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RESEARCH ON EMULSIFIED TYRE PYROLYSIS OIL AS A COAL FLOTATION COLLECTOR

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Abstract: In this paper the possibility of using the pyrolysis oil derived from waste tyres as a collector in flotation of coal was evaluated. The pyrolysis oil was obtained at the initial and final pyrolysis temperatures of 400 and 700 ^{o}C, respectively, and the heat holding time of 30 min. Flotation results indicated that the pyrolysis oil emulsion showed stronger collecting ability than diesel and the concentrate ash content just slightly increased in comparison to flotation in the presence of diesel. The contact angle measurement and immersion microcalorimetry test correlated well with the flotation data. The Fourier Transform Infrared Spectroscopy results demonstrated that diesel and pyrolysis oil emulsion is physically adsorbed on the coal surface.

Keywords: *pyrolysis oil, coal flotation, contact angle, interaction heat, adsorption*

Introduction

With depletion of fossil fuel, increase in energy demands and rising concerns of environmental pollution, it is imperative to develop alternative and renewable sources of energy (Yi et al., 2015). Worldwide, about 1 billion tyres are manufactured every year and almost equal number is permanently removed from vehicles and defined as a waste. Disposal of scrap tyres in the piles is no longer an alternative way to fire the tyres since it provides habitats for disease vectors such as mosquitoes (Stefano et al., 2014). Nowadays, there are several methods to manage the scrap tyres. Among them, the production of fuel from the waste tyres, especially in combination with a pyrolysis process, is an environmentally friendly and efficient way to take advantage of scrap tyres (Miranda et al., 2010; Chen et al., 2010; 2013). In relation to production of the pyrolysis oil, various approaches, such as non-catalytic, catalytic, plasma and hydrous pyrolysis have been applied (Shen et al., 2006; Huang et al., 2009; Rushdi et al.,

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2013). The pyrolysis oil from the scrap tires was tested as a fuel in boilers and internal combustion engines and it was reported that the pyrolysis oil had a potential source of chemical feedstock in industrial processes such as benzene, toluene, xylene and limonene (Aylon et al., 2008).

The tyre pyrolysis oil (TPO) is mainly constituted by paraffins, olefins, aromatics and aliphatic hydrocarbons (Stefano et al., 2014; Gyung-Goo et al., 2014). These compounds have a good collecting ability to coals, and thus make TPO possible to be a potential collector in flotation of coal. It could be an economic and efficient way to replace diesel with a new flotation reagent.

Flotation is widely applied in separation of complex ores such as sulphides, oxides, non-metallic ores as well as coal (Wills and Napier-Munn, 2006). Coal is the main fuel in China, therefore many researchers study flotation behaviour of coal slimes (Xia et al., 2015; Xie et al., 2015; Zhang and Liu, 2015; Zhang, 2015). Diesel and kerosene are commonly used as the collector in coal preparation plants in China. A huge dosage of oil products is consumed every year. In China, the total coal production in 2013 was 3.7 billion tons (Pg). According to the China 12th five-year plan of energy development, an about 65% of the raw coal should be washed in the coal preparation plants. The total amount of coal slimes produced during washing, which need to be further proceeded, is about 15% of the total coal washing amount, while the flotation amount of coal slime is about 0.33 billion tons (Pg). Therefore, the diesel demand for coal flotation is about 0.3 Tg which leads to a huge petroleum consumption, and also increase the production costs of coal preparation (Yi et al., 2015).

In this paper, emulsified TPO was used as the collector for three different coal samples. The flotation results with TPO and were compared diesel which is commonly used as the collector in flotation of coal.

Experiment method and procedure

Materials

Coal samples were obtained from three coal preparation plants in Shanxi, Inner Mongolia and Henan province, respectively. The size composition of coal samples are given in Tables 1-3.

Table 1. Size composition of coal 1# (long flame coal)

Size fraction (%)	Weight (%)	Ash content (%)
−0.5 + 0.25	2	14.2
−0.25 + 0.125	5	10.5
−0.125 + 0.074	16	11.1
−0.074+0.045	77	31.9
Total	100	27.1

Table 2. Size composition of coal 2# (meager lean coal)

Size fraction (%)	Weight (%)	Ash content (%)
−0.5 + 0.25	19	6.3
−0.25 + 0.125	24	8.4
−0.125 + 0.074	20	9.0
−0.074+0.045	37	15.2
Total	100	10.6

Table 3. Size composition of coal 3# (fat coal)

