Journal of Energy Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem

http://www.journals.elsevier.com/journal-of-energy-chemistry/

Oxidative depolymerization of lignin improved by enzymolysis pretreatment with laccase☆

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ARTICLE INFO

Article history:
Received 17 March 2017
Revised 24 April 2017
Accepted 27 April 2017
Available online xxx

Keywords:
Lignin
Depolymerization
Enzymolysis
Pretreatment
Aromatic monomer

ABSTRACT

A new lignin depolymerization approach for improving the yield of aromatic monomers (YAM) by enzymolysis pretreatment was investigated, in which lignin was pretreated with laccase followed by oxidative depolymerization of lignin. It was found that lignin depolymeirzation was enhanced significantly by enzymolysis. The oxidative depolymerization contributed to 21.37% of YAM after the enzymolysis pretreatment, whereas the conventional oxidative depolymerization only gave 14.10% of YAM. The addition of ethanol in enzymatic pretreatment process improved the efficiency of enzymolysis, which effectively improved the solubility of pretreated lignin and depolymerization degree (DD) of lignin. The enzymolysis pretreatment increased the content of syringyl (S) style aromatic monomers, which hindered the recondensation among polymerized products. As lignin has low solubility in acidic aqueous solution, ethanol was added into enzymolysis system to improve the efficiency. However, the enzymolysis of lignin should be carried out for a limited time to prevent the inactivation of laccase.

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1. Introduction

Lignocellulosic biomass composed of cellulose, hemicellulose and lignin is the most abundant renewable resource. With the fast consumption of fossil resource, it is very important to produce advanced carbon neutral liquid biofuels and chemicals using renewable lignocellulose [1–4]. As lignin is the only renewable compound containing aromatics, increasing concerns are focused on the depolymerization of lignin by hydrolysis [5], oxidation [6–9], liquefaction [10,11], supercritical alcoholysis [12], hydrogenolysis [8,13], pyrolysis [14,15] etc. for the efficient preparation of aromatic monomers from lignin. However, the yield of aromatic monomers (YAM) is still low because lignin has complicated structure highly random linked with C–C and C–O bonds by syringyl (S), guaiacyl (G) and p-hydroxyphenyl (H) subunits [16,17]. Oxidative depolymerization is one of the most common methods to depolymerize lignin for obtaining aromatic monomers with a higher depolymerization degree (DD) of lignin. Fe and Cu were widely used as the catalyst for oxidative depolymerization of lignin [18]. Santos et al. [19] used $CuSO_4$ as the catalyst to depolymerize lignin in the O_2/NaOH system and got the highest 16.1% of syringaldehyde and 4.5% of valillic aldehyde. However, oxidation of lignin easily produces highly reactive free radicals, which results in the recondensation among the depolymerized lignin fragment molecules, and hence decreases the YAM [20]. Therefore, it is still a great challenge to develop an efficient approach to preventing the recondensation of depolymerized lignin fragments.

In order to improve depolymerization efficiency of lignin, a novel and effective two-step technology was proposed, in which the depolymerization of oxidized lignin under mild conditions in aqueous formic acid resulted in more than 60 wt% yield of low molecular mass aromatics [21]. For hindering condensation among depolymerized products, the combination of base-catalyzed lignin hydrolysis with addition of boric acid protecting agent was used to shift the product distribution to lower molecular weight compounds and increase product yields beyond 85% [22]. A highly active and selective nickel-based catalyst was used in birch wood lignin conversion into monomeric phenols, in which 97% of selectivity and 50% of monomeric phenols were obtained [23]. However, native lignin is relatively easier to depolyemrize than alkali lignin.

Biotechnology was also used in the depolyerization of lignin. Laccase was widely used in the selective delignification [24], but it has a relatively low efficiency for lignin depolymerization [25] because recalcitrant barriers exited in real lignin would have impeded the enzymolysis. Many of the chemical and physical pretreatments, such as autohydrolysis, dilute acid, organosolv, alkaline green liquor, ionic liquid and steam explosion, have been studied to improve the enzymolysis efficiency [26]. However, there is little available reference on enzymolysis as the pretreatments for

Q2 Q3 ☆ This work was financially supported by the National Natural Science Foundation of China (No. 21576104, 21690083).

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http://dx.doi.org/10.1016/j.jechem.2017.04.018
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Please cite this article as: Y. Zhu et al., Oxidative depolymerization of lignin improved by enzymolysis pretreatment with laccase, Journal of Energy Chemistry (2017), http://dx.doi.org/10.1016/j.jechem.2017.04.018

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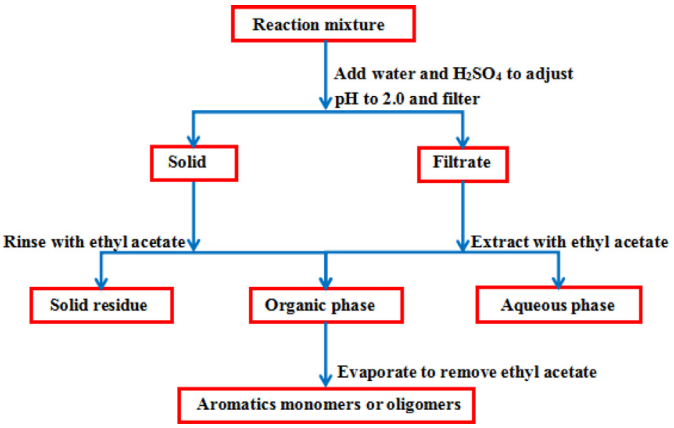

Fig. 1. Brief scheme of the product-treating process.

chemical depolymerization of lignin. Considering mild and environmentally friendly method of enzymolysis pretreatment of lignin, it may be a promising approach in the depolymerization of lignin.

