Fuel Processing Technology 137 (2015) 124–130

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Effect of hydrophobicity on viscosity of carbonaceous solid–water slurry

Amrita Mukherjee [a,b], Peter Rozelle [c], Sarma V. Pisupati [a,b,*]

[a] John and Willie Leone Family Department of Energy and Mineral Engineering, The Pennsylvania State University, 110 Hosler Building, University Park, PA 16802, USA
[b] EMS Energy Institute, The Pennsylvania State University, 110 Hosler Building, University Park, PA 16802, USA
[c] US Department of Energy, Germantown, MD, USA

ARTICLE INFO

Article history:
Received 5 August 2014
Received in revised form 6 December 2014
Accepted 8 December 2014
Available online 25 April 2015

Keywords:
Coal
Petcoke
Hydrophobicity
Aggregation
Optimum particle-size distribution
Viscosity

ABSTRACT

Carbonaceous solid–water slurry rheology is greatly affected by the surface properties of the carbonaceous solids used. Slurriability studies showed that, for the same solids loading, viscosities of highly hydrophobic petcoke and bitumen–water slurries were approximately one order of magnitude higher than the viscosity of non-hydrophobic Illinois #6 (bituminous) coal–water slurry. Apart from slurriability, the hydrophobicity of the carbonaceous solids was found to influence the type of additives used to reduce the viscosity. Selected to reduce viscosity, the addition of non-ionic additive Triton X-405 caused a drastic reduction in petcoke and bitumen–water slurry viscosities, whereas anionic additive ammonium lignosulfonate reduced Illinois #6 coal–water mixture viscosity more effectively. Optimum particle-size distribution was also found to be dependent on the surface properties of the solids. Experimentally determined optimum particle-size distributions were observed to deviate from the theoretical predictions. A deviation of 8% was noted in the case of Illinois #6 coal–water slurry, whereas deviations of 30% were observed in the case of hydrophobic bitumen and petcoke–water slurries. Viscosity predictions of semi-empirical models were compared to experimentally measured viscosities. The predicted viscosities did not match the experimental results, especially at higher solids loading. A thixotropic model taking into account particle aggregation was found to predict viscosity more accurately in the case of these hydrophobic carbonaceous solid–water slurries.

1. Introduction

Carbonaceous solid–water slurry (CSWS) fuel has received worldwide attention since 1970 [1] as a substitute for oil. Currently, carbon-rich, hydrophobic by-products from the petroleum industry such as bitumen or petroleum coke are being used as fuel in slurry-fed gasification units for Integrated Gasification Combined Cycle plants [2,3]. A typical CSWS consists of 60–75% carbonaceous solid, 35–40% water, and about 1% of chemical additive [4]. For higher gasification efficiency, CSWS should have a high solids content but a low viscosity for ease of handling and to reduce pumping energy. The industrially expected Brookfield viscosity value for a typical CSWS is 1000 cP at 100 rpm [5].

Hydrophobicity is one of the most important surface properties of carbonaceous solids. It plays a crucial role in determining the rheological behavior of the solids suspension in water [6]. Hydrophobic interaction resulting from higher carbon content of these solids gives rise to the formation of aggregation networks in the suspension [7]. Higher mineral matter and oxygen contents in carbonaceous solids result in greater hydrophilicity, leading to increased adsorption of water on the solid surface [7,8]. The rheology of the suspension gets affected in both of these cases. Chemical additives are important ingredients in controlling such behavior and maintaining fluidity and stability of the slurries [9–11]. The type of additive also depends on the hydrophobic/hydrophilic character of the solids. Therefore, in order to study and control slurry rheology, it is very important to understand the behavior of these carbonaceous solids when in suspension. The main objective of this work is to study the effect of hydrophobicity on CSWS viscosity.

Along with surface properties, particle-size distribution is the other most important factor that determines CSWS viscosity. Optimum particle-size distribution ensures tight packing of the particles and thus maximizes solids volume fraction [12]. Several models have been proposed to calculate optimum particle-size distribution. Some of the most notable works were done by Furnas, Andreasen and Andersen, and Farris [1,13,14]. Henderson and Scheffe modified the Farris equation by expressing the model in a more practical form. These models were developed for spherical non-interacting particles [15]. This work experimentally tests the applicability of the Henderson and Scheffe equation for the determination of optimum particle-size distribution for these carbonaceous solids–water slurries which differ in surface properties.

This work also tests the applicability of semi-empirical models and a thixotropic model for viscosity prediction of carbonaceous solids–water slurries. One of the earliest works by Einstein predicts the viscosity of infinitely dilute suspensions of rigid spheres [16]. Mooney, Krieger–Dougherty, Liu, Dabak et al., Chong et al., Simha, and many others

---

[*] Corresponding author.
E-mail address: sxp17@psu.edu (S.V. Pisupati).

http://dx.doi.org/10.1016/j.fuproc.2014.12.055
0378-3820/

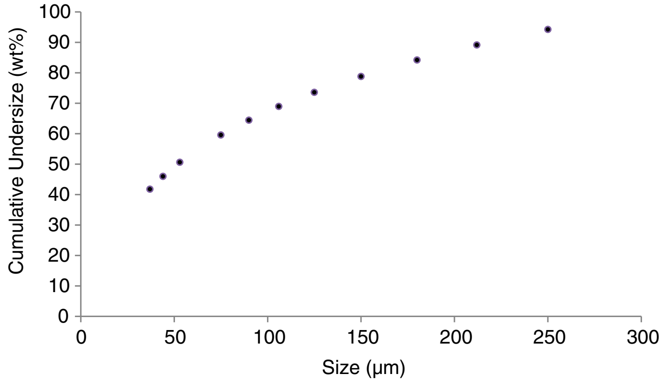

Fig. 1. Particle-size distribution used in slurriability study, analysis of effect of additives and viscosity prediction experiments.

