



## Effect of temperature on structure evolution in char from hydrothermal degradation of lignin



Jun Hu, Dekui Shen, Shiliang Wu, Huiyan Zhang, Rui Xiao\*

Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, Southeast University, Nanjing 210096, PR China

### ARTICLE INFO

#### Article history:

Received 1 November 2013

Accepted 3 January 2014

Available online 11 January 2014

#### Keywords:

Lignin

Char

Structure evolution

Subcritical water

Hydrothermal degradation

### ABSTRACT

Hydrothermal degradation of lignin was carried out at 280–365 °C and the structure of solid char residue was extensively examined by means of scanning electron microscopy (SEM), nitrogen absorption/desorption, X-ray spectroscopy (XRD) and Fourier transform infrared spectroscopy (FTIR). The thermal stability of the produced char was estimated by Thermogravimetry–Fourier transform infrared spectroscopy (TG–FTIR). The char yield was 16.8% at 310 °C, which then increased with the temperature and reached the maxima value of 26.77% at 365 °C. SEM photo indicated that decomposition of lignin was enhanced with the increasing temperature, producing char with rough surface and few vesicles. The char at 330 °C had the largest surface area (2.5936 m<sup>2</sup>/g) and the largest pore volume (0.0189 cm<sup>3</sup>/g). XRD spectrum revealed that the char prepared at higher temperature produced higher ordered crystalline structure. Most of functional groups in char identified by FTIR were eliminated at 350 °C, except for the hydroxyl group. The char produced under high hydrothermal temperature exhibited high thermal-stability according to the right-shifted DTG curve against temperature. A mechanism was proposed to explain the possible steps for char structure evolution during lignin hydrothermal process in subcritical water, involving cleavage of the weak bonds at low temperature, and elimination of functional groups and carbonization at high temperature. The results would help improve the understanding of lignin degradation in subcritical water and optimize the hydrothermal process for producing value-added chemicals from lignin.

© 2014 Elsevier B.V. All rights reserved.

### 1. Introduction

Annually, a large amount of black liquor is emitted from industrial pulping process, being harmful for the underwater and soil system. Containing various active functional groups, lignin isolated from black liquor is a potential kind of feedstock for producing energy, fuels, and chemicals [1–3].

Hydrothermal degradation is estimated as a promising technique to convert lignin to gas, liquid, solid fuels, and chemicals (especially phenolic compounds) [4–7]. Wahyudiono et al. investigated the decomposition of alkali lignin in near and supercritical water, reporting monomeric compounds as the primary liquid product. They also found that the distribution of the functional groups of char changed greatly during the decomposition [8]. Pińkowski et al. examined the effect of temperature on hydrothermal decomposition of alkali lignin in subcritical and supercritical water, finding that both degradation of alkali lignin and repolymerization of decomposition products were promoted with the temperature increasing [9]. The degradation of organosolv

lignin was tested in subcritical water with different adding gas by Bembenic et al., and the widest variety of liquid products were presented when using CO as adding gas [10]. Except for the non-catalytic degradation in water, lignin has also been decomposed in some organic solvents, such as ethanol, with various catalysts [11–14]. Kang et al. studied the hydrochars produced by hydrothermal carbonization of lignin, cellulose, xylose and wood meal between 225 and 265 °C, focusing on the carbon content and higher heating value of the different chars [15]. Although considerable work has been carried out on the hydrothermal of lignin, most of these work only focused on the liquid products, giving little detailed description on the solid char.

Investigation of char can help to understand the degradation mechanism of lignin comprehensively, and give guidance on how to promote the degradation of incompletely reacted lignin and how to inhibit the repolymerization of liquid products [16]. Besides, a better understanding of char will propel its commercial use, bringing added-value to the black-liquor lignin. The structure of char from pyrolysis lignin or biomass has been widely investigated, and a specific understanding of the char evolution is available [17–19]. However, the char of hydrothermal degradation will present different properties due to the complex hydrothermal process. Therefore, it is important to study the physico-chemical characteristics of

\* Corresponding author. Tel.: +86 25 83795626/+86 25 83795726.  
E-mail address: [ruixiao@seu.edu.cn](mailto:ruixiao@seu.edu.cn) (R. Xiao).

hydrothermal char and to elucidate its evolution mechanism during hydrothermal process.

In this work, the physico-chemical characteristics of char produced from hydrothermal degradation of black-liquor lignin in sub-critical water was identified, including the morphology of the char characterized by a scanning electron microscopy (SEM), the surface areas and pores distribution information by nitrogen absorption/desorption, the crystalline structures by X-ray spectroscopy (XRD) and functional groups evolutions by Fourier transform infrared spectroscopy (FTIR). Thermogravimetry–Fourier transform infrared spectroscopy (TG–FTIR) was used to investigate the thermal stability of the char under pyrolysis. A mechanism was proposed for char evolution based on the obtained information in terms of the morphology, the surface areas, the pores distribution, the crystalline structure, the functional groups distribution and the thermal behavior of pyrolysis.

## 2. Materials and methods

### 2.1. Materials

The solvents used in the study were purchased from Nanjing Reagent Co. and used as received. Black liquor was obtained as the condensed byproduct from a pulping company in Yueyang (China).

