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FLOTATION OF LONG FLAME COAL PRETREATED BY POLYOXYETHYLENE SORBITAN MONOSTEARATE

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Abstract: In this investigation, polyoxyethylene sorbitan monostearate (Tween 60) was used to improve flotation of fine long flame coal. The flotation recovery of long flame coal could be increased when long flame coal was either pretreated or conditioned with Tween 60 in a flotation cell for a period before the addition of collector. Fourier Transform Infrared (FTIR) technique was used to indicate surface properties of long flame coal. The results of FTIR show that there are many oxygen functional groups on the surface. Contact angle measurements were used to indicate changes in hydrophobicity of coal surface before and after Tween 60 and/or diesel pretreatments. The results of contact angle measurements show that hydrophobicity of coal can be increased by Tween 60. Tween 60 can also enhance adsorption of diesel on the coal surface, and hence floatability of long flame coal can be further improved. Tween 60 primarily enhances the flotation recovery of low density coal fractions (<1.5 and 1.5-1.8 kg/dm^3). However, the increase in flotatation recovery is less significant with an excessive addition of Tween 60.

Keywords: *flotation, hydrophobicity, low rank coal, Tween 60, pretreatment*

Introduction

Flotation is widely used in beneficiation of fine coal slimes (<0.5 mm) and is based on the difference in hydrophobicity between coal matter and minerals. It is well known that coal particles are usually much more hydrophobic than gangue ones (Drzymala, 2007). During conventional flotation processes, coal particles are floated into the froth, which is treated as a clean coal after dewatering processes, whereas hydrophilic particles are retained in a system and transported to tailings.

It is well recognized that low rank coals, such as peat, lignite and long flame coal are difficult to float using common oily collectors. However, universal oily collectors after special treatments, such as emulsification and addition of oxygenated functional groups into collector molecule can significantly improve flotation of low rank coals

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(Jia et al., 2000; Boylu and Laskowski, 2007). The addition of pitch in a dry grinding process of low rank coal before flotation enhance the combustible matter recovery and reduce the ash content of clean coal (Atesok and Celik, 2000). A low temperature heating process can be also useful for improvement in hydrophobicity of lignite (Celik and Seyhan, 1995; Ye et al., 1988; Cinar, 2009). Floatability of low rank coal can be improved by microwave pretreatment since microwave pretreatment reduces the moisture content of low rank coal (Ozbayoglu et al., 2009). The low moisture content might be beneficial to the flotation performance of lignite. Furthermore, microwave treatment was also used to improve Taixi oxidized coal flotation since both dehydration and oxidation reactions could occur on the oxidized coal surface after microwave radiation (Xia et al., 2013).

Surfactants are widely used in food processing technology since they can decrease the surface tension of solutions. Thus, surfactants are also applied in improvements in low rank coal flotation (Burkin and Bramley, 1963; Aston et al., 1981; Chander et al., 1987; Moxton et al., 1987; Yu et al., 1990; Jia et al., 2000; Sahbaz, 2013). In some cases, surfactants added at low concentration can make low rank coal more hydrophobic, whereas, at high concentration, they can decrease hydrophobicity of low rank coal (Zhang and Tang, 2014). On the other hand Kowalczuk et al. (2015) showed that frothers do not change the real hydrophobicity of particles, but they improve their effective hydrophobicity. Furthermore, the foaming ability and froth stability can be improved by addition of surfactants into flotation processes (Aktas and Woodburn, 1995; Pugh, 1996; Cho and Laskowski, 2002; Ozmak and Aktas, 2006; Kosior et al., 2011).

In this investigation, polyoxyethylene sorbitan monostearate (Tween 60) was used to improve flotation of low rank coal slimes (long flame coal). The effect of different Tween 60 dosages on the flotation performance of long flame coal was investigated. Fourier Transform Infrared (FTIR) technique was used to indicate the surface properties of long flame coal. Contact angle measurements were used to indicate the changes in hydrophobicity of coal surface before and after Tween 60 and diesel pretreatments. In this paper, Tween 60 will be found to be a good promoter in the flotation of long flame coal.

Materials and methods

Materials

Long flame coal samples were obtained from the Shandong Province of China. The proximate composition of coal samples is shown in Table 1, where M^{ad} is the moisture content, V^{ad} volatile content, FC^{ad} fixed carbon content, and A^{ad} is the ash content on an air dry basis.

The particle size distribution of coal samples is shown in Table 2. It indicates that the yield of <0.045 mm size fraction with an ash content of 43.40% plays the most important role in the size distribution of this coal samples. It is deduced that the coal samples contain a certain number of heterogeneous minerals, which might deteriorate the flotation performance of combustible matters due to the particle interaction in the flotation system (Bokanyi, 1996).

