



Comparison on structural modification of industrial lignin by wet ball milling and ionic liquid pretreatment



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ABSTRACT

As the most abundant aromatic compounds, lignin is still underutilized due to its relatively low quality. In order to improve its quality, two pretreatment technologies, wet ball milling (WBM) and ionic liquid pretreatment (ILP) were tested on the industrial lignin and evaluated on the average molecular weight and polydispersity, surface morphology, and functional groups changes. The results showed that the lignin pretreated by the WBM with phosphoric acid presented dramatic decrease of polydispersity (23%) and increase of phenolic hydroxyl content (9%). While, the ILP treated samples exhibited the significant reduction of the average molecular weight and polydispersity. The decrease on the particle size and the emergence of the porous structure were found when treated with [Emim][OAc]. In addition, the remarkable reduction of the methoxy groups were observed to be 50% and 45% after treated with [Bmim]Cl and [Emim][OAc], respectively.

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1. Introduction

As one of the major components in the plant cell wall, lignin is the most abundant natural aromatic compounds on earth [32]. Presently, there are two main lignin resources from the existing industry: papermaking industry and bio-refining industry [18]. The papermaking industry alone produces 50 million tons of lignin annually which is mostly used as energy source by combustion and not more than 2% for producing phenolic resins, polyurethane foams, bio-dispersants and epoxy resins etc. [11]. To make good use of lignin can not only alleviate pollution to the environment caused by papermaking industry, but also improve market competitiveness of bio-refining industry, and thus relieve the energy crisis related to the shortage of petrochemical resources [13]. Two main reasons have been identified to restrict the high valorization of the industrial lignin: high dispersity of molecular weight and relatively low reactivity [16]. In order to improve the reactivity of lignin, many methods have been proposed, including methylation, demethylation, acetylation, etc. Wu and Zhan's study (2001) showed that the content of methoxyl groups in wheat straw soda lignin, decreased from 10.39% to 6.09% after demethylation, while the contents of the phenolic hydroxyl and carboxyl groups increased from 2.98% and 4.58% to 5.51% and 7.10%, respectively

[33]. investigated the methylation of pine Kraft lignin which revealed that about 0.36 mole of hydroxymethyl group per C₉ unit was introduced. The adhesive made from the hydroxymethylated Kraft lignin and phenol-formaldehyde resin (50%:50%, w/w) could reach bond strength of 65 psi in a lab test. With up to the 30% substitution of the phenolated lignin to phenol in the synthesis of lignin-based phenol-formaldehyde resin, the obtained resin had the similar mechanical and physical properties to the commercial phenol-formaldehyde resin [6]. However, these methods use toxic organic reagent and the operation process is complicated. Therefore, it is necessary to find green and feasible method to improve the lignin quality. Pretreatment is one of the most important operation unit in biorefinery process [12]. Many physical and chemical pretreatment methods have been successfully employed to overcome the recalcitrance of biomass and improve the yields of monomeric sugars, including ball milling, dilute acid, steam expansion, hot water, ionic liquids and organic solvent [5]. Among these biomass pretreatment techniques, wet ball milling (WBM) seems to be one of the promising pretreatment process in terms of polydispersity reduction and reactivity improvement. Compared to the traditional acid hydrolysis technologies, which causes equipment corrosion and further degradation of biomass to form inhibitor, mild acid hydrolysis coupling ball milling at room temperature could provide a simpler and less harsh treatment [34]. Yamashita et al. [31] revealed that the combination of ball milling and phosphoric acid swelling is an effective pretreatment method for the production of ethanol from paper sludge. In addition, the investigation of [17] indicating that

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the treatment effect of wet ball milling is better than that of dry milling.

Recently, ionic liquids (ILs) have become very popular solvents for the dissolution of biomass [9]. Ionic liquids pretreatment (ILP) can reduce the cellulose crystallinity by partially removing hemicellulose and lignin, and thus enhance the digestibility of biomass [24]. ILP are less energy demanding, more environmentally friendly and easier to handle [25]. Lee et al. [15] found that 1-ethyl-3-methylimidazolium acetate ([Emim][OAc]) can selectively extract lignin from wood with less crystalline cellulose remaining. Pu et al. [23] observed that the properties of the anion are extremely important in the solubility of lignin in ionic liquids. The recyclability of ionic liquids also has been demonstrated by some studies [19].

To our knowledge, no investigation has been reported in implementing the existing pretreatment process in biorefinery on lignin which might be helpful to improve the lignin quality. WBM and ILP were employed to treat industrial lignin in the present study. The changes of molecular weight, polydispersity, surface morphology and functional groups were also investigated.

2. Material and methods

2.1. Material

Industrial lignin was purchased from Changzhou Peaks Chemical Co., Ltd. (Changzhou, China). Its main composition was 93.35% lignin, 2.31% carbohydrates and 2.11% ash. *N*-methylimidazole, 1-chlorobutane and 1-bromoethane were purchased from Shanghai Jingchun Chemical Reagent Company; phosphoric acid, potassium acetate, toluene, dichloromethane, acetic anhydride, pyridine, chloroform and diethyl ether were purchased from Beijing Chemical Reagent Company. All reagents were used as supplied without further purification.

