



Effects of aluminum chloride-catalyzed hydrothermal pretreatment on the structural characteristics of lignin and enzymatic hydrolysis



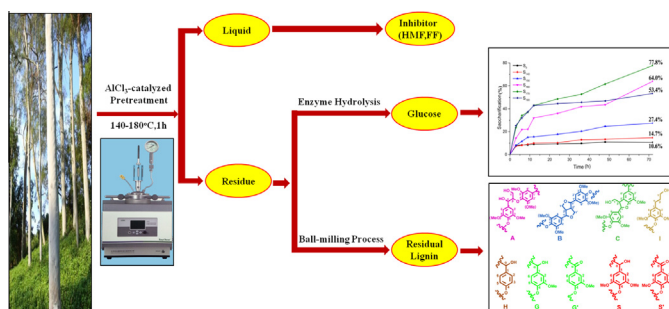
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HIGHLIGHTS

- AlCl_3 -catalyzed pretreatment can obtain digestible substrate for glucose and lignin.
- Removal of hemicelluloses is correlated with the pretreatment severities.
- The structural characteristic of the lignin was comprehensively elucidated.
- The pretreatment greatly facilitates the enzymatic hydrolysis of the substrates.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, *Eucalyptus camaldulensis* was pretreated with 0.02 M aluminum chloride (AlCl_3) at 140–180 °C to obtain digestible substrates for glucose and lignin. The effects of AlCl_3 -catalyzed hydrothermal pretreatment on the degradation of carbohydrates, structural changes of lignin, crystallinity, morphologic changes, and cellulose conversion of the pretreated biomass have been investigated by HAPEC, HPLC, FT-IR, XRD, CP/MAS NMR, SEM, and 2D-HSQC NMR. Results showed that the pretreatment significantly removed hemicelluloses and cleaved β -O-4 linkages of lignin at high temperatures. Under an optimum condition (at 170 °C for 1 h), almost all of hemicelluloses were removed and most of β -O-4 linkages in lignin were cleaved, and 77.8% cellulose conversion of the pretreated biomass was achieved, which was 7.3-fold higher than that of the original biomass. In short, this process was regarded as a promising approach to achieve an efficient conversion of lignocellulosic biomass to fermentable glucose and residual lignin.

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1. Introduction

Facing the impending depletion of fossil resources and environmental problems, utilization of lignocellulosic biomass as an alternative for fossil carbon sources in fuel and chemicals is one of the greatest challenges in the current world (Alvira et al., 2010). Lignocellulosic biomass has a complex structure consisting of three main polymeric components, namely, cellulose, hemicelluloses, and lignin. Cellulose and hemicelluloses, which are both

composed of monomer sugars, can be converted into fermentable sugars by pretreatment and enzymatic hydrolysis. Lignin is composed of randomly cross-linked phenylpropanoid units and fills in the spaces between the cellulose fibers and hemicelluloses to protect them from any kinds of degradation assisted by enzyme or catalysts (Sanderson, 2011). Moreover, lignin is an irregular and reticulated polymer, which greatly limits the further utilization of lignocellulosic biomass. Hence, an efficient pretreatment is crucial to break the lignin seal to increase the accessibility of the cellulase enzyme to the cellulose. The targets of a typical pretreatment are relocation of lignin and hemicelluloses, increase the porosity of the biomass so as to improve the enzymatic

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digestibility and increase the conversion yield of mono-sugars (Wyman et al., 1992).

Up to now, many pretreatments have been developed and investigated, including physical, chemical, biological methods, and a combination of these methods (Isroi et al., 2011; Kamireddy et al., 2013; Zhu et al., 2009; Lloyd and Wyman, 2005). Among these, hydrothermal pretreatment (also known as hydrothermolysis, uncatalyzed solvolysis, hot-compressed water treatment, or liquid hot water pretreatment) has been considered to be an economical and eco-friendly pretreatment that can improve sugar release performance of biomass and achieve some important bio-products, such as hemicelluloses, oligosaccharides and furfural (Garrote et al., 1999). During hydrothermal pretreatment, organic solvents and catalysts are not required and equipment corrosion can be minimized (Alvira et al., 2010). In fact, the ionization constant (K_w) of water rapidly increases with the elevated temperatures and is about one thousand times higher than that of water at room temperature (Kumar et al., 2011). Therefore, the high ionization constant promotes the hydrolysis of lignocellulosic biomass since acidic medium facilitates the cleavage of ether and ester bonds and hydrolysis of hemicelluloses (Savage, 1999). The hydrothermal pretreatment has been widely investigated for several lignocellulosic materials such as poplar (Yang et al., 2012); wheat straw (Safari Baboukani et al., 2012), sugarcane bagasse (Duarte et al., 2012). Unluckily, long reaction time, high temperature and high energy consumption of hydrothermal pretreatment restricts its large-scale application (Stephanopoulos, 2007). More importantly, as compared to pure water at high temperature alone, inorganic acid (sulfuric acid and phosphoric acid) forms more hydronium ions (H_3O^+) at lower temperatures. It has the advantage of recovering 91% of xylose after dilute sulfuric acid pretreatment (Lloyd and Wyman, 2005). Some researchers also have investigated the dilute sulfuric acid pretreatment of coastal *Bermuda* grass from 120 to 180 °C over a range of acid concentrations (0.3–1.2% w/w) and residence time (5–60 min) (Redding et al., 2011). The optimal pretreatment condition was found to be 1.2% dilute sulfuric acid for 60 min, yielding about 94% of the total sugars from the biomass. However, the dilute acid pretreatment required a special reactor to resist corrosion concerns. To overcome this shortcoming, the use of metal salt solutions instead of inorganic acid has been proposed (Liu et al., 2009). Recently, the enhancement effects of NaCl, KCl, CaCl₂, MgCl₂, FeCl₃, FeCl₂, Fe₂(SO₄)₃, and FeSO₄, on the production of furfural from xylans (hemicelluloses) and degradation of cellulose have been evidenced (Liu et al., 2009; Yu et al., 2011; Cai et al., 2014). As shown by a previous report (Ma et al., 2012), the conversion ratio of cellulose increased from 40.4% (without catalyst) to 86.8%, and the content of glucose in the final products increased from 25.9% (without catalyst) to 64.5% after the extremely low AlCl₃ catalyzed pretreatment.

