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**DEVELOPMENT AND USE OF AN APPARATUS TO MEASURE
THE DYNAMIC SURFACE PROPERTIES OF COAL-WATER SLURRY FUELS**

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ABSTRACT

Experiments were conducted to measure dynamic surface tension of various coal-water slurry (CWS) fuel samples containing different surfactants and coal loadings. A maximum air bubble pressure technique was used to measure dynamic surface tension. The coal used for the CWS had 50 μm volume mean diameter (VMD) mined from the Upper Elkhorn Seam in Virginia. Five surfactants were selected for the study: Witconol NP-100, Ammonium DDBS (hard), Ammonium DDBS (soft), Witconate 1223H and Witconate 1840X. To determine critical micelle concentration (CMC), static surface tension was also measured using a Du-Nouy ring tensiometer. Detailed and comprehensive data for dynamic surface tension for a 50% CWS mixture are documented and presented.

INTRODUCTION

CWS has been receiving attention as an alternative fuel because of its similarity to oil with respect to convenience in transporting and handling. However, CWS fuel needs to be atomized into fine droplets to provide for acceptable combustion. Atomization characteristics of liquid or slurry fuels significantly affect the combustion performance. The basic physics of atomizing coal slurry mixtures is not well developed, consequently, there is a weak theoretical base for characterizing droplet sizes with defined properties. On the other hand, an intrinsic difficulty in studying CWS fuels is their diversity in chemical and physical contents, depending on the

geographic location of the coal. A universal correlation cannot be expected for CWS atomization, and an individual study of coal from a particular seam is essential.

To characterize CWS fuel atomization, several basic properties must be measured, including surface tension and viscosity (Kihm et al., 1993). Although CWS mixture is known to exhibit a weak non-Newtonian behavior, a number of rheological studies show that CWS viscosity approaches a constant value when the shear rate is relatively high, as in atomization. One of the most important fluid properties associated with droplet formation in CWS fuel sprays is the dynamic surface tension. Static, not dynamic, surface tension is normally measured in conventional rheology. The static surface tension measurement is relatively simple and allows enough time for surfactants to disperse to the liquid interface. The static and dynamic surface tension values are the same for pure fluids, such as pure water. The dynamic surface tension, however, may be much different than the static surface tension for certain classes of mixtures. An example of such a fluid mixture is water mixed with a surfactant. CWS fuels usually contain 1% or more of additives, and these additives keep suspended coal particles from sedimenting too quickly and also reduce the surface tension for better mixing. For these fluid mixtures, droplet formation is dependent on the amount of surfactant which reaches (migrates and/or disperses to) the mixture surface. If the frequency of droplet formation is low, sufficient surfactant reaches the surface and the effects of the surfactant may be fully appreciated. On the other hand, if the frequency of droplet formation is high, insufficient time may exist for the surfactant to reach the interface. In this case, dynamic surface tension is the governing property for atomization, and values of dynamic surface tension may be much higher than the corresponding static surface tension because insufficient time exists for migration of surfactant.

The CWS preparation industry has historically concentrated on improving the mixing and stability of coal powder suspended in water. Little attention has been paid to the effect of different surfactants on dynamic and/or static surface tension of the CWS mixture. This paper presents an experimental study of static and dynamic surface tension properties of CWS fuels for selected surfactants, using a maximum bubble pressure technique. Parametric variations in the study include coal loading, surfactant concentration, and bubble frequency.

EXPERIMENTAL PROCEDURES

Properties of Tested Coal Powder

The test coal mined from the Upper Elkhorn seam in Virginia was pulverized at the DOE-PETC grinding facility. Size distributions of the coal particulate were measured with a Leeds and Northrup Microtrac Standard Range Analyzer at the PETC and the results are presented as volume fraction versus VMD in Fig. 1. The proximate and the ultimate analyses of the coal were also

made at the PETC and are summarized in Table 1. The ash contents of 2.56% and the relatively large VMD of 55 μm indicated that the coal powder would be suitable for boiler applications. For firing internal combustion engines, the coal is generally micronized to less than 5 μm VMD, and the ash contents need to be less than 1% (Hsu and Branyon, 1993).

