EFFECT OF DISPERSING AND STABILIZING ADDITIVES ON RHEOLOGICAL CHARACTERISTICS OF THE UPGRADED BROWN COAL WATER MIXTURE

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ABSTRACT

The preparation of upgraded brown coal water mixture (UBCWM) by using an Indonesian upgraded coal that was produced by an upgraded brown coal (UBC) process in pilot scale, was carried out to obtain the effect of dispersing and stabilizing additives on rheological behaviour of the UBCWM. Three kinds of anionic dispersing additives, naphthalene sulfonate formaldehyde condensate (NSF), polymethacrylate (PMA) and polystyrene sulfonate (PSS) and three kinds of stabilizing additives, carboxyl methyl cellulose (CMC) an organic material a derivative of cellulose, rhansam gum (S-194) and gellan gum (S-60) some kinds of bio poly sacharide the trade mark of Dainippon Pharmaceutical Co. Ltd. were used in this study. Results indicate that the addition of NSF 0.3 wt% together with S-194 0.01 wt% is effective in preparing UBCWM with good slurry ability and stability, based on its rheological characteristics (apparent viscosity at shear rate of 100 s^{-1} and yield stress at zero point of shear rate). Since the price of S-194 is expensive, the addition of CMC 0.01 wt% is also effective in preparing stable UBCWM.

Keywords: Dispersing additive, stabilizing additive, rheology, apparent viscosity, yield stress

1. INTRODUCTION

After the increasing of oil price in the world, coal began to be reviewed as a substitute fuel for oil. However complete conversion of oil fired facilities to coal fired ones would involve substantial capital expenditure. Coal water mixture (CWM) consisting of mixture of ground powder coal, water and small quantities of additive, is a fluid having a viscosity equivalent to crude or heavy oil offers potential as a replacement for fuel oil in oil fired facilities with only modest retrofits of existing equipment. CWM technology also offers a lower risk technology relative to other coal conversion technologies. Since a mixture of coal and water, CWM is free from some of the major problems of solid coal, such as powder dust and spontaneous combustion during storage and transportation. Unlike solid coal, moreover, CWM does not require large handling facilities (Hashimoto, 1999).

The preparation of CWM was investigated after the oil crises in 1973 and 1978 (Usui *et al*., 1997). On the other hand, oil prices have been kept low and stable and then increase again in the middle of 2006. Therefore, the investigation of CWM should be restarted for stable energy supply. Normally, CWM is prepared by using pulverizing bituminous coal, since the surface nature of bituminous coal is more hydrophobic than lignite. However subbituminous coal and lignite, which are commonly referred to as low rank coals constitute about 85% of the measured coal resources in Indonesia could be changed to be a hydrophobic nature by an upgrading process.

Many studies have been done on the upgrading of low rank coals. Willson et al, 1987, have put forward the hot water drying (HWD) method in comparison with alternate methods (drying by a rotary kiln, superheated nitrogen, superheated steam and saturated steam). However the high pressure condition of this upgrading process is a significant disadvantage. Usui *et al.*, 1999, proposed the upgrading method by a combined process of vacuum drying and tar coating at low pressure. The additional of tar was needed to seal and plug the pores of coal to prevent moisture reabsorbed after upgrading process.

One of the upgrading methods, which has been developed and applied, is upgraded brown coal (UBC) process. The schematic diagram and operational procedure of UBC process has been reported in a previous paper (Umar *et al.*, 2006a). In the future, UBC pilot plant product is available in the form of upgraded brown coal water mixture (UBCWM).

There are three principal objects to obtain a good CWM (Usui and Sano, 1986). The first object is to maximize the solid content in CWM. This is necessary to maintain the energy from unit mass of CWM as roughly same as those of oil. However, the increase of solid content in CWM causes a rapid increase in viscosity, and the fluidity of CWM may be lost under highly loaded conditions. Thus it is important to find out the preparation conditions that accomplish the reduced viscosity requirement in CWM. This is the second object. The third one is to obtain a stable CWM. As the CWM is the suspension of pulverized coal particles in water, unsuitably prepared CWM causes rapid settling of the coal particles, and this settling may cause many troubles in coal utilization process.

