



Research article

Effect of solvent on hydrothermal oxidation depolymerization of lignin for the production of monophenolic compounds



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ABSTRACT

Lignin was hydrothermal oxidation depolymerized by using H_2O_2 as the oxidant and $\text{CuO}/\text{Fe}_2(\text{SO}_4)_3/\text{NaOH}$ as catalysts. The effect of the solvents, including water, methanol, 1,4-dioxane, tetrahydrofuran, ethanol, and their co-solvent, on the depolymerization of lignin were investigated. It is found that the yield of monophenolic compounds reaches 17.92% by using 1:1 (v/v) of methanol/water as the reaction medium. The suitable proportion of methanol to water not only effectively maintains the alkalinity of the reaction medium and the solubility of lignin, but also suppresses the demethoxylation during the process of depolymerization reaction, resulting in an increase of contents of syringyl style monophenolic compounds which prevents the re-polymerization. Consequently, the yield of monophenolic compounds is increased.

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1. Introduction

Lignocellulosic biomass composed of cellulose, hemicelluloses and lignin is the most abundant renewable resource in the world. The efficient conversion of cellulose and hemicellulose into fuel ethanol and platform chemicals has been making great progress. However, the high-valued utilization of lignin is very limited due to its complex structure, and therefore becomes the bottleneck of the utilization of biomass [1]. Lignin is a three-dimensional polymer consisting of three phenylpropane units (syringyl, guaiacyl and p-hydroxyphenyl) linked by C–C bond and C–O bond. In recent years, more and more attentions are paid on the depolymerization of lignin for the preparation of monophenolic compounds, which is the key process for preparing liquid fuel.

Many attempts have been made to depolymerize lignin for the production of aromatic compounds, including pyrolysis [2], enzymolysis [3], hydrolysis [4], photolysis [5], hydrogenolysis [6], supercritical alcohol depolymerization [7] and microwave-assisted depolymerization [8]. And hydrothermal depolymerization is considered to be a promising approach as green solvent water is used as the reaction medium. Wang et al. [9] reported that the hydrothermal conversion of lignin at 310 °C for 30 min without the presence of catalyst, and 3.17% of monophenolic compounds were obtained, showing that subcritical water could depolymerize lignin into phenols to a certain degree. Based-catalyzed depolymerization of Kraft lignin was carried out in near-critical water, where more than 17% of aromatic products were

obtained. However, a 22% yield of bio-char was also found [10]. Gosselink et al. [11] converted organosolv hardwood and wheat straw lignin to a phenolic oil using a supercritical fluid consisting of carbon dioxide/acetone/water, and a total yield of 10–12% was obtained. Yan et al. [12] investigated Pt/C or Pd/C catalytic depolymerization of lignin in the presence of H_3PO_4 and H_2 , and found that 1:1 (v/v) 1,4-dioxane/water as the solvent can increase by 8.5% of monophenolic compounds compared with water as the solvent. Onwudili and Williams [13] studied the Pd/C catalytic depolymerization of lignin in subcritical water and found that the addition of formic acid can improve the yield of bio-oil to 33.1%. The depolymerization of lignin by using $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ as the catalyst [14] showed that compared to water, 1:1 (v/v) methanol/water as the solvent increased the yield of vanillin and Methyl vanillin by 3.05%. Zhu et al. [15] investigated the cornstalk liquefaction in methanol, water or methanol/water mixed solvents at 250–320 °C, which showing that the isometric methanol and water mixed solvent was found to be most effective for the liquefaction at 300 °C for 30 min.

As mentioned above, the reaction medium may play an important role in the depolymerization of lignin. However, the corresponding mechanism is not very clear. Since H_2O_2 is a green oxidant, an alkali- H_2O_2 system is widely used in the oxidative depolymerization of lignin, which is one of the promising strategies to utilize lignin [16]. In addition, Cu^{2+} can result in the deprivation of side chains from structural units of lignin to form some phenolic compounds, and Fe^{3+} can form new reactive intermediates with $\bullet\text{OOH}$ radicals generated by dissociation of hydrogen peroxide [17], facilitating oxidative degradation of lignin. Therefore, the oxidative depolymerization of lignin was carried out using H_2O_2 as the oxidant and $\text{CuO}/\text{Fe}_2(\text{SO}_4)_3/\text{NaOH}$ as the catalyst in the present work. The effect of reaction medium on the depolymerization

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of lignin for preparing monophenolic compounds was investigated in order to explore the mechanism of reaction medium in the alkaline hydrogen peroxide depolymerization of lignin.

2. Experimental

2.1. Materials

Wheat alkali lignin (WAL) was provided from Shandong Quanlin Paper Group Co., China. To remove carbohydrates from the resulting black liquor, 2 M hydrochloric acid was added to adjust pH to 2–3. After being stirred at 50 °C for 30 min, the mixture was separated by vacuum filtration. The resulting lignin was washed with water for three times and then dried at 50 °C. WAL was further purified by ultra-filtration (Wuxi Membrane Science and Technology Co., China) with a 30,000 Da cutoff membrane. Elemental analysis of the purified WAL is shown in Table 1. All other chemicals were purchased from Aladdin Chemistry Co., Ltd.

2.2. Catalytic depolymerization of lignin

0.3 g lignin, 20 mL solvent, 0.08 g CuO, 0.004 g Fe₂(SO₄)₃, 2.4 g NaOH and 2 mL H₂O₂ (30 wt.%) were placed in a 100 mL of stainless steel autoclave (Beijing Shijishenglang Chemical Machinery Co., Ltd., China). The catalytic reaction was carried out at 150 °C for 60 min with a stirring speed of 400 rpm. And then the autoclave was cooled down to room temperature with cooling water. The depolymerized products were acidified with sulfuric acid at pH of 2.5. After filtration, the filtrate was diluted to 100 mL to identify monophenolic compounds by LC–MS analysis.

