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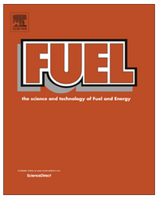

Full Length Article

Effect of molecular weight on the pyrolysis characteristics of alkali lignin

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HIGHLIGHTS

- Molecular weight of lignin was not affected on the volatile product species.
- Low molecular weight lead to the yields of CH_4, CO_2, phenol and alkyl phenol increased.
- High molecular weight favored the generation of guaiacol and alkyl guaiacol.

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ABSTRACT

The effects of molecular weight on the pyrolysis products properties of alkali lignin were investigated by using thermogravimetric analyzer coupled with Fourier transform infrared spectrometry (TG-FTIR) and tube furnace. Four lignin samples, including pure alkali lignin (AL), more than 10 kDa lignin fraction (AL-10kDa), 5–10 kDa lignin fraction (AL-5kDa) and 1–5 kDa lignin fraction (AL-1kDa) were firstly prepared by ultrafiltration membrane technology. Then the thermal behavior and volatile evolution patterns of the four lignin samples were investigated by TG-FTIR, and the component properties of condensable and incondensable products obtained from tube furnace were characterized by the gas chromatography/mass spectroscopy (GC/MS) and gas chromatography (GC). TG-FTIR results indicated that the molecular weight of lignin was not significantly affected on the evolution temperature ranges and volatile product species, while has an obviously effect on the total yields of CH_4, CO_2, phenols and aromatics products. GC/MS and GC results indicated that low molecular weight helps to crack the methoxy groups of lignin leading to the yields of CH_4, CO, CO_2, phenol and alkyl phenol increased, while high molecular weight favored the generation of guaiacol and alkyl guaiacol. Meanwhile, the effect of molecular weight on the yields of aromatics was also affected by the pyrolysis temperature.

1. Introduction

The depleting stocks of fossil fuels have forced researchers to investigate renewable fuels and chemicals as an alternative to petrochemical products [1,2]. Recently, more and more attentions have been paid to lignin for product bio-fuels [3–5]. Meanwhile, lignin is one of the main components of biomass and the chemical structure of lignin suggests that it may be a promising material for producing bio-based phenolic chemicals [6–8].

Based on the previous researches [9,10], lignin is an amorphous and highly branched polymer through C—O or C—C bonds, and the polymer molecular structure of lignin is very difficult to be degraded into phenyl propane monomers. Therefore, the selective depolymerization of lignin structure into smaller molecular units is the major challenge for converting it to value-added chemicals. Pyrolysis is the most studied method for the conversion of lignin for recent decades [11–14]. It was found that the major pyrolysis products of lignin include gaseous hydrocarbons with carbon monoxide and carbon dioxide, volatile liquids (alcohols, ketones, aromatics and phenols) and solid chars. Furthermore, the proportions and components of lignin pyrolysis products were mainly affected by several factors, such as its feedstock type, heating rate, reaction temperature and catalysts. Wang [12] studied the pyrolysis behaviors of four type lignins including alkali lignin (AL), klason lignin (KL), organosolv lignin (OL), and milled wood lignin (MWL) by using TG-FTIR and Py-GC/MS. They found pyrolysis of AL and KL produce more phenols than OL and MWL at low temperature

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by the breakage of ether bonds. Kim [13] investigated the effect of various parameters on catalytic pyrolysis of lignin over HZSM-5 catalysts. They concluded that aromatic hydrocarbon and other phenolics were the main products, and the yield of aromatic hydrocarbon gradually increased with increasing pyrolysis temperature between 500 and 700 °C. Wang [14] studied the effect of KCl, $CaCl_2$ and $FeCl_3$ on alkali lignin pyrolysis using TG-FTIR and Py-GC/MS. They found that different metal chlorides have notable differences catalytic effects on lignin pyrolysis performance. According to our previous research [15,16], the pyrolysis products components of alkali lignin appear to be readily influenced by the organic bound Na groups of lignin structure.

In addition, alkali lignin is a degradation product of lignin from soda pulping process, and it has a large molecular weight distribution. Toledano [17] investigated the chemical structure and thermal behavior differences of three lignin fractionations obtained by ultrafiltration processes. They proposed that there was not clear evidence that the fractions are different in their thermal behavior. We studied the pyrolysis characteristics of three different lignin fractions obtained from alkali black liquor of Cunninghamia lanceolate by selective precipitation [18]. The difference was that we found the higher molecular weight lignin fraction exhibited the lower weight loss value. Meanwhile, there is no consensus achieved as to the effect of molecular weight on the pyrolysis products properties of alkali lignin. Therefore, in this paper, we made a further study to confirm the effect of molecular weight distribution on the pyrolysis characteristics of alkali lignin.

