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**Development and Use of an Apparatus to Measure the Dynamic Surface Properties
of Coal-Water Slurry Fuels for Applications to Atomization Characteristics**

K. D. Kihm, Principal Investigator
Department of Mechanical Engineering
Texas A&M University
College Station, Texas 77843-3123
Tel. (409) 845-2143
Fax (409) 862-2418

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 (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 has been documented and presented.

INTRODUCTION

Properties of Tested Coal Powder

The tested coal was originally mined from the Upper Elkhorn seam in Virginia and 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 USDOE-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 DOE-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 maintained 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.

ACCOMPLISHMENT

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) presents measured dynamic surface tension versus bubble frequency for a water mixture and for 50% CWS mixture, respectively. For each mixture, five different weight 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 measured 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 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.

SUMMARY OF PROGRESS

Progress has been made to characterize the rheological behavior of CWS by measuring both the static and dynamic surface tensions. 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. The summary of the progress is the following:

1. The maximum air bubble pressure technique has been successfully applied to measuring dynamic surface tension of CWS mixtures.
2. The critical Micelle concentration for 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 counterpart and values of dynamic surface tension of CWS mixture increased with increasing bubble frequency.
4. For the tested surfactants, dynamic surface tension showed sharp decreases up to 1% surfactant concentration, and gradual decreases were observed thereafter, at higher concentration.

FUTURE RESEARCH PLAN

For future investigation, a correlation between the dynamic surface tension and atomization characteristics will be studied. A simple orifice atomizer will be used to generate CWS sprays and the droplet SMDs will be measured using a Malvern diffraction particle sizer. For CWS mixtures to be tested, DDBS (soft) and 1840X are being considered as the best and the worst surfactant candidates, respectively.

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

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

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

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. 4 Static surface tension of CWS mixture with Witconol NP-100 for three different coal weights: 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 Ammon DDBS (soft)

Fig. 6 Static and dynamic surface tension of 50% weight CWS mixture with NP-100 (The numbers in the parentheses represents 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 50% weight CWS mixture with different surfactant concentrations (unit of surface tension: dyne/cm or mN/m)

<i>Bubble freq.</i> (10/sec)	Water Solution					CWS Mixture (50% coal weight)				
WEIGHT %	0	0.1	0.5	1	5	0	0.1	0.5	1	5
1223H	72	72	60	49.8	44	84	80.5	70.5	54	49.5
1840X	72	72	69	68	52.7	85	77	65	64	55
NP-100	71.5 (0.01)	57.5	49 (0.2)	40	-	-	62.5	42.7 (0.62)	39.5	-
DDBS (hard)	72	67.7	46.8	44	38.5	80.5	70.5	46.5	44	43
DDBS(soft)	72	70	50	47.5	38.5	81.5	73	46	43	39.5
<i>Bubble freq.</i> (1/sec)	Water Solution					CWS Mixture (50% coal weight)				
WEIGHT %	0	0.1	0.5	1	5	0	0.1	0.5	1	5
1223H	72	69.5	47	41	38.2	77.5	74	38.5	38.3	36.5
1840X	72	71	60	53	44.5	78	70	50	48	45
NP-100	60.5 (0.01)	38.6	37 (0.2)	35.5	-	-	40.5	36 (0.62)	34	-
DDBS (hard)	72	54	38	37	34	77.5	52	34.7	34.3	33.9
DDBS(soft)	72	57	41	40	33.5	77.7	64.5	35	34	33.7

*numbers in the parenthesis represent actual surfactant concentrations tested

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