Fuel 207 (2017) 214–225

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

# Wetting thermodynamics of low rank coal and attachment in flotation

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## HIGHLIGHTS

- The wetting ability of modified diesel oil for coal sample did not entirely increase with the decrease of surface tension, and liquid viscosity was also a relevant factor.
- Great viscosity is good for adhesion, but excessive viscosity was bad for its wettability.
- The induction time between coal particles and reactive oily bubbles modified by 2-ethylhexanol and DDAB showed a significant decrease.
- It was crucial to the flotation of low rank coal that proper surfactant was used to generate reactive oily bubbles.

## ARTICLE INFO

*Article history:*
Received 24 March 2017
Received in revised form 31 May 2017
Accepted 2 June 2017

*Keywords:*
Low rank coal
Wettability
Surfactant
Induction time
Reactive oily bubble flotation

## ABSTRACT

It is critical for flotation to accomplish the bubble-mineral particle attachment as well as mineralization process. The surface free energy of mineral particle and liquid is a key parameter which affects the wettability and wetting process of mineral in mineralization. In this paper, the surface free energy components of coal sample were calculated by Washburn equation and Oss Chaudhury-Good-Van theory. Additionally, the wetting ability of modified diesel oil for coal sample was studied by Washburn dynamic capillary method while Lipophilic Hydrophilic Ratio and relative contact angle were calculated. Furthermore, the effect of both surfactants, 2-ethylhexanol and didodecyldimethylammonium bromide (DDAB), on the induction time between oily bubbles and coal particles was investigated. Results indicated that wetting ability of modified diesel oil for coal sample did not entirely increase with the decrease of surface tension, and liquid viscosity was also a relevant factor. The adhesion strength enhanced whereas the detachment probability reduced with the increase of collector viscosity. But too large viscosity was bad for fluidity of liquid, which therefore decreased its wettability for coal sample. The induction time between coal particles and reactive oily bubbles modified by 2-ethylhexanol and DDAB decreased by 74.35% and 86.45% respectively. As a result, the maximum combustible matter recovery of 72.20% (increasing by 22.23%) and highest flotation efficiency index of 56.50% were obtained when the weight ratio of 2-ethylhexanol to diesel oil was 0.04, while that of using reactive oily bubbles modified by DDAB showed an apparent decrease. It indicated that it was crucial to the flotation of low rank coal that proper surfactant was used to generate reactive oily bubbles.



## 1. Introduction

Coal is taken as the main energy source, and coal's share of China's primary energy consumption is 64% in 2015. What's more, there are abundant resources of low rank coal in China, which accounts for 45.68% of proven coal reserves [1]. Production of low rank coal reached to 1.8 billion tons in 2013, accounting for about 50% of total coal production capacity, which had been an important part of China's coal energy production and supply.

However, the economical recovery of low rank coals is difficult to achieve, which restricts its clean and efficient utilization. For low rank coal molecule, it has the characterize of less condensed aromatic ring, high H/C ratio, much aliphatic chains and great amount of oxygen which exists mainly in the form of polar hydroxyl (both phenol and alcohol), carbonyl and some peroxide type oxygenated moieties [2–5]. These hydrophilic functional groups decrease hydrophobicity of low rank coal thus lead to poor floatability [6,7]. The adhesion efficiency of diesel oil droplets onto low rank coal surface is so small that large amount of collector is

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http://dx.doi.org/10.1016/j.fuel.2017.06.018

required to achieve satisfactory yields [7,8]. Furthermore, there are a lot of oxygen and nitrogen atoms on the surface of low rank coal, which are easily negatively charged and then bring about the stable hydration film. Hydroxyl and carbonyl of coal surface can also be ionized, which can influence the flotation process by controlling the thickness of liquid film on coal surface. Consequently, it is difficult to float the low rank coal using common oily collectors, such as diesel oil and kerosene [9].

For fine materials under 0.5 mm, flotation is the most efficient separation technology [10]. Bubble-mineral particle attachment and mineralization process are critical to flotation which can realize the effective separation of coal and gangue. The surface free energy (for liquid also called surface tension) of mineral particle and liquid is a critical parameter which affects the wettability and wetting process of mineral in mineralization [11]. Therefore, the attachment and mineralization process between bubbles and particles can be analyzed from the respect of thermodynamics. If the free energy of the system is reduced, the adhesion process can be carried out spontaneously. The strong surface hydrophobicity of ore particles is corresponding to the great contact angle of the water to the coal sample and the strong spontaneous tendency. For liquid, the surface free energy is equal to that of the surface tension in values. While, for solid, according to the Van Oss–Chaudhury–Good theory, the total surface free energy can be decomposed into the non-polar Lifshitz-vander Waals force and polar Lewis acid–base interaction force [12–16]. Van Oss, Good et al. [17,18] thought that H-bonds were attributed to polar Lewis acid–base which was composed of acid part and base part. Washburn dynamic method and Oss Chaudhury-Good-Van theory can be used to measure and calculate the total surface free energy of solid and its components thus learn the wetting behavior of mineral dust. The detailed description can be found in other literatures [11,12,19]. Additionally, Lipophilic Hydrophilic Ratio [12,20], wetting energy, film flotation and induction time measurement are also used to determine surface energy [21,22].