Basic process of CWM production technology consists of the selection of raw material, the use of appropriate dispersing and stabilizing additives, pulverization of raw material into appropriate particle size and mixing for providing suitable rheological properties as a fluid fuel. The simplest parameter for showing the property of a slurry under the fluidable condition will be a viscosity. Different from fuel handled with boiler previously, CWM change in apparent viscosity with a change in shearing rate (velocity gradient). In many practical cases, the viscosity at a given shear rate is defined as an apparent viscosity at that shear rate.

CWM usually exhibits non-Newtonian pseudoplastic or Bingham plastic behaviour with a small yield stress. The yield stress is a property commonly exhibited by concentrated suspensions, in particular those with a flocculated network structure. It is a measure of the strength of flocculated network structure, since it represents the force per unit area required to exceed the deformation of the structure and initiate flow, and therefore can be used as a quantitative measure of the ease of redispersion of the sediment, since it is envisaged that CWM will be stored in unagitated tanks (Tudor *et al.*, 1996).

The yield stress is calculated by relating shear stress to shear rate. Stability may be established by the buildup of stiff internal structure between the solid particles. The increases in yield point at zero shear rate produces a slight increase in slurry stability against settling, but may not adversely affect on the quality of atomization.

This paper reports the rheology of the UBCWM to obtain the most suitable of dispersing and stabilizing additives to produce a stable UBCWM. Three kinds of dispersing additives, naphthalene sulfonic acid (NSF), poly (meth) acrylate (PMA) and poly styrene sulfonic acid (PSS) and three kinds of stabilizing additives, carboxyl methyl cellulose (CMC) an organic material a derivative of cellulose, S-194 (rhansam gum) and S-60 (gellan gum) some kinds of bio poly sacharide produced by Dainippon Pharmaceutical Co. Ltd. were used in this study.

2. EXPERIMENTAL

In this study, a low rank coal from Berau, East Kalimantan was used as raw coal. The coal was upgraded by the UBC process in pilot scale. The result of proximate and ultimate analyses and the calorific value of upgraded Berau coal is shown in Table 1.

From the Table 1, it can be seen that the inherent moisture, ash and sulfur contents of the upgraded coal are 4.81, 3.12 and 0.48 % respectively. It is clear that the upgraded coal could be accepted as raw material for the preparation of a UBCWM.

The upgraded coal was milled by using an ultra fine mill to produce coal with particle size passed through 60 mesh screens. The solid particle size was measured by using a HORIBA LA-920, a laser type particle size measurement. The size of coal feed was passed of 60 mesh screens.

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The solvent of the sample was ethanol of 98%, to make a homogeneous suspension. The percent solid was about 70% to 90%. From this study, some parameters such as frequency of particle size distribution and median can be derived.

Table 1. Characteristics of coal used in UBCWM preparation

Analysis, adb	Result
Proximate	
Moisture, %	4.81
Ash, %	3.12
Volatile matter, %	46.69
Fixed carbon, %	45.38
Ultimate:	
Carbon, %	65.91
Hydrogen, %	6.28
Nitrogen, %	1.03
Sulfur, %	0.48
Oxygen, %	23.18
Calorific value, cal/g	6,274

The BET (Brunauer-Emmet-Teller) specific surface area was measured using SHIBATA APP.SA-100 based on the amount of nitrogen absorbed on the surface of the solid particle. The nitrogen flow rate was 150 ml/min. Before subjected to the test, coal samples were dried in the nitrogen atmosphere at 180°C.

Figure 1 shows that all of the upgraded coal particle size was passed through 60 mesh screen. The number coal particle size of less than 75 µm was 58% with an average diameter of 61.8 µm and the BET specific surface area was 5.28 m^2/g. These characteristics mean the advantage in

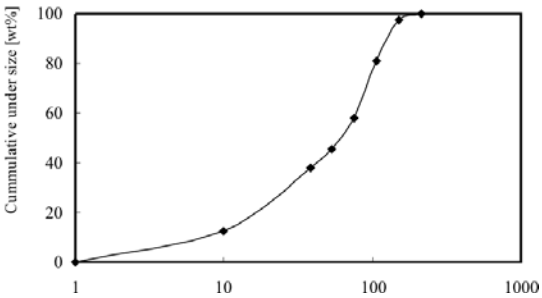

Figure 1. Particle size distribution of the upgraded co

slurry preparation, because it will produce UBCWM with high solid concentration.

