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

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ABSTRACT

In this study, the Fourier transform infrared (FTIR) spectrometry and the ^{13}C - ^1H correlation two-dimensional (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 *p*-hydroxyphenyl 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.

Keywords: Lignin; Chemical structure; 2D HSQC NMR; Pyrolysis; Phenols

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 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 side-chain 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 ^{13}C - ^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 - ^1H 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 experiment, 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 µm 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.

Fig. 1. FTIR spectra of SAL and AOL

3.1. 2 Side-chain linkages and aromatic units by 2D HSQC NMR

2D HSQC NMR could identify the ^{13}C - ^1H correlations of lignin and provide important internal structural information. Thus, the side-chain linkages and aromatic units within lignin samples were characterized by the 2D HSQC NMR technique. The side-chain ($\delta_{\text{C}}/\delta_{\text{H}}$ 50-90/2.5-6.0) and the aromatic ($\delta_{\text{C}}/\delta_{\text{H}}$ 100-135/5.5-8.5) regions in the HSQC spectra of the two lignin samples were shown in Fig. 2.

Fig. 2. Side-chain (left column) and aromatic regions (right column) in the 2D HSQC NMR spectra of SAL (a, b) and AOL (c, d)

As shown in Fig. 2(a) and (c), in the side-chain regions in the HSQC spectra of SAL and AOL, ^{13}C - ^1H correlations about the methoxy groups, the β -O-4' aryl ether linkages with a free OH at the γ -carbon (A), the β -O-4' aryl ether linkages with a acetylated OH at γ -carbon (A'), the resinol substructures formed by β - β' , α -O- γ' , and γ -O- α' linkages (B), and the phenylcoumarane substructures formed by β -5' and α -O-4' linkages (C) (see Fig.

3) were recognized according to the previous literatures [21, 22, 26-28]. These linkages were the major internal connections of lignin, which construct the three-dimensional structure of lignin [2]. Owing to the different preparation methods, the relative contents of these linkages in the two lignin samples were quite different. In contrast to 68% β -O-4' linkages in AOL, SAL only contained 14% β -O-4' linkages. Furthermore, the relative contents of β - β' and β -5' linkages in SAL were 59% and 27%, and those in AOL were 13% and 19%.

Fig. 3. Side-chain linkages and aromatic units identified by 2D HSQC NMR of lignin: (A) β -O-4' aryl ether linkages with a free OH at the γ -carbon; (A') β -O-4' aryl ether linkages with a acetylated OH at γ -carbon; (A'') C_{α} -oxidized β -O-4' aryl ether linkages; (B) resinol substructures formed by β - β' , α -O- γ' , and γ -O- α' linkages; (C) phenylcoumarane

substructures formed by β -5' and α -O-4' linkages; (D) spirodienone substructures formed by β -1' and α -O- α ' linkages; (I) *p*-hydroxycinnamyl alcohol end groups; (J) cinnamaldehyde end groups; (PB) *p*-hydroxybenzoate substructures; (H) *p*-hydroxyphenyl units; (G) guaiacyl units; (G') oxidized guaiacyl units with a C $_{\alpha}$ ketone; (S) syringyl units; (S') oxidized syringyl units with a C $_{\alpha}$ ketone.

In order to further clear the contents of these linkages in SAL and AOL, the semi-quantitative results (based on per 100 Ar) were conducted [18, 21]. Under this standard, the frequency of β -O-4', β - β ', and β -5' linkages in SAL presented the amount of 0.7, 3.0, and 1.4, which were completely different from Wen and co-workers' results [21]. This phenomenon can be explained by the fact that SAL used in this study was isolated from the soda alkali pulping black liquor (the detailed preparation conditions can be found in Fig. S1). The black liquor lignin had low ether bonds, and this was in accordance with the pulping theory. The feedstock used by Wen and co-workers was extracted by the NaOH solution, which preparation conditions were relatively mild with more ether bonds retained. As for AOL, the semi-quantitative contents of β -O-4', β - β ', and β -5' linkages were 12.0, 2.3, and 3.3. These amounts were similar with Guo and co-workers' results [22], in which the raw material and the preparation method were the same. Moreover, the ^{13}C - ^1H correlations of the carbohydrates (2-O-Ac-xylp, β -D-xylp, and cellulose) [21, 29] were also observed in the side-chain region of SAL, which were caused by the residual lignin-carbohydrate complex (LCC).