Size fraction (%)	Weight (%)	Ash content (%)
−0.5 + 0.25	17	10.9
−0.25 + 0.125	22	14.2
−0.125 + 0.074	21	15.4
−0.074+0.045	40	21.7
Total	100	16.9

The yield and composition of tyre pyrolysis oil (TPO) mainly depend on the specific characteristics of pyrolysis process such as temperature, pressure and less on type of tyres since their basic components are similar (Ucar et al., 2005). The TPO used in this experiment was obtained at the initial pyrolysis temperature 400^{o}C, heat holding time 30 min and final temperature 700 ^{o}C. An about 45% of pyrolysis oil was obtained. Then, the pure TPO was emulsified by 10 wt% sorbitan oleate (Span 80) and 10 wt% emulsifier OP-10 ($C_{34}H_{62}O_{11}$) to improve its dispersity in the water solution. The concentration of the tyre pyrolysis oil emulsion (TPOE) was 80% in weight. Octanol was used as a frother, while diesel and TPOE as the collector. The analytically grade Span 80, OP-10, octanol and diesel were obtained from Aladdin Reagent (China).

Methods

Flotation

Flotation tests were carried out in a 1 dm^3 XFD laboratory flotation cell. In all flotation tests, a 100 g sample was used. The impeller speed in both conditioning and flotation processes was 1800 rpm. The aeration rate was 1.33 dm^3/min. The coal sample was first pre-wetted in the flotation cell for 1 min. Then, the collector was added and conditioned for 2 min. After that the frother (100 g per Mg of coal) was added and conditioned for additional 30 s. Each flotation test was performed for 3 min. The concentrates and tailings were filtrated, dried and weighed to calculate the mass of flotation products.

Water used in flotation tests was tap water with pH value of 7.6. Each flotation test was repeated at least three times. The data points represent the mean values (n = 3) with standard deviation.

Contact angle measurements

DSA 30 from KRUSS, Inc. (Germany) was used to measure the contact angle on the coal surface by the sessile drop method. In each test, 1 g of clean coal (ash content less than 8%) and collector (1 g/Mg) were first stirred with a magnetic stirrer for 30 min. Then, the suspension was filtered and dried at 30 ^{o}C and pressed for 1 min using a FW-4A powder compressing machine (China). The contact angle measurements were repeated and the contact angle values presented in this paper were presented as the average value of at least three measurements.

Immersion microcalorimetry experiments

Microcalorimetric measurements of adsorption of three coal samples were performed at 30 °C in a SETARAM C80 calorimeter (France). In each test, 100 mg coal sample was put into the lower part of the calorimetric cell, with a circular PTFE thin membrane cover on it. In the upper part of mixing cell, a volume of 2.0 cm^3 of collector solution (corresponding to 1 kg/Mg dosage) was added. After complete stabilization of the calorimeter base line, a movable rod break the membrane and enabled the collector solution to be pushed into the container with the mineral sample.

A thermal effect, which was corrected by subtracting the wetting effect of the coal sample in the deionized water, was obtained in each experiment. The effect of membrane breaking was found to be negligible in the test. The measurements results were analysed using the SETARAM software. The tests were repeated at least three times and each data point presented in this paper was the average value.

FTIR measurements

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 6700 spectrometer at 25 ^{o}C in the range from 4000 to 400 cm^{-1}. Prior to the tests, the coal samples were ground to less than 5 μm in an agate mortar before being conditioned with collector. Then, the coal samples conditioned with collectors were mixed with KBr (the mass ratio of the coal sample-to-KBr was 1:100) and pressed at 10 MPa for 1 min using a FW-4A powder compressing machine (China).

Results and discussion

Flotation results of the three coal samples are showed in Fig. 1. It can be seen that much higher concentrate yield and combustible matter recovery were obtained in the presence of TPOE. The TPOE showed good versatility for the three coal samples. For coal 1#, 72% concentrate yield and 84% combustible matter recovery were obtained in the presence of 1.6 kg/Mg TPOE compared with 31% concentrate yield and 37% combustible matter recovery in the presence of 1.6 kg/Mg diesel. For coal 2#, 92% concentrate yield and 96% combustible matter recovery were obtained in the presence of 1.5 kg/Mg TPOE compared with 41% concentrate yield and 43% combustible matter recovery in the presence of 1.5 kg/Mg diesel. For coal 3#, TPOE also showed good collecting ability. Since tyre pyrolysis oil (TPO) is mainly constituted by paraffin, olefins, aromatics and aliphatic hydrocarbons, these compounds may have synergistic effect in the flotation process of coals.