The UBCWM was prepared by dispersing the fine upgraded coal in distillated water to form a homogeneous suspension. The variables of this experiment were coal concentration in the UBCWM, 50, 55, and 60 wt%, kinds of dispersing additives, NSF, PMA and PSS and kinds of stabilizing additives, CMC, S-194 and S-40 with a fixed amount of 0.3 and 0.01 wt%, respectively. Besides that, the UBCWM without the addition of dispersing and stabilizing additive were also prepared as references. The effectiveness of these dispersing and stabilizing additives has been discussed elsewhere (Saeki *et al.*, 1994 and Usui *et al.*, 1987).

The flow characteristics of UBCWM, were measured by a stress control type rheometer (Rheometric Scientific Co. Ltd., SR-5) in steady shear mode using a para-plate system. The apparent viscosity measurements were performed at 25°C. The UBCWM was generally prepared at apparent viscosity of 1.00 Pa s at shearing rate of 100 s^{-1} as a target. The high viscosity more than 1.00 Pa.s was considered difficult in handling during transportation and combustion.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Effect of dispersing additive

The effect of dispersing additive on the apparent viscosity of the UBCWM using a stabilizing additive of CMC 0.01 wt% is shown in Figure 2.

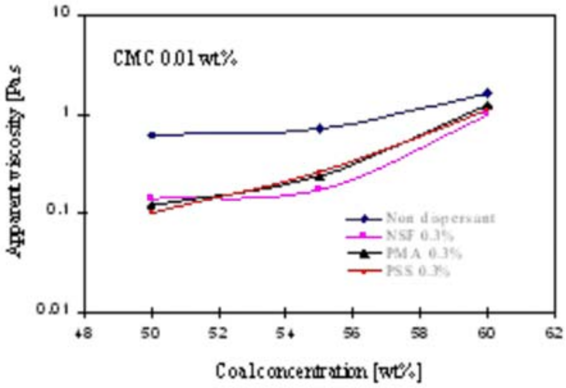

Figure 2. Effect of dispersing additive on the apparent viscosity

From Figure 2, it can be seen that the increase of coal concentration in the UBCWM causes a rapid increase in viscosity, and the fluidity of the UBCWM may be lost under highly loaded conditions. Thus it is important to use a dispersing additive in the preparation condition that accomplishes the reduced viscosity requirement in the UBCWM. The UBCWM without the addition of dispersing additive has higher apparent viscosity by comparison to that the UBCWM with the addition of dispersing agent. The addition of NSF at coal concentration larger than 55 wt% causes the best dispersion of coal particles and the apparent viscosity of the UBCWM is the lowest by comparison to that by the addition of PMA and PSS. In the previous paper (Umar *et al.*, 2006b), NSF has been reported to be a good surfactant for UBCWM preparation. It was examined the effectiveness of NSF to produce UBCWM with good slurry ability.

The rheogram of the UBCWM between shear rate and apparent viscosity and between shear rate and shear stress by using CMC 0.01 wt% as stabilizing additives in several dispersant at coal concentration of 60 wt% can be seen in Figures 3 and 4 respectively. The UBCWM exhibits non-Newtonian fluid behavior Bingham plastic with a yield stress. To define the yield stress, the higher shear rate portion of each rheogram was extrapolated to zero shear rate. The increase in yield stress would produce a stable UBCWM. Figure 5 shows the effect of dispersing additive on the yield stress of the UBCWM by using CMC 0.01 wt% as stabilizing additive.

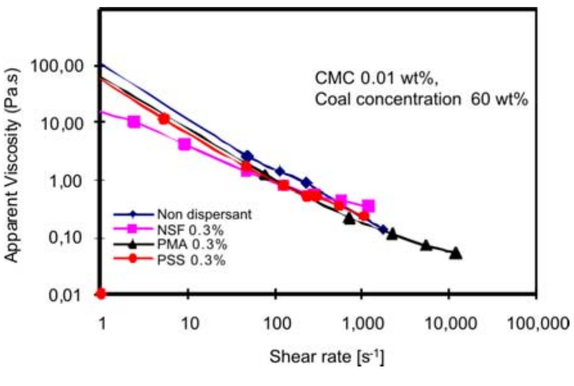

Figure 3. Effect of dispersing additive on the rheogram of the UBCWM (Shear rate Apparent vs viscosity)

