



## Effect of tetrahydrofuran extraction on lignite pyrolysis under nitrogen



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### ARTICLE INFO

#### Article history:

Received 12 August 2014  
Received in revised form 3 February 2015  
Accepted 4 February 2015  
Available online 7 February 2015

#### Keywords:

Lignite  
Tetrahydrofuran extraction  
Pyrolysis  
Tar  
GC  
NMR

### ABSTRACT

Based on the host-guest model of coal, the fixed and mobile phase of coal which can be separated by solvent extraction will present different characteristics during thermal conversion. The pyrolysis of Xilin-guole and Huolinhe lignites and their extraction residues with tetrahydrofuran were investigated at 450–700 °C under N<sub>2</sub> atmosphere. The results indicate that the temperature at the maximum tar yield of extraction residue is lower than that of coal. Compared with raw coal, residue pyrolysis process exhibits lower water yield, higher gas yield and similar char yield. Similar H<sub>2</sub> yield, more CO and CO<sub>2</sub> yields but less CH<sub>4</sub> yield are obtained during residue pyrolysis than those in coal pyrolysis. GC analysis of tar shows that contents of phenols and mononuclear aromatics from residue tar are higher than those from raw coal tar. <sup>1</sup>H NMR and <sup>13</sup>C NMR of tar indicate that the tar from residue has higher aromaticity factor than that from coal. The total acidity and acid distribution in raw coal, extraction residue and their chars obtained at 600 °C show that phenolic –OH is the main oxygen contained group in extract. The activity of O in coal could be improved by extraction, and more O will be translated to –OH during pyrolysis.

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### 1. Introduction

Coal provides around 30% of global primary energy needs, generates 41% of the world's electricity and is used in the production of 70% of the world's steel in 2013 [1]. It will still be an important energy resource in the foreseeable future, especially in China. Lignite which accounts for about 12% of China's total coal resource will also be an important resource even if its high moisture and low heating value. As the basis of the coal utilization and lignite upgrading, pyrolysis has been investigated for a long time, nevertheless, it is still difficult to accurately describe the pyrolysis process because of the complicated structure of coal. In order to describe the coal structure, many structure models were built and two phases structure concept of coal was gradually recognized since 1980s [2]. It was thought that the organic matters in coal could be divided into two parts: mobile phase and fixed phase. Only the mobile phase and the peripheral parts of the macromolecular structure (comprising mainly of the polycyclic aliphatic substances) could be decomposed during pyrolysis [3]. Therefore, it is necessary to study the effect of different parts during coal pyrolysis to understand the mechanism of coal pyrolysis.

Besides significant differences between mobile phase and fixed phase in structure and composition, there are also many different non-covalent bonds (hydrogen bond, charge-transfer interaction,  $\pi$ - $\pi$  interaction) [4–6] and weak covalent bonds (ether bond, ester bond) [7,8] which play an important role in combination among organic structure units. Their existence also results in the complex reactivity during coal pyrolysis. Hydrogen bonds, especially self-associated OH and OH- $\pi$  hydrogen bonds are considered to be the main non-covalent components in lignite [9]. Miura et al. [10] found seven –OH Gaussian distribution absorption peaks using FT-IR by a curve-resolving method. These –OH absorption bands mainly consisted of free OH groups, OH- $\pi$  hydrogen bonds, self-associated OH, OH-ether O hydrogen bonds, tightly bound cyclic OH tetramers, OH-N hydrogen bond (acid/base structures) and COOH dimers. Chen et al. [11] studied the thermal stability of these hydrogen bonds by in-situ pyrolysis FT-IR, and found that the thermal stability of hydrogen bonds followed the order of OH- $\pi$  < OH-N < self-associated OH  $\approx$  cycle OH tetramers < OH-ether O. It was reported that solvent extraction could break the non-covalent bonds and weak covalent bonds during extraction, and the mobile phase and fixed phase could be effectively separated [12]. Therefore, the effect of non-covalent bonds and weak covalent bonds during pyrolysis can be investigated by solvent extraction pretreatment.

In this paper, tetrahydrofuran (THF) was used as solvent, and two Chinese lignites from Inner Mongolia Autonomous Region,

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Xilinguole lignite (XLGL) and Huolinghe lignite (HLH), were chosen as coal samples. The pyrolysis experiments of raw coals and their extraction residues (XLGL-R and HLH-R) were carried out on the fixed-bed reactor at 450–700 °C under N<sub>2</sub> atmosphere. The pyrolysis gas was analyzed by GC and the tar was analyzed by GC and <sup>1</sup>H and <sup>13</sup>C NMR techniques.

## 2. Experimental and equipment

### 2.1. Materials and extraction process

The lignite sample was pulverized to pass through the 100 mesh sieve followed by desiccation in a vacuum oven at 80 °C for 24 h prior to the experiments. THF was selected as extraction solvent and purified by distillation before use. About 100 g coal and 500 mL fresh THF were placed into a 1000 mL conical flask and extracted about 2 h under stirring at room temperature followed by suction filtration. The filter cake was returned to conical flask and added another 500 mL fresh THF for extraction. The total extraction time was more than 100 h to ensure a complete extraction. Because of the miscibility of THF and water, the solution was dehydrated by anhydrous CaCl<sub>2</sub> and condensed by rotary evaporator after filtration. Extract (XLGL-E and HLH-E) was obtained after drying condensed solution to constant weight in the vacuum drying oven at 60 °C. The extraction yield was defined as the percentage of extract weight to coal weight in dry and ash-free basis (daf). The extraction yield of XLGL and HLH are 1.73% and 5.09%, respectively. The proximate and ultimate analyses of samples are shown in Table 1, which were measured by SUNDY SDTGA5000 industrial analyzer and Vario EL III elemental analyzer, respectively.

