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Full Length Article

Thermal conversion of lignin to phenols: Relevance between chemical structure and pyrolysis behaviors



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HIGHLIGHTS

• Aromatic units and side-chain linkages within lignin were analyzed by 2D HSQC NMR.

• Relevance between lignin structure and pyrolysis behaviors was explored by Py-GC/MS.

• Selectivities of phenols derived from AOL vs. SAL reached 86.73% vs. 87.37%.

• More β -O-4' linkages led to the easier pyrolysis conversion and less demethoxylation.

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ABSTRACT

In this study, the Fourier transform infrared (FTIR) spectrometry and the ¹³C-¹H correlation twodimensional (2D) heteronuclear single-quantum coherence (HSQC) nuclear magnetic resonance (NMR) were introduced to determine the chemical structure of soda alkali lignin (SAL) and Alcell organosolv lignin (AOL), and the relevance between chemical structure and pyrolysis behaviors was evaluated by thermogravimetric analysis (TGA) and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). Results showed that the two lignin samples had similar functional groups and S/G ratio, excepting side-chain linkages. SAL was mainly cross-linked by β - β' linkages, while the main linkage within AOL was β -O-4'. This difference proposed that AOL had the worse thermal stability and was easier to be pyrolyzed to phenols than SAL. Herein, the pyrolysis transformation of SAL was always promoted by the increased temperature, whereas the generated phenols from AOL would be redecomposed at high pyrolysis temperature (800 °C). Moreover, the priority of demethoxylation occurring in SAL pyrolysis was higher than that in AOL pyrolysis. Further analysis on the types of phenols suggested that the formation of syringyl phenols benefitted from the increasing temperature. However, the formation of phydroxyphenyl phenols was inhibited as temperature increased, and the highest selectivity of guaiacyl phenols was obtained at 600 °C. The reveal of the relevance between lignin chemical structure and pyrolysis behaviors is meaningful for the efficient thermal conversion of lignin to phenol compounds.

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1. Introduction

In response to the current environmental crisis and energy shortage, more attention has been paid to the renewable and sustainable source derived from biomass. In the three major components of lignocellulosic biomass (lignin, cellulose and hemicellulose), lignin accounts for 15–35% of the weight and 40% of the fuel value [1]. Therefore, lignin is a promising alternative to produce fossil-based fuels. Furthermore, as a natural aromatic polymer composed of methoxylated phenylpropane units, known as syringyl (S), guaiacyl (G), and *p*-hydroxyphenyl (H) units, lignin is also

* Corresponding author. E-mail address: ruixiao@seu.edu.cn (R. Xiao). regarded as the renewable source to generate aromatic chemicals [2,3]. As industrial solid waste, most available lignin could be isolated from the waste liquid of pulp and paper industry [4]. Moreover, a large number of industrial lignin could be separated from lignocellulosic bio-ethanol process [3,5].

Among those reported lignin utilization forms, pyrolysis is identified as one of the most promising thermochemical technologies [6]. During pyrolysis, lignin can be rapidly transformed into liquid products, gaseous products and solid residue, in which, the liquid products are known as bio-oil. After mixture with other fuels or optimization the combustion system, pyrolysis bio-oil could be burnt for heating and energy as a replacement of petroleum fuels [7,8]. Excepting as liquid fuels, pyrolysis bio-oil could be used to produce value-added chemicals, such as modified phenolic resins



because of the enriched phenols [9–11]. Moreover, supercritical carbon dioxide is also introduced to extract the bio-oil to enrich the value-added phenols [12,13]. Catalytic upgrading is another efficient way to add the value of bio-oil. Through hydrodeoxygenation processes, the bio-oil can be transferred into light olefins and aromatic hydrocarbons [14,15].

The efficient utilization of bio-oil was greatly associated with its quality, which is influenced by the pyrolysis parameters (mainly the temperature), as well as the chemical structure of lignin samples. The contents of S, G, and H units in lignin samples largely determined the distribution of S, G, and H phenols in bio-oil [16,17]. The side-chain linkages are another sticking point to the chemical structure of lignin samples. In protolignin, the sidechain linkages are ether bonds (β -O-4', α -O-4', 4-O-5', α -O- γ ') and carbon–carbon bonds (5-5', β -5', β -1', β - β ') [2,3]. While, after various isolation processes, these side-chain linkages, especially the β -O-4' ether linkage, are fractured in a certain range [18–21]. The effect of side-chain linkages (types and contents) on the thermal stability of lignin samples has been revealed with the thermogravimetric analyzer previously [18,22]. However, few studies focus on the deep-seated relevance between side-chain linkages and lignin pyrolysis behaviors.

