



## Short Communication

# Thermogravimetric–Fourier transform infrared spectrometric analysis of CO<sub>2</sub> gasification of reed (*Phragmites australis*) kraft black liquor

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## ABSTRACT

CO<sub>2</sub> gasification of the reed (*Phragmites australis*) kraft black liquor (KBL) and its water-soluble lignin (WSL) was analyzed by thermogravimetry coupled with Fourier transform infrared spectrometry (TG–FTIR). In KBL gasification, major mass loss of KBL occurred between 150 and 1000 °C, followed by a further slow mass loss until the heating was stopped and the TG curve leveled off. The TG profiles of the WSL and the KBL were similar during gasification; however, the differential thermogravimetry (DTG) curves and mass decrease from 300 °C of the TG curves of the WSL and the KBL were different because of their dissimilar ingredients. The CO formation mechanism was the same and independent of structural types of lignins between reed and wood in their KBL CO<sub>2</sub> gasification.

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## 1. Introduction

With the depletion of fossil fuels and increasing concern for the environment, the use of biomass resources as a potential renewable energy source to substitute for fossil fuel resources has attracted attention (Silva et al., 2009; Frombo et al., 2009). Black liquor is a by-product from the kraft process, which is an alkali pulping process used to separate the fiber from non-wood or wood chips. The black liquor contains both inorganic and organic substances. It is an important fuel in paper manufacture, and provides about  $2.5 \times 10^9$  GJ per year worldwide, which is roughly one-half of the energy consumed by pulp and paper mills (Sutinen et al., 2002). Although the proportion of chemical pulp that is from non-wood sources has decreased gradually over time in China, the absolute yield of non-wood chemical pulp has increased. In 2008, 18% of pulp was from non-wood origin (10.9% of this pulp originated from straw, and 2.2% from reed (*Phragmites australis*) (Huang, 2009). Black liquor from non-wood is particularly difficult to recover and use for energy production because of its high viscosity arising from its high content of silica (Li, 2009). Black liquor gasification is an alternative to traditional methods for converting this waste into valuable fuel products (Sricharoenchaikul, 2009). The gasification of kraft black liquor (KBL) from wood has been investigated previously, and Gea et al. (2004, 2005) have discussed the kinetics of CO<sub>2</sub> gasification of alkaline black liquor from wheat

straw. However, the gasification characteristics of reed KBL have not been investigated to date. For industrialization of black liquor gasification in China, basic data is required from studies on the gasification of black liquor from non-wood chemical pulp.

Unlike gas chromatography, which provides discontinuous analysis, thermogravimetry coupled with Fourier transform infrared spectrometry (TG–FTIR) can be used for continuous measurement of the devolatilization of materials. TG–FTIR can be used to identify the major volatile species and the typical temperature ranges in which they are released (Biagini et al., 2006).

The objective of this work was to investigate the CO<sub>2</sub> gasification characteristics of reed KBL through analysis of the CO<sub>2</sub> gasification properties of lignin isolated from it.

## 2. Experimental

### 2.1. Samples

Reed KBL collected from a kraft pulp mill in Yiyang (Hunan Province, China) was dried by blast drying at 105 °C (0% water content) for analysis. The black liquor solid (6 g) was mixed with 80 mL of dioxane/deionized water (5:3 v/v) and heated at 87 °C for 2 h. The mixture was centrifuged for 10 min at 86 g and the supernatant was mixed with 50 mL of chloroform. The solution was left undisturbed for 10 min and separated into three layers (transparent, garnet and black layer). The black layer was collected and slowly evaporated under reduced pressure to a thick solution,

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**Table 1**  
Elemental and proximate analysis of water-soluble lignin and kraft black liquor (wt.%, dry basis).

Sample	Organic element analysis					Inorganic element analysis	Proximate analysis	
	N	C	S <sup>a</sup>	H	O <sup>b</sup>		Na	Ashes
WSL	0.07	40.47	0.65	4.31	54.50	19.38	19.07	54.06
KBL	0.04	32.46	0.23	6.43	60.84	23.50	39.20	49.96

<sup>a</sup> Organic sulfur.

<sup>b</sup> By difference.

which was dried with a spray dryer. This material was designated as the reed water-soluble lignin (WSL). The results of elemental and proximate analyses of the WSL and KBL are shown in Table 1.

## 2.2. <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) analysis

Solution-state <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using a Bruker DRX-400 spectrometer operating in Fourier transform mode at 74.5 MHz. For analysis, the lignin sample (20 mg for <sup>1</sup>H, 200 mg for <sup>13</sup>C) was dissolved in 1 mL of dimethyl sulfoxide-d<sub>6</sub> (99.8% D) at room temperature.

