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Wettability and flotation modification of long flame coal with low-temperature pyrolysis

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ABSTRACT

The purpose of this investigation was to explore the effect of low-temperature pyrolysis on the wettability and floatability of the long-flame low-rank coal particles. Changes in surface functional groups of long-flame coal were measured before and after pyrolysis and the surface free energy of the coal particles was calculated by the van Oss–Chaudhury–Good theory. As the pyrolysis temperature was increased to 500 °C, the total surface free energy γ_S and the base part γ_S^- of the long-flame coal decreased from 42.63 to 41.26 mN·m^{-1} and from 28.19 to 2.18 mN·m^{-1}, respectively. The reductions in γ_S and γ_S^- indicated a significant increase in hydrophobicity of the long-flame coal after pyrolysis. In addition, the wetting heat of the coal became less negative, indicating significant restriction of the hydrophilicity of the coal surface. The zeta potential of the coal was measured before and after pyrolysis; pyrolysis significantly affected the coal's zeta potential, which became less negative as the pyrolysis temperature was increased. Thus, the electrostatic repulsion between bubbles and coal particles decreased after pyrolysis, and therefore the attachment time of bubbles to coal particles decreased by up to 72.73%. The flotation recovery of the coal particles increased by up to 38.20% as the pyrolysis temperature was increased to 500 °C.

1. Introduction

Coal is an important energy source in some countries, especially China [1], Australia [2], and Turkey [3]. Although global coal deposits are abundant, about 50% of coal reserves comprise low-rank coal [4]. The quality of low-rank coal is usually very low and upgrading processes, such as burning, liquefaction and gasification, are required to enhance the coal quality prior to use. Many separation methods have been developed for the clean and efficient utilization of low-rank coal, including magnetic separation, gravity separation, bio-beneficiation, and froth flotation [5,6]. Froth flotation, a physicochemical separation process based on the attachment of hydrophobic mineral particles to air bubbles, is considered a versatile mineral processing technique for fine coal particles below 0.5 mm in particle size [7]. However, low-rank coal possesses many oxygenated functional groups, including phenolic hydroxyl, alcohol hydroxyl, carbonyl, and carboxyl moieties, which induce poor floatability [5]. The flotation of the low-rank coal has become a worldwide problem due to the poor floatability of the low-rank coal. Different pretreatment methods have been developed to improve the floatability of low-rank coals, such as dry grinding with the addition of collectors [8], heat pretreatment [9], ultrasound pretreatment [10–15], and oily-bubble flotation [16]. It was also reported that the heating process could lead to some significant changes in the coal surface properties [17,18]. Among these changes in the properties of the coal surface, the hydrophobicity of the coal particles surface is an important issue to the fine coal flotation process [18,19]. It was partially reported that the wettability of the anthracite as well as bituminous coal particles was significantly altered after the heating process [20]. In addition, Xia [17] studied the influence of heating on lignite wettability and found that heating altered not only the lignite surface properties but also its hydrophobicity. Ye et al. [18] reported that the floatability of lignite was improved after low-temperature heating. However, few have investigated the influence of low-temperature pyrolysis on the wettability of coal particles, particularly for low-rank coal. In addition, enough attention is also not given to combine the change in the properties of the coal particles surface to the change in hydrophobicity as well as floatability of the coal particles before and after low-temperature pyrolysis process, especially for low-rank coal particles. Therefore, it is significant to investigate the influence of low-temperature pyrolysis on the surface properties, particularly the wettability and floatability of low-rank coals.

In this research, the changes in wettability and floatability of long-

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flame coal (a low-rank coal) before and after low-temperature pyrolysis were studied. Fourier-transform infrared (FTIR) spectroscopy and zeta potential measurements were performed to reveal the surface property changes. The surface free energy of mineral particles can affect the wetting of mineral particles during bubble–particle attachment and mineralization [7]. Because very little research has been done regarding the influence of pyrolysis on the surface free energy of coal, the surface free energy was calculated to permit a quantitative interpretation of the flotation response of the coal before and after pyrolysis. Finally, the wetting heat of long-flame coal before and after pyrolysis was measured to reflect the change in hydrophilicity, and the attachment probability of bubbles to pyrolyzed coal particles was estimated based on the attachment time.

2. Experimental

2.1. Materials

Long-flame low-rank coal obtained from Shendong, China, was used in this investigation. To reflect the influence of pyrolysis on the surface properties and flotation response of the coal, low-ash coal was obtained from the as-received coal samples by the float-and-sink method and used in experimentation. The low-ash product was crushed to a particle size of < 0.5 mm and the < 74 μm particle size fraction was 24.68%; this crushed material was tested as the final coal sample. Proximate physical characterization results for the final coal samples are presented in Table 1. The $S_{t,daf}$ value of the final samples was 0.26%.