Table 1. Proximate composition of coal samples

M^{ad} (%)	A^{ad} (%)	FC^{ad} (%)	V^{ad} (%)
8.63	35.09	23.35	32.93

Table 2. Particle size distribution of coal samples

Size fraction (mm)	Mass (%)	Ash content (%)	Cumulative	
			Yield (%)	Ash content (%)
0.5-0.25	1.79	7.43	1.79	7.43
0.25-0.125	8.17	11.45	9.97	10.73
0.125-0.074	14.96	20.15	24.93	16.38
0.074-0.045	8.51	24.93	33.44	18.56
<0.045	66.56	43.40	100.00	35.09

The density distribution of coal samples is shown in Table 3. It indicates that the materials with the density smaller than 1.6 kg/dm^3 are clean coal with the ash content of 8.84%. The yield of 1.6-1.8 kg/dm^3 density fraction is 25.83% with 29.18% ash content, which demonstrates there is a certain number of composite particles in the coal sample (Dyrkacz and Horwitz, 1982; Luttrell et al., 2000). In addition, the yield of >1.8 kg/dm^3 density fraction takes the largest proportion at 43.72% with the ash content of 56.88% in the density distribution. The high density particles are mainly gangue particles. It indicates that a low ash content clean coal may be difficult to obtain due to the contamination of fine gangue particles (Zheng et al., 2005).

Table 3. Density distribution of coal samples

Density fraction (kg/dm^3)	Mass (%)	Ash content (%)	Cumulative lights	
			Yield (%)	Ash content (%)
<1.3	1.54	2.99	1.54	2.99
1.3-1.4	5.74	4.58	7.28	4.24
1.4-1.5	13.18	7.75	20.46	6.50
1.5-1.6	9.99	13.64	30.45	8.84
1.6-1.8	25.83	29.18	56.28	18.18
>1.8	43.72	56.85	100.00	35.09

Methods

FTIR measurements

A Perkin Elmer Spectrum 2000 model spectrometer was used for Fourier Transform Infrared (FTIR) analyses, and the spectrum was obtained at 2 cm^{-1} resolution in the interval between 4000 and 400 cm^{-1}. The FTIR spectra of coal samples were obtained with analytical grade KBr pellets. The ratio of the coal to KBr was 1 to 100.

Flotation tests

Diesel and 2-octanol were used as the collector and frother, respectively. The flotation tests were conducted in a 1.5 dm^3 XFD flotation cell using 90 g of coal for each flotation test. The impeller speed of flotation machine was kept as 1800 rpm, and airflow rate was 4.0 dm^3/min. Collector dosage was 2 kg/Mg coal, and frother dosage was 1 kg/Mg coal. Tween 60 dosages were 1, 2, 3, 4, 5 and 6 kg/Mg coal. Both 2-octanol and Tween 60 were obtained from Sinopharm Chemical Reagent Co. Ltd of China, and they were in analytical grades. Diesel was industrial product grade, which was obtained from a coal preparation plant of China.

For each test, the pulp was first agitated in the flotation cell for 2 min, and then Tween 60 was added and agitated for an additional 3 min. After this, diesel was added to the pulp and agitated for another 2 min. Then, the frother was added, and the pulp was conditioned for the next 30 seconds. At last, the air inlet was opened and the froth products were collected.

The flotation concentrates were analyzed using two parameters: the combustible matter recovery and ash content. The combustible matter recovery can be calculated by using formula:

$$\text{Combustible Matter Recovery (\%)} = \frac{M_C(100 - A_C)}{M_F(100 - A_F)} \cdot 100 \tag{1}$$

where M_C and M_F are concentrate and feed yields (%), respectively, A_C and A_F are ash contents in concentrate and feed (%), respectively.

Contact angle measurements

Coal samples before and after Tween 60 and diesel pretreatments were firstly pressed to tablets. Four types of coal tablets were investigated: raw coal tablet (without any pretreatment), coal pretreated by Tween 60 only (3 kg/Mg), coal pretreated by diesel only (2 kg/Mg) and coal pretreated by both Tween 60 and diesel (Tween 60 1, 2, 3, 4, 5 and 6 kg/Mg, diesel 2 kg/Mg).

The coal samples were pretreated in a 1.5 dm^3 XFD flotation cell at a speed of 1800 rpm, and the pulp density was 60 g/dm^3. When the coal sample was pretreated by Tween 60 only, the pulp was first agitated in the flotation cell for 2 min, and then Tween 60 was added and agitated for an additional 5 min. Afterwards, the pulp was filtered, and dried at a temperature of below 40 degrees. The process of coal samples pretreatment by diesel only was the same with that by Tween 60 only. However, when the coal sample was pretreated by Tween 60 and diesel together, the Tween 60 was added into the pulp and agitated for 3 min first. Then diesel was added into the pulp and agitated for another 2 min.

