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Influence of surfactants and experimental variables on the viscosity characteristics of coal water mixtures

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Abstract−To improve the fluidity of a coal water mixture (CWM) having lower viscosity and higher solid concentration, the effects of surfactants (five kinds) and experimental variables such as temperature (5-65 °C), pH (1-11), particle size distribution (PSD) on the viscosity characteristics of two different coals (Shenhua and Kideco Coal) were investigated. Relatively economical surfactants were chosen in this study: sulfonated melamine formaldehyde polymer (SMF-30), naphthalene formaldehyde sulfonate (Sikament-NN), naphthalene sulfonate water reducer (NSWR), naphthalene formaldehyde sulfonate (PC-1000) and poly-carboxylate (PC). The SMF-30, an anionic surfactant, revealed the most significant reduction in viscosity of CWM among the five surfactants since the SMF-30 forms electric double layer on the surface of coal, and the repulsive force of this layer surpasses the aggregation of coal particles. In addition, the viscosity of CWM decreased with increasing pH and temperature, in particular, the increase in OH- on the surface of coals by the addition of NaOH caused the increase in the repulsive force between the negatively charged coal particles. Furthermore, the very fine particles (less than 45 μm) of coals should be removed before making CWMs since it revealed the increase in viscosity of CWMs.

Keywords: Coal Water Mixture (CWM), Viscosity, Surfactant, pH, Particle Size Distribution (PSD)

INTRODUCTION

There has been a growing interest in alternative energy resources due to the steep reduction in easily accessible oil reserves. Among the alternatives, coal exhibits advantages of relative price stability as well as the possibility of long-term supply, attributed to its enormous reserves widely distributed worldwide.

In thermochemical conversion plants such as conventional coal-fired power plants, coal to liquid (CTL), integrated gasification combined cycle (IGCC) and synthesis natural gas (SNG) plant using coal as a main fuel, coal feeding is divided into two feeding technologies: dry and wet method. When dry feeding method is used in these thermochemical coal conversion technologies, fine particles (or dust) are necessarily generated and it not only serves as an environmental threat, but also can inadvertently drift into the air, resulting in harm to human health. For solving this problem, some researches for production of the CWM, which will transform ash from solid state (ash) to liquid state (slurry), are underway [1]. For wet feeding method, coal water mixture (CWM) or coal water slurry (CWS) that is easy to handle and feed to plant especially at high pressure operating condition using a high pressure slurry pump is used. The CWM is generally composed of pulverized coal particles (60%-70%), water (30%-40%), and a small amount of surfactant, characterized as a non-Newtonian fluid having a yield stress.

To achieve both stable supply of CWM to the plant and high reaction efficiency (e.g., carbon conversion efficiency and cold gas efficiency in case of coal gasification process), a lower viscosity value and higher solid concentration of CWM should be maintained. It is known that the type and concentration of coals and surfactants are the most crucial factors on the viscosity characteristics of CWM [2,3].

Coal is a solid matter with a complicated chemical structure. According to Atesok et al. [4] and Yun et al. [5], inherent moisture, equilibrium moisture, ash, fixed carbon, the ratio of fixed carbon/volatile matter, O/C ratio, ratio of oxygen-containing functional groups, and porosity of particles in coals play an important role in the rheological characteristics, especially, the viscosity of CWM.

The most common method to maintain low viscosity and high solid concentration of CWM is to add a small amount (1-2 wt%) of surfactant into the mixture of coal and water. Typically, water-soluble anionic surfactants are used to increase dispersibility among coal particles, which finally can improve the fluidity of CWM.

Currently, a number of studies are underway to better understand the fluidity of CWM with respect to the type and structure of surfactants [7]. Among the surfactants used to produce CWM, poly-carboxylate (PC) is mainly used as a water-reducing agent for concrete manufacture, composed of a side chain grafted with a main chain, which is flexible and supports the transformation of its molecular structure; hence, it is possible to compound it in various forms including one having a long-side chain structure [8,9]. Zhang et al. observed the effect of amount of each type of surfactant (sulfonated acetone formaldehyde; SAF, sulfonated phenol formaldehyde; SPF, and sulfonated 2-naphthol-formaldehyde; SNF) having simi-

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lar chemical structure on the viscosity characteristics of CWS, and concluded that SNF shows the lowest viscosity of CWM [10]. Umar et al. also investigated the effect of three anionic surfactants, naphthalene sulfonate formaldehyde condensate (NSF), poly-methyl acrylate (PMA), and polystyrene sulfonic acid (PSS) on the apparent viscosity of CWM and indicated that compared with the addition of three kinds of surfactants, the apparent viscosity of CWM with NSF were the lowest than those of CWMs with PMA and PSS [11]. Kim et al. looked at the effect of surfactants as a water-reducing agent on the viscosity of CWM and reported that anionic surfactant SLES $(EO)_3$ was the most effective surfactant. Das et al. [19] revealed that the rheological characteristics of CWMs compounded with low rank Indian coal and three starch additives, starch xanthate, starch xanthide, and starch phosphate were affected by the amount of coal and additives, temperature and pH.

In this study, to make available CWM having lower viscosity and higher solid concentration in commercial coal plant, we determined the viscosity characteristics of CWM with two coals (Shenhua coal, Kideco coal) and five economical surfactant candidates (sulfonated melamine formaldehyde polymer; SMF-30, naphthalene formaldehyde sulfonate; Sikament-NN, naphthalene sulfonate water reducer; NSWR, naphthalene formaldehyde sulfonate; PC-1000 and poly-carboxylate; PC). In addition, with the verified two superior surfactants, the effects of experimental variables such as temperature, pH, and coal particle size on viscosity characteristics of CWM were observed.

