



Effects of chemical form of sodium on the product characteristics of alkali lignin pyrolysis



Da-liang Guo^a, Hong-you Yuan^{a,b}, Xiu-li Yin^{a,*}, Chuang-zhi Wu^a, Shu-bin Wu^{a,b}, Zhao-qiu Zhou^a

^aThe CAS Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, PR China

^bThe State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, PR China

HIGHLIGHTS

- Organic bound Na and inorganic Na catalyzed alkali lignin pyrolysis.
- The evolution of volatiles is affected by the two chemical forms Na additives.
- Na additives increase the elimination of phenolic hydroxyl and alkyl substituent.
- Effect of chemical forms Na on char gasification was determined by temperature.

ARTICLE INFO

Article history:

Received 9 August 2013

Received in revised form 8 October 2013

Accepted 15 October 2013

Available online 26 October 2013

Keywords:

Alkali lignin

Na

Chemical form

Pyrolysis

Gasification

ABSTRACT

The effects of Na as organic bound form or as inorganic salts form on the pyrolysis products characteristics of alkali lignin were investigated by using thermogravimetric analyzer coupled with Fourier transform infrared spectrometry (TG-FTIR), tube furnace and thermo-gravimetric analyzer (TGA). Results of TG-FTIR and tube furnace indicated that the two chemical forms Na reduced the releasing peak temperature of CO and phenols leading to the peak temperature of the maximum mass loss rate shifted to low temperature zone. Furthermore, organic bound Na obviously improved the elimination of alkyl substituent leading to the yields of phenol and guaiacol increased, while inorganic Na increased the elimination of phenolic hydroxyl groups promoting the formation of ethers. It was also found the two chemical forms Na had different effects on the gasification reactivity of chars. For inorganic Na, the char conversion decreased with increasing the char forming temperature, while organic bound Na was opposite.

Crown Copyright © 2013 Published by Elsevier Ltd. All rights reserved.

1. Introduction

Alkali lignin, a heterogeneous aromatic polymer, represents an important by-product stream within chemical pulp mills (Nakamura et al., 2008; Pandey and Kim, 2011). The chemical structure of alkali lignin suggests that it may be a good source of phenolics and aromatics (Effendi et al., 2008; Gosselink et al., 2012; Li et al., 2012; Wahyudiono et al., 2008). Traditionally, alkali lignin is as low value fuel fired to product heat and steam in pulp mill (Gosselink et al., 2012). With the increasing demand for alternatives to fossil fuels, the utilization of alkali lignin has attracted worldwide interest, and thermochemical method (pyrolysis and gasification) is considered as a potential conversion method to product bio-chemicals or bio-fuels (Amen-Chen et al., 2001; Azadi et al., 2013; Pandey and Kim, 2011).

In the soda pulping process, sodium hydroxide is used as cooking chemical to extraction and degradation lignin. Important

delignification reactions include the cleavage of phenolic α -O-4 linkages, cleavage of non-phenolic β -O-4 linkages, and cleavage of some phenolic β -O-4 linkages (Sun et al., 1999). Meanwhile, chemical action and solubilization make sodium ions connect with phenolic hydroxyl and carboxyl groups of lignin by chemical bonds, forming phenolic sodium and carboxylate sodium groups (Guo et al., 2012). Similarly, Quyn et al. (2002, 2003) investigate the catalytic effects of alkali and alkaline earth metallic species on the pyrolysis and gasification of Victorian brown coal. They concluded that the Na loaded into coal substrate as NaCl and as sodium carboxylates ($-\text{COONa}$) can have very different catalytic effects on the char reactivity. Chen and Yang (1997) proposed a mechanism for alkali and alkaline earth catalyst gasification. They believed that the net charge of the edge carbon active site is substantially changed by gaining electron density from the alkali or alkaline earth element (by forming C-O-M, where M stands for metal). The relative catalytic activities of these elements can be correlated with their abilities of donating electrons and changing the net charge of the edge carbon atom. Based on these previous studies, the organic bound Na group in the chemical

* Corresponding author. Tel.: +86 02087057731; fax: +86 02087057737.

E-mail address: xylin@ms.giec.ac.cn (X.-l. Yin).

structure of alkali lignin can be considered as a key factor for converting it into value-added chemicals. Therefore, the effect of organic bound Na group on the distribution of pyrolysis products, especially phenols were studied in this paper. Meanwhile, the catalytic effects of organic bound Na groups on the steam gasification of residual char were investigated.

