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# Effect of pyrolysis temperature on lignite char properties and slurrying ability



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#### ARTICLE INFO

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Keywords: Lignite Pyrolysis Lignite char-water slurry Slurrying ability Functional group Pore structure This work investigates the influence of different pyrolysis temperatures in lignite char properties and slurrying ability. Baorixile lignite was pyrolyzed under nitrogen atmosphere from low to high temperatures. The pyrolyzed chars were then used in preparing lignite char–water slurry fuels. The apparent viscosities and rheological behaviors of different slurries were obtained by using a rotating viscometer. Pyrolysis can effectively improve lignite char–water slurry concentration, and the influence of such mechanism can be determined by analyzing oxygen-containing functional groups and pore structures. Result suggests that pyrolysis not only removes the moisture content but also causes an apparent increase in lignite coal rank. Pyrolysis also evidently reduces the number of oxygen-containing functional groups and the hydrophilicity of lignite char, consequently improving slurry concentration but decreasing slurry static stability. The pore structure of the lignite char changes significantly after pyrolysis. With increasing pyrolysis temperature, average pore diameter initially decreases and eventually increases, whereas specific surface area and pore volume exhibit an opposite trend. Experimental results reveal that the slurry concentration of lignite char does not increase monotonically with the increase of pyrolysis temperature and 600 °C–800 °C is the most suitable pyrolysis temperature range for lignite slurrying ability improvement. © 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Coal water slurry (CWS), as a fuel derived from coal, consists of 60%– 70% coal, 29%–39% water, and ~1% additives. This fuel was first developed as an oil replacement for slurry combustion during the energy crisis in the 1980s. Since then, CWS has been widely used in combustion and gasification process. With the rapid development of integrated gasification in combined cycle (IGCC) and coal gasification in the recent years, CWS fuel has been recognized as an important fuel for high-pressure gasifier with high energy efficiency. CWS feedstocks have been extended from bituminous coal to petroleum coke [1] and lignite [2] because of the short supply of high-rank coal. Given its high pore volume and high moisture content, it was extremely challenging for lignite to produce highly concentrated CWS fuel. Thus, the use of low-rank coal, which has abundant reserves accounting for approximately 53% of the global total coal reserve, has attracted the attention of researchers around the world.

Various lignite upgrading technologies have been reported in the literature [3–5]. Lignite is characterized by having an enriched volatile matter content; a high H/C ratio; a large amount of carboxyl groups, carbonyl groups, and methylene; and a positive reactive behavior. As such, lignite is highly reactive during pyrolysis. Pyrolysis has been widely investigated as a thermal treatment upgrading method that can upgrade lignite quality in terms of heat value, stability, and moisture absorption [6–8]. After being pyrolyzed, lignite can be converted into liquid, gas, and solid products. Kaji et al. [9] found that after pyrolysis at 400 °C, the water-holding capacity of lignite char decreased by more than two-thirds compared to that of raw lignite. Previous studies indicate that pyrolysis can increase specific surface area [10] and reduce oxygen content [11], which is preferable for making high-concentration lignite char-water slurry (LCWS). Fan et al. [12] investigated the additive effects on slurrying activity and pointed that lignite char-water slurrying ability is considerably higher than that of raw coal. However, most of the coal pyrolyses were conducted at a low or moderate temperature range [13,14], lacking the understanding of high temperature pyrolyzed char properties. The primary aim of this work is to investigate the effect of the pyrolysis temperature, from low to high range, on slurrying ability of lignite char by using selected additives as dispersant and stabilizer to gain insight into the global comprehensive utilization of lignite.

Baorixile (BRXL), a typical lignite with total water concentration of 25.68% from Inner Mongolia, where it is one of the largest reserve areas of lignite in China, was studied in this article. Pyrolysis was performed in the absence of oxygen and at a temperature ranging from 400 °C to 1000 °C. The influence of different pyrolysis temperatures on LCWS

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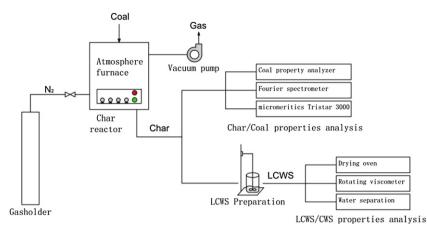


Fig. 1. Schematic diagram of the experimental setup.

properties, including slurry concentration, rheological behavior, and stability, was investigated.