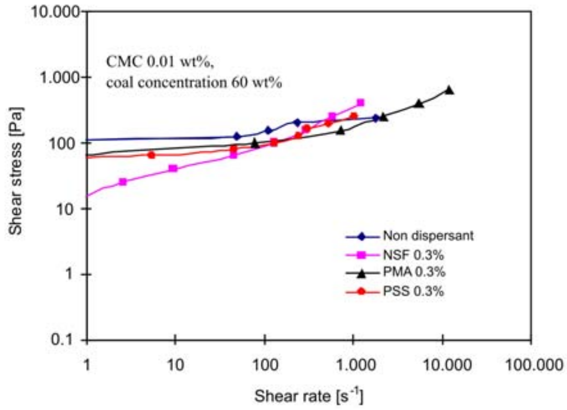

Figure 4. Effect of dispersing additive on the rheogram of the UBCWM (Shear rate vs shear stress)

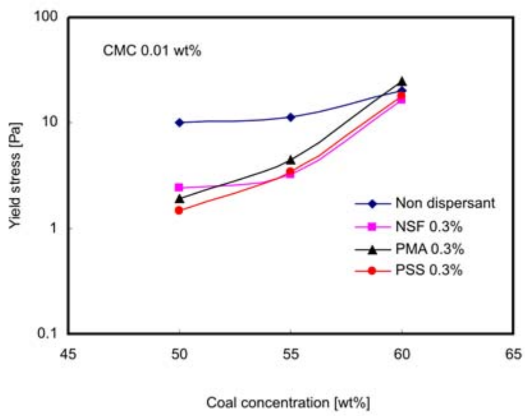

Figure 5. The effect of dispersing additive on the yield stress

From Figure 5, it can be seen that the yield stress value increases with the increases of coal concentration. At coal concentration of 60 wt%, the addition of dispersing additive did not increase the yield stress, event stabilizing additive (CMC 0.01 wt%) was used. It may be explained that the dispersing additive, effective in reducing apparent viscosity. When viscosity is reduced, the settling of coal occurs more rapidly. This phenomenon is frequently observed when anionic surfactant such as the NSF, is used (Usui and Sano, 1984). This anionic surfactant is adsorbed on the coal surface, and it increases the electrostatic repulsion force between the coal particles. As a result, the addition of dispersing additive together with stabilizing additive is very important in UBCWM preparation.

3.2. Effect of stabilizing additive

The effect of stabilizing additive on the apparent viscosity of the UBCWM by using NSF 0.3 wt% as dispersant is shown in Figure 6. This figure shows that the UBCWM without the addition of stabilizing additive has low apparent viscosity. In low coal concentration (50 wt%), the addition of S-194 to the UBCWM, the increasing of the apparent viscosity was not significant different from CMC and S-60. In high coal concentration (60 wt%), the addition of stabilizer causes a rapid increase in the apparent viscosity of the UBCWM.

It has been explained above, that the increasing of the apparent viscosity, the tendency of coal sedimentation will decrease. From Figure 6, it can be seen that the addition of S-194 and S-60 is more effective in preparing a stable UBCWM. These stabilizers may entangle together and some of the functional cites adsorb on the surface of coal particles. As a result, an interparticle (network) structure of the coal particle can be constructed. In the case of ship transportation or long term tank storage, a network structure of the UBCWM might prevent sedimentation of the coal particles. The rheogram of the UBCWM between shear rate and apparent viscosity and between shear rate and shear stress by using NSF 0.3 wt% and several kinds of stabilizer of 0.01 wt% at coal concentration of 60 wt%, are shown in Figures 7 and 8 respectively.