For this purpose, the different chemical forms Na loaded lignin was firstly prepared by different adding pattern (Guo et al., 2012). Secondly, the two chemical forms Na loaded lignin and pure lignin were pyrolyzed in thermogravimetric analyzer coupled with Fourier transform infrared spectrometry (TG-FTIR). TGA was adopted to keep a detailed recording of the mass loss data, and FTIR was used to obtain the evolution patterns of volatiles. Thirdly, these three lignin samples were pyrolyzed at 400, 500, 600, 700 and 800 °C in a tube furnace to obtain the pyrolysis products (residual char, condensable and incondensable products). Finally, the steam gasification experiments of residual chars were carried out on TGA at 800 °C to investigate the influence of the char forming temperature on the catalytic effect of this two chemical forms Na.

2. Experiment

2.1. Sample preparation

Pure alkali lignin sample was separated from the soda-AQ wheat straw black liquor by acid precipitation with 1 N H₂SO₄ 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.

Organic bound Na (Or-Na) loaded lignin sample was prepared by impregnating method. A known amount of L₁ was first added into a beaker. 0.1 mol/L NaOH solution was then added into the beaker, until L₁ completely dissolved. The process of addition needed to be as gradual and slow as possible in order to avoid loading excessive NaOH solution. Finally, the lignin solution was dried, and then the organic bound Na loaded lignin sample was obtained.

Inorganic bound Na (Inor-Na) loaded lignin sample was prepared by physical mixing. The addition amount of inorganic bound Na was in accord with organic bound Na.

3. Experimental methods

3.1. 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.

3.2. Pyrolysis experiment

Pyrolysis experiment was conducted in a tube furnace. 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, 500, 600, 700 and 800 °C, respectively. After the desired temperature was reached, the sample was rapidly moved into the furnace to pyrolysis. Each experiment was made at atmospheric pressure and at the desired temperatures ranging from 400 to 800 °C under approximately 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. The condensed liquid products were absorbed in the condenser. At the end of each experiment, the solid products (char) were allowed to cool to ambient temperature before being recovered.

3.3. Gasification experiment

The steam gasification reactivity of the char samples was investigated using a TGA (NETZSCH STA409C). The experimental procedures used to perform char gasification as follows: firstly, about 10 mg char sample was loaded into TGA; secondly, the temperature of TGA was increased from ambient temperature to 850 °C with a heating rate of 20 °C/min, under N₂ of a flow rate of 100 mL/min; finally, the steam was introduced into TGA at a flow rate of 200 mL/min at 850 °C, and then the reaction zone was kept at an isothermal temperature about 25 min for char gasification. Char conversion (x_t) of gasification stage was calculated using the following Eq. (1):

$$x_t = \frac{m_0 - m_t}{m_0 - m_{Na}} \quad (1)$$

where m_0 is the sample weight at the start of gasification; m_t is the weight at gasification time t ; m_{Na} is the weight of Na additives.

3.4. Analytical methods

3.4.1. Incondensable products analysis

The incondensable products released from each pyrolysis experiment were analyzed on a gas chromatograph (SHIMADZU GC-20B Japan) with a thermal conductivity detector (TCD). The C-RID area method was used to calculate the volume percentage of a gas component (V_i). According to Clapyron equation and chemical mole law, the producing gas ability of each sample were defined as following Eq. (2):

$$m_i = \frac{\frac{P}{RT} * V_0 * V_i * M_i}{m_0} \quad (2)$$

where m_i is defined as gas yield, it meant that the mass (mg) of a gas component releasing from per gram of sample; m_0 is the sample weight; V_0 is the total volume of gas products; M_i is the mole mass of a gas component; P is the gas pressure; R is the equilibrium constant of ideal gas; T is the gas temperature.

3.4.2. Condensable products analysis

The condensable products were dehydrated by anhydrous sodium sulfate, filtrated by Millipore filtration, and then detected on a GC/MS analyzer (HP5890 Series II, HP5971 detector, USA) operating in an electron ionization (EI, 70 eV) mode. The initial oven temperature was set to 40 °C (held 5 min) before increasing at 5 °C/min to 200 °C, and then heated up to 250 °C with 20 °C/min and kept it for 5 min. Carrier gas was the highest purity helium with a flow rate of 0.8 mL/min. The separated components were determined by the mass spectrogram of standard compounds, and the relative concentrations of specific compounds identified by the methods of areas of peak normalization.

Download English Version:

<https://daneshyari.com/en/article/7080110>

Download Persian Version:

<https://daneshyari.com/article/7080110>

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