Fuel Processing Technology 144 (2016) 290–298

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Research article

Rheological modifiers for petroleum coke–water slurry

David J. Marchand [a], Alexander Abrams [a], Brennan R. Heiser [a], Yongkwang Kim [b], Juhoe Kim [b], Seong H. Kim [a,]*

[a] Department of Chemical Engineering and the Materials Research Institute, The Pennsylvania State University, University Park, PA 16802, USA
[b] Green Coal Lab, Energy R&D Center, SK Innovation, 325 Expo-ro, Yuseong-gu, Daejeon 305-712, Republic of Korea

ARTICLE INFO

Article history:
Received 13 October 2015
Received in revised form 7 January 2016
Accepted 11 January 2016
Available online 23 January 2016

Keywords:
Petroleum coke
Petcoke
Slurry fuel
Rheological properties

ABSTRACT

The rheological properties of petroleum coke–water slurries (PWS) were examined and modified using polyvinyl alcohol (PVA), naphthalene sulfonate (NS), and xanthan gum (XG). PVA and NS were both very effective at reducing the slurry viscosity. Adsorption isotherms showed that PVA and NS must be adsorbed to the particle surface to be effective; the viscosity cannot be reduced further once the particle surface is saturated. Decreasing the slurry viscosity also caused very poor stability against settling due to gravity. Adding XG to PVA-treated slurries gave strong shear-thinning behavior, which allowed for excellent stability. PVA and XG are practical and effective for producing PWS with ideal rheological behaviors.

1. Introduction

The dwindling supply of easily accessible oil has led to the exploration of slurry fuels – highly loaded suspensions of solid carbonaceous particles in liquid media – as a means to supplement liquid fuels using solid fuel sources. Coal–water slurries (CWS) are one of the most notable examples of this trend [1–5]. Research into their creation and use started as a result of the oil shortages in the 1970s, and now the majority of CWS research and usage occurs in China, where there are large coal reserves but little oil. Various other slurry fuels have also been investigated, including those that use biomass for the solid component [6], or black liquor [7] or sludge as the liquid phase [8–10].

Recently, the buildup of petroleum coke (petcoke), the solid byproduct of petroleum distillation, has led to an increased interest in petroleum coke–water slurries (PWS) [7,10–12]. Petcoke has desirable properties as a fuel since it has high carbon content, high heating value, and low ash content. However, it is inconvenient to burn directly as a fuel source because of difficulty in transporting the solid material and the high SO_X emissions — petcoke can contain 5 wt.% sulfur [9]. Producing a slurry from the petcoke may solve the transportation issues, and the presence of water suppresses the combustion temperature, which could reduce the production of SO_X [3]. Petcoke is also more desirable than coal for slurry applications because of its lower ash content, since ash species cause abrasion and other costly maintenance issues in a boiler [13,14]. While the ash content of coal varies from 2 wt.% to above 20 wt.% depending on the coal rank [1,15], petcoke is typically only about 0.5 wt.% ash [7,10,12]. The desire to fully utilize petcoke stocks, the advantages of slurry preparations, and the improved performance of PWS over CWS have all contributed to the increased interest in producing and burning PWS [16].

Unfortunately, some fundamental issues hinder the creation of PWS with optimum properties [1,17,18]: (1) petcoke is hydrophobic, so dispersing petcoke particles in water requires either a surfactant or some surface treatment to render them hydrophilic; (2) the petcoke particles in the slurry can be up to 100 μm in diameter, and they are much more dense than water, so some stabilizing agents are required to prevent settling due to gravity; (3) the viscosity of the slurry must be low (<1 Pa-s) to facilitate pumping through a power plant like an oil, but the low viscosity also increases the rate of settling due to gravity; (4) the solid loading must be quite high (>55 wt.% petcoke) so that it has an appreciable heating value (~20,000 kJ/kg), but the high loading leads to a high viscosity. These goals are, in part, mutually exclusive, so creating a slurry with optimum properties is difficult.