Although some researchers investigated the effects of metal salts solution on the enzymatic hydrolysis of lignocellulosic biomass (Kamireddy et al., 2013), the effects of metal salts solution on the structural features of lignin, and structural features of residual lignin in the substrates as well as the corresponding enzymatic hydrolysis has been generally ignored. Lignin is principally comprised of three main lignin building blocks, *p*-hydroxyphenyl, guaiacyl, and syringyl units, linked by carbon–carbon (e.g., β - β , β -5, β -1 and 5–5) and ether bonds (e.g., α -O-4 and β -O-4) (Wen et al., 2013). In fact, the existence of lignin after pretreatment inhibits subsequent enzymatic hydrolysis, and the inhibitory mechanism was proposed as follows: Lignin limits the enzyme access to cellulose by forming a physical barrier; meanwhile, it also non-productively adsorbs enzyme, which probably reduces the enzymatic efficiency (Kumar and Wyman, 2013; Kumar et al., 2012). However, the structural characteristic of the residual lignin

in the substrates, which affects the efficiency of enzymatic hydrolysis of the pretreated biomass, still needs to be deeply investigated.

In this study, low concentration of aqueous aluminum chloride (AlCl₃) was used to pretreat the feedstock (*Eucalyptus camaldulensis*) for understanding the effects of AlCl₃ pretreatment on the chemical structures of lignin and subsequent enzymatic hydrolysis of the pretreated substrates (see Fig. 1). The liquid fractions obtained after pretreatment were analyzed by a high performance liquid chromatography (HPLC) and a high performance anion exchange liquid chromatography (HPAEC). The chemical and morphological characterizations of original and the pretreated residues were analyzed by using different analytical techniques, such as Fourier Transform Infrared (FTIR), X-ray diffraction (XRD), cross-polarization magic angle spinning carbon-13 nuclear magnetic resonance (CP/MAS ¹³C NMR), and scanning electron microscopy (SEM). Moreover, structural features of lignin, such as S/G ratios and the percentage of major substructures (inter-coupling bonds, β -O-4, β - β , β -5, etc.), were qualitatively and quantitatively acquired according to two-dimensional hetero-nuclear single-quantum coherence nuclear magnetic resonance (2D-HSQC NMR). In short, all the results will provide useful information in the value-added applications of *Eucalyptus* species for producing of glucose and residual lignin for the production of phenol formaldehyde adhesive.

2. Methods

2.1. Materials

The raw biomass, *E. camaldulensis*, was obtained from Guangxi province, China. It was cut into pieces, milled and screened in a mill (DFT-200A, Shanghai) to obtain a 20–40 mesh fraction. The composition of *Eucalyptus* wood was 43.5% glucan, 15.7% xylan, 0.6% galactan, 0.8% mannan, 26.3% Klason lignin and 3.94% acetyl groups in terms of dry weight, which was analyzed by the standard NREL method (Sluiter et al., 2008b). AlCl₃·6H₂O (>97%) and CH₃COONa (>99%) were purchased from Xilong Chemical Co., Ltd (Guangdong, China). H₂SO₄ (95–98%) was supplied by Beijing Chemical Company (Beijing, China). Liquid-state cellulase (100 FPU/mL) were supplied by Novozymes, Beijing, China.

2.2. AlCl₃-catalyzed hydrothermal pretreatment in a batch reactor

The pretreatment experiments of the biomass were performed in a batch reactor (100 mL internal volume, Sen Long Instruments Company, Beijing, China). The reactor was made of Hastelloy C-276 to mitigate the effects of acid corrosion at high temperatures. A 7 g (oven dried) quantity of dry biomass was added to 70 ml of 0.02 M aqueous AlCl₃ (equivalent to 1:10, solid:liquid ratio). The batch reactor was heated by electrical heating, the temperature was kept constant at the target temperature of 140, 150, 160, 170 or 180 °C for 1 h, and the reactor was stirred at 1000 rpm in order to provide homogeneous mixing in the batch reactor. After the desired temperature achieved, the reaction time was initiated and the temperature in the reactor was maintained constant. When the reaction was finished, the reactor was immediately cooled by passing the cold water into the external jacket until ambient temperature. After releasing the gas and pressure, the reaction mixture was filtrated with a Buchner funnel. The filtrate was stored in refrigerator for further analysis, and the solid residue was washed thoroughly with distilled water until the liquid in the filter flask became colorless and further freeze-dried by a 216V-230 freeze dryer (Thermo Fisher Scientific, Shanghai, China). The pretreated substrates were labeled as S₁₄₀, S₁₅₀, S₁₆₀, S₁₇₀ and S₁₈₀, respectively, corresponding

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