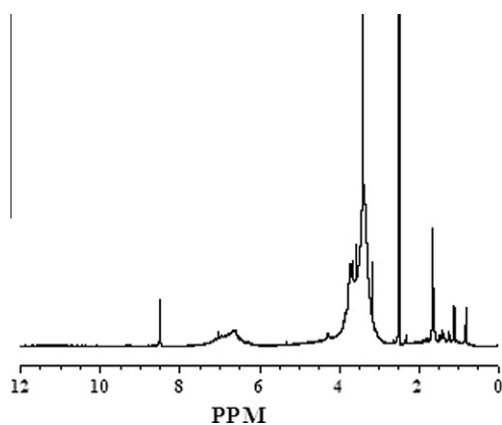
## 2.3. TG–FTIR analysis

CO<sub>2</sub> gasification of the KBL and WSL were tested on a Netzsch STA499C integration thermal analyzer. High purity N<sub>2</sub> and CO<sub>2</sub> were used as the protective and reactive gases at flow rates of 20 and 40 cm<sup>3</sup>/min, respectively. About 10 mg of the sample was heated from 40 to 1000 °C at 20 °C/min, and then held at this temperature for 1 h. The volatiles released in KBL and WSL gasification were detected online by a Bruker FTIR Tensor 27 spectrometer. FTIR spectra were recorded from 4000 to 400 cm<sup>-1</sup>. A blank test was carried out first to eliminate the buoyancy effect.

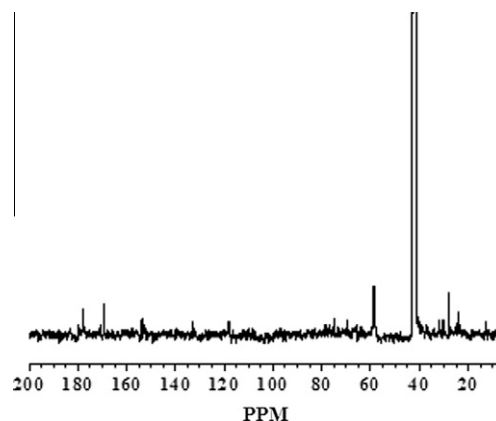
## 3. Results and discussion

### 3.1. Analysis of <sup>1</sup>H and <sup>13</sup>C spectra of WSL

The structural features of WSL were analyzed by <sup>1</sup>H NMR (Fig. 1) and <sup>13</sup>C NMR (Fig. 2). Based on available data (Faix, 1991; Xu et al., 2007; Yuan et al., 2009), assignments of most of the observed peaks in Figs. 1 and 2 are listed in Tables 2 and 3, respectively. The analyses showed that the WSL extracted from reed KBL contained guaiacyl, syringyl, and p-hydroxyphenyl units and hemicellulose impurities attached to the lignin.



**Fig. 1.** <sup>1</sup>H NMR spectra of water-soluble lignin.



**Fig. 2.** <sup>13</sup>C NMR spectra of water-soluble lignin.

### 3.2. Analysis of TG and differential thermogravimetric (DTG) curves from KBL to WSL

TG and DTG curves were obtained for KBL (Fig. 3(a)) and WSL (Fig. 3(b)) gasification under CO<sub>2</sub>.

The TG and DTG curves of the KBL (Fig. 3(a)) showed that thermal reaction occurred over a wide temperature range, and started at approximately 150 °C. Three large and two small peaks in the DTG profiles (Fig. 3(a)) indicated that different reactions occurred at distinct times during heating of the samples. At <500 °C, the main reactions were depolymerization of hemicellulose and lignin in the KBL, which corresponded to the first and second peaks in the DTG curve, respectively (Guo et al., 2006). A very small peak appeared in the DTG curve at 500 °C, which is indicative of mass loss by vaporization of sodium (Sams and Shadman, 1986; Li and van Heiningen, 1986). A second weak peak at 650 °C in the DTG curve showed that mass loss occurred through reduction of Na<sub>2</sub>SO<sub>4</sub> by carbon and CO (Li, 1989). When the temperature reached 840 °C, a large peak was observed in the DTG curve, which was a result of a fast chemical reaction between the reduced Na<sub>2</sub>CO<sub>3</sub>–carbon complex and CO<sub>2</sub> (Sams and Shadman, 1986; Cerfontain et al., 1987) occurred over a wide temperature range starting at approximately 150 °C. Both the WSL and KBL showed major mass loss during gasification between 150 and 1000 °C, and further slow mass loss until the heating of the sample was complete. The mass decrease from 300 °C was different for WSL and KBL because the black liquor is a complicated mixture containing lignin, hemicellulose, fatty acid, resin, sodium, etc. (Xie and Zhan, 2001) whereas, the WSL was not as complex. In the DTG curves, a weak peak was observed at 500 °C for the WSL (Fig. 3(b)) but not the KBL (Fig. 3(a)), which could result from different components of the two samples.

**Table 2**  
Analysis of <sup>1</sup>H NMR spectrogram of water-soluble lignin.

Shift δ (ppm)	Assignments
0.8–1.7	H in aliphatic groups in the side chains of lignin
2.5	DMSO
3.2	H in water in DMSO
3.4	H in methoxyl
4.3	H <sub>γ</sub> attached to carbons involved in aryl-ether bonds or hydroxyl bonds
5.3	H <sub>β</sub> in condensed structures and/or H <sub>α</sub> in phenyl coumaran structures
6.7–6.8 and 7.0	Ar–H in syringyl and guaiacyl units
8.5	H in phenolic hydroxyl

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