The target of the work is to reveal the relevance between lignin chemical structure and pyrolysis behaviors, which is meaningful for the efficient thermal conversion of lignin to phenol compounds. Therefore, the Fourier transform infrared (FTIR) spectrometry and the ¹³C-¹H correlation two-dimensional (2D) heteronuclear single-quantum coherence (HSQC) nuclear magnetic resonance (NMR) were introduced to characterize the chemical structure of two typical lignin samples (soda alkali lignin and Alcell organosolv lignin). Then, the relevance between chemical structure of lignin samples and their pyrolysis behaviors under various temperature parameters was studied by thermogravimetric analysis (TGA) and pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS).

2. Materials and methods

2.1. Materials

Materials used in this study were soda alkali lignin (SAL) and Alcell organosolv lignin (AOL), which were separately isolated from the pulping black liquor of triploid *Populus tomentosa* Carr. and further purified with the mild acidolysis method [23]. Preparation, isolation, and purification procedures for SAL and AOL were shown in Fig. S1.

2.2. Structural characterization

Chemical structure of lignin was characterized by the Fourier transform infrared (FTIR) spectrometry and the $^{13}C^{-1}H$ correlation two-dimensional (2D) heteronuclear single-quantum coherence (HSQC) nuclear magnetic resonance (NMR). FTIR spectra of the two lignin samples were programmed on a Nexus 670 FTIR spectrometer (Thermo Nicolet, USA). Samples were pressed into a KBr disc with a mass ratio of 1:50. The spectra were scanned in the range from 400 cm⁻¹ to 4000 cm⁻¹ with a resolution of 4 cm⁻¹. The 2D HSQC NMR was performed on 100 mg of lignin dissolved in 600 µL of dimethylsulfoxide-d₆ (DMSO-d₆) using an AVANCE III HD 600 spectrometer (Bruker, Germany). The central peak of DMSO-d₆ at 39.5/2.49 was used as the internal standard. Pulse widths of 8.35 and 16.00 µs were used for protons and carbons, respectively.

2.3. Thermal stability

Thermal stability of lignin was investigated on a TA Q50 thermogravimetric analyzer (TA Instruments, USA). In each exper-

iment, approximately 10 mg of lignin sample was placed in a platinum crucible and heated from room temperature to 700 °C with a heating rate of 10 °C/min. High-purity nitrogen (99.999%) was used as the carrier gas with a flow rate of 40 mL/min. The weight loss data was automatically collected by the software.

2.4. Fast pyrolysis

Lignin pyrolysis was carried out on a CDS 5200 pyrolyser (CDS Analytical, USA) connected to a 7890A gas chromatograph coupling with a 5975C triple axis detector mass spectrometer (Agilent Technologies, USA). The feedstock was pyrolyzed under 400, 500, 600, and 800 °C respectively for 15 s with the heating rate of 10 °C/ ms. The split ratio was 50:1, and the flow rate was 1.00 mL/min. The injector, detector, and interface temperatures were all set at 250 °C. The separation column was an HP-5MS capillary column (30 m, 0.25 mm inner diameter, 0.25 μ m film thickness). The column temperature starting from 50 °C was raised until 250 °C for 5 min with a heating rate of 8 °C/min. The ionizing voltage of mass spectrometer was 70 eV, and the mass was scanned range from *m*/*z* 5 to 400 with a speed of 1.0 s/decade. Data processing was performed using Perkin Elmer NIST Spectral Version 5 software (USA).

3. Results and discussion

3.1. Structural characterization of lignin

3.1.1. Functional groups by FTIR

The structural features of SAL and AOL analyzed by FTIR spectroscopy were illustrated in Fig. 1. Meanwhile, all notable peak assignments were referenced according to the previous works [17,20,24,25] and listed in Table S1. As can be seen from the summary, peak 1 was the absorption signal of O-H stretching vibration, ascribed to the OH groups in both phenolic and aliphatic structures. Peak 2 and peak 3 were separately the C-H stretching vibration signals in methyl and methylene groups. The carbonyl stretching vibration signal was recognized as peak 4. The aromatic skeletal vibration signals were assigned clearly in peak 5, peak 6 and peak 8. Furthermore, typical absorptions of syringyl and guaiacyl rings in lignin samples were identified. Peak 9 was the syringyl ring breathing with C–O stretching vibration, and peak 10 was the guaiacyl ring breathing with C=O stretching vibration. A comparison between SAL and AOL was further carried out, and the results showed that the FTIR characteristics of the two lignin samples were rather similar, which indicated the similar functional groups of the lignin fractions.

3.1.2. Side-chain linkages and aromatic units by 2D HSQC NMR

2D HSQC NMR could identify the ¹³C-¹H correlations of lignin and provide important internal structural information. Thus, the



Fig. 1. FTIR spectra of SAL and AOL.

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