Lignin was isolated from the black liquor according to the method described in our previous work [20]. In brief, black liquor was first acidified to a pH value of about 2.0 with 50% (wt%)  $H_2SO_4$ , and stirred for 1 h at 55 °C. Then the acidified black liquor was filtrated under vacuum. The filtrated cake were collected as isolated lignin and washed with deionized water to neutral. After dried at 80 °C for 12 h, the isolated lignin was extracted with benzene–ethanol (1:2, v/v) for 12 h in a Soxhlet extractor at 90 °C to remove some low molecular sugar residues. The extracted liquid was heated at 40 °C under 0.4 Mpa to remove the benzene–ethanol solvent and the remained solid lignin was dried at 80 °C for 12 h. The purified lignin was stored in dry atmosphere for following hydrothermal degradation.

### 2.2. Process of hydrothermal degradation

The hydrothermal degradations of lignin were conducted in a high pressure autoclave (AC 150, ESTANIT). The 150 mL autoclave was made of 316 TI, with a maximum working pressure of 40 MPa at 600 °C. Lignin sample (3 g) were loaded into the reactor with 100 mL deionized water. Air in the reactor was removed with five successive purges with nitrogen. Then the reactor was injected with nitrogen to 3 MPa, and heated by electricity. This heating process took about 40 min. After keeping at the desired temperature for 2 h at a stirring speed of 400 rpm, the reactor was cooled to the room temperature by a water coil. Each reaction condition was repeated for 2–3 times. The gas products were collected for GC with Flame ionization detector (FID) and Thermal Conductivity Detector (TCD) analysis [21], which mainly composed of  $CH_4$ , CO and  $H_2$ . Because of the relative low temperature used in this study, the gas products yields were negligibly low. After releasing the pressure, the reactor was opened, and all liquid and solid products were collected. The reactor was rinsed with ethyl acetate and solid product adhered to the wall was removed with a metal spatula. The solid product was isolated by filtration under vacuum, and then dried at 105 °C for 12 h. This solid product was defined as char.

### 2.3. Characterization methods

The SEM analysis was carried out for the surface morphology. Lignin and the chars were coated to the finest thickness prior to

measurement with Au/Pd film using a Cressington 208 HR sputter coater, and then observed and imaged with a JEOL JSM-6300 SEM. Nitrogen absorption/desorption was carried out on a micropore analyzer (Micromeritics ASAP 2400 instrument) using nitrogen as an adsorbate at 77 K. The pore size distribution was obtained in the size range of 0.4–250 nm. Brunauer–Emmett–Teller (BET) theory and Brrett–Joyner–Halenda (BJH) theory were used to determine the pore surface area and the pore size distribution of char particle. XRD for the crystal structure was performed in a D/max 2500 VL/PC X-ray diffractometer using Cu K $\alpha$  radiation (40 kV, 200 mA) from 5° to 85° with a step of 0.02°/s. The FTIR spectra were recorded on a FTIR spectrophotometer (Bruker Vector 22) using a KBr disc containing 1% samples. Sixteen scans were conducted for each sample in the range from 4000 to 400  $cm^{-1}$ , with a resolution of 4  $cm^{-1}$ . The precision was no more than 0.01  $cm^{-1}$ . A thermogravimetric analyzer (Setsys-1750, Setaram) coupled to an FTIR spectrophotometer (Bruker Vector 22) was employed to investigate the mass loss of lignin and on-line formation of gas products. About 20 mg lignin sample was placed into the furnace and heated from 30 to 900 °C at a heating rate of 20 °C/min under a nitrogen flow of 60 mL/min to maintain an inert atmosphere. The FTIR instrument was connected to the thermogravimetric analyzer by a flow cell which was heated to 180 °C to prevent condensation of the produced gas. The scanning range was set at 4000–400  $cm^{-1}$ .

## 3. Results and discussion

### 3.1. Yield of char residue

The char yield decreased from 28.25% at 280 °C to the lowest value of 16.8% at 310 °C, followed by an increasing to 26.77% at 365 °C. Ye et al. carried out the hydrothermal degradation of lignin in ethanol/water and observed the same trend with the lowest solid yield obtained at 250 °C [22]. The relative high yield at 280 °C was attributed to the existence of incompletely degraded lignin. With temperature increasing, lignin was further degraded and less char was collected. Repolymerization reaction was promoted along with the degradation reaction, and this repolymerization was severe at higher temperature, leading to the higher char yield at 365 °C.

### 3.2. Physico-chemical characterization of char residue

#### 3.2.1. SEM analysis

The SEM micrographs of lignin and the chars prepared by hydrothermal degradation are shown in Fig. 1. It can be observed that the shape of original lignin (Fig. 1a) was irregular polygonal, with a few pores on the relatively smooth surface. After hydrothermal degradation, the surface became rough gradually and many pores were formed due to the releasing of volatiles (Fig. 1b). In addition, many vesicles adhered to the surface could be found. As temperature increased to 350 °C, the size of the char particles became smaller and pores and vesicles disappeared (Fig. 1c). However, some irregular fluffy products were found which may be the result of carbon deposition. When the temperature came to 365 °C, the shape of the some char particles evolved to near needle (Fig. 1d).

Compared to the pyrolysis char of lignin observed by Sharma et al. [17], the hydrothermal char had less vesicles and more open pores. This might be attributed to the water which could permeate into the pores, and this permeation inhibited the formation of vesicles to some extent. Vesicles, which were widely distributed in pyrolysis char, could lead to the pore blockage and reduce of surface area. In addition, lignin particles presented a better dispersion under the stirred hydrothermal condition.

Download English Version:

<https://daneshyari.com/en/article/1196865>

Download Persian Version:

<https://daneshyari.com/article/1196865>

[Daneshyari.com](https://daneshyari.com)