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Pyrolysis behaviors of four lignin polymers isolated from the same pine wood

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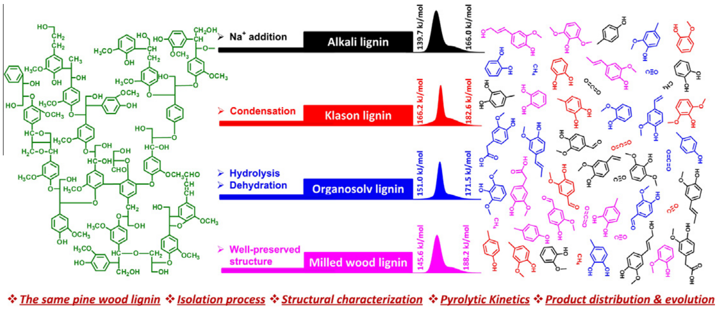
HIGHLIGHTS

- Isolation process greatly influences lignin structure and pyrolysis behavior.
- AL and MWL have poor thermal stability due to well-preserved weak ether linkages.
- Weights of two reactions in DG-DAEM vary among the four lignins pyrolysis.
- Higher phenols yield in the pyrolysis of AL and MWL *via* breaking of weak ether bonds.

GRAPHICAL ABSTRACT



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ABSTRACT

Four lignin polymers, alkali lignin (AL), klason lignin (KL), organosolv lignin (OL), and milled wood lignin (MWL), were isolated from the same pine wood. Structural characterization by FTIR and ^{13}C NMR indicated that the four lignins have different structural features. Their pyrolysis behaviors were analyzed by TG-FTIR and Py-GC/MS. Thermally unstable ether bonds and side branches were well-preserved in AL and MWL, but were broken in OL and KL. Pyrolysis of AL and KL produce more phenols at low temperature by the breakage of ether bonds. AL and KL show lower activation energies in the main degradation stage, quantified by a distribution activation energy model with two linearly combined Gaussian functions. The evolution behaviors of typical gaseous products, CH_4, CO_2, and CO, were analyzed, and insights about the correlation between chemical structure and pyrolysis behavior were obtained.

1. Introduction

Fast pyrolysis is a promising thermo-chemical method for directly converting biomass into liquid biofuels (Mohan et al., 2006). As one of the three main components in lignocellulosic biomass, lignin has a significant influence on the pyrolysis behavior of biomass. Lignin is a three-dimensional, complex polymer comprised of *p*-hydroxyphenyl, guaiacyl, and syringyl, all of which are randomly connected with each other by C—O—C (β-O-4, α-O-4, 4-O-5) or C—C (5-5, β-5, β-1) bonds, where β-O-4 is most frequent. Lignin usually has a content of 18–35% in lignocellulosic biomass, and is covalently linked with hemicellulose (Mohan et al., 2006). However, the pyrolysis mechanism of lignin remains unclear. The current popular model compounds used in lignin pyrolysis mechanism studies include monomers (Kotake et al., 2013), dimers (Kawamoto et al., 2007), and oligomers (Chu et al., 2013). They have simplified structures and could be considered as basic fragments in lignin. However, lignin polymer that is directly isolated from biomass has a structure more closely related to its natural form, *i.e.*, high degree of polymerization and more complete branches. Lignin polymers could be isolated from bio-

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mass by many different methods. Alkali lignin (AL) and klason lignin (KL) are isolated by removing carbohydrates that are linked with lignin using alkali and acid, respectively. Lignin could also be isolated using neutral solvents. Most popularly, an ethanol–water mixture is used to extract the organosolv lignin (OL) at high temperature. Milled wood lignin (MWL) is another lignin polymer isolated by using neutral organic solvent with the help of ball milling at room temperature. Selecting the lignin isolation method has a significant influence on the chemical structure of the isolated lignin, because lignin's weak ether linkages and side branches are sensitive to chemical treatments (El Hage et al., 2010; Pan et al., 2006). AL, KL, OL, and MWL have often been used as model compounds in the mechanistic study of lignin pyrolysis. Wang et al. (2009) performed pyrolysis of MWLs isolated from hardwood and softwood, and found that methoxy group content has a significant influence on the resulting pyrolysis behaviors. Yang et al. (2007) found that AL decomposes over a wide temperature range of 160–900 °C, and the final solid char yield was about 40%, much higher than that of cellulose pyrolysis. Bährle et al. (2014) used KL as a model compound for comparing the pyrolysis behaviors of hardwood and softwood lignins. They suggested that radical formation during hardwood KL pyrolysis was more frequent than that of softwood KL pyrolysis, and was mainly due to high methoxy group content in hardwood KL. Patwardhan et al. (2011) studied the effect of pyrolytic temperature on the product distribution of lignin pyrolysis by using a commercial OL, and found that the pyrolytic products from OL were mainly monomeric phenols with alkyl or methoxy groups. Since the chemical structure of lignin changes with the isolation process, it is necessary to compare the structural features and pyrolysis behaviors among lignins isolated by different methods.