Maximum Bubble Pressure Technique

Figure 2 illustrates the operating principle of the maximum bubble pressure tensiometer technique for dynamic surface tension measurement (Brian and Chen, 1987). The CWS sample was contained in a vessel into which is inserted a specially designed capillary tube with a small outlet diameter of one millimeter. As bubbles were formed, grew, and detached from the capillary tube orifice, variations of the bubble pressure occurred because of the change in bubble radius. For each bubble, maximum pressure was recorded when the bubble radius reached its minimum at the orifice radius. For different bubble generation frequencies, the dynamic surface tension was calculated from the measured maximum bubble pressure substituted into a simple relation

$$\sigma = (p_{\max} - \rho gh) r_c / 2 \quad (1)$$

where ρ is the sample fluid (CWS) density, g is the gravitational acceleration, h is the height above the capillary outlet, and r_c is the radius of the capillary outlet. The maximum bubble pressure, $p_{\max}$, corresponds to the inside air pressure when the radius of the growing bubble is equal to the capillary radius, r_c . The KRUSS Model BP1 tensiometer was adopted to measure dynamic surface tension of CWS fuels. The accuracy of the tensiometer was tested by measuring surface tension for distilled and deionized water. The result ensured a satisfactory measurement accuracy showing less than 2% deviations from the surface tension values listed in the CRC Handbook (Weast, 1988).

Tested Additives/Surfactants

Two different kinds of additives were considered: a stabilizer and a surfactant. Without a stabilizing additive, the coal particles separated from the mixture very rapidly and within minutes produced a thick layer of coal powder at the bottom of the container. We concluded that a stabilizer had to be considered as an essential component in all CWS fuel formulations. Flocon, a commonly used stabilizer for CWS mixing, was selected as the stabilizer. After some trial-and-error procedures, an optimal concentration of Flocon was determined to be between 0.3 - 0.5% in weight of the tested CWS. A rotary shaker was used to mix the CWS with deionized and distilled water.

Guidance and suggestions in identifying appropriate surfactants for testing were based on Berger (1992). The selected surfactants and their critical micelle concentration (CMC) data are

presented in Table 2. The static surface tension is minimized for concentrations higher than the CMC. Surfactant concentrations greater than CMC do not further decrease the surface tension significantly. These CMCs were measured for a water-based solution using a Du-Nouy ring tensiometer. Figure 3 shows the measured static surface tension as a function of weight % for the case of Witconol NP-100 showing the CMC of 0.0041%. When coal powder is added, a significant increase of CMC is expected primarily because of the absorption of surfactant occurring on the porous surface of the coal particles.

RESULTS AND DISCUSSION

Critical Micelle Concentration of CWS Mixtures

Measurement of static surface tension of CWS mixtures was carried out using a Du-Nouy ring tensiometer. Figure 4 shows the variations of static surface tension of 40, 50 and 60% CWS fuels with Witconol NP-100 concentration changes. Measured values of static surface tension were nearly insensitive to the coal loading ranges considered. For all three coal loadings, about 0.1% CMC was measured for Witconol NP-100 surfactant. Compared with the water-based solution, more than an order of magnitude increase in CMC was observed for CWS mixture. This is believed to be primarily due to the absorption of the surfactant by coal particulate.

Dynamic Surface Tension

Figures 5(a) and 5(b) present measured dynamic surface tension versus bubble frequency for a water mixture and for 50% CWS mixture, respectively. For each mixture, five different concentrations of Ammonium DDBS (soft) surfactant were considered. The dynamic surface tension of pure water (0% curve in Fig. 5(a)) remained constant, yielding approximately 72 dyne/cm regardless of bubble frequency. As we shall see, the measured static surface tension of CWS was comparable to pure water. For the case of the dynamic surface tension of CWS without surfactant, however, a gradual increase was observed with increasing bubble frequency and the values of dynamic surface tension were higher than that of pure water at all bubble frequencies. This higher dynamic surface tension is believed to be due to the higher viscosity of the suspended coal powder in CWS. The dynamic surface tension behaved similarly when the surfactant concentration was relatively low (0.1%). When the surfactant concentration was sufficiently high (5.0%), excessive amounts of surfactant overrode the negative effect of coal powder, and dynamic surface tensions for both mixtures were essentially the same. The other four surfactants demonstrated qualitatively very similar behaviors.

Figure 6 presents diverse results of surface tension measurement versus weight % of Witconol NP-100 surfactant. The regular symbols represent the water mixture case and the solid

symbols represent the 50% weight CWS case. The solid circles and squares denote static and dynamic surface tension, respectively. The three curves for the dynamic surface tension results correspond to three different bubble frequencies of 1, 6, and 10/sec. For the same surfactant concentration, CWS showed higher static surface tension than did the water mixture. CWS also exhibited higher CMC concentrations. This is likely due to the absorption of surfactants by coal particles and the reduction in active concentration of surfactant in the mixture. The dynamic surface tension showed a dramatic increase with increasing bubble frequency. Since the bubble expansion rate was faster with higher bubble frequency, less surfactant can migrate to the bubble surface, which resulted in higher surface tension. The static surface tension can be considered as an equivalent dynamic surface tension measured with zero bubble frequency.

