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Separation and characterization of lignin obtained by catalytic hydrothermal pretreatment of cotton stalk

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ABSTRACT

A catalytic method for the isolation of lignin in high purity from cotton stalk was presented in this study. Lignin fractions were obtained by the extraction of cotton stalk under catalytic hydrothermal conditions in the presence of metal chlorides including $AlCl_3$, $CrCl_3$, $FeCl_3$ and $ZnCl_2$ as catalysts. Structural elucidation of these lignin samples was investigated by high-performance anion-exchange chromatography (HPAEC), gel permeation chromatography (GPC), and 2D HSQC NMR spectroscopy. The results showed that the separated lignin fractions possessed higher purities than milled wood lignin (MWL). 2D NMR spectra demonstrated that guaiacyl (*G*) and syringyl (*S*) units were predominant in these lignin fractions, similar to the typical lignin types of hardwood. Moreover, the obtained lignin fractions consisted mainly of β-*O*-4′ aryl ether linkages, followed by resinol and phenylcoumaran structures. It was also found that the cleavages of β-*O*-4′ linkages occurred remarkably due to the presence of catalysts, and their decreasing severities were consistent with the acidity of the metal chlorides. In addition, the degradation was accompanied by a mild repolymerization during the catalytic hydrothermal pretreatment. In consideration of the relatively high yield and purity, isolation of lignin from raw materials by using catalytic hydrothermal pretreatment catalyzed by $AlCl_3$ provided us a more effective approach for biomass pretreatment.

1. Introduction

Lignocellulosic biomass, the fibrous materials derived from plant cell walls, is potentially a clean and sustainable feedstock for liquid fuel and chemical production in future biorefineries (Himmel, 2007). However, its use as a raw material for biorefinery still contains considerable technological challenges, particularly because of its chemical complexity and recalcitrance. Lignin, one of the three major components in lignocellulosic biomass, is an irregular and reticulated polymer network and composed of randomly cross-linked phenylpropanoid units (Ämmälahti et al., 1998). The phenylpropanoid units impregnate the preexisting hemicelluloses–cellulose network, thereby imparting both rigidity and biological resistance to the lignocellulosic structure. With the unique structure and chemical properties of lignin, a wide variety of fine chemicals are potentially obtainable, such as aromatic compounds and fuels (Zakzeski et al., 2010). Nevertheless, the tight physical bindings and chemical linkages between lignin and cell wall polysaccharides make it difficult to isolate lignin with a high yield in an unaltered form.

Over the last few decades, the separation and structural characterization of lignin have been extensively studied (Björkman, 1956; Chang et al., 1975; Crestini et al., 2011). Milled wood lignin (MWL) was obtained by the classical Björkman method after ball-milling which disrupted the crystallinity of the cellulose in the cell wall and depolymerized the lignin polymers to some extent. Solvent could then penetrate the cell wall and extract some low molecular weight lignin at a maximum yield of less than 50% of the theoretical value (Björkman, 1956). Even with an inability to isolate the whole lignin, MWL, which has recently been reported to be a linear oligomer based on a new method for the evaluation of the polymerization of lignin (Crestini et al., 2011), has been typically considered to be representative of native lignin structure. Further improvements in the yield of lignin isolated from ball-milled wood have arisen through the use of cellulolytic enzymes (Chang et al., 1975). However, novel and efficient solvents and process technologies are still required to help break the bottleneck for efficient utilization of lignocellulose. In this case, a concept of the hydrothermal

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pretreatment might be capable of facing challenges by virtues of their tremendous potential (Carr et al., 2011).

Hydrothermal pretreatment, based on the utilization of water as the sole fractionation agent, is an environmentally friendly pretreatment that can be used as the first stage of processes that produce an integral benefit to the raw materials (Xiao et al., 2011a, 2013). The versatility of hydrothermal system is related to the tunable polarity of water, an effective solvent for both polar and non-polar compounds, which is directly dependent upon the temperature. As the temperature of water is increased, the polarity of water decreases (Lu and Ralph, 2011), resulting in more dissolution of insoluble compounds. Simultaneously, the ionization degree of water enhances at high temperature, and as a consequence, water generates an elevated level of hydronium ions and acts as a weak acid. Moreover, another important reason why the hydrothermal pretreatment of biomass is developed is that the major part of the unused biomass is wet with water content of 80% or more. Therefore, the drying cost has been saved by using hydrothermal pretreatment due to the absence of drying processes. However, in spite of the extensive researches about hydrothermal, the relatively mild hydrothermal pretreatment with low temperature in the presence of catalysts is still obscure and needed to be further investigated.