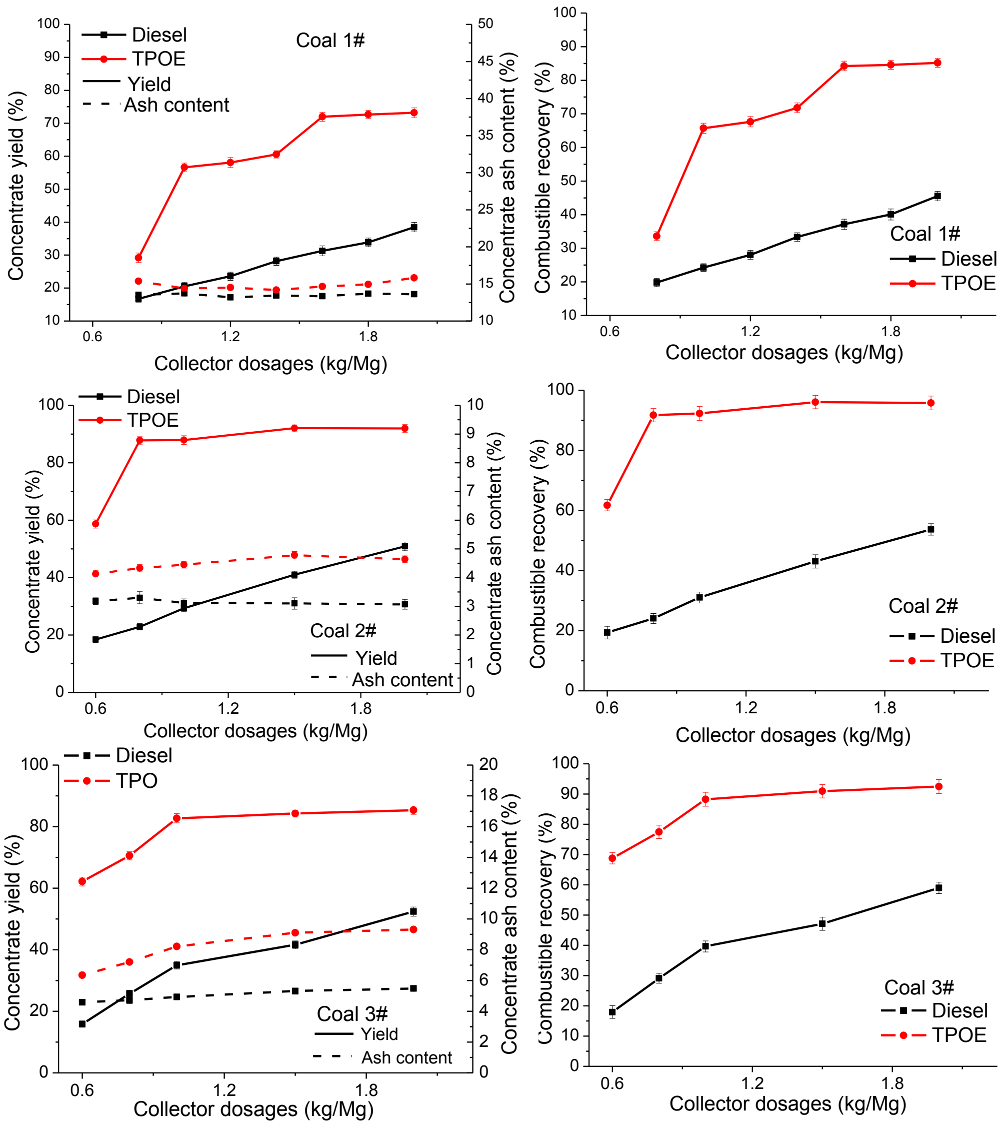

Fig. 1. Flotation results of coal 1#, coal 2# and coal 3# in the presence of TPOE and diesel. The data points represent the mean values (n = 3) ± standard deviation

In order to investigate the wetting behaviour of diesel and TPOE on coal surfaces, the contact angle measurements of were carried and the results are presented in Fig. 2. As shown in Fig. 2, the values of contact angle of pure coal 1#, coal 2# and coal 3#

were 63, 80 and 85°, respectively. The presence of TPOE increased the values of contact angle to 91°, 95°, 105°, respectively. Figure 2 also indicates that the coal samples become more hydrophobic in the presence of TPOE compared with that of diesel. The contact angle measurement results corresponded well with the flotation results.