### 2.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA851<sup>e</sup> analyzer. During experiments, about 15 mg sample was placed in a ceramic crucible and heated from 25 °C to 850 °C with a heating rate of 10 °C/min under N<sub>2</sub> atmosphere. Because of high volatilization of the extract, only 5 mg sample was used during TGA of the extract.

### 2.3. Pyrolysis process

Pyrolysis experiments were carried out in a fixed-bed reactor and the schematic diagram of reactor was shown in the reference [13]. About 5 g sample placed in the center of the reactor was heated to the desired temperature by the preheated furnace, and N<sub>2</sub> with a flow rate of 300 mL/min was used as carrier gas. The total pyrolysis time was 40 min and N<sub>2</sub> was stopped when the reactor temperature dropped below 100 °C. The char was removed from the reactor and weighted after the experiment. The liquid products (tar plus water) collected by a cold trap were separated into tar and water by the method of ASTM D95-05<sup>e1</sup> (2005) after the experiment. The yields

of tar, water, char and gas in dry basis of lignite or residue sample are calculated by the following equations:

$$Y_{\text{tar}} = \frac{W_{\text{tar}}}{W_d} \times 100\%$$

$$Y_{\text{water}} = \frac{W_{\text{water}} - W_{\text{ad}} \times M_{\text{ad}}}{W_d} \times 100\%$$

$$Y_{\text{char}} = \frac{W_{\text{char}}}{W_d} \times 100\%$$

$$Y_{\text{gas}} = 100 - Y_{\text{tar}} - Y_{\text{water}} - Y_{\text{char}}$$

where *Y* is the yield of products, *W*<sub>tar</sub>, *W*<sub>water</sub>, and *W*<sub>char</sub> are the weight of tar, water and char obtained during pyrolysis, *W*<sub>d</sub> is the weight of coal sample on the dry basis (*d*), *W*<sub>ad</sub> is the weight of coal sample on the air dry basis (*ad*).

### 2.4. Analysis of products

A TECHCOMP GC7890 II was used for gas analysis. A thermal conductivity detector (TCD) coupled with a 5A molecular sieve column was used to analyze H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and CO, and a flame ionization detector (FID) coupled with GDX-502 column was used to analyze CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>.

A SHIMADZU GC-2014 was used for the analysis of tar. The BPX-5 (methylsiloxane, 25m × 0.32 mm × 0.25 μm) capillary column coupled with the FID was used to analyze tar sample and N<sub>2</sub> was used as carrier gas with 2 mL/min. The operating conditions were injection port temperature, 280 °C; interface temperature, 280 °C; column oven temperature, 50 °C for 5 min, ramped at 3 °C/min to 110 °C with a 5 min hold, followed by 2 °C/min to 190 °C with a 5 min hold, and then 1 °C/min to 220 °C with a 30 min hold. Because not all macromolecules in tar can be detected by GC or GC-MS, 63 kinds of standard materials including aliphatics, aromatics, phenols and oxygen heterocyclic compounds (such as phenol, toluene, methyl-naphthalene, acenaphthene, C12–C28 aliphatics) with relatively high content in tar were used as external standards to determine their contents in tar. Prior to GC analysis, the tar sample was dissolved in CH<sub>2</sub>Cl<sub>2</sub> followed by dehydration and desalination.

<sup>1</sup>H NMR and <sup>13</sup>C NMR analyses of tar were performed on a Bruker Avance II 400M. Na<sub>2</sub>SO<sub>4</sub> was added into the tar sample dissolved in CH<sub>2</sub>Cl<sub>2</sub> to remove the water via stir and filtration, and the solvent was removed by rotary evaporation, then the tar sample was dissolved in CDCl<sub>3</sub> before analysis; the extract was dissolved in deuterated methanol (CD<sub>3</sub>OD) because the solubility of extract in CDCl<sub>3</sub> is lower than that in CD<sub>3</sub>OD. TMS was used as internal standard substance. The total acidity and acid distribution in the lignite and residue samples were determined by a modified Schafer method [14,15].

## 3. Results and discussion

### 3.1. TG/DTG analysis of coal, residue and extract

TG/DTG curves of XLGL, HLH, their extraction residues (XLGL-R and HLH-R) and extracts (XLGL-E and HLH-E) are shown in Fig. 1. It can be seen that slight difference between residues and raw coals exists below 200 °C, which is ascribed to the different moisture contents of coal and residue. But almost similar weight loss curves were obtained at high temperature, which may be attributed to no significant change of volatiles content after extraction by THF. However, the weight loss of their extract is different from the raw coals and there are three significant weight loss peaks. Take XLGL-E as sample; the first weight loss occurs below 120 °C, which is

**Table 1**  
Proximate and ultimate analyses of the samples.

Sample	Proximate analysis (wt.%)			Ultimate analysis (wt.%, daf)				
	<i>M</i> <sub>ad</sub>	<i>A</i> <sub>d</sub>	<i>V</i> <sub>daf</sub>	C	H	N	S	O <sup>a</sup>
XLGL	5.42	15.60	40.91	61.28	3.98	0.70	0.80	33.24
XLGL-R	0.21	15.76	40.76	61.67	3.78	0.70	0.85	33.00
HLH	5.07	9.01	43.67	66.89	4.50	1.25	0.26	27.10
HLH-R	3.69	9.06	43.41	67.39	4.66	1.17	0.26	26.52

*M*<sub>ad</sub> is the moisture content in air dry basis; *A*<sub>d</sub> is the ash content in dry basis; *V*<sub>daf</sub> is the volatile matter in dry ash-free basis.

<sup>a</sup> By difference.

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