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The resource utilization of oily sludge by co-gasification with coal

Menghan Xu, Jie Zhang, Haifeng Liu *, Hui Zhao, Weifeng Li

Key Laboratory of Coal Gasification and Energy Chemical Engineering of Ministry of Education, East China University of Science and Technology, No. 130 Meilong Road, Shanghai 200237, People's Republic of China
Shanghai Engineering Research Center of Coal Gasification, No. 130 Meilong Road, Shanghai 200237, People's Republic of China

HIGHLIGHTS

- Oily sludge and coal are mixed to prepare coal–oily-sludge slurry (COSS).
- Different methods of adding oily sludge have great influence on the slurryability.
- Oily sludge could forms thin hydrophobic membranes on coal particle surface.
- Added oily sludge decreases viscosity and yield stress of COSS.
- The maximum solids load can be either increased or decreased in different methods.

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ABSTRACT

The utilization of oily sludge produced from refinery processes was evaluated in this study. Oily sludge was added to coal–water slurry (CWS) in different ways to prepare desirable coal–oily-sludge slurry (COSS). The slurryability and rheological characteristics of COSS were investigated and compared to CWS. The viscosity and yield stress of COSS sharply decrease with increasing the addition of oily sludge that preferentially wets coal particles. Microscopic structure and surface functional groups examination proved that oil droplets present in oily sludge could form a thin hydrophobic membrane on coal particle surface and modify its surface properties. The maximum solids loading can be either increased or decreased depending on the slurry preparation method. The maximum solids loading of COSS increases from 62.2 wt% to 64.0 wt% when oily sludge that preferentially wets coal was added in a ratio of 10.0 wt%.

1. Introduction

Petroleum industries generate large quantities of oily sludge that accumulated in crude oil tanks, refinery products tanks, and desalters et al. during oil production and processing [1–3]. Oily sludge is a complex mixture containing different quantities of waste oil, wastewater, sand, and mineral matter. A lot of components such as benzene, phenol, anthracene, and pyrene are also contained in it, and most of them are toxic, mutagenic, and carcinogenic [4]. Therefore, oily sludge is classified as priority environmental pollutant by the US Environmental Protection Agency and has been listed as dangerous solid waste in China, due to its adverse impact on human health and environment [5,6]. It is mandatory for industries to undertake the task of effective treatment and safe disposal of the wastes. A variety of methods have been suggested to treat oily sludge such as solvent extraction, membrane filtration, ozonation, incineration and biodegradation [6–8]. However, most of them are expensive and requiring elaborate equipment and substantial amounts of additional fuel. Simple and cheap technologies are needed for oily sludge treatment. A new concurrent disposal method for oily sludge is preparing coal–oily-sludge slurry (COSS) by adding oily sludge to coal–water slurry (CWS), and processing this slurry fuel in an entrained-flow gasifier [9,10]. This new disposal method for oily sludge are hoped to be a good strategy to address issues associated with using organic waste as direct fuel [11–14].

COSS should exhibit optimum rheological behaviors and good stability during its storage and transfer through pipelines. The primary factors responsible for the rheological behaviors of COSS depend upon physicochemical properties of coal particle such as its functional groups, roughness, wettability and inherent moisture [15–18]. During the slurry formation, hydrophilic functional groups on the coal surface will easily combine with water resulting in the loss of free water, which leads to the increase in the slurry viscosity. Therefore, the solids loading of COSS can be improved

* Corresponding author. Tel.: +86 21 64251418; fax: +86 21 64251312.
E-mail address: hfliu@ecust.edu.cn (H. Liu).

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by modifying the surface of coal particles. The oil present in oily sludge can work as adhesive to coat coal particle surfaces and form thin hydrophobic membranes [19]. In the preparation of COSS, the hydration layer [20,21] of coal particles become thinner consequently, which means the water is extremely repelled from the surface of coal particles, with more free water left. Therefore, the viscosity of COSS could be dramatically reduced.

In this study, a new way to dispose oily sludge by co-gasification with coal was proposed. Through different methods of adding oily sludge, the surface of coal could be modified, and therefore the slurry formation of COSS will be improved. The objective of the present work was to study the influence of oily sludge on slurryability of CWS. The rheological properties and stability of COSS were investigated, and compared to CWS. Fourier transform-infrared spectroscopy (FT-IR) and laser scanning confocal microscope were used to investigate mechanisms of co-slurrying of oily sludge and coal.

2. Experimental

2.1. Materials

Oily sludge from Gaoqiao Petrochemical Company (located in Shanghai, China) and Shenfu coal from Inner Mongolia were chosen for this study. The properties of sludge sample was tested mainly according to Taiwo [1]. Proximate and ultimate analysis and properties of the oily sludge are shown in Tables 1 and 2, respectively. Since the value of the API gravity is less than 22.3, the oily sludge can be classified as heavy oil.