One of the biggest challenges in using lignin polymer as a model compound for pyrolysis mechanism studies is the limited understanding of its chemical structure. While many previous studies mainly focus on the characterization of pyrolytic products, characterization of the original lignin structure and its influence on pyrolysis behavior are inadequate. In this study, four lignin polymers, AL, KL, OL, and MWL, were isolated from the same pine wood (*Pinus bungeana*). Their chemical structures were characterized using Fourier transform infrared spectroscopy (FTIR) and ^{13}C nuclear magnetic resonance spectroscopy (^{13}C NMR). Subsequently, the lignin polymers were used to study the mechanistic influence of structural features on pyrolysis behavior.

2. Experimental

2.1. Materials

The pine wood (*Pinus bungeana*) used in this study was obtained from a local timber mill (Hangzhou, China). Before each experiment, the raw material was dried and ground into coarse powder approximately 0.15–0.18 mm in size. The isolation of AL was based on the method proposed by Sun et al. (2000), where the NaOH concentration was 5% and the process was performed at 50 °C for 6 h. KL was obtained from the acid–insoluble fraction by NREL standard procedures (Sluiter et al., 2008). In the method previously described by Pan et al. (2006), OL was extracted by adding a small amount of sulfuric acid (1.2 wt% of raw biomass) to a mixed solution of ethanol and water (65:35, v/v) at 170 °C for 80 min. The solid-to-liquid ratio for this process was 1:8. MWL was isolated by a neutral solvent at room temperature using a method developed by Bjorkman (El Hage et al., 2010). The purity of lignin was calculated by quantitative acid hydrolysis method, and the isolated lignin was treated by 4% H_2SO_4 for 1 h at 120 °C (Ahmed et al., 2013). The purities of each lignin were 87.3%, 92.2% and 88.7% for AL, OL and MWL, respectively. KL was considered to be pure since it was isolated by high concentration acid treatment. The content of ash in lignin was measured by using thermogravimetric analysis operating under air atmosphere.

2.2. Structural characterization of lignins

The ultimate analysis of each lignin polymer was performed on a Vario MICRO Elemental Analyzer (Elenemtar Analysensysteme GmbH, Germany). Information about the functional groups of the four lignin polymers were recorded by a Nicolet 5700 Fourier transform infrared spectroscopy over the wavenumber range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. Each spectrum was accumulated from 36 scans. Solution-state ^{13}C NMR spectra of MWL, AL, and OL were recorded on an Agilent 600 MHz DD2 spectrometer at 25 °C. For each run, 80 mg sample was dissolved in 0.5 mL dimethyl sulfoxide-d_6 (DMSO-d_6). Tetramethylsilane was selected as the internal standard. Each spectrum was collected for 21,000 scans. Since KL is difficult to be dissolved, a solid-state ^{13}C cross-polarization magic angle spinning (^{13}C CP/MAS) NMR was employed to analyze the KL structure. The carbonyl carbon resonance of glycine was used as the external reference. The spectrum was averaged over 1200 scans.

2.3. Pyrolysis characterization of lignins

The devolatilization behavior of four lignin polymers were identified by a Netzsch STA 409 thermogravimetric (TG) analyzer with a heating rate of 20 °C/min from 25 to 800 °C. The released volatiles were immediately swept into a coupled FTIR spectrometer for on-line analysis (TG-FTIR). Spectra were recorded between 4000–400 cm^{-1} with a resolution of 4 cm^{-1} and a scan rate of 32 scans per minute. Pure nitrogen was used as the carrier gas and held at a flow rate of 60 mL/min. To minimize the influence of heat transfer, samples were held constant at 5 mg. The product distributions from the pyrolysis of each sample at different temperatures were further analyzed on a pyrolyzer coupled with a gas chromatography–mass spectrometer (Py-GC/MS). Approximately 0.5 mg of sample was loaded in the micro-pyrolyzer (CDS5200, CDS Analytical Inc., USA), and was immediately heated to the required temperature with a residence time of 10 s. The pyrolytic products were analyzed by a GC–MS (Thermo scientific, Trace DSQII, USA) equipped with a DB-WAX capillary column (30 m × 0.25 mm × 0.25 μm). Pure helium was used as the carrier gas with a constant flow rate of 1 mL/min. The GC oven was heated from 40 °C (held for 1 min) to 240 °C (held for 24 min) at a heating rate of 8 °C/min. The MS was operated in EI mode with an ion-source electron energy of 70 eV. The detected mass-to-charge ratio ranged from 35 to 450. All of the chemicals were identified according to the NIST MS library and previous work (Brebu et al., 2013; Kim et al., 2013).

3. Results and discussion

The color of isolated KL was dark brown, while the colors of the other three samples were much lighter. All samples had higher carbon content and lower oxygen content than raw biomass (see Table 1), indicating that lignin is an important carbon source for the resulting pyrolytic products. OL contains the lowest oxygen content, suggesting an intense deoxygenation reaction occurring during its isolation. Elemental sulfur was only found in KL because of the sulfuric acid addition during the isolation process. The ash contents of lignins were 6.22%, 1.66%, 1.73% and 2.37% for AL, KL, OL and MWL, respectively. This indicated that the alkali treatment introduced some extra alkali metal in the AL structure.