2.2. Wet ball milling pretreatment (WBM)

The ball-milling process was performed in a WL-IA planetary ball mill (Rishengjiuyuan Co., Ltd., Tianjing, China) equipped with four zirconia milling jar (500 ml for each one). Each jar was loaded with 30 g industrial lignin, 80 ml phosphoric acid (4%, w/v) and 30 zirconia balls ($\varphi = 10$ mm) and milled at 400 rpm for 30 min. The sample prepared by WBM with water (WBM-H₂O) was used as control. The mixture after WBM was filtered and washed with five times volume of water until the filtrate were approaching neutral. The residue was dried in vacuum oven at 40 °C overnight, then sealed for the following analysis. Duplicates were run for WBM with phosphoric acid (WBM-H₃PO₄) or WBM-H₂O. The solid recovery rate (R_s) was calculated as following:

$$R_s = \frac{m_1}{m_0} \times 100 \quad (1)$$

m_0 : Mass of raw feedstock, dry weight, g;

m_1 : Mass of pretreated samples, dry weight, g.

2.3. Ionic liquid pretreatment (ILP)

1-Butyl-3-methylimidazolium chloride ([Bmim]Cl) and 1-ethyl-3-methylimidazolium acetate ([Emim][OAc]) were mixed with industrial lignin at a ratio of 20:1, respectively. After 120 °C for 30 min, deionized water was added at a ratio of 5:1 to recover the lignin by vacuum filtration. The recovered solid was washed repeatedly with deionized water until the filtrate appeared colorless before it was dried in vacuum oven at 40 °C overnight. The dried sample was used for the following analysis. Each

treatment was carried out twice. The solid recovery rate (R_s) was calculated based on Eq. (1).

2.4. Analysis methods

2.4.1. Dry matter content

Dry matter content was determined by the moisture analyzer, Mettler Toledo HR83. Duplicate experiments were run for each sample.

2.4.2. Gel permeation chromatography (GPC) analysis

GPC was used to determine the weight average molecular weight (M_w) and number average molecular weight (M_n) of industrial lignin before and after pretreatment. The GPC analysis was done as described by [8]. The sample (50 mg) was dissolved in 2 ml mixture of acetic anhydride/pyridine (1:1, v/v) and shaken at room temperature, 150 rpm. After 24 h, the reaction was terminated by adding anhydrous ethanol (25 ml), and shaken at room temperature, 150 rpm for another 30 min, the solvent was then removed by vacuum rotary evaporation. The acetylated lignin was dissolved in chloroform (2 ml) and precipitated with diethyl ether (100 ml), followed by centrifugation at 4000 rpm, for 10 min. The precipitate was washed with diethyl ether for three times and dried under vacuum at 40 °C overnight. The dried acetylated lignin was dissolved in THF (20 mg/ml) and filtered through a 0.45 μ m organic membrane filter. The GPC analysis was carried out by HPLC (Agilent Technologies, 1260 Infinity) using a Styragel columns (PLgel mixed-C) at 25 °C and THF as eluent at a flow rate of 0.5 ml/min. A refractive index detector (RID) was used. Polystyrene standards were used as the calibration for the molecular weight of lignin [30].

2.4.3. Scanning electron microscopy (SEM) analysis

SEM was used to characterize the changes on morphology before and after different pretreatments. The sample for SEM was prepared by spray-gold processing to make it conductive, avoiding degradation and buildup of charge on the specimen [24]. A Hitachi S-4800 scanning microscope (Hitachi High-Technologies Corporation, Japan) operated at 15 kV was used to observe the samples.

2.4.4. Fourier transform infrared spectroscopy (FTIR)

The investigation of lignin by Fourier transform infrared spectroscopy was carried out using a JASCO FT/IR-660 plus spectroscopy. Each sample was prepared by KBr disk method [3]. The region between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1} and 80 scans were recorded.

2.4.5. Ultraviolet/visible (UV/vis) lignin analysis for ionization spectra

The lignin samples were characterized by differential UV/vis spectroscopy. The method is based on the difference in absorption between lignin in alkaline and neutral solution [1]. In alkaline solution, phenolic hydroxyl groups are ionized and the absorption changes towards longer wavelengths and higher intensities. By subtracting the spectrum derived from the neutral solution from that of the alkaline solution, an ionization difference spectrum is obtained. The UV/vis data was obtained by using an UV765 spectrophotometer (Shanghai Precision & Scientific Instrument Co., Ltd). The absorption spectra were recorded from 200 to 500 nm with a bandwidth of 1 nm and a fast scan speed mode was used. The spectra were determined by adding 5 ml of lignin solution (0.06 g/l in 1:1 v/v 2-mercaptoethanol and water) to 1 ml of either 0.6 M NaOH (alkali spectra) or phosphate buffer at pH 6.5 (neutral spectra) [7].

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