Water content (WC): The American Society for Testing and Materials (ASTM) standard method D95 was used for measuring the water content of oily sludge. The oily sludge was heated with petroleum ether (solvent, boiling range 90–120 °C) which co-distilled with the water present in the sample in a fume cupboard. Condensed solvent and water were continuously separated in a trap, and the water settled as the bottom layer. The condensed liquid containing water and hydrocarbon was transferred to a graduated cylinder. A water layer with higher density was at the bottom of the cylinder. The volume of the water was then used to calculate the water content.

Volatile hydrocarbon content (VHC): Sample with known mass was put in an oven (with ventilation) at 105 °C to constant weight. The reduction in mass indicated the moisture and light hydrocarbon content in the sludge. As water content was measured previously, the light hydrocarbon content (wt%) was calculated as follows:

$$\text{VHC} = \frac{\text{reduced mass(g)}}{\text{mass of tested sample(g)}} \times 100\% - \text{WC(wt\%)} \tag{1}$$

Solids content (SC): Dried samples (105 °C) were placed in a furnace at 550 °C for 30 min. The residue was weighed. The solids content of the oily sludge was calculated in weight percent using the equation:

$$\text{SC} = \frac{\text{mass of residue remaining after burning(g)}}{\text{mass of tested sample(g)}} \times 100\% \tag{2}$$

Table 1
Properties of oily sludge.

Parameters	Values
Viscosity/mPa s	273.6
WC/wt%	59.86
VHC (105 °C)/wt%	17.63
NHC/wt%	14.98
SC/wt%	7.53
pH	7.4
API gravity/15.6 °C	19.69

Nonvolatile hydrocarbon content (NHC): After measuring the water content, light hydrocarbon content, solids content, and the nonvolatile hydrocarbon content can be calculated in weight percent as follows:

$$\text{NHC} = 1 - \text{WC} - \text{VHC} - \text{SC} \tag{3}$$

2.2. Experimental procedure

Raw coal was dried in a dry oven at 105 °C for 2 h, and then the dried coal was comminuted in a ball-milling machine to obtain particles of two particle size distributions. The size of the particle was determined by automatic laser granularity analyzer (Malvern mastersizer 2000) by suspending in ethanol and subjecting to ultrasonic diffusion. The mean volume diameters of coarse particles and fine particles are 18.3 μm and 219.6 μm, respectively. Coarse and fine coal particles were mixed by a mass ratio of 6:4, and the mean volume diameter of the mixed particles is 114.4 μm. Sodium naphthalene sulfonate formaldehyde condensate (NSF) was used as dispersant at a constant dosage of 0.8 g/100 g dry fuel (oil and coal) in the preparation of CWS and COSS. Because of the high calorific value of oil, the oil and solids of oily sludge contribute to the total solids content of COSS.

2.3. Analytical procedure

The rheological property measurements of COSS were performed using Malvern Bohlin CVO rheometer. The temperature was controlled at 25 ± 0.1 °C. The maximum solids loading is defined as solids content of slurry with viscosity (1000 ± 100) mPa s at a shear rate of 100 s^{-1} [22,23]. For measurements of viscosity, the shear rate is varied smoothly from 0 to 100 s^{-1} in 100 s. Later on, the shear rate is kept constant at 100 s^{-1} for 30 s for obtaining additional viscosity measurements. The results are averaged for determining the viscosity. The determination of yield stress: The shear stress ramp is conducted between 0 Pa and 10 Pa with 50 sample points over 500 s. Experiments are repeated three times to ensure that the ramp limits are sufficient and results are consistent. For the measurements of thixotropy, rheological curves were tested by gradually increasing the shear rate from zero to 100 s^{-1} in 3 min, and then decreasing from 100 s^{-1} to zero within the same time.

The stability of slurry was measured according to "glass rod penetration test" described by Zhan et al. [24]. Slurry was poured into a glass cylinder (3 cm in diameter) to 15 cm in height at room temperature for 24 h. A glass rod (5 mm diameter, 20 g) was spontaneously dropped from the slurry surface to the bottom of cylinder at a certain time interval, and it stopped when the tip got in contact with the hard sediment. The penetration ratio is calculated as follows:

$$\text{Penetration ratio } (\%) = d/d_t \times 100\% \tag{4}$$

where d is the distance of rod travel (cm), and d_t is the maximum distance of rod travel (cm). The slurry is graded into excellent stability (marked A), good stability (marked B), fair stability (marked C) and poor stability (marked D) according to the different penetration ratio ranges of 95–100%, 85–95%, 70–85% and 0–70%, respectively.

The microstructure of slurry was observed using laser scanning confocal microscope (Nikon A1R). The composite images (Fig. 1) are created by merging an unfiltered real-light image with a filtered, UV-light image using hydrophobic fluorescent dye [DiIC1(5) iodide, Fanbo Biochemicals Co., Ltd.] stained in the oily sludge. The intensity of the UV-light image is colored red in the composite image for clarity. Infrared spectrum of the sample was analyzed using