Many of these issues with PWS have been addressed in the research on CWS. The effects of many variables on the properties of CWS have been investigated, including coal type [1,16,19–23], loading [16,19,22,24–26], particle size distribution [16,19,27,28], temperature, and the addition of various surfactants, dispersants, and stabilizers [7,29–33]. The addition of additive molecules, in particular, can drastically change the rheological behavior of a slurry, since those additives can fundamentally change the interaction between particles in water. Hydrophobic particles in water naturally tend to agglomerate due to the van der Waals and hydrophobic interactions [34]. Disrupting the network of interacting particles requires energy, which means those interactions lead to a higher slurry viscosity.

Some additive chemicals can negate the interparticle interactions that cause agglomeration and high viscosity. Naphthalene sulfonate (NS) is a common additive in CWS formulations [4,14,17]. NS adsorbs to the coal particle surfaces, and the sulfonate group dissociates in

---

* Corresponding author.
E-mail address: shkim@engr.psu.edu (S.H. Kim).

http://dx.doi.org/10.1016/j.fuproc.2016.01.011
0378-3820/

water to become negatively charged. The coal particles are then electrostatically repelled from each other, which overcomes the net attractive forces between the bare particles, and the viscosity decreases [4]. Many polymers have also been used as additives for CWS to reduce the viscosity [35–38]. If the polymer has hydrophobic and hydrophilic regions, the hydrophobic regions will adsorb to the coal surfaces, and the hydrophilic regions will be suspended in solution [5]. The coal particles then repel each other due to steric hindrance from the polymer chains.

Another issue with PWS and CWS is that the particles can be quite large – on the order of 10 or 100 μm, which is well above the range of colloidal stability – so the particles will settle due to gravity. The stability of CWS has been improved by adding stabilizers that can impart shear-thinning behavior on the slurry [18,30]. The stabilizers act to create a network structure in the slurry that increases the viscosity at low shear rates, but that network is easily disrupted and cannot reform at high shear rates, so the viscosity is lower [34,39]. Since settling due to gravity for a small particle is a very low shear process, the particles are stabilized by the high viscosity under that static condition. Xanthan gum (XG) is one of the most common stabilizers used in the food and consumer goods industries, and it has also found favor in CWS formulations, since it is cheap, abundant, and can impart strong shear-thinning behavior at low concentrations (<1 wt.%) [39–41].

In this paper, we discuss the use of various additives to reduce the viscosity and increase the stability of the petcoke slurries. Following the success of using NS to reduce viscosity of CWS, we show that NS is also effective in PWS. However, NS is undesirable for practical use with PWS, because the sulfur in NS adds to the inherent sulfur in petcoke, which is already problematic. Polyvinyl alcohol (PVA) was investigated as a possible alternative to NS, because PVA contains a mixture of hydrophobic and hydrophilic regions, it is comprised only of carbon, oxygen, and hydrogen, and is cheap and easily available in large quantities. PVA is shown to be as effective as NS at reducing the slurry viscosity as well as allowing for higher solid loading. However, PVA decreases the viscosity at all shear rates, so slurries with PVA are not stable against settling. This issue is solved by adding xanthan gum to impart shear-thinning behavior onto the slurries. The combination of PVA and XG gives PWS with ideal properties: low viscosity, high solid loading, and good stability.

2. Experimental

2.1. Petroleum coke and additives

Petcoke was provided pre-ground by SK Innovation Global Technology, and was sourced from India. Fig. 1a shows the size distribution of the ground petcoke, for which the volume median diameter is D [v,0.5] = 31.7 ± 0.3 μm. Fig. 1b shows the XPS spectrum obtained from as-received petcoke. Table 1 gives the bulk elemental concentration obtained from ultimate analysis (elemental analysis of combustion products) of the petcoke, as well as the surface concentration obtained from XPS. The two techniques show that the surface and bulk compositions are similar. The oxygen concentration is higher at the surface, probably due to oxidation from the environment [42], and the sulfur content is slightly lower, perhaps due to the surface oxidation.

