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RESEARCH PAPER

Oxidative degradation of lignin for producing monophenolic compounds

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Abstract: Oxidative degradation of lignin for producing monophenolic compounds was carried out under microwave irradiation, with H_2O_2, CuO and $Fe_2(SO_4)_3$ as the oxidants. The results indicated that the yield of monophenolic compounds and degradation rate of lignin feed reach 11.86% and 90.88%, respectively, under the relatively benign conditions of 180°C. Oxidative degradation of lignin with H_2O_2 as a single oxidant gives a high degradation rate but a lower yield of monophenolic compounds, due to the aromatic ring opening reaction; however, Cu^{2+} present in the oxidant system is able to promote the cleavage of side chain and ether bond, whereas Fe^{3+} to enhance the oxidation ability of H_2O_2, which are then conducive to improving the yield of monophenolic compounds. A moderate increase of degradation temperature and reaction time are favorable for improving the yield of monophenolic compounds. Owing to the coexistence of lignin degradation and recondensation of degraded fragments, the prevention of degraded lignin from recondensation turns to be a key issue to achieve a high yield of monophenolic compounds.

Keywords: alkaline lignin; microwave irradiation; oxidative degradation; monophenolic compounds

The production of fuels and chemicals from renewable biomass has become a research hotspot in recent decades due to increasing concerns on the world energy crisis, high price of petroleum and petrochemicals, and the environmental pollution from fossil fuel utilization. It is relatively easy from cellulose and hemicellulose composed of repeated structural units to prepare biomass liquid fuel via depolymerizing into saccharide compounds, fermention and hydrodeoxygenation. However, it is difficult to depolymerize lignin, the largest renewable natural macromolecule containing aromatic compounds, accounting for 15%–30% by weight of plants[1], due to its complex structure. Therefore, the bottleneck in converting lignin to biomass liquid fuel is how to convert lignin into monophenolic compounds.

It is generally recognized that lignin is mainly composed of three main phenylpropane units, namely guaiacyl, syringyl, and *p*-hydroxyphenyl, which is linked together through C–C bond and C–O bond. Accordingly, monophenolic, dimers or oligomers can be obtained from lignin by different strategies, including oxidation, hydrolysis, liquefaction, pyrolysis, enzymolysis, and so on[2–5]. Nowadays, more and more attentions have been paid to the conversion of lignin to biomass liquid fuel via depolymerization and further hydrodeoxygenation[6,7].

Due to the low reactive activity of lignin, the chemical degradation of lignin is mostly carried out at high temperature of 300–600°C and high pressure of 4.5–20 MPa, or in a supercritical/subcritical media, except the time-consuming biodegradation. However, the yield of monophenolic compounds reported is usually less than 11% even under such harsh conditions[8]. Microwave assistance is increasingly applied to chemical reaction, as it greatly shortens the heat transfer time, accelerates the molecular movement, enhances the average energy of reactant molecules, as well as reduces the activation energy of the degradation reaction[9]; however, very limited reference is available on the degradation of lignin under microwave irradiation. Gu et al[10] studied the oxidative degradation of lignin by H_2O_2 with lanthanum-modified SBA-15 as a catalyst; high yield of monophenolic compounds was obtained (31.48% by mole or 2.7% by weight) under the microwave power of 200 W at 150°C for 10 min. Therefore, the optimization of process variables on the degradation of lignin is still essential to improve the yield of monophenolic compounds under relatively benign conditions. In the present work, the oxidative degradation of lignin for producing the monophenolic compounds was then carried out with H_2O_2,

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CuO and $Fe_2(SO_4)_3$ as the oxidants under microwave irradiation.

1 Experimental

1.1 Materials

Wheat straw alkaline lignin was provided by Quanlin Paper Group Co., China. After acidolysis and purification, alkaline lignin with the molecular weight of 2500–30000 Dalton (Da) was used for further study by using an ultrafiltration apparatus (Wuxi Membrane Science and Technology Co., China) with 2500 and 30000 Da cutoff membranes. Gallic acid, 4-hydroxybenzoic acid, 4-hydroxybenzaldehyde, vanillin, vanillic acid, syringate, syringaldehyde, 4-coumaric acid, ferulic acid, acetosyringone, and erucic acid were used as the standards to identify the monophenolic compounds, which were purchased from Aladdin Co. Hydrogen peroxide (30%), sodium hydroxide, hydrochloric acid, copper oxide (powder), ferric sulfate (powder), copper sulfate pentahydrate, and formic acid used were in reagent grade; methanol and acetonitrile were in HPLC grade.

