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Influence of heating rate on reactivity and surface chemistry of chars derived from pyrolysis of two Chinese low rank coals

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ABSTRACT

A series of char samples were derived from pyrolysis of two typical low-rank coals in China (Shengli lignite and Shenmu bituminous coal) at low, medium and fast heating rates, respectively, to the same pyrolysis temperature 750 °C. Then these chars were characterized by means of thermogravimetric analysis and Fourier transform infrared spectrometer with the aim to investigate the influence of heating rate in pyrolysis process on gasification reactivity and surface chemistry of them. Besides, a homogeneous model was used to quantitatively analyze the activation energy of gasification reaction. The results reveal that Shengli lignite and its derived chars behave higher gasification reactivity and have less content of oxygen functional groups than Shenmu coal and chars. Meanwhile, chars derived from Shengli lignite at 50 °C/min and Shenmu coal at 200 °C/min have the greatest gasification reactivity, respectively. The oxygen functional groups in Shengli lignite are easily thermo-decomposed, and they are less affected by the heating rate, while that in Shenmu coal have a significant change with the variation of heating rate. In addition, there is no good correlation between the change of oxygen functional groups and that of the gasification reactivity of the derived chars from pyrolysis at different heating rates.

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1. Introduction

China has the third largest coal reserves in the world, and low rank coal, including lignite and low rank bituminous coals, accounts for more than 55% of the proven reserves [1,2]. Low rank coal has more side chains in chemical structure, with high hydrogen and oxygen content, resulting in its high volatile content, water content, easy oxidation, low calorific value, inconvenience for storage and long-distance transport [3,4]. In accordance to the characteristics of low rank coals, it has been an established technology to utilize low rank coal efficiently by pyrolysis-based poly-generation in China [5,6], which results in a large number of solid products. Meanwhile, several technologies have been developed and used to upgrade the low rank coals, the productivity of char from these processes is generally more than 50%.

As concerned as the gasification, low rank coals are often used as feedstock for entrained flow gasification. It is a common knowledge that coal particles experience the pyrolysis process before they contact with the gasification agent during the coal gasification. In other words, pyrolysis can be considered as the initial stage of thermal conversion process of coal and the coinstantaneous processes of gasification reaction [7,8]. Thus, the composition, structure, and surface chemistry of solid product derived from pyrolysis have great influence on the subsequent gasification process [9–11]. Consequently, it is self-evident that how to get the char with higher reactivity from pyrolysis of low rank coal become the key to efficient utilization of low rank coal.

Low rank coal and its derived char, which are important gasification materials, have high chemical reactivity. Coal gasification is the core technology of clean and efficient coal utilization, the leading in modern coal chemical industry, the basis of integrated gasification combined cycle power generation, multi-generation systems and other process industries [12,13]. As coal gasification technology has been progressed from the traditional fixed-bed gasification using coarse coal as feedstock to entrained flow gasification process using pulverized coal in dry state or coal-water slurry, the period of coal pyrolysis stage is becoming shorter and shorter, which means that the heating rate in pyrolysis prior to gasification becomes faster. So far, extensive researches on char reactivity have been conducted, in which the effect of temperature on char was the primary factor and aroused wide attention. Cetin et al. found that at a higher final temperature, a faster pyrolysis will increase coal's fluidity in the process, thereby reducing the resistance of gas escaping, making char a developed pore structure which is in favor of gasification reaction [14]. Cai et al. studied the

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effect of temperature and heating rate on coal reactivity with the aid of screen-reactor, drawing a conclusion that at the 1500 °C, it is proportional to the relationship between the reactivity and heating rate when the heating rate exceeds 1000 K/s [15]. Jayaraman et al. investigated the pyrolysis of high-ash coal with different heating rates at temperatures less than 1000 °C, presuming that specific surface area of the char and production rate of light gases, such as CO_2 and H_2, are proportional to heating rate [16]. So far, studies mentioned above are operated in a tube furnace, thermal gravimetric analyzer or screen reactor, and dropper furnace either at slow (≤20 °C/min) or ultra fast (≥1000 °C/min) heating rates, in which heating rate could not be controlled precisely [17,18]. However, the actual temperature rise of coal particles in commercial reactors, including fixed bed, fluidized bed and entrained bed, covers in the range of 20–1000 °C/min. Therefore, it is necessary to study the variation of the reactivity of char derived from pyrolysis of low rank coal in a broader range of heating rates, especially similar to practical operating condition, in order to better understand the effect of heating rate on gasification reactivity of the derived char and improve the efficiency of low rank coal's utilization.