Heretofore, numerous inorganic salts have functioned as catalysts by many scholars, such as KCl, $CaCl_2$, $MgCl_2$, $FeCl_2$, $CoCl_2$, $CrCl_3$, FeS, $FeSO_4$, $Fe_2(SO_4)_3$ and KAc (Liu et al., 2009a; Lu et al., 2011; Wang et al., 2011; Zhang et al., 2013). And among these catalysts, some inorganic salts have been confirmed to have a remarkable catalysis effect. For instance, $AlCl_3$ has been found to be an effective catalyst in hydrolysis of xylan into furfural and would achieve faster cellulose hydrolysis at a lower temperature and get a high glucose content within short residence time (Ma et al., 2012; Yi et al., 2013). For iron-based catalysts, $FeSO_4$ had a more significant effect on enhancement of both production of the oils and biomass conversion as a catalyst than FeS (Xu and Etcheverry, 2008). Afterwards, $FeCl_3$ was then found to be the most effective catalyst on the hemicelluloses degradation and xylose recovery from corn stalk among $FeCl_2$, $FeSO_4$, $Fe_2(SO_4)_3$ and $FeCl_3$ (Liu et al., 2009a, 2009b). As a consequence, it is inferred that the metal chloride is an appropriate catalyst for the biomass pretreatment. Nevertheless, based on the previous literature, it has been also found that the catalytic effects of metal chlorides are mainly focused on removal and conversion of carbohydrates, while their effects on lignin fractionation and structure changes during the hydrothermal pretreatment are still limited. Therefore, our emphasis focused on the separation efficiency and structural changes of lignin component from biomass with the catalytic hydrothermal pretreatment in the presence of metal chlorides.

As for the experimental raw material, cotton stalk was chosen since it is an abundant lignocellulosic by-product from cotton production in many countries, such as China, Egypt and Turkey (Tutus et al., 2010). In China, it is estimated that more than 20 million tons (dry weight) of cotton stalk are generated annually (Deng et al., 2011). Lignocellulose is the main component in cotton stalk, which is a compact structure of cellulose (32–46%), hemicelluloses (20–28%) in close association with lignin (26%) (Jha et al., 2008). This cellulose-rich biomass has gained increasing importance as a raw material for paper and cardboard industries because of its low cost, high yield and low non-fibrous materials content. In fact, although cotton stalk has been partly used for making paper and paperboard in China, the practical scale is still small. Therefore, more investigations need to be carried out to utilize cotton stalk cleanly and efficiently.

Therefore, the aim of our work was to establish a more effective lignin separation method from cotton stalk based on catalytic hydrothermal pretreatment in the presence of metal chlorides. In order to avoid the extensive degradation of hemicelluloses during the catalytic hydrothermal pretreatment, the materials were firstly extracted with hot water at 150 °C without catalysts to remove hemicelluloses (Bobleter, 1994), then the residual materials were treated separately with catalytic hydrothermal systems in the presence of catalysts of $AlCl_3$, $CrCl_3$, $FeCl_3$, $ZnCl_2$ to isolate lignin components. As a comparison, milled wood lignin (MWL) extracted according to the classic method and the control lignin sample obtained by hydrothermal pretreatment without catalyst were both prepared. All of these lignin fractions were comparatively characterized with spectroscopic and chromatographic techniques including high-performance anion-exchange chromatography (HPAEC), gel permeation chromatography (GPC), and 2D heteronuclear single quantum coherence nuclear magnetic resonance (2D HSQC NMR) spectroscopy.

2. Experimental details

2.1. Materials

Cotton (*Gossypium hirsutum*) stalk was harvested in an agricultural field in Xinjiang Province in China. After sample collection, the husks and branches were removed. The cotton stalk sample was then dried (50 °C, 24 h), and milled with a cutting mill to pass a 40-mesh sieve. The milled sample was extracted with acetone/water (9:1) in a Soxhlet apparatus for 24 h, and the extractive free sample was dried under vacuum for five days. The main composition (%, w/w) of the dried cotton stalk was: cellulose 36.5%, hemicelluloses 39.7%, lignin 18.6% and ash 1.25%. For determining the content of cellulose, the cotton stalk was first delignified using sodium chlorite under acidic condition, and the holocellulose obtained was then extracted with 10% potassium hydroxide at room temperature for 16 h to remove the hemicelluloses. Ash was determined according to the TAPPI standard method T211 om-93. Klason lignin was also detected according to the TAPPI standard method T-222 om-98 (Meng et al., 2012a). All chemicals used were analytical grade, and sugar reference materials were purchased from Sigma–Aldrich Company (Beijing).

2.2. Separation of lignin fractions

In order to avoid extensive degradation of hemicelluloses during catalytic hydrothermal pretreatment, the material (40–60 mesh) was firstly extracted with hot water at 150 °C for 2 h with a solid to liquid ratio of 1:6. After filtration, the residue was treated under hydrothermal conditions with and without catalysts at 170 °C for 2 h with a solid to liquid ratio of 1:10. Afterwards, the separation and purification procedures were performed as described in a previously published paper (Wang et al., 2010). The lignin fractions separated based on the catalytic hydrothermal systems in the presence of catalysts of $AlCl_3$, $CrCl_3$, $FeCl_3$ and $ZnCl_2$ were labeled as L_1, L_2, L_3 and L_4, respectively. Meanwhile, the lignin fraction obtained with the hydrothermal pretreatment without catalysts was named as L_5. The isolation sequence for lignin preparations based on the catalytic hydrothermal pretreatment is shown in Fig. 1.

2.3. Physicochemical characterization of lignin fractions

Sugar analysis of the lignin fractions was performed by a high-performance anion-exchange chromatography (HPAEC) system (Dionex ICS3000, USA) with a pulsed amperometric detector and an ion exchange Carbopac PA-1 column (4 × 250 mm). The carbohydrate moieties associated with the lignin fractions were determined by hydrolyzing ca. 5 mg samples in 1.475 mL of 10% H_2SO_4 for 2.5 h at 105 °C with occasional vibration. After hydrolysis, the mixture was filtered and diluted 50-fold prior to injection. Calibration was