In the aromatic regions in the HSQC spectra of SAL and AOL (Fig. 2(b) and (d)), cross-signals from *p*-hydroxyphenyl (H), syringyl (S and S'), and guaiacyl (G) lignin

units, as well as the *p*-hydroxybenzoate substructures (PB) [22, 26, 30] were observed. As can be seen from the relative contents listed in Fig. 2(b) and (d), SAL had more S and S' units, almost the same G units, less H units, and no PB substructures compared with AOL. Furthermore, no cross-signals from the *p*-hydroxycinnamyl alcohol end groups (I) and the cinnamaldehyde end groups (J) (see Fig. 3) were found in both SAL and AOL. These two substructures were common in MWL and MAL of triploid *Populus tomentosa* Carr. [26]. The absence of I and J suggested that both of the two preparation methods used in this work could degrade those substructures completely. In general, all these features were the nature characteristics of the two lignin samples, originating from the different preparation methods.

3.2 Thermal stability of lignin

In the field of lignin thermochemical conversion, it is extremely important to investigate the thermal properties of lignin samples, which could clarify the potential relationship between chemical structure and degradation, and forecast the yield of pyrolysis products [18]. Thus, the thermal stabilities of SAL and AOL were conducted on a TA Q50 thermogravimetric analyzer with the heating rate of 10 °C/min, and the thermogravimetry (TG) and differential thermogravimetry (DTG) curves were depicted in Fig. 4. During the thermogravimetric processes of SAL and AOL, three degradation stages can be recognized: dehydration stage, active pyrolysis stage, and passive pyrolysis stage [31]. Generally, attentions are paid to the active stages, i.e., the major decomposition phase.

Fig. 4. TG and DTG curves of SAL and AOL with the heating rate of 10 °C/min

As shown in Fig. 4, the maximum decomposition temperatures of SAL and AOL were separately 353.3 °C and 346.2 °C, which intuitively indicated the poor thermal stability of AOL because of its high content of β -O-4' linkages. Meanwhile, it was noteworthy that the thermal decomposition rate of AOL was slightly higher than that of SAL in the initial decomposition phase (200-350 °C). This phenomenon can be explained by the fact that the initial decomposition was correlated to the decomposition of the weak internal linkages, such as β -O-4' linkages [18, 22]. When the temperature reached 400 °C, the degradation of aromatic rings and the cracking of C-C linkages (mainly 5-5' and β - β' linkages) became dominant [32]. Furthermore, the demethoxylation reaction, i.e., the OCH₃ group releasing from aromatic rings, occurred in the temperature range from 400 °C to 550 °C [33]. Therefore, the high thermal decomposition rate of SAL in this temperature range suggested its priority of the demethoxylation reactions.

3.3 Pyrolysis products by Py-GC/MS

Pyrolysis products from SAL and AOL under various temperatures were separately summarized in Table S2 and S3. As can be seen from the data, chemical compounds from the pyrolysis of the two lignin samples were roughly similar, mainly the oxygenated aromatic compounds. However, because of the different pyrolysis mechanism and formation routes of each compound, the maximum selectivity of different product was obtained under different temperature. Taken those pyrolysis products from SAL for example, the highest selectivity of 2-methoxy-4-vinyl phenol, which derived from G units, was 5.86% and appeared at 500 °C. 2,6-Dimethoxy phenol was the end product from S units, and its maximum selectivity was 7.43% at 600 °C. Furthermore, the C_α-OH group in S units could be oxidized into the C_α=O group, and then the C_α-C_β bond or the C_β-C_γ bond was cracked, forming 4-hydroxy-3,5-dimethoxy benzaldehyde or 1-(4-hydroxy-3,5-dimethoxy phenyl) ethanone with the maximum selectivity of 6.49% or 4.41% at 400 °C. Finally, 2,6-dimethoxy-4-(2-propenyl) phenol, the dominant product, was another typical degradation product from S units, and its highest selectivity was up to 20.77% at 400 °C.

From the above analysis, a phenomenon can be observed that the maximum selectivities of these main products were basically obtained at low temperatures. This was because that these products mainly originated from the cleavage of the weak side-chain linkages along with the formation pathways that Hu et al. summarized [24]. Due to the low bond dissociation energies, the cleavage of these weak side-chain linkages (especially β-O-4' linkages) can be carried out at low temperatures. With the temperature rising up, pyrolysis reactions became vigorous, and those free-radical intermediates would undergo series of subsequent transformation to other end products. Therefore,

selectivities of these products decreased at high temperatures. In addition, selectivities of certain products derived from AOL were always slightly higher than those from SAL. This can be explained by the results of 2D HSQC NMR and thermal stabilities that AOL contained more β -O-4' linkages than SAL, so that, it was easier to be degraded than SAL.

