Full Length Article

Thermal decomposition of pyrolytic lignin under inert conditions at low temperatures

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HIGHLIGHTS

- Chars prepared from the pyrolysis of pyrolytic lignin (PL) at 100–350 °C are characterised.
- Chars prepared at temperatures above 300 °C consist of mainly heavy aromatic oligomers.
- Light and heavy aromatic fractions interact and enhance char formation during PL pyrolysis.
- Polymerization of heavy aromatic oligomers in PL enhances char formation at T > 250 °C.

ARTICLE INFO

ABSTRACT

A pyrolytic lignin, separated from the bio-oil generated from biomass fast pyrolysis bio-oil at 500 °C via cold-water extraction, was thermally decomposed in a drop-tube/fixed-bed reactor under inert conditions at 100–350 °C. It is found that the char yield of the pyrolytic lignin under such fast pyrolysis conditions decreases rapidly from ∼82% at 100 °C to ∼23% at 350 °C. The majority of the weight loss is contributed by the significant reduction in the fraction of light aromatic oligomers (i.e., the CH_2Cl_2-soluble fraction) retained in the pyrolytic lignin chars, with such reductions increasing with temperature. On the contrary, there is insignificant change in the fraction of heavy aromatic oligomers (i.e., the CH_2Cl_2-insoluble fraction) retained in the pyrolytic lignin chars during pyrolysis at such low temperatures. It is evident that there are strong interactions between the light and heavy aromatic oligomers during thermal decomposition of the pyrolytic lignin, leading to the observed additional char formation. The main reactions during thermal decomposition of the pyrolytic lignin are the release of aliphatic and small phenolic compounds (i.e., via demethylation and decarbonylation reactions), mainly due to the breaking of ether bonds in the pyrolytic lignin structure. The char structure becomes more aromatic as temperature increases, due to the enhanced polymerization reactions at high temperatures (>250 °C).

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1. Introduction

Bio-oil from biomass fast pyrolysis is considered as an important feedstock that may be further refined into liquid transportation fuels in existing petroleum refineries [1,2]. However, bio-oil is of low quality (e.g., high acidity, low heating value, high viscosity, poor stability, and immiscibility with petroleum fuels) and needs to be upgraded before it can be processed in existing petroleum refinery infrastructure [3,4]. There may be various technologies for bio-oil upgrading, such as catalytic hydrotreating, steam reforming, cracking, and esterification [5–9]. One of the key problems associated with bio-oil upgrading is related to the poor thermal stability of bio-oil [2]. The reactive functional groups in bio-oil,

i.e., organic acids, carbonyl groups, sugars and aldehydes [10], have the tendency for decomposition, polymerization and/or condensation upon heating, resulting in coke formation during upgrading [11,12]. Coke formation causes significant operation problems (e.g., catalyst deactivation and reactor plugging) during bio-oil upgrading [13–15].

Bio-oil has very complex chemical composition and consists of compounds with a wide range of different functional groups and molecular weights [16]. Due to the large molecular weight, the lignin-derived oligomers (so-called pyrolytic lignin) in bio-oil can easily polymerize upon heating, contributing significantly to coke formation [17,18]. Pyrolytic lignin can be isolated from bio-oil as the water-insoluble fraction via cold-water extraction [19–21]. Previous studies were devoted to characterise the physical and chemical properties of pyrolytic lignin [16,19–22]. However, the knowledge on the thermal decomposition of pyrolytic lignin is still

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scarce, especially the fundamental mechanisms responsible for coke formation. A previous TG-FTIR study [23] reported that pyrolytic lignin is thermally unstable and can even start to decompose at temperatures as low as 160 °C. Therefore, it is of critical importance to understand the fundamental reaction mechanisms during the thermal decomposition of pyrolytic lignin at low temperatures. Consequently, this is the main objective of this study that carries out a systematic investigation into the formation and characteristics of chars during thermal decomposition of the pyrolytic lignin at 100–350 °C.

2. Experimental

2.1. Sample preparation

The bio-oil sample used in this study was produced from fast pyrolysis of pine wood using a fluidised-bed reactor at 500 °C. The bio-oil was stored in a freezer at around −10 °C prior to experiment. The pyrolytic lignin sample was prepared from bio-oil by cold-water extraction [24]. The pyrolytic lignin sample was further separated into the CH_2Cl_2-soluble and CH_2Cl_2-insoluble fractions via CH_2Cl_2 extraction. Generally, the CH_2Cl_2-soluble and CH_2Cl_2-insoluble fractions represent the light and heavy aromatic oligomers in the pyrolytic lignin [10,25], respectively. The solvent in all samples was removed by evaporation at 40 °C, and the dry residues were stored in a freezer for subsequent experiments.

