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Separation and characterization of pyrolytic lignins from the heavy fraction of bio-oil by molecular distillation

Yurong Wang, Shurong Wang *, Furong Leng, Junhao Chen, Lingjun Zhu, Zhongyang Luo

State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China

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ABSTRACT

Different fractions of bio-oil could be enriched with various chemical families by molecular distillation. The distilled fraction could be upgraded by catalytic esterification, cracking, or steam reforming, whereas the heavy fraction was difficult to dispose of. In this study, we adopted the methanol–water method for primary separation of pyrolytic lignins and sugars in the heavy fraction to improve the efficiency of utilization of the heavy fraction. Ultimate analysis, gel-permeation chromatography, Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, and pyrolysis–gas chromatography/mass spectrometry were employed to characterize the pyrolytic lignins obtained by methanol–water and water extraction methods. The pyrolytic lignins consisted of similar elements, and their basic structures included etherified and non-etherified syringyl and guaiacyl units. However, low-molecular-weight pyrolytic lignin from the heavy fraction differed from the high-molecular-weight pyrolytic lignin and water-extracted pyrolytic lignin in molecular weight distribution, side chains, and interunit linkages. As the low-molecular-weight pyrolytic lignin consisted of tri- to pentamers and 0.14/Ar carbonyls, it had high reactivity. Interunit linkages of the three pyrolytic lignins contained β–β′ resinol moieties, while the low-molecular-weight pyrolytic lignin had the most abundant alkyl ether linkages.

1. Introduction

Biomass, which can be converted into chemicals and liquid fuels, is renewable, widely distributed, and abundant, and it has low amounts of sulfur and nitrogen [1]. Fast pyrolysis is a promising technology that can convert solid biomass into the primary liquid fuel, bio-oil. However, crude bio-oil has high oxygen content, low heating value, and complex composition [2], which limit its use. Although various upgrading technologies such as catalytic cracking, hydrotreatment, steam reforming, and catalytic esterification have been applied to bio-oil upgrading [3,4], whole bio-oil cannot be converted with high efficiency because of the various reactivities and interactions of its more than 300 compounds. Researchers have attempted to separate the bio-oil into different fractions followed by fraction upgrading. Most studies, however, used only bio-oil model compounds or the aqueous phase obtained by water extraction for the production of hydrogen, polyols, hydrocarbons, and so forth [5,6]. The aqueous phase of bio-oil contains mainly small-molecule acids and ketones, which have high reactivity and can convert under moderate conditions [7,8]. In contrast, sugars in the aqueous phase easily deposit on catalysts, forming coke and rapidly deactivating the catalyst [9,10]. A combination of high-efficiency separation and appropriate upgrading technology of bio-oil may effectively relieve catalyst deactivation during bio-oil upgrading. Primary enrichment of various chemical families with graded separation of bio-oil not only provides a platform for extraction of such chemicals, but also aids the selection of upgrading technology for obtaining high-grade fuels.

Traditional distillation easily leads to polymerization and coking problems associated with bio-oil [11,12]. In contrast, molecular distillation enables the high-efficiency separation of bio-oil at low temperatures, which allows bio-oil to retain its original properties. We investigated the separation properties of bio-oil by molecular distillation under different conditions [13,14]. Our results show that small molecules such as acetic acid, acetol, furfural, and water could reach the second condensation trap and form a water-rich light fraction. Monophenols such as phenol and guaiacol accumulated in the middle fraction, while sugars and phenolic oligomers remained in the heavy fraction because of their high molecular weights. Various technologies based on the enrichment properties of bio-oil compounds were employed for the upgrading of various bio-oil fractions obtained from molecular distillation, and bio-oil fractions were utilized at high efficiency [15,16]. Since the heavy fraction was very viscous, emulsion fuel was produced with the

* Corresponding author at: State Key Laboratory of Clean Energy Utilization, Zhejiang University, Zheda Road 38, Hangzhou 310027, China.
E-mail address: srwang@zju.edu.cn (S. Wang).

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emulsification of diesel and alcohol-diluted heavy fraction [17]. Nevertheless, the existence of pyrolytic lignins led to the instability of emulsion fuel, and the enrichment of valuable sugars in the heavy fraction provided a means for extracting sugars for the production of ethanol [18]. As a result, an optimal upgrading scheme for bio-oil heavy fraction is necessary.

Pyrolytic lignin, an important bio-oil constituent, can occur at a high content (up to 30 wt%) [19,20] and can remain in the heavy fraction during molecular distillation. It can increase the viscosity and complexity of bio-oil and is therefore difficult to be upgraded [21]. Since pyrolytic lignin mainly derives from the fragments of lignin pyrolysis, its side-chain functional groups and interunit linkages may undergo change. Therefore, the separation and characterization of pyrolytic lignin may improve the extraction of monophenols and sugars from heavy fraction, and may aid in understanding the structural variation of lignin after pyrolysis. Moreover, these characterization results are also references for its applications such as targeted upgrading for biofuels [22–24] as well as synthesis of phenolic resin, adhesive, and carbon fiber [25,26]. The water solubilities of pyrolytic lignin and sugars are different. Sugars have strong hydrophilicity due to their polyhydroxyl moieties, whereas pyrolytic lignin has complex structures and many hydrophobic groups. Consequently, water can be used for fast separation of these two chemical families. As the water content of crude bio-oil is around 30 wt% [2], water or water combined with organic solvents and pH control can be used to extract pyrolytic lignins with various reactivities from bio-oil [20,27]. However, the heavy fraction has very low water content and appears in semi-solid at room temperature. It flows slowly even at above 40 °C. As a result, direct addition of water to the heavy fraction cannot result in good miscibility due to the strong intermolecular interactions of heavy fraction. These chemical bonds are difficult to break and thus prevent separation of pyrolytic lignin from other chemicals. Meanwhile, the heavy fraction is rich in sugars, so direct pH control [27] is not useful for further separation and purification of sugars. The present study effectively separated pyrolytic lignins from the heavy fraction through the methanol–water extraction method. Various characterization methods were used to investigate the functional groups, structural units, side chains, and interunit linkages of pyrolytic lignins obtained from two extraction methods. We also evaluated semiquantitatively the typical functional groups such as carbonyls and methoxyls, as well as the interunit linkages.