In the present work, a two-step approach for depolymerization of lignin combining laccase pretreatment with hydrothermal oxidation was explored to increase the YAM. The effects of laccase activity, enzymolysis time, and medium on the YAM were investigated. Moreover, the mechanism of oxidative depolymerization of lignin improved by enzymolysis pretreatment was proposed by analyzing the distribution of the identified aromatics in depolymerized products.

2. Experimental

2.1. Materials

Alkali lignin was purchased from Sigma-Aldrich (St. Louis, USA) from industrial black liquor with β–O–4 linkage of being 17–28/100 C_9 units by 2D NMR analysis. DENYKEM PAP-5 laccase was purchased from Denykem Biological Technology Co. Ltd (Shanghai, China) with enzyme activity of 6.55 U/g. Alkali lignin after enzymolysis pretreatment (ALEP) was obtained by repetitively rinsing the enzymolysis mixtures with deionized water until no protein detected in rinsing water and drying overnight at 50 °C. Other chemicals were purchased from Aladdin Chemisty Co. Ltd. (China) without further purification.

2.2. Depolymerization of lignin

0.30 g of lignin, 10 ml of ethanol, 10 ml of sodium acetate/acetic acid buffer (pH = 5.0) and appropriate amount of laccase were added into a 100 ml of conical flask. Then, the flask was placed on HZQ-X160 Constant Temperature Oscillation Incubator (Suzhou Experiment Equipment Co. Ltd., China) for incubation at 50 °C with a stirring speed of 200 rpm for 2 h. After the enzymolysis pretreatment, the reaction mixture was transferred to a stainless steel autoclave (Beijing Century SenLong Experimental Apparetus Co., Ltd., China), and then subjected to a optimized hydrothermal oxidative depolymerization at 150 °C for 2 h by adding 2.4 g of NaOH, 0.080 g of CuO and 2 ml of H_2O_2 [6]. The post-treatment process was shown in Fig. 1. For comparison, a hydrothermal oxidative depolymerization under the same conditions except without laccase pretreatment was also carried out, in which 14.10% of YAM was obtained and 81.83% of DD was reached.

2.3. Analysis of depolymerized products and pretreated lignin

The depolymerized products were identified by gas chromatography-mass spectrometry (GC–MS, GCMS-QP2010, Shimadzu Co., Japan) equipped with an electron impact ion source (ionization energy at 70 eV). The capillary column was DB-5 column (30 m × 0.32 mm × 0.25 mm). The column temperature was programmed to keep at 50 °C for 2 min, ramp to 280 °C at 10 °C/min, and then hold at 280 °C for 5 min. Helium was used as a carrier gas at 0.6 ml/min. The injector temperature and ion source were set to 260 and 200 °C, respectively. The aromatic monomers were identified by comparing their mass spectra with those in a computer library (NIST) followed by comparing their retention time with those of standard compounds.

The DD and the YAM were calculated by the following equations, respectively.

$$\mathrm{DD}\,(\%) = [(W_L - W_S)/W_L] \times 100\% \quad (1)$$

$$\mathrm{YAM}\,(\%) = \left(W_{A}/W_L\right) \times 100\% \quad (2)$$

where W_L, W_S and W_A were the weight of the initial added lignin, solid residues and aromatic monomers, respectively.

NMR analyzed was carried out on a Bruker Avance III 600 MHz instrument (Bruker Co., Germany) equipped with a cryogenically cooled 5 mm TCI gradient probe with inverse geometry, where 100 mg of lignin and ALEP were dissolved in 0.5 ml dimethyl sulphoxide-d_6 (DMSO-d_6), respectively. Heteronuclear single quantum coherence (HSQC) spectra were recorded using a standard Bruker pulse sequence 'hsqcedetgpsisp2.3' with a 90 pulse, 250 ms acquisition time, 3 s pulse delay, $^1J_{C-H}$ of 145 Hz, 16 scans and the acquisition of 8192 data points (for ^{1}H) and 256 increments (for ^{13}C). The pulse widths of ^{1}H and ^{13}C were p1 = 6.9 us and p3 = 12.9 us, respectively. The spectral widths of ^{1}H and ^{13}C were 20 ppm and 240.00 ppm, respectively (16,025.6 and 48,275 Hz). HSQC correlation peaks were assigned by comparing with the literature [1,27–29] and the percentages of the G, S, and H were obtained via analyzing the integrals of the peaks, which were performed using the MestReNova v10.0.0 software default processing template.

3. Results and discussion

3.1. Effect of enzymolysis pretreatment on the YAM

As oxidative depolymerization of lignin gave a relatively low YAM, enzymolysis pretreatment with laccase was introduced into oxidative depolymerization of lignin. The effect of enzymolysis pretreatment time on the YAM and DD is presented in Fig. 2.

It was found from Fig. 2 that conventially oxidative depolymerization of lignin gave a 14.10% of YAM, whereas enzymolysis pretreatment with laccase for 2 h before oxidative depolymerization contributed to an as high as 20.36% of YAM. However, when the enzymolysis pretreatment time prolonged to 4 h, the YAM decreased to 16.80%, and then almost kept a constant when enzymolysis pretreatment time exceeded 4 h. This was because Laccase could remain active for several hours in the solvent containing organics [30], and then the laccase activity decreased. Fig. 2 also presented that enzymolysis pretreatment for 2 h together with oxidative depolymerization contributed to a 92.83% of DD, which is greater than 81.83% of DD from conventionally oxidative depolymerizaiton. This meant that enzymolysis pretreatment effectively promoted the depolymerization of lignin, and hence improved the YAM.

It was worth noting that both DD and YAM were decreased after enzymolysis pretreatment for 2 h. However, the extent of decrease for YAM was greater than that for DD, which indicated

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