[17–22] developed semi-empirical equations for suspensions of finite concentrations. These models were originally developed for hard spheres and did not take into account the surface properties of the solids. Dooher et al. developed a phenomenological model for viscosity prediction in their work [23]. Surface properties were taken into account through statistical correlations. Their work was based on only bituminous and lignite coal and did not include highly hydrophobic solids like petcoke and bitumen. Moreover, the correlation developed by Dooher is proprietary and is not accessible to all. Based on the phenomenological model proposed by Cheng and Evans, Usui proposed a thixotropic model for predicting viscosity of highly concentrated coal–water mixture [24–27]. This model takes into account the agglomerative nature and non-sphericity of the suspended solids and is based on the assumption that only the smallest particles take part in aggregation [28].

2. Experimental

2.1. Materials

Experiments were carried out with Illinois #6 coal (bituminous coal), bitumen, and petcoke–water slurry samples. The particle sizes of each of these samples were reduced to less than 500 μm using a laboratory-size ball mill, and the particles were screened and separated into the following size ranges: −250 + 212 μm, −212 + 180 μm, −180 + 150 μm, −150 + 125 μm, −125 + 106 μm, −106 + 90 μm, −90 + 53 μm, −53 + 44 μm, −44 + 37 μm, −37 μm. The following particle-size distribution, as shown in Fig. 1, with weighted mean size equal to 72 μm, was used in the following experiments:

a. studying the effect of surface properties of different carbonaceous solids on their slurriabilities (Section 3.2)
b. analyzing the effect of additives on slurry viscosity (Section 3.3)
c. testing the applicability of the existing viscosity models to predict viscosity of carbonaceous solid–water slurry (Section 3.5)

For experiments involving the determination of optimum particle-size distribution (Section 3.4), the particle-size distribution was varied. The Henderson and Scheffe formula was utilized to determine the particle-size distribution, which would result in optimum viscosity and stability of the CSWS.

The proximate and ultimate analyses of the three samples are presented in Table 1:

2.2. Additives

For experiments involving additives, the additives tabulated in Table 2 were used.

Table 1
Proximate and ultimate analyses results:

	Proximate analysis (weight %, dry basis)				Ultimate analysis (weight %, dry basis)				
	M	VM	A	FC	C	H	N	S	O
Petcoke	0.32	10.96	0.17	88.55	89.08	3.64	1.47	5.43	0.20
Bitumen	0.16	49.51	0.47	49.86	91.1	2.96	1.3	4.09	0.11
Illinois #6	7.71	38.46	12.48	49.05	68.76	4.73	1.53	5.47	7.02

Note: M,VM, A, and FC stands for moisture, volatile matter, ash, fixed carbon, respectively; C, H, N, S, and O denote carbon, hydrogen, nitrogen, total sulfur, and oxygen, respectively.

2.3. Preparation of CSWS

For the preparation of CSWS, the calculated amount of carbonaceous solids (calculated on the basis of targeted slurry concentration) was added to a weighed amount of distilled water. The mixture was then stirred by a propeller agitator for 10 min and viscosity was measured [29]. For experiments involving additives, the additives were directly added to distilled water. Solids loading of the CSWS was calculated and reported on a moisture-free basis.

2.4. Viscosity measurements

The viscosity of the coal–water mixture was measured using a Bohlin 88 Viscometer (a product of Malvern Instruments Ltd., U.K.), which comprises of a constant speed motor with a torque detecting system. For all the experiments conducted in this work, measuring systems no. 8 (i.e., the system designated as “wide gap” with the inner cylinder diameter 25 mm and outer cylinder 33 mm) was used. This measuring system was designed for use with the range of viscosity values from 10 cP to 5,000 cP. The shear rate used for all the measurements was $100\ s^{-1}$. All viscosity measurements were performed in the temperature range of 23 to 26 °C and 30–40% humidity (ambient conditions).

2.5. Contact angle measurement

Contact angles were measured using a goniometer (ramé-hart Model 295). Coal particles were made into pellets with a pressure of 750 psi, and the contact angles of water on the carbonaceous solid surface were measured using the sessile drop technique.

2.6. Uncertainty analysis

To determine the repeatability, each experiment was repeated five times. Important factors that might have led to errors in viscosity measurement include variation in particle shape, sieve analysis limitations, weighing balance tolerance, and measurement error. Using the recommended manufacturer's procedure, the viscometer was calibrated prior to each experiment. Relative standard deviations (representing combined error due to all of these factors) of around 10% in lower viscosity values and around 5% in higher viscosity values were observed. The slight variation in relative standard deviation from lower to higher viscosity measurements can mainly be attributed to measurement errors caused due to wall slip conditions and agglomerate formation in concentrated suspensions [29].

Table 2
Additives used in this work.

Commercial name	Chemical name	Type
Norlig TSD	Ammonium lignosulfonate	Anionic
Kayexalate	Sodium polystyrene sulfonate	Anionic
Triton X-405 (70% active)*	Octylphenol ethoxylate	Non-ionic

* Note: 70% active indicates concentration (by weight) of additive in water as provided by the supplier.