The tablets of coal samples were measured by the sessile drop method using a water contact angle analyzer (JC2000D) such as a water droplet on the surface of coal tablets in the air. Static contact angles were adopted to determine hydrophobicity of coal samples. Each coal sample was measured three times and the average value of contact angles was used in this investigation.

Results and Discussion

The FTIR spectrum obtained for the long flame coal (Fig. 1) shows CH_3 and CH_2 regions at 2927 cm^{-1} and 2852 cm^{-1}, respectively. The peak at 1447 cm^{-1} is -CH_3 stretching vibration. The peaks around 1112 cm^{-1}, 1278 cm^{-1} and 1035 cm^{-1} may be attributable to C-O-C vibration (Sun et al., 2010). The peak at 3400 cm^{-1} is for OH, and peaks at 1607 cm^{-1} may be for C=O or COOH functional groups. The peaks around 800 cm^{-1} and 697 cm^{-1} usually indicate the presence of benzene rings. The peaks at 3695 cm^{-1} and 3623 cm^{-1} can be considered as attributable to the kaolin mineral. The peak at 3050 cm^{-1} may be C-C=C (olefins) stretching vibration. It indicates that the long flame coal sample represents a really low rank coal. Long flame coal has many oxygen bearing functional groups which are hydrophilic. Meanwhile, long flame coal as low rank coal is usually difficult to float with common oily collectors since there are many oxygenated functional groups on low rank coal surface (Zhang and Tang, 2014).

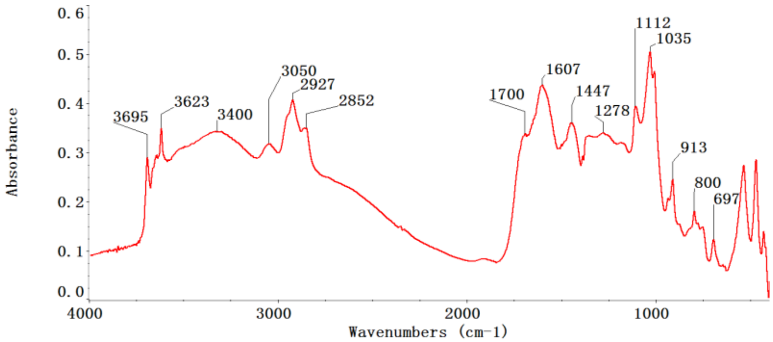

Fig. 1. FTIR spectrum of long flame coal

Figure 2 shows that the combustible matter recovery increases with the increase of Tween 60 dosage, while Tween 60 dosage is less than 3 kg/Mg. After then, the combustible matter recovery decreases with the increasing Tween 60 dosage. The concentrate ash content decreases with the increase of Tween 60 dosage (while Tween 60 dosage is less than 2 kg/Mg). The ash content of concentrate then shows no change with the increasing Tween 60 dosage. It indicates that the hydrophobicity of long flame coal surface may be effectively enhanced by Tween 60 at low dosages (optimal dosage is 3 kg/Mg). Under a higher dosage of Tween 60, the flotation performance of the coal samples deteriorates.

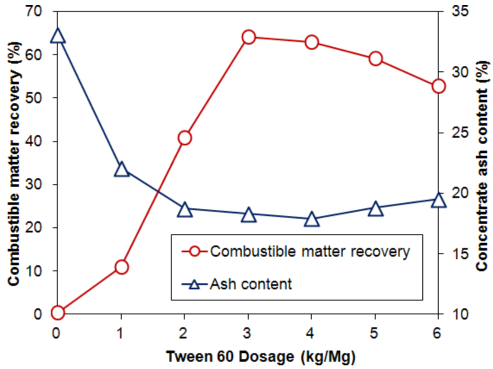

Fig. 2. Flotation results at different Tween 60 dosages

The concentrate at Tween 60 dosage of 3 kg/Mg was collected and screened into five size fractions, 0.5-0.25, 0.25-0.125, 0.125-0.074, 0.074-0.045 and <0.045 mm. The combustible matter recoveries and ash contents for different size fractions were obtained calculating that the flotation feed of each size fraction was regarded as 100%.

