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Effect of low-temperature pyrolysis on surface properties of sub-bituminous coal sample and its relationship to flotation response

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ABSTRACT

Coal spontaneous combustion makes coal suffer a high-temperature heating process (similar to a low-temperature pyrolysis). Additionally, low rank coal is considered to be friendly utilized through two steps, i.e. low-temperature pyrolysis of low rank coal to gain gas/liquid components and then coal char forwarded to the burning or other chemical applications. Therefore, it is necessary to investigate the effect of low-temperature pyrolysis on the surface properties of low rank coal and its role in the floatability of coal particles because coal already suffering spontaneous combustion should be upgraded before usage. In this investigation, SEM, XPS, attachment time and flotation tests were employed to reveal the changes of surface properties and floatability of sub-bituminous coal before and after the pyrolysis. After the pyrolysis, a significant mass loss was observed and many pores/cracks were newly created as well as the content of hydrophobic functional groups on coal surface was increased whereas the content of hydrophilic oxygen-containing functional groups was reduced. The attachment time of coal-bubble was significantly decreased after the pyrolysis, which directly made an increase in the hydrophobicity and floatability of sub-bituminous coal. The findings of this paper may be useful for a better use of sub-bituminous coal resources because sub-bituminous coal is well known as difficult to float and sub-bituminous coal fines are usually wasted in coal preparation plants. This paper proposes that coal char from sub-bituminous coal may be forwarded to a further upgrading process (i.e. flotation) because the floatability of sub-bituminous coal is significantly improved by the pyrolysis.

1. Introduction

Coal is a matter consisting of organic and inorganic components. Nowadays, coal is usually utilized as energy resources and chemical raw materials. Even though new energy and oil/gas are becoming more popular today, coal still plays an important role in energy supply in many countries, such as China [1], Turkey [2], Australia [3] and the US [4]. For chemical applications, coal is widely used to produce formaldehyde, activated carbon and etc [5–7]. In general, the upgrading and beneficiation processes are required to improve coal quality prior to the utilization of coal, such as burning, gasification, and liquefaction. The common beneficiation methods for coal include gravity separation, flotation, screening, etc.

Because coal consist of organic matters, coal oxidation usually occurs accompany the mining processes of coal. The oxidation processes usually release plenty of heat which makes coal mine/piles suffer a spontaneous combustion [8]. As is known, coal spontaneous combustion makes coal bear a high-temperature heating process. To some extent, this high-temperature heating process is similar to a low-temperature pyrolysis with the heating temperature of 500–700 °C [9]. If a coal mine suffered a spontaneous combustion, the properties of coal will be significantly changed. Among these changes in coal properties, the surface hydrophobicity of coal is the most important issue which determines the flotation cleaning of fine coal particles in coal preparation plants. Chinese coal fires are mainly distributed in Inner Mongolia, Xinjiang, Ningxia, Shanxi, etc. There are over 30 km^2 of coal fire area in China [10]. The properties of coal particles from the coal fire area are different from the conventional coals. For example, a part of raw coal for Ningxia Taixi coal preparation plant supplied from coal fire area that after artificial fire-extinguishing is treated as waste, which is not reasonable for coal resource saving [11]. It is necessary to investigate how to upgrade the coal fines already suffering the spontaneous combustion or the high-temperature heating process. It has been partially reported that the surface wettabilities of bituminous and anthracite coals are increased after the heating process while the surface wettability of lignite is reduced [12,13]. However, there is little

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attention already paid to combine the changes in the surface properties to the changes in the hydrophobicity and floatability of coal particles to date.

Furthermore, a recommended usage of low rank coal in energy supply is considered as the two-step utilization. In the two-step usage, low rank coal is first treated under a low-temperature pyrolysis to gain gas/liquid components and then coal char is forwarded to the burning or other chemical applications [14]. After the pyrolysis process, the ash content of low rank coal will be increased and hence affects the burning application [15,16]. How about forwarding the heated low rank coal to beneficiation processes?

As is known, the primary beneficiation processes are gravity separation and flotation based on the difference in the density and the surface hydrophobicity, respectively [17]. Traditionally, low rank coal is difficult to float using the common oily collectors, such as diesel and kerosene [18,19]. However, the surface properties of low rank coal will be significantly changed after the pyrolysis and hence the surface hydrophobicity of coal is also varied. In our previous studies, the wettability of lignite surface was reduced after a high-temperature heating process in quartz crucibles whose atmosphere is a lack of oxygen. It meant the surface hydrophobicity of lignite was enhanced after the heating process [20]. However, little attention was paid to a comprehensive study into the relationship between the physical/chemical properties and the hydrophobicity/floatability of coal particle before and after the heating process as well as the low-temperature pyrolysis.