For all five different surfactants, dynamic surface tension measured with bubble frequency of 10/sec is presented for 50% weight CWS mixtures in Fig. 7, and also tabulated in Table 3. For pure CWS mixture without any surfactant, the dynamic surface tension ranged from 80.5 to 84.0 dyne/cm showing approximately a $\pm 2\%$ scatter based on a constant ideal case. This scatter included the inhomogeneity of coal powder, the uncertainty of coal concentration and mixing, the repeatability of the tensiometer measurement, and other experimental factors. For the variable nature of the experiment, a $\pm 2\%$ scatter is considered to be acceptable. For all the surfactants, dynamic surface tensions showed sharp decreases up to about 1% surfactant concentrations, which were roughly equivalent to the CMC of NP-100, and gradual decreases were observed thereafter. An important thing to note here is that the dynamic surface tension of CWS mixture can be widely varied, depending on both added surfactant and its concentration. According to the results presented in Fig. 7, NP-100 can be considered as the best surfactant, yielding a minimal dynamic surface tension.

CONCLUSION

This experimental study was made to characterize the rheological behavior of CWS by measuring both the static and dynamic surface tensions. Most experiments were performed with a 50% weight CWS. Five different surfactants were studied: Witconol NP-100, Ammonium DDBS (hard), Ammonium DDBS (soft), Witconate 1223H, and Witconate 7840X. Fundamental conclusions reached are the following:

1. The maximum air bubble pressure technique has been successfully applied to measuring the dynamic surface tension of CWS mixtures.
2. The critical micelle concentration of CWS mixtures was generally higher than that of a water mixture mainly because of the absorption of surfactant by coal particles.

3. Dynamic surface tension was significantly higher than its static surface tension and increased with an increasing bubble frequency.
4. For the tested surfactants, the dynamic surface tension showed sharp decreases as the surfactant concentration reached to 1%, and gradual decreases were observed thereafter, at the higher concentration.

FUTURE RESEARCH PLAN

For future investigation, the surface tension measurements will be repeated for CWS samples containing higher coal loadings of up to 70 % in weight. The PI is pursuing a cooperative effort with WITCO in Houston in developing a new dispersant that will allow CWS samples with such high solid contents. Another direction of the research will be to design and construct an atomizer to test the correlation between the surface property measurement and the atomization characteristics of CWS fuels. For more comprehensive investigation, a cross-injecting spray system into convective air stream will be devised.

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Table 1. Results of coal analyses (Upper Elkhorn Seam coal, Virginia)

Proximate Analysis (dry basis)	
% Volatile Matter	36.75
% Fixed Carbon	60.69
% Ash	2.56
High Heating Value	14,950 Btu/lb 34,741 kJ/kg
Ultimate Analysis (dry basis)	
% Carbon	83.66
% Hydrogen	6.38
% Nitrogen	1.56
% Sulfur	0.77
% Oxygen (diff)	7.63

Table 2. Critical micelle concentration (CMC) of selected surfactants (water-base solutions)

Surfactants	CMC (weight %)
Witconol NP-100	0.0041
Ammon DDBS (Hard)	0.11
Ammon DDBS (soft)	0.083
Witconate 1223H	0.12
Witconate 1840X	0.05

Fig. 1 Measured volume fraction of coal particulates (VMD = 55 um)

Fig. 2 Schematic illustration of maximum air bubble pressure technique for dynamic surface tension measurement

Fig. 3 Static surface tension of Witconol NP-100 mixed with distilled water

Fig. 4 Static surface tension of CWS mixture with Witconol NP-100 for three different coal concentrations: 40%, 50%, and 60%

(a) water solution

(b) 50% weight CWS mixture

Fig. 5 Dynamic surface tension of (a) water solution, and (b) 50% weight CWS mixture with Ammonium DBBS (soft).

Fig. 6 Static and dynamic surface tension of 50% weight CWS mixture with NP-100
(The numbers in the parentheses represent the bubble frequency per second.)

Fig. 7 Dynamic surface tension of 50% weight CWS mixture with different surfactant weightings under bubble frequency of 10/sec

Table 3 Dynamic surface tension of 40 and 50% weight CWS fuel samples containing different surfactant concentrations measured at 10 bubbles/sec (unit of surface tension: mN/m or dyne/cm)

Coal Loading	40%					50%				
Surfactant Concentration (%)	0	0.1	0.5	1	5	0	0.1	0.5	1	5
1223H	74.5	71.5	48	40	48.7	84	80.5	70.5	54	49.5
1840X	71.5	70.3	64.2	59.2	49.3	85	77	65	64	55
NP-100	75.5	67	41.2	39.5	39	83.5	78	52	49	-
DDBS (hard)	74	66.5	41.2	39.8	37.2	80.5	70.5	46.5	44	43
DDBS(soft)	74	72.3	40.3	38.6	37.7	81.5	73	46	43	39.5

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