Research article

Relationship of thermal degradation behavior and chemical structure of lignin isolated from palm kernel shell under different process severities

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ABSTRACT

Lignin has been considered to be a potential feedstock to produce phenols chemicals by fast pyrolysis technology because of its aromaticity. In this work, four types of lignin were isolated from palm kernel shell with different severities: milled wood lignin (MWL), alkali lignin (AL), Klason lignin (KL), and organosolv ethanol lignin (OEL). A deep investigation of the relevance of the pyrolysis behaviors and chemical structure was carried out by FTIR, GPC, 2D-HSQC-NMR, TGA-FTIR and Py-GC/MS. AL contained highest content of β-O-4 aryl ether bond (53.9/100 Ar) and highest value of S/G ratio (1.68). MWL showed the widest temperature range (126–536 °C) of thermal degradation because of its inhomogeneous distribution of molecular weight. Highest content of oxygen-containing non-condensable gas components (H_2O, CO_2, CO) was observed in AL. The dominant organic components from lignin pyrolysis were S-type phenols, G-type phenols, P-type phenols, and C-type phenols. G-type (9.74–26.01%) was the dominant phenols products in AL, while P-type (44.23–56.01%) for KL, P-type (29.38–56.07%) for OEL, and G-type (9.08–25.81%) and P-type (22.60–29.04%) in MWL. Higher pyrolysis temperature promoted the formation of aromatics. As the conversion rate increased from 0.1 to 0.8, the activation energy estimated from DAEM model of four types of lignin, all gradually increased.

1. Introduction

As the nature's dominant aromatic polymer, lignin is heterogeneous, and present in the different layers of the plant cell wall (the middle lamella, primary wall, and secondary wall) [1]. It contributes about 15%–35% weight and 40% energy of the dry lignocellulosic biomass [2,3]. In the lignin polymer, three typical phenylpropane units, namely hydroxyphenyl (H), guaiacyl (G), and syringyl (S), are randomly bonded together by the ether bond (β-O-4, α-O-4, and γ-O-4) and the carbon-carbon bond (5-5, β-1, and β-5) [4–7]. According to different isolation methods, it can be divided into the following types: milled wood lignin (MWL), organosolv ethanol lignin (OEL), alkali lignin (AL), Kalson lignin (KL), enzymatic/mild acidolysis lignin (EMAL), *etc*. By now, lignin can be used to produce surfactant, resin, composites, bio-fuels, and bio-chemicals.

In the recent years, fast pyrolysis technology operating at a fast heating rate and a short residence time with an atmosphere of absence of oxygen, has been extensively developed as a promising technology to convert various types of renewable biomass into liquid bio-fuels or bio-chemicals, known as bio-oil [8,9]. Due to the particular structure characteristic of being rich in phenylpropane units, lignin has been considered to be a potential feedstock to produce phenolic-rich bio-oil [10]. In addition, after a series of upgrading processes including separation and purification, catalytic cracking, and hydrodeoxygenation, the phenolic-rich bio-oil could be transferred into other value-added chemicals of olefins and aromatic hydrocarbons (benzene, toluene, and xylene (BTX)) [11,12].

The property of bio-oil was mainly affected by the lignin source, reactor type, pyrolysis temperature, and residence time [8,11,13]. However, lignin type derived from different isolation methods, has been reported to be the most important native influence factor due to the different chemical structures. References [14, 15] investigated the relevance of the lignin source and the pyrolysis behaviors using soda alkali lignin (SAL) and Alcell organosolv lignin (AOL). The result showed

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that AOL had higher content of β-O-4 type ether bond (with very low bond dissociation energy) than SAL which leads to poorer thermal stability of AOL, and higher selectivity production rate of phenolic chemical components of AOL at low-to-medium pyrolysis temperature. Wang et al. [16] compared the basic properties and pyrolysis behaviors of milled wood lignin (MWL), organosolv lignin (OL), alkali lignin (AL), and Klason lignin (KL). OL had the highest content of carbonyl groups (C=O) which resulted in highest content of non-condensable gases of CO and CO_2. In addition, higher content of ether linkages preserved in the AL and KL lead to more phenols production at low pyrolysis temperature. Wang et al. [17] found that pyrolysis lignin (PL) extracted from bio-oil had lower molecular weight, lower content of S unit, G unit, methoxy groups, ether linkages than MWL, therefore, the yield of CO, methanol, formaldehyde and phenols from PL are lower than from MWL as well as poorer thermal stability. Other researchers [18–21] also confirmed the result that lignin source from different isolation methods had remarkable effect of on the pyrolysis behaviors of lignin.

In this study, four types of lignin isolated from the same biomass with different severities, namely ball-milling and extracted by neutral organic solvent, mild organic solvent with faintly acid, strong acid solvent, and strong alkali solvent, were used to evaluate the effect of the chemical structure on the pyrolysis behaviors. MWL, also named Björkman lignin, was isolated in a neutral condition's extracting solvent (dioxane/water solution) after milling pretreatment which was recognized as the most ideal one to keep the chemical structure of protolignin. OEL was isolated in mild acid condition's solvent (ethanol/water solution with little sulfuric acid as a catalyst) with little variation of chemical structure compared to the protolignin. AL and KL were isolated in a strong alkali condition's solvent (NaOH/water) and a strong acid condition (sulfuric acid/water). Therefore, compared to the protolignin, a certain degree of modification of the chemical structure of lignin would occur depending on different isolation methods.