#### 2. Material and methods

#### 2.1. Experimental setup

As Fig. 1 shows, the experimental setup, which consists of a char reactor with power supply, a LCWS preparation process, and two analysis systems, namely, char/coal property analysis system and LCWS/CWS property analysis system. BRXL was first pyrolyzed in a nitrogen atmosphere furnace at different temperatures. Char properties, involving proximate and ultimate analyses, functional groups, and physical structures were tested accordingly. Pyrolyzed chars were made into LCWS, whose solid loading, rheological behavior, and static stability were evaluated with the use of the LCWS/CWS property analysis system.

#### 2.2. Material

In the experiment, air-dried raw coal was milled to particles of less than 75 µm to ensure the thoroughness of pyrolysis and the homogeneity of the lignite char. As the moisture content is one of the main challenges in the preparation of high-concentration LCWS, coal was oven-dried at 105 °C for 2 h; the slurrying abilities of which were then compared with that of the pyrolyzed lignite chars. Results of the proximate and ultimate analyses of raw coal and oven-dried coal are listed in Tables 1 and 2.

#### 2.3. Methods

#### 2.3.1. Pyrolysis process

Pyrolysis experiments were conducted in a controlled atmosphere furnace (HMX1700-30). The temperature ranged from 400  $^\circ\text{C-}$ 

Table 1
Proximate and ultimate analyses of coal and different temperature pyrolyzed chars.

1000 °C, with an interval of 100 °C at a heating rate of 10 °C/min and an isothermal treatment of 30 min. Approximately 300 g of raw coal powder was paved in a ceramic container under N<sub>2</sub> gas environment. After a complete purging process by N<sub>2</sub> gas, a sufficient amount of N<sub>2</sub> was fed into the furnace until a tiny positive pressure was achieved to guarantee an inert atmosphere.

#### 2.3.2. Lignite char-water slurry preparation

The LCWS was prepared as follows. First, the required masses of char/coal powder, deionized water, and additives were calculated and weighed in predetermined ratios. A copolymer of methylene naphthalene, sulfonate styrene, and sulfonate maleate (an NDF additive) was adopted as a dispersant and a stabilizer in this experiment. The abovementioned dispersant accounted for 0.8% of the weight of the char/coal samples. The coal/char powder was gradually added into the dispersant solution under low speed agitation of 200 rpm. The solution was then stirred at 1000 rpm for 20 min to ensure that the dispersant solution with coal/char powder is mixed well. During the preparation of LCWS/CWS, the temperature was maintained at 25 °C–30 °C.

#### 2.3.3. Physicochemical characterization of lignite char

Functional group analyses of raw/dried coal and lignite chars were performed on a Nicolet 6700 Fourier transform infrared (FTIR) spectrometer. During the test, KBr pellets were prepared by grinding 2.5 mg of specimens with 200 mg of KBr. The FTIR spectra of the specimens for the 4000 cm<sup>-1</sup>–400 cm<sup>-1</sup> region were studied by curve-fitting analysis.

The pore structure of raw coal and lignite chars was determined by using an automatic surface area and a porosity analyzer (TriStar 3000, MicroMeritics). The samples were kept under 200 °C in a vacuum for 3 h to remove the contaminants inside the pore structures. Then, a 0.5 g sample was retained in liquid nitrogen for analysis. The pore structure properties were assessed during nitrogen absorption and separation

Specimen	Proximate analysis (%)				$Q_{net,ad}$ (J/g)	Ultimate analysis (%, ad)				
	M <sub>ad</sub>	A <sub>d</sub>	$VM_d$	FCd		С	Н	Ν	St	0
Raw coal	8.68	10.50	37.89	51.61	22,989	60.06	3.38	0.59	0.11	17.59
400 °C char	1.41	12.05	25.60	62.35	27,278	70.25	3.51	0.91	0.19	11.85
500 °C char	1.76	13.63	15.61	70.76	29,000	75.55	2.93	1.03	0.18	5.16
600 °C char	1.00	14.90	7.17	77.93	29,891	80.02	1.22	0.80	0.19	2.02
700 °C char	1.04	15.46	3.64	80.89	29,702	80.60	2.00	0.91	0.20	0
800 °C char	0.66	16.03	2.09	81.88	28,930	82.01	0.56	0.59	0.18	0.08
900 °C char	0.52	16.52	1.65	81.84	28,825	82.30	0.17	0.60	0.18	0
1000 °C char	0.62	16.74	1.31	81.95	28,639	82.50	0	0.46	0.17	0

Note: ar = as received. ad = air dry basis. d = dry basis. M = moisture content. A = ash content. V = volatile matter. FC = fixed carbon.

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