2. Experimental

2.1. Separation of pyrolytic lignins

Bio-oil was produced by pyrolysis of lauan sawdust using a fast-pyrolysis fluidized bed designed by Zhejiang University. The feeding rate was 5 kg/h, and the pyrolysis temperature was 500–550 °C. The detailed operation can be found in the literature [28]. Before experiments, the crude bio-oil was filtered to remove fine solid particles.

Water extraction of pyrolytic lignin from the original bio-oil was done by adding 4.98 g of bio-oil dropwise to 49 g of ice-cooled water while stirring at 5000 rpm. Subsequently, the suspension was filtered through a 0.45 μm organic membrane to obtain the precipitate named as water-extracted pyrolytic lignin (PLO), which was dried at 38 °C under vacuum.

The heavy fraction of bio-oil was obtained by molecular distillation of bio-oil using a KDL-5 molecular distillation apparatus (UIC Company). The evaporation temperature and operation pressure were 70 °C and 120 Pa, respectively. The feeding rate was 2 mL/min, and the rotational speed of the roller wiper was 120 rpm. The detailed operation is described in our earlier report [14]. The heavy fraction of bio-oil (3.03 g) was dissolved directly in methanol (6.45 g) with the aid of ultrasound and then precipitated with two volumes of deionized water. The precipitate, high-molecular-weight pyrolytic lignin (HPLH), was obtained by centrifugation at 8000 rpm. The residual solution was evaporated at 25 °C to remove the methanol, and the suspension was re-centrifuged at 8000 rpm to obtain low-molecular-weight pyrolytic lignin (LPLH). To eliminate residual moisture, tetrahydrofuran (THF) was used to redissolve the pyrolytic lignins. The obtained solutions were evaporated at 30 °C to remove the residual water and solvent.

2.2. Analysis of pyrolytic lignins

Carbon (C), hydrogen (H), and nitrogen (N) in the heavy fraction and pyrolytic lignins were analyzed on a Vario Micro elemental analyzer (Elementar Analysensysteme GmbH, Germany). The oxygen content was estimated by difference. The heating value of each sample was calculated from the formula: $3.55C^2 - 232C - 2230H + 51.2C \times H + 131\,N + 20600$ [29]. The molecular weight distributions of pyrolytic lignins were determined by gel-permeation chromatography using a PL GPC 50 Plus. Each sample was dissolved in THF and centrifuged at 8000 rpm for 15 min. Subsequently, the upper layer was filtered through a 0.45 μm organic membrane. Three PL gel columns (103, 105, and 500 Å; 300 × 7.5 mm) were connected in series, and their temperatures were kept at 50 °C.

The chemical structure of pyrolytic lignins was characterized through spectroscopic techniques. The functional groups of pyrolytic lignins were analyzed on a Nicolet 5700 Fourier transform infrared spectrophotometer (FTIR) manufactured by Thermo Fisher Company. Each sample was dissolved in THF, and the solution was allowed to dry on the surface of a solid KBr slide under an infrared lamp. Each sample was scanned within a wavenumber region of 4000–400 cm^{-1}. One-dimensional (1D) and two-dimensional (2D) nuclear magnetic resonance (NMR) spectroscopy were both carried out at 25 °C on an Agilent 600 MHz DD2 NMR apparatus. For ^1H NMR, about 20 mg sample was dissolved in 0.5 mL of deuterated dimethyl sulfoxide (DMSO-d_6), and tetramethylsilane was used as the internal standard. Experimental parameters were as follows: 45° pulse angle, 1 s relaxation delay, and 32 scans. For 2D ^{13}C—^1H heteronuclear single quantum coherence (HSQC) correlation NMR, about 100 mg of each sample was dissolved in 0.5 mL of DMSO-d_6 with the aid of ultrasound. The relaxation delay for ^1H dimension was 1.5 s, while that for ^{13}C dimension was 2 s. The total acquisition time lasted 10 h. The central cross signal of DMSO-d_6 (δ_C/δ_H = 39.5/2.49) was used as a reference point for the internal chemical shift, and the $^1J_{C\text{-}H}$ value used was 146 Hz.

Pyrolytic lignins were subjected to pyrolysis using a pyrolyzer (CDS5200) connected to gas chromatograph (Trace DSQ II) and a mass spectrometer (Py–GC/MS). Each sample (0.35 mg) was pyrolyzed in a quartz tube at 600 °C for 20 s at a heating rate of 1000 °C/s. The desorption temperature was 280 °C. GC/MS was performed by using a DB-wax polar capillary column (Agilent Company). Chromatography was carried out from 40 to 240 °C by ramping at 8 °C/min. The final temperature was held for 20 min. The char residue and small molecular volatiles were detected with a Mettler-Toledo TGA/SDTA851e thermo-balance coupled with a Nicolet NEXUS 670 FTIR spectrometer (TG–FTIR). Experiments were carried out from ambient to 800 °C at a heating rate of 20 °C/min with a steady nitrogen flow of 80 mL/min. The volatiles were identified with FTIR, and the spectrum scope was located in the range of 4000–400 cm^{-1} at a resolution of 16 cm^{-1}.