1.2 Methods for lignin degradation and characterizations

0.3 g of alkaline lignin, 14.0 g of sodium hydroxide solution (1–5 mol/L), and desired amount of oxidants were added into the reactor placed in a microwave digestion instrument (Ethos 1, Milestone, Italy); the initial power of microwave used in this work was 300 W. After the reaction test, the degraded products were cooled down to room temperature, and filtered to remove any insolubles; the filtrate was then acidified with hydrochloric acid at a pH value of 2.0. After the second filtration, the resultant solution was used to identify the monophenolic compounds by LC-MS analysis.

The degradation rate (x) of alkaline lignin and the yield of monophenolic products (w) were calculated by

$$\eta(\%) = [(m_{\text{lignin}} - m_{\text{res}})/m_{\text{lignin}}] \times 100\% \quad (1)$$

$$w(\%) = (m_{\text{mono}}/m_{\text{lignin}}) \times 100\% \quad (2)$$

where m_{lignin}, m_{res} and m_{mono} were the masses of alkaline lignin used in the degradation reaction, residual lignin (insolubles), and identified monophenolic compounds, respectively.

Table 1 Effect of the H_2O_2, Cu^{2+} and Fe^{3+} amounts used on the oxidative degradation of alkaline lignin

H_2O_2 V/mL	$CuSO_4 \cdot 5H_2O$ m/g	CuO m/g	$Fe_2(SO_4)_3$ m/g	Degradation rate η/%	Yield w/%
–	0.02	–	–	28.16	3.04
–	–	0.02	–	34.22	2.65
2.0	–	–	–	93.17	4.01
2.0	0.02	–	–	80.20	6.34
2.0	–	0.02	–	81.33	6.00
2.0	0.02	–	0.002	85.77	6.76
2.0	–	0.02	0.002	93.47	6.97

0.3 g alkaline lignin and 14 g NaOH (2 mol/L) were used; the degradation reaction was carried out at 165°C for 90 min

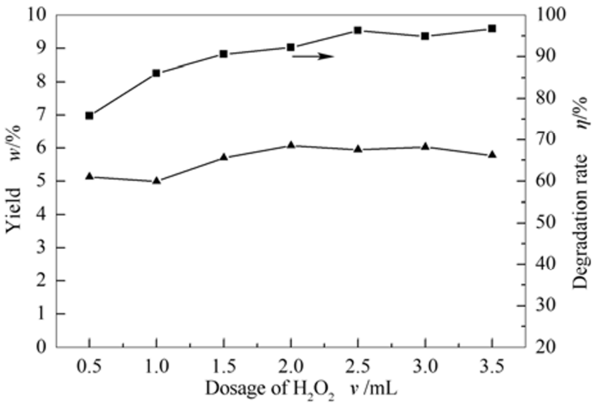

Fig. 1 Effect of H_2O_2 dosage on the degradation rate of alkaline lignin and the yield of monophenolic compounds

0.3 g alkaline lignin, 14 g NaOH (2 mol/L), 0.02 g CuO, and 0.002 g $Fe_2(SO_4)_3$ were used; the degradation reaction was carried out at 165°C for 30 min

The degradation products of alkaline lignin were analyzed by LC-MS with a ultra-high performance tandem mass spectrometry (maXis impact, Bruker Co., USA) and a LC system (1290 Infinity, Agilent Co., USA) equipped with a capillary column (Agilent RRHD SB-C18, 2.1×150 mm, 1.8 μm). The mobile phase was composed of eluent A (formic acid, 0.1%) and eluent B (methanol in acetonitrile, 10%). The gradient elution was programmed as 10% B for 1 min, 20% B for 5 min, and then 20% B for 16 min. The column was held at 30°C and the detector was set at a wavelength of 280 nm. The flow rate and injection volume were 0.2 mL/min and 5 μL, respectively. The monophenolic compounds were identified from their mass spectra by comparing their retention time with those of authentic compounds; the yields of resultant monophenolic compounds were determined by the standard curves.