Low-temperature pyrolysis was performed in a furnace under a controllable atmosphere. The terminal pyrolysis temperatures of 300, 400, and 500 °C were selected and the pyrolysis time of 30 min was used throughout. For each pyrolysis experiment, the coal sample was placed in a quartz container under 180 mL/min N_2 flow. After pyrolysis, the product was cooled to atmospheric temperature ($\sim$20 °C) under N_2. The pyrolyzed samples were sealed under N_2 until use.

2.2. FTIR spectroscopy measurements

An FTIR spectrometer (Nicolet iS5, Thermo Fisher) with the wavenumber range of 4000–400 cm^{-1} was employed to evaluate the changes in the oxygenated functional groups of the long-flame coal before and after pyrolysis. For the FTIR measurements, coal samples pyrolyzed at the various temperatures were first ground to less than 74 μm in diameter. Then, 2 mg of the ground coal was mixed with 300 mg KBr and pressed into a pellet at 28 MPa for FTIR measurement. A blank scan was taken before measuring and all experiments were performed at 20 °C.

2.3. Contact angle measurements

The sessile drop technique was employed to carry out the contact angle measurement. Prior to the contact angle measurement, the coal samples were firstly ground to < 74 μm and then pressed under a 40 MPa pressure using a tablet machine to form a plate. Subsequently, a drop of desired solution was produced, and then was conducted to contact with the coal plate. The contact angle value could be obtained by capturing the droplet image using a drop shape analyzer (DSA100, Krüss GmbH, Germany). For each experiment, a set of 3 times measurements were performed and the average value was adopted.

Table 1
Proximate analysis results for the final coal samples.

M_{ad}, %	A_{ad}, %	V_{ad}, %	FC_{ad}, %
8.95	3.83	37.49	49.73

ad = air-dry basis; M = moisture content; A = ash content; V = volatile matter; FC = fixed carbon.

2.4. Wetting heat measurements

The wetting heat of the coal before and after pyrolysis was measured using a microcalorimeter system (C80, Setaram, France). For the wetting heat measurements, the coal samples were first ground to < 74 μm. Then, 8-mg samples were sealed in stainless steel cells under aluminum foil films that divided the cells into two parts each. Next, 2 mL deionized water was placed in the upper part of the stainless steel cell. Then, stainless steel cells with and without coal samples, as test and reference cells, respectively, were placed in the calorimeter. The aluminum foil film was pierced when the system reached equilibrium. Subsequently, the wetting heat was analyzed using the software accompanying the C80 microcalorimeter system.

To quantitatively evaluate the influence of pyrolysis on the hydrophobicity of the coal, the inhibiting efficiency IE(%) was calculated according to the following equation [21]:

$$IE(\%) = (1-\Delta H_p/\Delta H_r) \quad (1)$$

where ΔH_r is the wetting heat of the raw non-pyrolyzed coal and ΔH_p is that after pyrolysis.

2.5. Zeta potential measurements

Zeta potential measurements of the coal samples before and after pyrolysis were performed using the ZetaPALS system (Brookhaven, USA). The coal samples were firstly ground to < 30 μm [22]. Then, 0.1 wt% suspensions of the ground coal were prepared using deionized water. The suspensions were stored for 10 h before the zeta potential measurements and 1.5 mL supernatants were removed using a pipette for measurement. The pH was adjusted using either NaOH or HCl. Zeta potential measurements were performed five times for each pyrolysis temperature, with the mean value reported. All measurements were conducted at a temperature of 20 ± 1 °C.

2.6. Bubble–particle attachment measurements

The attachment time measurements between bubbles and coal particles before and after pyrolysis were conducted using the 2015EZ Induction Timer Instrument (manufactured by Alberta University, Canada). It has been reported that the bubble–particle attachment time was sensitive to the particle size. In the influence of bore water on the coal flotation performance reported by Ozdemir et al., three different coal particle sizes (0.106 × 0.038 mm, 0.25 × 0.106 mm and 0.5 × 0.25 mm) were employed for the bubble–particle attachment time measurements [23]. And, 0.053–0.106 mm mineral particles were used for the bubble–particle induction time measurements in the experiment reported by Albijanic et al. [24]. In addition, the coal particles of 0.074–0.125 mm were employed for attachment time measurements in the experiment reported by Chen et al. [25]. In this experiment, the coal particles of 0.074–0.125 mm were employed for the bubble–particle attachment time measurements, 1 g coal particles obtained by wet screening was transferred to a small measuring container filled with distilled water and the measurement was performed by moving a bubble to touch the coal particle bed at a given contact time. Then, as the distance between the bubble and particles bed was increased, we used a macro lens to observe whether the coal particles became attached to the bubble.

The bubble size (1.25 mm), the initial distance between the bubble bottom and coal particle bed (0.2 mm), the approach and retraction time of the bubble (10 ms), and the amplitude of air bubble motion (3 V) were held constant in this experiment. The contact time for which the pickup efficiency was 50% was defined as the attachment time. Each experiment was repeated 10 times at different positions of the particle bed and the mean value was reported.