In order to enhance surface hydrophobicity of low rank coal, pretreatments are always necessary. The main pretreatment methods consist of preconditioning and grinding [23,24], thermal [25] and microwave [26], ultrasound [27], direct contact mixing of the reagents with dry coal before wetting [28], which improve the hydrophobicity of low rank/oxidized coals by reducing the oxygenated functional groups on the coal surface thus making some fresh surfaces, removing pore water and hydration water, avoiding formation of a thick wetting film on the coal surface or modifying the surface. Furthermore, it is called reactive oily-bubble flotation that air bubbles are replaced by reactive oily bubbles (i.e., bubbles covered by a thin layer of non-polar collector modified by surfactants) as a carrier in flotation [29]. For minerals difficult to float, the experimental results showed better flotation efficiency using reactive oily bubbles than that of air bubbles because of former's stronger collecting power, better selectivity and shorter induction time. Therefore, reactive oily-bubble flotation has been proven to be a more effective technology [30–36]. There are a number of advantages in reactive oily-bubble flotation in which a non-polar collector modified by surfactants is not directly added into the pulp, but as a thin hydrophobic layer covering on bubble surface comparing with the conventional flotation. It reduces the actual amount of collector required by greater degree of dispersion on target particles and minimizes undesired activation of gangue particles. What's more, a higher concentration of collector molecules localized on the oil-water interface gives rise to a stronger collecting power [29]. When adsorption between the collector film and the mineral particles happens, the mineral particles also adheres to the bubbles, thus reducing the adhesion work and greatly decreasing the induction time.

The thinning and rupture of wetting thin films between the air/water and solid/water interfaces, and the formation and expansion of the gas–liquid–solid contact lines must be done after collision for bubble-particle attachment to occur. The attachment time is defined as the time for the attachment process involving three events, while the induction time is a part of attachment time and is referred to the time for the first two processes [37]. For attachment and mineralization to occur, the induction time must be less than the contact time. Therefore, the induction time is a quite important parameter for the separation of coal and mineral matter. Albijanic et al's [37] work reviewed the experimental studies into the induction and attachment times between minerals and air bubbles as well as oil droplets and air bubbles. The results showed that the changes of surface of pure minerals in both flotation surface chemistry and physical properties could be determined by the time parameters. Su et al's [36] research, which focuses on the mechanisms of oily bubbles improving bitumen recovery, indicated that the spreading of oily bubbles on a bitumen surface was much faster than that of air bubbles, the induction time between oily bubbles and bitumen was much shorter than that of air bubbles and bitumen, which was well correlated with higher recovery using oily bubbles as a carrier in flotation.

In the present work, the reactive oily-bubble flotation was employed to enhance the flotation of low rank coal. While, 2-ethylhexanol and didodecyldimethylammonium bromide were used as emulsifiers to improve the performance of oily bubbles. The wetting ability of modified diesel oil for coal sample was studied by Washburn dynamic capillary method while it was evaluated by Lipophilic Hydrophilic Ratio. Moreover, the attachment efficiency between reactive oily bubbles and coal particles was estimated by induction time.

## 2. Washburn equation and Van Oss–Chaudhury–Good theory

According to Poiseuille law [38] and Laplace equation, the Washburn equation can be expressed as follows [39]:

$$\omega^2 = c\frac{\rho^2\gamma_L cos\theta}{2\eta}t \qquad (1)$$

where ω is the liquid weight gain. $c$ is the geometric factor of Washburn tube (The geometric factor c of the packed Washburn tube is the same for one kind of sample and the same Washburn tube). ρ is the density of the liquid. $\gamma_L$ is the surface tension of liquid. η is the liquid viscosity. $\theta$ is the contact angle. And t is the wetting time.

The geometric factor of packed Washburn tube is

$$c = rC^2\pi R^2 \qquad (2)$$

where r is the effective radius of capillary. $C$ is fine particle filling rate in Washburn tube. R is the radius of Washburn tube.

The slope of $w^2$-$t$, $k$ is

$$k = \frac{\rho^2\gamma_L cos\theta}{2\eta} \qquad (3)$$

The geometric factor of packed Washburn tube can be determined by choosing one kind of probe liquid as a reference liquid with the fastest wetting rate for particle sample. The difference of wettability of liquids for particle samples can be evaluated by wetting rate and relative contact angle.

Lipophilic Hydrophilic Ratio (LHR) is used to evaluate the difference of wettability of oil (L) and water (H) for the solid sample and is given by:

$$LHR = \frac{cos\theta_L}{cos\theta_H} = \frac{k_L\eta_L}{k_H\eta_H} \times \frac{\rho_H^2\gamma_H}{\rho_L^2\gamma_L} \qquad (4)$$