The degree of depolymerization (DD) of WAL and the yield of monophenolic products (YMC) were calculated by following equations, respectively.

$$DD(\%) = [(w_{\text{lignin}} - w_{\text{solid}}) / w_{\text{lignin}}] \times 100 \quad (1)$$

$$YMC(\%) = (\sum w_{pi} / w_{\text{lignin}}) \times 100 \quad (2)$$

where w_{lignin} , w_{solid} , $\sum w_{pi}$ were the weight of the initial lignin, solid residues, sum of identified monophenolic compounds, respectively.

2.3. Analysis of depolymerized products

The depolymerized products of WAL were analyzed using LC–MS on an Agilent 1290 Infinity Liquid chromatograph (Agilent Co., USA) and a maXis impact tandem mass spectrometer (Bruker Daltonics, USA). The separation was carried out on an Agilent RRHD SB–C18 column (2.1 × 150 mm, 1.8 μm). The gradient comprised of a binary solvent system consisting formic acid aqueous solution (0.1 vol.%) (A) and methanol (B) at a flow rate of 0.2 mL · min⁻¹. The starting condition of gradient was 90% of A and 10% of B. Subsequently, B was linearly increased to 27% in 10 min, then to 35% in 10 min and to 55% in 15 min. Thereafter, the mobile phase was reverted to the initial condition in 5 min and held for 5 min for re-equilibration of column before the next injection. The injection volume was 5.0 μL, column temperature was set at 30 °C, and the detector was set at a wavelength of 280 nm, respectively. The monophenolic compounds were identified from their mass spectra followed by comparing their retention time with those of standard compounds (refer to Figs. S1–2). The yields of resulting monophenolic compounds were determined by standard curves.

Table 1
Elemental analysis of purified lignin.

C (wt.%)	H (wt.%)	N (wt.%)	O (wt.%)	S (wt.%)
57.01	6.04	0.81	35.61	0.53

Electrospray ionization mass spectrometry (ESI-MS) was carried out on a maXis impact (Bruker Co., Germany). Scans were acquired in positive ion mode from m/z 50 to 1000 with sodium formate solution as an internal standard to correct molecular weight. The ability of different solvents to dissolve lignin was analyzed by UV–Vis spectroscopy on an UV-2550 spectrophotometer (Shimadzu Co., Japan).

3. Results and discussion

3.1. Solvent effect on alkaline hydrothermal oxidative depolymerization of lignin

The effects of water, methanol, 1,4-dioxane, tetrahydrofuran, ethanol, and their mixture solvents on the depolymerization of lignin under the optimal conditions at 150 °C for 60 min is presented in Table 2.

It can be found from Table 2 that compared to methanol, dioxane, tetrahydrofuran and methanol, water exhibits a better effect in the alkaline hydrothermal oxidation depolymerization of lignin, reaching 81.60% of DD and 13.19% of YMC, whereas ethanol gives only 32.50% of DD and 4.04% of YMC, respectively. It is reported that the alkalinity of the reaction medium plays an important role on alkaline depolymerization of lignin [18]. The pH of different reaction media with addition of NaOH is shown in Table 3, which indicates that the pH of NaOH aqueous is greater than 14; whereas those of selected organic solvents are lower than 14. This means that NaOH is highly soluble in water, with a lower solubility in methanol, dioxane, tetrahydrofuran or ethanol. It can be found by combining Table 2 with Table 3 that the pH of reaction medium is correspondence with the YMC, where the higher pH of the medium is, the higher YMC is obtained. It is worth noting that a very low YMC obtained in ethanol solvent may be because ethanol can be oxidized to form acetic acid which neutralizes the alkalinity of the reaction system [19]. However, methanol is most likely to be oxidized to CO₂ and H₂O₂.

Table 3 also shows that when water is added into the selected organic solvent to form the co-solvents, the DD and YMC are improved dramatically compared to single organic medium. One of the reasons may be that the addition of water into selected organic solvents increases the solubility of NaOH, and hence increases the alkalinity of reaction medium.

3.2. Effect of the proportion of methanol to water on the hydrothermal depolymerization of lignin

As a higher of 17.92% YMC is obtained under the mixture of methanol and water (Table 2), the effect of the volume ratio of methanol to water on the YMC is shown in Table 4.

Table 4 shows that the YMC increases from 13.19% to 17.92% with the increase of the volume ratio of methanol to water increases from 0:20 to 1:1, whereas the ratio of methanol to water is greater than 1:1, the YMC decreases with the increase of content of methanol. It is

Table 2
Effect of medium on the hydrothermal depolymerization of lignin.

Solvent	YMC (%)	DD (%)
20 mL H ₂ O	13.19	81.60
20 mL methanol	11.43	78.46
20 mL dioxane	8.78	77.70
20 mL tetrahydrofuran	6.96	53.66
20 mL ethanol	4.04	32.50
10 mL dioxane + 10 mL H ₂ O	14.91	83.64
10 mL methanol + 10 mL H ₂ O	17.92	86.54
10 mL ethanol + 10 mL H ₂ O	16.11	86.24
10 mL tetrahydrofuran + 10 mL H ₂ O	8.20	81.97

(Lignin: 0.3 g, H₂O₂: 2 mL, CuO: 0.08 g, Fe₂(SO₄)₃: 0.004 g, NaOH: 2.4 g, temperature: 150 °C, time: 60 min).

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