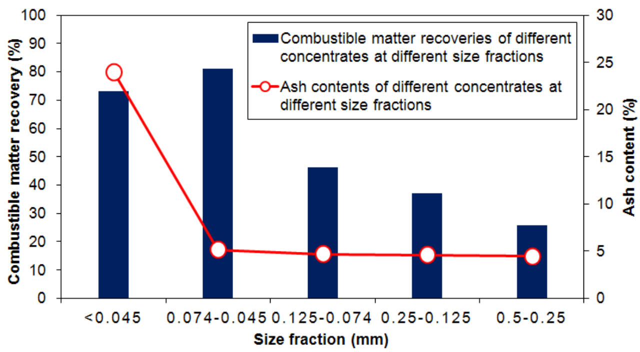

Fig. 3. Combustible matter recovery and ash content of concentrates with different size fractions at Tween dosage of 3 kg/Mg

Figure 3 shows that the combustible matter recovery increases with the decrease of size fraction but it has a little decrease, while the size fraction is <0.045 mm. The ash content increases with decrease of size fraction steadily. As shown in Fig. 3, the ash content of <0.045 mm size fraction is about 24%, while the ash contents of other size fractions are about only 4~5%. It indicates that the selectivity of <0.045 mm size fraction is lower than those of other size fractions. The combustible matter recovery of

0.074-0.045 size fraction is the highest, around 80%, with the ash content of about 5%. This is the size fraction with the best flotation performance. The high ash content of <0.045 mm size fraction increases the ash content of total concentrate since the particles of size below 0.045 mm show a very low selectivity and are recovered by various ways, including entrainment, entrapment and slime coatings (Trahar, 1981).

In order to investigate the effect of Tween 60 dosage on the flotation recovery of coal fines of different density fractions (<1.5, 1.5-1.8 and >1.8 kg/dm^3), the concentrates at different Tween 60 dosages were collected and treated by a sink-float test using organic heavy liquids. As it shown in Fig. 4, the combustible matter recoveries of <1.5 and 1.5-1.8 kg/dm^3 density fractions increase with increase of Tween 60 dosage but it has a little decrease while Tween dosage is higher than 3 kg/Mg. A higher Tween 60 dosage has a deleterious effect on the flotation recovery of low ash content coals (<1.5 and 1.5-1.8 kg/dm^3). The combustible matter recovery of >1.8 kg/dm^3 density fraction increases with the increase of Tween 60 dosage but with little range. The addition of Tween 60 can enhance the recovery of low density coal fractions (<1.5 and 1.5-1.8 kg/dm^3) much more than that of high density coal fraction (>1.8 kg/dm^3). Therefore, Tween 60 may be used as a good promoter in the flotation of long flame coal.

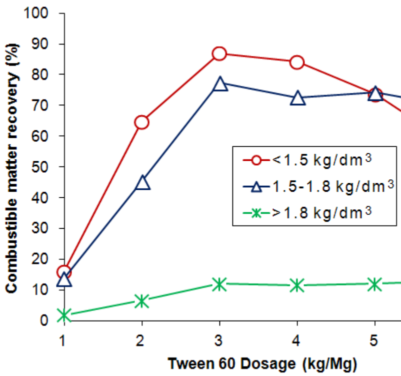

Fig. 4. Combustible matter recovery of various density fractions at different Tween 60 dosages

As shown in Fig. 5, the static contact angle of raw coal is about 43°, pretreated by Tween 60 only is about 51°, pretreated by diesel only is also about 51°, while the contact angle of coal pretreated by both Tween 60 (3 kg/Mg) and diesel is about 59°. Figure 6 shows that the contact angles increase with the increase of Tween 60 dosages when the Tween 60 dosage is less than 4 kg/Mg. After then, the contact angles decrease with the increasing Tween 60 dosages. However, it is clear that the contact angles at the Tween 60 dosage of more than 1 kg/Mg (include 1 kg/Mg) are greater than 51°, which demonstrates that the contact angle of coal sample pretreated by

Tween 60 and diesel together is greater than that of the coal sample pretreated by diesel only.

The results of contact angle measurements indicate that the hydrophobicity of coal surface can be improved by Tween 60, i.e. the contact angle increases from 43° to 51°. The collector (diesel) also can improve the hydrophobicity of coal surface, i.e. the contact angle increases from 43° to 51°. If the coal is pretreated by Tween firstly and then the pretreated coal is conditioned with collector (diesel), the hydrophobicity of coal surface can be further improved, i.e. the contact angles at all Tween 60 dosages are greater than 51°, and the maximum contact angle is up to approximately 60°. It indicates that Tween 60 has a good effect on the flotation improvement.