Although the pyrolysis behaviors of MWL [16,17,22], OEL [18,20,21,23–25], AL [26–28], and KL [29–32] have been studied, most of the previous research focused on the weight loss characteristics, kinetics, and components of bio-oil. However, detailed chemical structure of lignin was still missed. Therefore, a deep relationship between chemical structure and pyrolysis behavior of the four types of lignin would be invaluable.

The aim of this study was to firstly investigate the detailed chemical structure of four lignins by FTIR, GPC, 2D-HSQC-NMR. Then the thermal degradation behavior of four lignins by TGA–FTIR and Py–GC/MS was studied. Finally, the relationship of thermal degradation behavior and chemical structure of lignin isolated from palm kernel shell under different process severities was established.

2. Experimental

2.1. Lignin isolation

The palm kernel shell (PKS, *Elaeis guineensis* Jacquin) with high lignin content (> 45% of acid-in soluble lignin estimated by the method of GB/T 2677.8-94 [33,34]) was chosen for the lignin isolation, and purchased from Sabah of Malaysia. The PKS powder with a particle size ranging from 0.25 to 0.38 mm (sieved using 40–60 mesh sifter) was used. Before the lignin isolation experiment, the PKS powder was extracted in benzene/ethanol solution (2:1 v/v) for 24 h, and dried at 105 °C for 24 h.

The isolation of PKS lignin was based on the following methods: (1) The isolation method of MWL was previously developed by Qiao et al. [35]. The powder sample was firstly milled in a ball mill (250 rpm, 72 h) at room temperature, then it was extracted in the dioxane/water solution (96% dioxane, biomass/solution = 1 g: 10 mL) for 24 h at 25 °C. The crude MWL was dissolved in the 1, 2-dichloroethane/ethanol solution (2:1 v/v), and precipitated in diethyl ether. After centrifugation, the solid material was washed with petroleum ether and dried in a

vacuum oven at 40 °C for 12 h. (2) The isolation method of AL was previously developed by Sun et al. [36]. The PKS (1 g) was treated with 10% NaOH (22 mL) at 80 °C with a continuous agitation of 6 h. Then, the 3 M HCl was gradually added into the former mixed solution until the pH reached 2.0, and the mixed solution was kept still for 3 h. The AL was obtained after the following steps of filtration, washing with DI water and dried in a vacuum oven at 40 °C for 12 h. (3) The isolation method of OEL was previously proposed by Pan et al. and EI Hage et al. [37,38]. The PKS (10 g) was treated with ethanol/water solution (65:35 v/v) with sulfuric acid (1.2 wt% of sample) as a catalyst in a Parr-4500 reactor (Parr Instrument, USA). The reaction was operated at 170 °C for 80 min with a solid/liquid ratio of 1:8. Then the solid residue was removed by filtration. The OEL was obtained from the solution by the following steps of centrifugation, rotary evaporation at 40 °C and dried in a vacuum oven at 40 °C. (4) The isolation method of KL was based on modified version of NREL procedure [39]. PKS was treated with sulfuric acid/water solution (72 wt% of sulfuric acid) at 20 °C for 2.5 h. KL was obtained from the insoluble precipitate after washing with DI water and drying in a vacuum oven at 40 °C for 12 h.

2.2. . Chemical structure analysis of lignin

2.2.1. Ultimate analysis

The ultimate analysis of the lignin was tested by the elemental analyzer (Vario EL III, Elementary, Germany) following the CHNS model. The calorific value of the lignin was tested by the automatic calorimeter (ZDHW-300A, Hebi Keda Instrument & Meters Co., LTD, China).

2.2.2. Molecular weight analysis

The molecular weight of lignin was established by the gel permeation chromatography (GPC) at 40 °C. The chromatographic column was a 300 mm × 7.5 mm i.d., 10 μm, PL-gel, with a 50 mm × 7.5 mm i.d. guard column of the same material (Agilent, USA). The GPC was composed of a Malvern Viscotek 3580 system, a Viscotek GPC 2502 refractive detector, and a GPC 1007 pump. HPLC grade THF was used as eluent with a flow rate of 1 mL/min. Mono-dispersed polystyrene was used as the standard to generate a universal calibration curve. All lignin samples were acetylated before analysis.

2.2.3. FTIR spectroscopy

The FTIR spectroscopy of lignin was carried out on a Nicolet-6700 (Thermo Fisher Scientific, USA) spectrograph. The mass ratio of KBr to lignin was 100. The resolution was 4 cm^{-1}, and the spectral region was 4000 to 500 cm^{-1}.

2.2.4. 2D-HSQC-NMR analysis

The NMR analysis of lignin was carried out in Bruker AVIII 400 MHz spectrometer at 25 °C [40]. 100 mg of lignin was dissolved in 0.5 mL of DMSO-d_6, and 20 μL of chromium (III) acetylacetonate (0.01 M) was added as a relaxation agent. For the quantitative 2D-HSQC spectra, the Bruker standard pulse program hsqcetgpsi2 was used. The central solvent peak at δ_C/δ_H of 39.5/2.49 was used as an internal reference. The spectral width of ^{1}H and ^{13}C were 5000 Hz and 20,000 Hz, respectively. For ^{1}H-dimension, the number of collected complex points was 1024 with a recycle delay of 1.5 s, while for ^{13}C-dimension, the number of transients was 64, and 256 time increments were recorded. The ^{1}JCH was 145 Hz.

2.3. Pyrolysis experiment and kinetics of lignin

2.3.1. TGA-FTIR analysis

The instrument of Thermogravimetric Analyzer (TGA 8000, PerkinElmer, USA) coupled with FTIR spectroscopy (Frontier, PerkinElmer, USA) was used to investigate the weight loss characteristics and identify the evolved gas components during lignin pyrolysis.