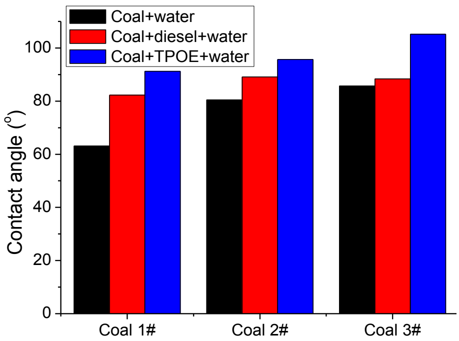

Fig. 2. Hydrophobicity of coal samples in water and in the presence of diesel and TPOE

All physical and chemical processes are accompanied by energy exchange. The energy change of a reaction is a fundamental thermodynamic quantity describing the amount of heat either released or absorbed during the course of the reaction (Atkins et al., 2006). In this section, the adsorption activity between either diesel or TPOE and three coal samples was compared by measuring the interaction heat. The measurement of adsorption energy can represent the total energy change in the adsorption process including wetting heat, energy required for desolvation and energy change after adsorbate binding heat (Cestari et al., 2010). Microcalorimetric plots for adsorption of diesel and TPOE on the coal samples are shown in Fig. 3. Generally, exothermic heat of interaction indicates the trend of attractive forces between the surface and adsorbate (Roselin et al., 2010). The interaction heat value can give an indication of the force between adsorbate and surface. As seen in Fig. 4, the interaction heat of TPOE and coals are much higher than that of diesel what indicates that TPOE is easily than diesel adsorbed on the coal surface.

Adsorption can be either physical or chemical. To a certain extent, physical adsorption and chemisorption can be classified by the magnitude of the energy change. It is well accepted that bonding strengths less than 84 kJ/mol can be classified into physical adsorption type bonds, and the typically chemisorption bond strengths can range from 84 to 420 kJ/mol. However, in this work we only got the total interaction heat in the immersion microcalorimetry test, and therefore the these tests cannot be used to determine the adsorption quantity of collector per gram of coal, and thus the type of adsorption process. In order to determine the adsorption type of TPOE on coals, the infrared spectrums of these three coals treated by diesel and TPOE (1 kg/Mg dosage) solution were measured and the results are shown in Fig. 5. Compared with the infrared spectrum of the pure coals, no new peak was observed for coal samples treated by either diesel or TPOE. Thus, it can be stated that diesel and TPOE physically adsorb on the coal samples.

