different processes on the molecular weights of the lignins, three lignin fractions were analyzed by GPC (Table 2). The molecular weight (M_w) of the AL was 1560 g/mol, and its polydispersity (M_w/M_n) was 2.00. It was observed that the M_w of the AHL was slightly decreased (1410 g/mol) as compared to that of the AL. This fact suggested that the lignin macromolecules underwent depolymerization during the AHP. It was noted that the more severe depolymerization reaction occurred during the HAP, which resulted in a distinctly reduced M_w of the lignin (1210 g/mol). In addition, as compared to the polydispersity index of

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