Therefore, the purpose of this paper was to investigate the effect of low-temperature pyrolysis on the surface properties of sub-bituminous coal and its role in the flotation behavior. A comprehensive study, including scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), induction time and flotation tests, was carried out to reveal the fundamental and applied aspects regarding the surface properties and the floatability of sub-bituminous coal particle before and after the low-temperature pyrolysis.

2. Experimental

2.1. Coal samples

Low-density sub-bituminous lump coal particles were selected crushed, screened to obtain < 0.5 mm size fraction as final coal samples. The proximate and elements analysis is listed in Table 1. Where *Mad* is the moisture content on air-dry basis; *FCd* is the fixed carbon content and *Ad* is the ash content on dry basis. *Vdaf* is the volatile matter content on dry ash free basis; The contents of elements (*C*, *H*, *O*, *N* and *S*) based on dry ash free basis. The volatile matter content is very high while the fixed carbon content is very low, which indicates the coal sample is one type of low rank coal. In addition, the ash content of coal sample is very low. Therefore, the ash content before and after low-temperature pyrolysis will be not analyzed in this paper.

2.2. Low-temperature pyrolysis process and mass loss analysis

Low-temperature pyrolysis experiments were conducted in a controlled atmosphere furnace (OTF-1200X). The terminal temperatures were fixed at 500, 600 and 700 °C, with an interval of 25 °C at a heating rate of 15 °C/min and an isothermal treatment of 30 min. Approximately 4 g of raw coal fines were paved in a quartz container under the N_2 gas environment with the air flow of 80 ml/min. After the pyrolysis process, coal char was heated under the N_2 gas until it was cooled to the normal atmospheric temperature. At last, coal char was stored under the N_2 gas and waited for other tests. In this paper, the mass loss of coal particles before and after low-temperature pyrolysis was analyzed to reveal the mass changes of coal char at different pyrolysis temperatures.

2.3. SEM tests

Quanta 250 SEM (FEI, USA) was used to analyze the surface morphology of coal particles before and after low-temperature pyrolysis. Before the SEM tests, coal particle surface was sputter-coated with a layer of gold. The magnification of SEM was fixed at 1000.

2.4. XPS tests

The XPS experiments of coal particles before and after low-temperature pyrolysis were carried out at room temperature in an ultrahigh vacuum (UHV) system with the surface analysis system (ESCALAB 250 Xi, America). The data processing (peak fitting) was performed with XPS Peak fitting software. The binding energies were corrected by setting the C1s hydrocarbon ($-CH_2-CH_2$-bonds) peak at 284.8 eV.

2.5. Attachment time tests

The coal particles before and after low-temperature pyrolysis were also forwarded to the attachment time tests. The bubble-particle attachment time measurements were conducted with the Attachment Timer (made by University of Alberta, Canada) [21].

First, the coal sample was transferred to a small cell filled with distilled water. A bubble holder was on the top of the coal bed. The bubble of about 1.5 mm in diameter was generated using a microsyringe and then held by the bubble holder. The distance between the bubble and the coal bed was adjusted as a constant in each test using the three-dimensional micro-translation stage. Next, the bubble was kept in contact with the coal bed for the controlled contact time from 10 ms to 5000 ms. The attachment behavior of coal particle to the bubble was visually observed through the lens and CCD camera linked to a monitor, as shown in Fig. 1. In order to obtain the accurate bubble-coal attachment time, repeated measurements were performed at different positions of the coal bed and the final attachment time was obtained using the arithmetic mean value.

2.6. Flotation procedure

All flotation tests were conducted in a 40 mL micro-flotation cell with the impeller speed of 1600 r/min. The pulp density was 50 g/L. The collector is not used in order to investigate the natural floatability of coal particles before and after low-temperature pyrolysis. The frother was *sec*-octyl alcohols at a dosage of 1.5 µl.

First, coal sample was added in flotation cell with water and prewetted for 3 min. Then, the frother was added and the pulp was conditioned for another 1 min. Third, the air flow (60 ml/min) was given and the flotation concentrate was collected within 2 min. At last, frother products and tailings were collected, dried and weighed to evaluate the difference in flotation behavior of coal particles before and after low-temperature pyrolysis. In this paper, low-ash coal particles were used and hence the ash contents of both concentrate and tailings were not analyzed. The concentrate yield was the sole index to evaluate the flotation results as well as the floatability of coal particles before

Table 1
Proximate and elements analysis of lignite sample.

Mad (%)	Ad (%)	FCd (%)	Vdaf (%)	Cdaf (%)	Hdaf (%)	Odaf (%)	Ndaf (%)	St,daf (%)
8.06	9.98	59.83	33.53	79.33	4.68	14.66	1.10	0.22