2.2. Thermal decomposition of pyrolytic lignin under inert conditions

A set of experiments on the thermal decomposition of the pyrolytic lignin were carried out using a pulse-feeding drop-tube/fixed-bed quartz reactor at 100–350 °C under inert conditions. With the detailed description given elsewhere [26], the reactor is essentially a drop-tube reactor connecting with a fixed-bed reactor in tandem, with the features of both reactors. Briefly, the reactor was preheated with argon (ultra-high-purity, ~1.1 L/min) as carrier gas. Once the reactor reached the desired temperature, approximately 0.4 g of the pyrolytic lignin sample was fed into the reactor in one shot. The pyrolytic lignin particles experienced fast pyrolysis in the drop-tube reactor section, with the volatiles subsequently passing through (but the char particles remaining on) the quartz frit of the connected fixed-bed reactor section. The reactor was then held at reaction temperature for 15 min. After the experiment was completed, the reactor was immediately lifted out of furnace and rapidly cooled to room temperature, with the inert carrier gas continuously flowing through the reactor. The condensed tar on the reactor outlet was burned off and the char yield was calculated by the weight difference of the reactor before and after the experiment. It should be noted that the char in this study is defined as the remaining solid residue after fast pyrolysis experiment.

2.3. Sample analysis and charaterisation

An array of analytical techniques were employed to characterise the pyrolytic lignin and char samples. The chemical composition of all samples was determined using an elemental analyser (Perkin-Elmer 2400 Series II). The water content was analysed by Karl Fischer titration according to a method described elsewhere [27]. The functional groups of char samples were analysed using a Fourier transform infrared (FT-IR) spectrometer (Bruker IFS 66) with a KBr pellet method [22]. Briefly, 2 mg of the pyrolytic lignin sample was ground with 150 mg of KBr for 3 min grinding time and the resulting mixture was pressed into a pellet. The FT-IR spectra were acquired at a resolution of 4 cm^{-1}, and 32 scans were taken to pro-

duce an absorbance spectrum for each sample. All spectra were corrected for background (e.g., water vapour and CO_2 contributions) and baseline then normalized to the unit mass (per gram on a dry basis) of the pyrolytic lignin.

The solid state ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR spectra of solid samples were acquired to study the changes of carbon structures in the pyrolytic lignin char samples, via a Varian 400 MHz NMR spectrometer equipped with a 4 mm CP/MAS probe. A high power decoupling sequence with a MAS spinning speed of ~7000 Hz was employed to produce high-resolution ^{13}C solid NMR spectra. The rotor loaded with a sample was spun at 25 °C with a 90° pulse, 0.04 s acquisition time and 4 s relaxation delay. Adamantane was used as an external standard for chemical shift calibration. The acquired spectra were processed using the software MestRenova.

The UV fluorescence spectra of solid samples were obtained using a fluorescence spectrometer (Perkin-Elmer LS 55), following a method detailed elsewhere [28], to understand the changes of aromatic ring structures in the char samples. Briefly, the sample was dissolved in chloroform-methanol solvent mixture (4:1 v/v), and the dissolved solution after filtration was diluted to a final concentration of 4 ppm for analysis. The spectra were recorded at the excitation wavelength range of 200–550 nm with a constant energy difference of −2800 cm^{-1}. The fluorescence intensity of solid sample was also normalized to the unit mass (per gram on a dry basis) of the pyrolytic lignin.

3. Results and discussion

3.1. Yields and elemental compositions of chars produced from thermal decomposition of the pyrolytic lignin

Fig. 1 shows that char yield from thermal decomposition of the pyrolytic lignin decreases with increasing pyrolysis temperature, from ~82% at 100 °C to ~23% at 350 °C. It is interesting to note that a large weight loss even takes place at a temperature as low as 100 °C. This can be attributed to the presence of some light aromatic compounds in the pyrolytic lignin as these light aromatic compounds can easily evaporate at low temperatures [23]. The pyrolytic lignin and char samples were further extracted with CH_2Cl_2 to obtain the distribution of the CH_2Cl_2-soluble and CH_2Cl_2-insoluble fractions in the char samples (see Fig. 1). It has been proven that the CH_2Cl_2-soluble fraction of the pyrolytic lignin mainly
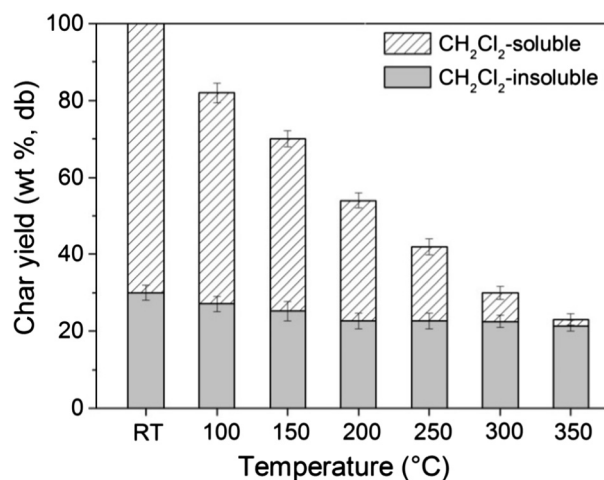

Fig. 1. Char yield from thermal decomposition of the pyrolytic lignin at 100–350 °C and the distribution of the CH_2Cl_2-soluble and CH_2Cl_2-insoluble fractions in the char samples.