For this purpose, three different lignin fractionations were firstly separated from alkali black liquor of wheat straw by using different cut-offs ultrafiltration membranes (1, 5 and 10 kDa). Secondly, the molecular weight distribution of the three lignin fractionations and unfractionated lignin were studied by gel permeation chromatography (GPC), and thermal behavior and volatile evolution patterns of the four lignin samples were investigated by TG-FTIR. Finally, the four lignin samples were pyrolyzed at 400, 600 and 800 °C in a tubular reactor to obtain the pyrolysis products, and then the characteristic of the condensable and incondensable products were analyzed by GC/MS and GC to confirm the effect of lignin molecular weight on the properties of volatiles products.

2. Materials and methods

2.1. Sample preparation

2.1.1. Black liquor

Black liquor (BL) used in this study, with a solids concentration about 572 g/ml, was supplied by a wheat straw soda-AQ pulp mill in Shandong province (China). Black liquor sample was filtered through a 200-mesh screen to remove any suspended matter. Alkali lignin (AL) was separated from the soda-AQ wheat straw black liquor by acid precipitation with 1 N H_2SO_4 to pH 2.5. The acid precipitated solids were filtered from the solution, washed thoroughly with distilled water, and dried by freeze-drying. Subsequently, the dried solids were dissolved in 1,4-dioxane, filtered to remove any inorganic impurities, and reclaimed by rotary evaporation of solvent under vacuum and dried.

2.1.2. Lignin fractionations

The different molecular weight fractions of black liquor were prepared by ultrafiltration (UF) membrane technology. Firstly, the concentration of black liquor was diluted to 10% with deionized water, and then the diluted black liquor was filtered through a G3 sand core funnel. Secondly, the ultrafiltration module of black liquor used in the present work was Pellicon tangential flow ultrafiltration unit (ZJMP 10-002, Millipore), equipped with a 1 L reservoir feed with a recirculation pump and a set of Omega cassette equipped with polyethersulfone (PES) membrane. The fractionation procedure was that the black liquor was first ultrafiltrated on a membrane with 10 kDa to collect the 10 kDa alkali lignin feedstock solution on the top, and then the filtrate was treated with the membrane with 5 kDa to collect the 5 kDa alkali lignin feedstock solution, and the remained liquor was ultrafiltrated on a membrane with 1 kDa to collect the 1 kDa alkali lignin feedstock solution. Lastly, the three different lignin fractions were prepared by using the same method with AL, and the three lignin fractions were marked as AL-10kDa, AL-5kDa and AL-1kDa.

2.2. Experimental methods

2.2.1. TG-FTIR experiment

TG-FTIR experiments were done on a Jupiter Thermo Gravimetric Analyzer STA 449 F3, coupled with a thermo electron corporation Fourier Transformation Infrared Spectrometer TENSOR 27 at a heating rate of 20 °C/min within the temperature range from 50 to 1000 °C. High purity nitrogen was used as carrier gas with a flow rate of 20 mL/min. In each case, the mass of sample was less than 10 mg to avoid possible temperature gradient in the sample and to ensure kinetic control of the process. The volatile released from pyrolysis would be swept into a Fourier Transform Infrared Spectrometer gas cell quickly by pure nitrogen. Moreover, the FTIR gas cell and the pipe were already preheated to 150 °C before each experiment. The spectrum scope was located in the range 4000–667 cm^{-1} and the resolution factor was set at 4 cm^{-1}.

2.2.2. Pyrolysis experiment

Pyrolysis experiment was conducted in a tube furnace, the experimental schema were presented in Fig. 1. The reactor consisted of a quartz glass tube that can be heated to 1000 °C with a stable heating rate. When pyrolysis experiments were to be carried out, the furnace initially was flushed with nitrogen about 30 min, and then the furnace was heated to the desired temperature of 400, 600 and 800 °C, respectively. After the desired temperature was reached, the sample was rapidly moved into the furnace to carry out the pyrolysis reaction, each reaction time was 5 min, and each experiment was made at atmospheric pressure and at isothermal conditions. The volatile products were purged from the furnace by nitrogen at a flow rate 100 mL/min. The incondensable products released through an ice-water condenser then were collected, and the condensed liquid products were absorbed in the condenser.

2.3. Analytical methods

2.3.1. Molecular weights distribution analysis

Prior to molecular weight determination, the four lignin fractions were acetylated according to the previous research [18]. The molecular weights distribution of the different acetylated lignin was determined by a Waters 515E equipped with a Waters U6 K refractive index (RI) detector, a Waters Model 510 pump, a Waters 848 UV absorbance detector and a column packed with 30 cm of Superdex 30 and 30 cm of Superdex 200. The lignin samples were heated to 40 °C in a water bath and kept at that temperature for at least 15 min before injection into the column, Tetrahydrofuran was used as the solvent and the flow rate of the solvent was 0.22 mL/min. To calibrate the system, standards of polyethylene glycol were used. The data was analyzed using Millennium 32 GPC software (Waters).