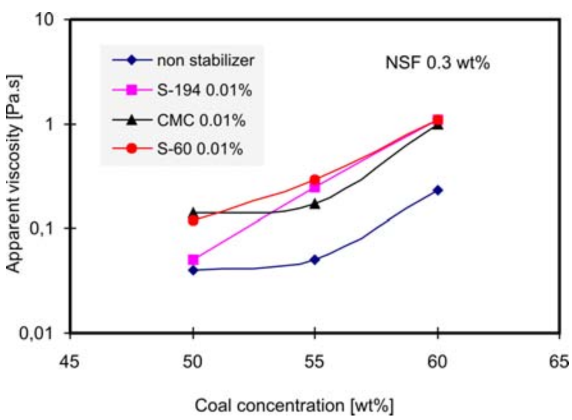

Figure 6. Effect of stabilizing additive on the apparent viscosity

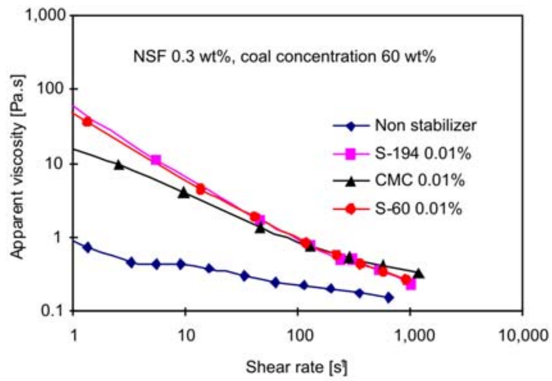

Figure 7. Effect of stabilizing additive on the rheogram of the UBCWM (Shear rate vs shear stress)

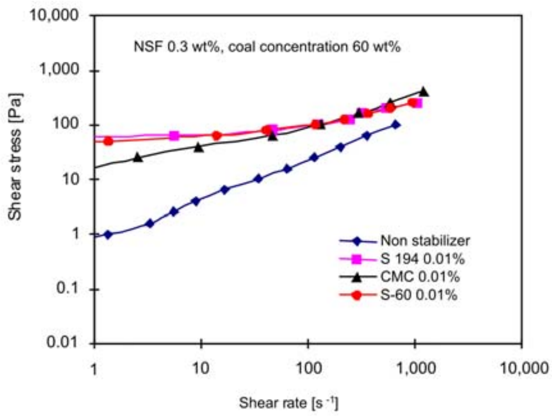

Figure 8. Effect of stabilizing additive on the rheogram of the UBCWM (Shear rate vs shear stress)

From Figure 8, it can be seen that all of the UBCWM with the addition of some kinds of stabilizing additive, exhibits non-Newtonian Bingham plastic with yield stress. The rheogram of the UBCWM by using S-194 and S-60 shows a same rheological behaviour, due to both stabilizing additive are the same kind of bio polysaccharides. The effect of stabilizing additive on the yield stress of the UBCWM by using NSF 0.3 wt% can be seen in Figure 9.

It is evident from Figure 7 that the stable UBCWM is obtained when the stabilizing additive is added. The UBCWM without the addition of stabilizer has low yield stress value. At the coal concentration in the UBCWM of 60 wt%, the yield stress values are almost the same for the three kinds of the

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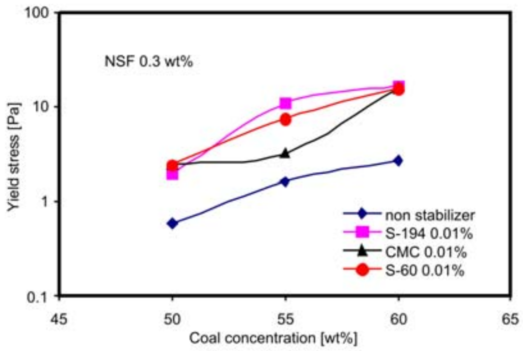

Figure 9. Effect of stabilizing additive on the yield stress using NSF as dispersant

stabilizers, even the S-194 shows the highest. This phenomenon suggests that long branches of S-194 are very effective to produce a network structure in the UBCWM (Saeki *et al*., 1994). Therefore, the addition of S-194 as stabilizer together with NSF as dispersant is effective in preparing UBCWM with good slurry ability and stability.

Although the experimental result of the UBCWM with the addition of PMA and PSS as dispersing additive and three kinds of stabilizing additives, CMC, S-194 and S-60 are not mentioned in diagrams, it was confirmed that the UBCWM with the addition of S-194 shows the best stabilizer for preparing a UBCWM, followed by CMC and S-60 together with PMA or PSS.

4. CONCLUDING REMARKS

It might be concluded that the addition of NSF 0.3 wt% as dispersing together with S-194 0.01 wt% as stabilizing additives is effective in preparing UBCWM with good slurry ability and stability based on its rheological characteristics. From the economical point of view, the price of S-194 is very expensive. On the other hand, CMC is abundant and cheap. Therefore, the addition of CMC 0.01 wt% together with NSF 0.3 wt% is also effective in preparing the UBCWM with good fluidity and stability.

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