Fuel 235 (2019) 687–695

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

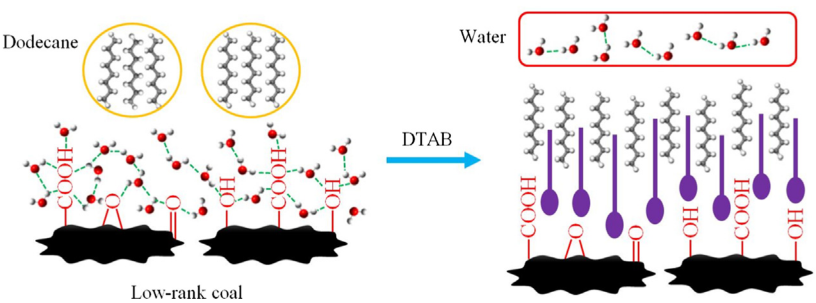
Full Length Article

Improving the adsorption of oily collector on the surface of low-rank coal during flotation using a cationic surfactant: An experimental and molecular dynamics simulation study

Yangchao Xia[a,b], Rui Zhang[a,b], Yaowen Xing[a,*], Xiahui Gui[a,*]

[a] Chinese National Engineering Research Center of Coal Preparation and Purification, China University of Mining and Technology, Xuzhou 221116, Jiangsu, China
[b] School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, Jiangsu, China

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Low-rank coal
Cationic surfactant
Adsorption
Oily collector
Molecular dynamics simulation

ABSTRACT

The effect of a cationic surfactant, dodecyltrimethylammonium bromide (DTAB), on low-rank coal flotation using an oily collector (dodecane) was investigated by a combination of experimental tests and molecular dynamics simulations. Flotation results showed that the addition of DTAB during pulp conditioning increased the clean coal yield, while a high concentration of DTAB exerted a negative influence. To explain the flotation behavior and analyze the interaction between low-rank coal, DTAB and dodecane, a series of experimental tests were conducted and the results indicated that a relatively lower concentration of DTAB is beneficial for the adsorption of dodecane on low-rank coal surface. In addition, by measuring the induction time, it was found that low-rank coal particles were easily adhered to bubbles in the presence of suitable concentration of DTAB. However, a high concentration of DTAB brings about an adverse effect. Later, molecular dynamics (MD) simulations were carried out to illustrate the positive effect of DTAB on the adsorption reaction between low-rank coal and dodecane. The results showed that the abundant number of oxygen-containing groups in low-rank coal are responsible for the limited adsorption of nonpolar dodecane molecules on its surface, while the pre-adsorption of DTAB on the surface of low-rank coal enhances dodecane adsorption. This can be ascribed to the exposed hydrophobic structure of the coal-DTAB complex. As a result, dodecane molecules were more easily adsorbed on the surface of low-rank coal and the attraction of low-rank coal to dodecane in the presence of DTAB resulted in a lower mobility of dodecane molecules, and a larger interaction energy between dodecane and low-rank coal. The simulation results are in good agreement with experimental results.

* Corresponding authors.
E-mail addresses: cumtxyw@126.com (Y. Xing), guixiahui1985@163.com (X. Gui).

https://doi.org/10.1016/j.fuel.2018.07.059
Received 10 April 2018; Received in revised form 12 June 2018; Accepted 14 July 2018
0016-2361/

1. Introduction

Low-rank coals involving sub-bituminous coal and lignite accounts for more than 50% of the world's coal reserves [1]. Due to the advantages of low mining costs and easy access, low-rank coals are widely used in energy production [2]. However, low-rank coals are characterized by low calorific values and high ash contents. Therefore, it is necessary to clean them before use in industry to improve resource utilization efficiency and protect the environment [3,4]. Froth flotation is an effective method for the beneficiation of fine coals, which depends on the natural hydrophobicity of coal [5–7]. Low-rank coals are difficult to float with oily collectors (kerosene, diesel oil, etc.) due to the abundant quantity of oxygenated functional groups on their surfaces, such as carboxyl, hydroxyl, carbonyl and methoxyl groups [8–10], which restrict the adsorption of oily collectors.

Numerous methods have been developed to improve the flotation performance of low-rank coals, most of which are focused on finding new oxygenated collectors [11–17]. In addition, particle surface pre-treatments, including mechanical grinding, ultrasonic, microwave and heating were studied [18–21]. However, the probability of finding a single efficient collector and surface pre-treatment technique to eliminate oxygenated functional groups on coal surface is limited.

At present, surfactants are mainly used as collectors or oily emulsifiers in low-rank coal flotation [5,22,23]. Jia et al. [7] used tetrahydrofuran ester in oxidized and low-rank coals flotation, and found that tetrahydrofuran ester was well bonded on coal surface. Vamvuka and Agridiotis [24] declared that dodecylamine, myristyltrimethylammonium bromide, sodium dodecyl sulfate and 2-ethyl hexanol significantly affected the flotation recovery of lignite. The blending of surfactants and oily collectors has been also used to improve the floatability of low-rank coals and reduce the dosage of oily collectors [6,23]. The lignite flotation response upon adding an emulsifier or a surfactant to kerosene was investigated by Cebeci [6], and the result indicated that a suitable surfactant (except anionic) could reduce the ash content and enhance combustible recovery. However, surfactants were seldom used to pre-treat coal surface in flotation.