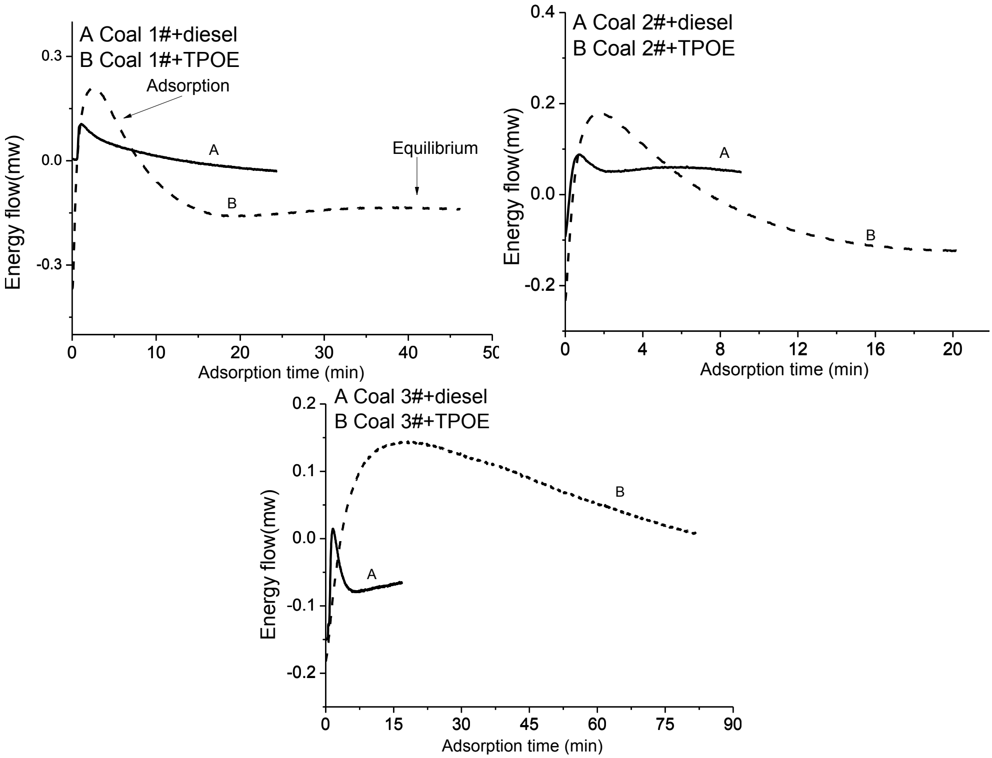

Fig. 3. Typical microcalorimetric plot for adsorption of diesel and TPOE on different types of coal surfaces (pH = 7.6, temperature 30°C)

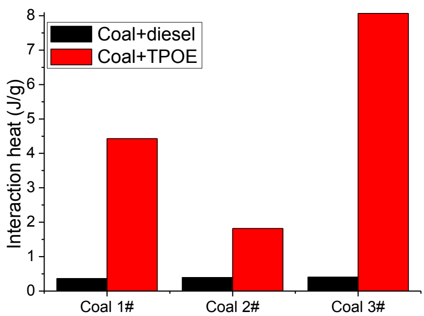

Fig. 4. Interaction heat of collector and coal samples

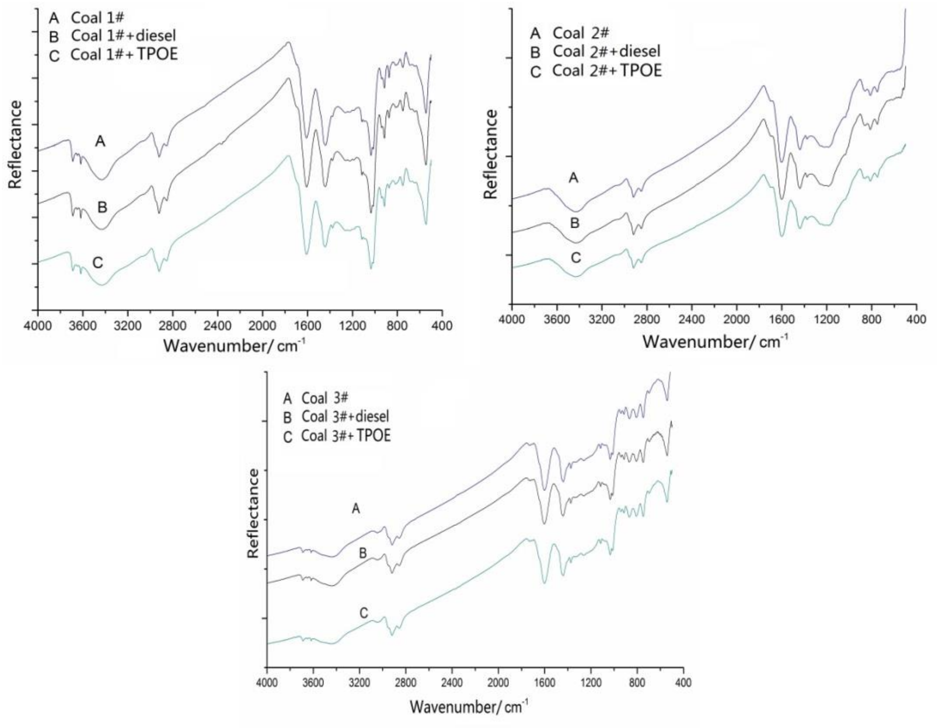

Fig. 5. Infrared spectra coal samples treated by diesel and TPOE
(collector dosage 1 kg/Mg, pH=7.8, temperature 25°C)

Conclusions

This paper proposed a new way to use the tyre pyrolysis oil emulsion (TPOE) as an efficient collector in flotation of coal. Flotation results indicated that the TPOE had stronger collecting ability than diesel. Over 90% combustible matter recovery can be obtained and the quality of the concentrate was acceptable as the concentrate ash content just slightly increased compared with that in the presence of diesel. The TPOE showed good versatility for three coal samples used in this work. The contact angle measurements and immersion microcalorimetry test correlated well the flotation data. Higher values of contact angle and interaction heat were obtained in the presence of TPOE than that of diesel. FTIR results suggested that diesel and TPOE physically adsorbed on the coal surfaces. It is apparent that each reduction in diesel consumption may bring a significant economic effect and this paper gives a new choice to the pyrolysis oil from waste tyre as an efficient flotation collector.

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