Tween 60 may screen the hydrophilic functional groups and hence increase the hydrophobicity of coal surface. The addition of Tween 60 may also enhance dispersion of the collector (diesel). The enhanced spread collector may adsorb on the coal surface more effectively, and hence the coal surface hydrophobicity will be further improved (Sis and Chander, 2003; Dey, 2012). However, the hydrophobicity of coal surface decreases at higher dosages of Tween 60 since higher dosages of Tween 60 might screen the coal surface and forms bilayer adsorption (Zhang and Tang, 2014). As a result, the flotation performance of coal samples at higher Tween 60 dosages was a little lower than that at proper Tween 60 dosages as shown in Fig .2.

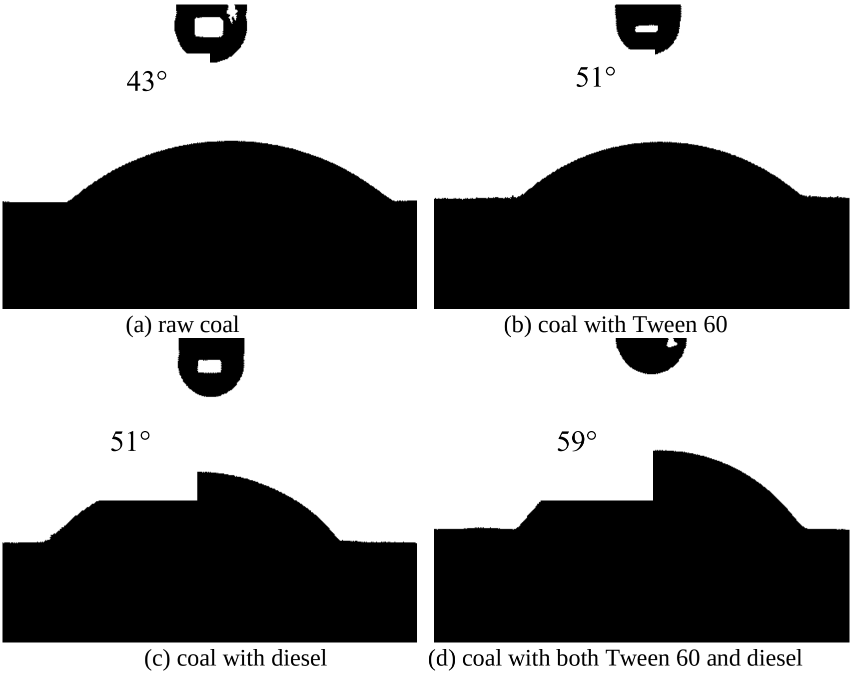

Fig. 5. Static contact angles of different coal tablets

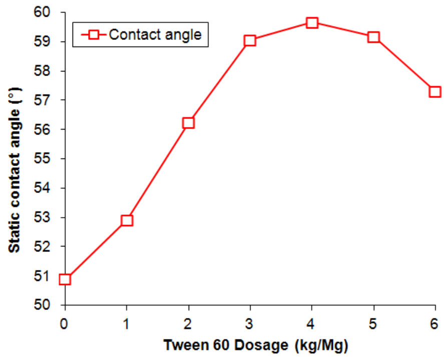

Fig. 6. Static contact angles of coal samples pretreated by Tween 60 and diesel (2 kg/Mg) together at different Tween 60 dosages

Conclusions

(1) The FTIR spectrum of long flame coal shows that there are many oxygen bearing functional groups, which are hydrophilic. Long flame coal is of a low rank and hence it is difficult to float it with common oily collectors.

(2) Flotation tests indicate that the flotation recovery of long flame coal can be improved by the addition of polyoxyethylene sorbitan monostearate (Tween 60) before flotation processes. The Tween 60 dosage is very important in the flotation recovery. The optimal Tween 60 dosage was found to be 3 kg/Mg in this investigation.

(3) Tween 60 can enhance the flotation of 0.5-0.25, 0.25-0.125, 0.125-0.074 mm size fractions. However, the high ash content of <0.045 mm size fraction increases the ash content of total concentrate since the particles of sizes below 0.045 mm show a very low selectivity. Meanwhile, Tween 60 can enhance the flotation recovery of low density coal fractions (<1.5 and 1.5-1.8 kg/dm^3) much more than that of high density coal fraction (>1.8 kg/dm^3).

(4) Tween 60 may screen the hydrophilic functional groups and hence increase the hydrophobicity of coal surface. The contact angle of coal pretreated by both Tween 60 and diesel is greater than 51°, while that of coal pretreated by diesel only is just about 51°. The addition of Tween 60 may also enhance dispersion of collector (diesel). The enhanced spread collector may adsorb on the coal surface effectively. Tween 60 can be used as a good promoter in the flotation of long flame coal.

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