3.4 Classification of chemical compounds

Lignin pyrolysis is a fast thermal degradation process, and the oriented conversion is hard to be realized. Hence, paying much more attention to one or some particular products is not meaningful. However, according to the typical functional groups, products in bio-oil could be classified into different groups [12, 23, 24]. These groups have similar chemical properties and can be further upgraded to the value-added bio-chemicals [14, 15]. Products from the pyrolysis of SAL and AOL could be divided into phenols (compounds containing a phenolic hydroxyl group), carbonyls (including aldehydes, ketones, acids, and esters), and others (mainly aromatic hydrocarbons). Selectivities of the three groups under various temperatures (400, 500, 600, and 800 °C) were illustrated in Fig. 5.

Fig. 5. Components of bio-oil from SAL and AOL: -400, -500, -600, -800: temperature in °C.

As can be seen in Fig. 5, phenols were the major products from the pyrolysis of SAL and AOL, whose selectivity was considerably higher than those of carbonyls and others. When the temperature rose from 400 °C to 800 °C, the selectivity of phenols from SAL continuously increased from 78.69% to 87.37%. However, the change law of the selectivity of phenols from AOL was different with that from SAL. When the temperature was less than 600 °C, the selectivity kept increasing from 80.74% to 86.73%. Whereas, the temperature was up to 800 °C, the selectivity dropped to 81.74%. This can be explained by the fact that at high temperature, the degradation reactions became much more vigorous and some phenolic hydroxyl groups were broken down synchronously. Furthermore, the selectivity of phenols from AOL was always higher than that from SAL

at low-to-medium temperature, which could be also explained by the results that AOL contained more β -O-4' linkages than SAL. Moreover, the selectivity of carbonyls kept decreasing when the temperature increased from 400 °C to 800 °C, and the trend of the selectivity of others with temperature increasing was irregular.

Considering from the types of aromatic rings, phenols could be further split into H, G, and S phenols [23, 24]. Fig. 6 showed the selectivities of the three kinds of phenols from the pyrolysis of SAL and AOL under different temperatures. As can be seen in Fig. 6(a), the selectivity of S phenols from SAL decreased continuously with the temperature increasing, which maximum selectivity was 41.92% at 400 °C. Opposite to S phenols, H phenols formed until 500 °C, and then its selectivity kept rising to 24.00% at 800 °C. Furthermore, an optimal temperature was screened in the G phenols formation. When the temperature was less than 600 °C, the formation of G phenols was promoted; whereas the temperature rose to 800 °C, the formation of G phenols was inhibited. Thus, the maximum selectivity (57.06%) was obtained at 600 °C. Similar trends of phenols from AOL could be drawn according to Fig. 6(b) and the details were not displayed again.

Fig. 6. Selectivities of phenols with different aromatic rings from the pyrolysis of SAL (a) and AOL (b): H phenols: *p*-hydroxyphenyl phenols; G phenols: guaiacyl phenols; S phenols: syringyl phenols.

S phenols only derived from S units within lignin. However, due to the inevitable demethoxylation reactions, especially at high temperatures, S units could be degraded into G and/or H units [34, 35]. Hence, the high temperature inhibited the formation of S phenols. As for these G phenols, their increasing selectivity before 600 °C mainly benefited from G units, as well as the demethoxylation of S units. However, when the temperature rose to 800 °C, demethoxylation reactions on G units became vigorous. Thus, its selectivity dropped. Furthermore, the formation of H phenols basically attributed from the demethoxylation of S and G units. Therefore, the selectivity of H phenols increased with the temperature rose up. Further comparing the selectivities of the three phenols from SAL and AOL under the same condition, it was found out that SAL always produced more G phenols, less S phenols, and almost the same H phenols (as shown in Fig. 6). These phenomena were consistent with the results in the high temperature zone of

TGA, and could be well explained by the fact that SAL had more β - β' linkages than AOL, which were harder to be degraded than those β -O-4' linkages. Thus, the competitive demethoxylation reactions in SAL pyrolysis occurred much more easily than those in AOL pyrolysis.

4. Conclusions

SAL and AOL had similar organic groups and were both consisted of guaiacyl and syringyl units. Main side-chain linkages within SAL and AOL were separately β - β' and β -O-4' linkages, in which the β -O-4' linkages determined the poor thermal stability and easy degradation of AOL. Prominent pyrolysis products from both SAL and AOL were phenols at all temperatures. Herein, the phenols from AOL were redecomposed by the high temperature (800 °C). Furthermore, the abundant β - β' linkages of SAL led to its priority of the demethoxylation reactions during pyrolysis. Meanwhile, the different demethoxylation degree under various temperatures determined the distributions of *p*-hydroxyphenyl phenols, guaiacyl phenols, and syringyl phenols.

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