Two typical low rank coals, Shengli lignite and Shenmu bituminous coal, were sampled and investigated in this study. These coal samples were prepared and then were pyrolyzed under slow (≤50 °C/min), medium and fast (100–750 °C/min) heating rates at the ending temperature of 750 °C. Then the derived chars were characterized by means of themogravimetric analysis (TGA) and Fourier transform infrared spectrometer (FT-IR) with the aim to investigate the influence of heating rate of pyrolysis process on the gasification reactivity and surface chemistry of the derived chars, and to better understand the effect of heating rate on the gasification characteristics of chars under conditions similar to those used in the modern coal chemical industry.

2. Materials and methods

2.1. Materials

Two coal samples were used in this study, one is lignite (Shengli lignite, SL, hereinafter), the other is bituminous coal (Shenmu bituminous coal, SM). Samples were collected by method of coning and quartering. The raw coals were ground in a mill, air-dried at room temperature, and then sieved to the particle size less than 74 μm. According to Chinese standards for coal analyses (GB/T 212 and GB/T 476), proximate analysis and ultimate analysis of the coal samples were preformed and the results are illustrated in Table 1.

2.2. Preparation of chars

Preparation of chars at low heating rates: weighing about 2 g of the coal sample in a quartz boat, then the boat was placed in a high temperature steel pipe of the tube furnace (R50/250/12 model, Nabertherm company, Germany). Prior to pyrolysis high purity nitrogen was introduced to the pipe for 10 min so that the air inside was discharged. The chars were produced at heating rates of 5 °C/min, 10 °C/min, 15 °C/min and 50 °C/min, respectively, to 750 °C in nitrogen ambience and then holding for 10 min before stopping heating insulation. After pyrolysis, the chars were cooled to ambient temperature in nitrogen atmosphere. The untreated Shengli lignite and Shenmu bituminous coal were marked as SL0 and SM0. The char of the parent coal was marked as combined abbreviation of coal sample and heating rate, for instance, SL5 means the char was obtained by pyrolysis of Shengli coal at heating rate of 5 °C/min to 750 °C and then holding for 10 min.

Preparation of chars at medium and fast heating rates: a special device, named mobile-lab, designed and manufactured by Tangshan Nayuan Microwave Thermal Instrument Co (China), was exploited to heat the coal sample at fast heating rates. With a thermo-transforming cavity which can absorb microwave and convert it to heating energy, the device can control the heating rate in a considerable range from 5 °C/min to 1000 °C/min, theoretically. The power of the device is distinctly at different heating rates. The power of the device is up to 12 KW at fast heating rates, while the power of the device is 2 kW at stable temperature phase. Weighing about 0.5 g of the sample in a quartz crucible with lid, and the crucible was placed in the cavity. Using the heating rates of 100 °C/min, 200 °C/min, 350 °C/min, 500 °C/min, 750 °C/min rise to 750 °C and then holding for 10 min before stopping heating insulation. After pyrolysis, chars were cooled to ambient temperature. The chars were also marked by the labelling method mentioned above.

2.3. Thermogravimetric analysis

In non-isothermal experiment, thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were conducted to understand gasification properties of the low rank coal and the derived chars. Themogravimetric experiments on the samples were carried out with a Pyris 1 thermogravimetric analyzer (PerkinElmer). About 10 mg of sample was spread evenly on a platinum crucible and heated at 5 °C/min to 1100 °C under a continuous carbon dioxide flow of 30 mL/min. According to the Eq. (1), carbon conversion rate x in terms of the sample weight loss can be obtained:

$$x = \frac{w_0 - w_t}{w_0 - w_\infty} \times 100\% \tag{1}$$

where w_0, w_t and w_∞ represent the initial weight of sample, the instantaneous weight at gasification time of t and final weight after gasification completely, respectively.

2.4. Kinetic model

Homogeneous model (HM) is the simplest and the most commonly used to analyze gasification reaction. It is assumed that the reaction occurs within the entire solid particles. With the reaction carried through, the size of solid particles remains the same, but the density of grain varied in uniform [19,20]. Combined with Arrhenius equation, the simplified dynamic Eq. (2) is obtained from CO_2 gasification reaction of coal (char):

$$\frac{dx}{dT} = \frac{A}{\beta}\exp(-\frac{E}{RT})(1-x)^n \tag{2}$$

Table 1
Proximate and ultimate analysis of coal samples (wt%).

Sample	Proximate analysis				Ultimate analysis				
	M_{ad}	A_d	V_{daf}	FC_{daf}	C_{daf}	H_{daf}	O_{daf*}	N_{daf}	$S_{t,d}$
SL	28.80	17.32	44.13	55.87	74.96	12.72	9.43	1.48	1.19
SM	7.29	9.66	38.54	61.46	80.35	7.06	10.63	1.38	0.53

Note: *M*: moisture; *A*: ash; *V*: volatile matter; *FC*: fixed carbon; ad: air dry basis; d: dry basis; daf: dry ash free; t: total; diff.: by difference.

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