During coal storage, transportation and utilization, a surfactant solution can be sprayed on the coal surface to restrict moisture adsorption. By altering the surface wettability, surfactants can be also used to improve the efficiency of fine coal dewatering and restrain fly coal dust [25,26]. Researches have shown that cationic surfactants can regulate the wettability of coal surface remarkably [27–32]. This is because the coal surface is generally negatively charged, which attracts cationic surfactants (such as quaternary ammonium surfactants) through electrostatic attraction and thus increases the hydrophilicity of coal surface through the alkyl chains of surfactants. However, a surfactant with a long alkyl chain can cause higher ash content, while a surfactant with a short alkyl chain has no obvious lipophilic effect. Hence, it is feasible to pre-treat low-rank coal using DTAB, which improves their flotation performance by enhancing their adsorption on oily collectors. Moreover, the application process is simple and may be used in industrial practice.

Recently, molecular dynamics (MD) simulations have been used to investigate the microscopic interaction behavior between chemicals with various mineral surfaces [33–37]. The adsorption and interaction mechanism of reagents on coal surface in an aqueous environment have been also investigated by MD simulation method [38–40]. Therefore, molecular dynamics simulations were carried out along with experiments in this study to investigate the effect of DTAB on the adsorption reaction between low-rank coal and dodecane during flotation. It emphatically revealed the microscopic interaction between low-rank coal, DTAB and dodecane, which will help in the development of a new method to improve the flotability of low-rank coals and understand the underlying adsorption mechanism.

2. Experimental and simulation

2.1. Materials and reagents

Low-rank coal samples were obtained from the Shendong Mine, China. The raw samples were crushed and ground to smaller than 0.5 mm in size for experimental study. The ash content of raw coal is about 13.8%, as determined by proximate analysis. Moreover, its oxygen content is 13.84% determined by ultimate analysis. This shows that this coal may be difficult to be floated. A cationic surfactant, dodecyltrimethyl bromide (DTAB, analytical grade, purity ≥ 99%), was obtained from the Sinopharm Chemical Reagent Co., Ltd, China. An oily collector dodecane and a frother 2-octanol (analytical grade, purity ≥ 99%), were purchased from Tianjin Damao Chemical Reagents Co., Ltd, China.

2.2. Flotation procedure

A XFD flotation machine with a cell of 1 L was used for flotation with a pulp concentration of 80 g/L. For each test, the dosage of dodecane and 2-octanol were maintained at 4 and 0.5 kg per ton of dry feed coal, respectively. Before pulp conditioning, DTAB was added into the cell filled with 1 L of deionized water. The concentrations of DTAB were varied between 0, 1, 1.75 and 5 mM. Subsequently, the surface pre-treatment of the coal was carried out under stirring at an impeller speed of 1800 r/min for 2 min. After this process, dodecane and 2-octanol were injected for contact times of 120 s and 30 s, respectively. The airflow rate was 1 L/min and the flotation concentrate product was collected until there was no froth product left in the flotation cell. The concentrates and tailings were filtered and dried in an oven at 80 °C to constant weight; later, ash measurement was conducted.

2.3. Induction time measurement

The induction time between air bubbles and coal particles was measured using self-constructed induction time measuring instrument consisting of a micro-displacement sensor, capillary tube, test bed, micro syringe, illumination device, high-speed camera and a PC (Fig. 1) [41]. Before measurement, the DTAB solution was prepared in the test bed; the solution concentration was set at 0, 1, 1.75 and 5 mM. After the low-rank coal samples were added and stirred for 2 min, dodecane was injected. The concentrations of coal and reagent in the test bed were consistent with those used in the flotation test. During measurement, an air bubble was moved towards and touched the coal particle spread on the test bed for a given time. The high-speed camera was used to record the attachment process and the results were observed using the PC. It is obvious that bubble-particle attachment occurs if the contact time is long enough; otherwise, no particles can be picked up by the bubble. The time at which the number of the bubble-particle attachment is 50% among a batch of tests, is defined as the induction time [42].

2.4. Wetting rate measurement

To analyze the wetting rate and adsorption heat of test samples, a series of adsorption experiments were carried out using the flotation machine used for flotation tests. DTAB and coal were added to the cell and then stirred for 2 min at 1800 r/min. The pulp concentration was 80 g/L and the concentrations of DTAB were 0, 1, and 5 mM. After each adsorption cycle, the mixtures were filtered and the obtained solid residues were dried in an air dry oven. Later, the wetting rates of the coal samples to dodecane were measured using a K100 surface tension analyzer (Krüss GmbH, Germany). The coal samples were accurately weighed to 2 g and fed into the test tube. The bottom of the test tube was sealed with a qualitative filter paper and screwed tightly. The head of the test tube was tightened with a screw cap. In order to reduce experimental errors, the height of the screw cap twist nail was kept