The rheological modifiers were purchased from Sigma Aldrich. These included: polyvinyl alcohol, 80% hydrolyzed, $M_W = 9000$–10,000 (cat. # 360627); sodium 2-naphthalene sulfonate (cat. # N6885); and xanthan gum (cat. # G1253). Polyvinyl alcohols with different molecular weights and degrees of hydrolysis were tested, but they all gave similar results.

2.2. Preparation of PWS

The necessary masses of petcoke, water, and any additives were measured on a scale. The concentrations of additives in the slurry are reported as weight percent based on the dry mass of petcoke, i.e., ignoring the mass of water. The additives were mixed into the water first, and the solution was mixed until no visible solids remained. The solution was allowed to settle until any bubbles produced during mixing disappeared, then the petcoke was added to the solution, and the slurry was vigorously mixed. Rheological measurements of the slurries were inconsistent in the first few hours after mixing due to the effects of bubbles, so all slurries were allowed to settle for at least 24 h before any measurements.

2.3. Characterization of PWS

Rheological measurements were performed using a Rheometric Scientific RM180 rheometer, a rotational, concentric cylinder rheometer that covers shear rates from 6.5 to 1290 s^{-1} and can detect torques from 0.25 to 7.5 mNm. The particle size distribution was found using a Malvern Mastersizer S laser diffraction system. Particle zeta potentials were measured with a Malvern Zetasizer ZS. X-ray photoelectron spectroscopy was performed using a Kratos Analytical Axis Ultra.

Attenuated Total Reflectance-Infrared Spectroscopy (ATR-IR) was used to measure adsorption isotherms via solution concentrations. A ThermoNicholet Nexus 670 FT-IR with a ZnSe ATR crystal was used for these measurements. The adsorption measurements were performed using ATR-IR instead of the simpler transmittance mode because the broad water absorption region obscured the PVA spectra in transmittance mode. The experimental procedure to create the adsorption isotherms was as follows:

(1) Create solutions of PVA in deionized water; measure IR absorption intensity of those solutions; plot the absorption peak area

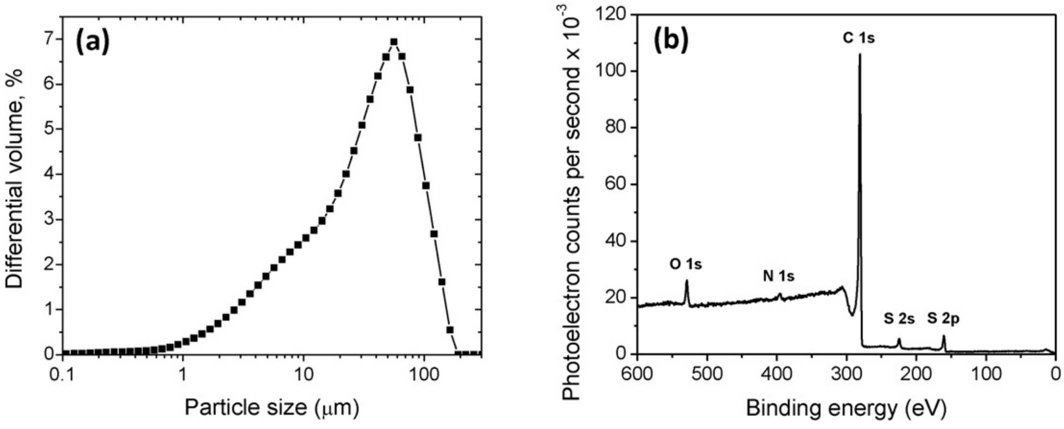

Fig. 1. (a) The particle size distribution of ground petroleum coke, and (b) the XPS spectrum of that sample.