EXPERIMENTAL

1. Materials and Measurements

Table 1 summarizes the results of proximate analysis, ultimate analysis, and calorific values of two different coals; Shenhua coal from China and Kideco coal from Indonesia. Shenhua coal and Kideco coal have different properties in terms of contents of moisture, ash, fixed carbon and oxygen. The caloric value of Shenhua coal was slightly higher than that of Kideco coal.

To make CWMs, both coals were initially crushed to a size of approximately 10 mm using a preliminary breaker and then, finally milled to less than 75 μm to feed into the entrained flow gasifier application using a pin mill. Fig. 1 shows the particle size distribution of two coals used in making CWM. The mean particle sizes of Shenhua coal and Kideco coal were measured as 61.79 μm and 53.88 μm, respectively.

In addition, the viscosity of CWMs made by all experimental conditions was measured under 20 rpm using Brookfield LV-3 rotor with a Brookfield DV-II viscometer and three times for reproducibility under same condition. The 20 rpm of rotor speed can be

Table 1. The proximate analysis, ultimate analysis, and calorific values of coals used in this study

Analysis \ Coal		Kideco	Shenhua
Proximate analysis (wt%, as received)	Moisture	29.78	6.34
	Volatile	32.96	29.20
	Fixed carbon	30.69	50.99
	Ash	6.57	13.47
Elemental analysis (wt%, daf)	Carbon	66.30	72.10
	Hydrogen	4.76	4.13
	Oxygen*	20.75	8.75
	Nitrogen	1.58	1.51
	Sulfur	0.04	0.04
Higher heating value (kcal/kg)		6,010	6,520

*Calculated by difference

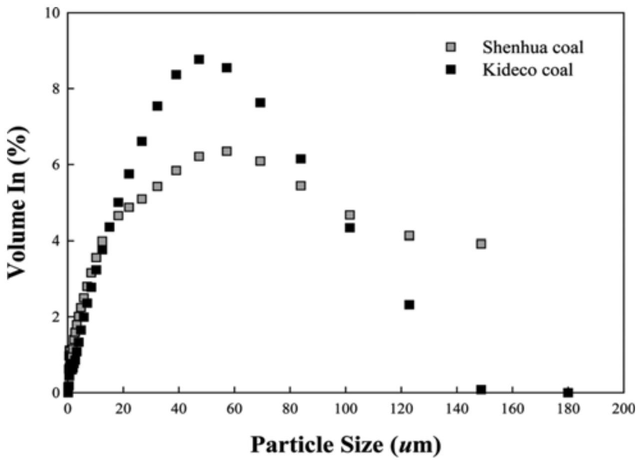

Fig. 1. Particle size distributions of each coal.

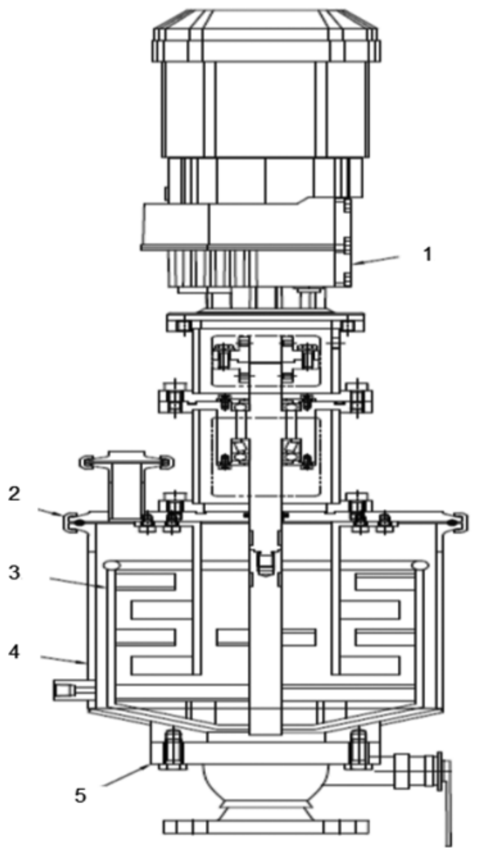

Fig. 2. Schematic diagram of CWM mixer.
1. Motor 2. Clamp 3. Agitator 4. Vessel 5. Bottom valve

converted into the shear rate value of 4.218 s^{-1}.

2. Manufacturing Procedure of CWM Samples

To make a CWM sample, the milled coal particles were initially mixed with distilled water in a CWM mixer, as shown in Fig. 2. And then, each concentration and type of surfactants was added into the mixture of coal and water. During this procedure, experiment temperature was kept at 22-25 °C for approximately 15 min. Five kinds of surfactants, sulfonated melamine formaldehyde polymer (SMF-30), naphthalene formaldehyde sulfonate (Sikament-NN), naphthalene sulfonate water reducer (NSWR), naphthalene formaldehyde sulfonate (PC-1000) and poly-carboxylate (PC) for this experiment, were selected to evaluate and adjust the viscosity for CWMs.

3. Experiment Conditions

First, to determine the optimum addition amount of the surfactant to make CWM having higher solid concentration and lower viscosity, experiments on the variation of the addition amount of each surfactant were performed without and with 0.4, 0.8, 1.2, 1.6 and 2.0 wt% of each surfactant under same amount of coals and distilled water. Second, the effect of solid concentration on the viscosity characteristics of CWM was observed for each sample by varying the concentration of coal from 54 wt%, 56 wt%, 58 wt% to 60 wt% (as received basis). From the results of these experiments, two superior surfactants, verifying the best performance related to each coal, were selected to investigate the viscosity characteristics of CWMs regarding other experimental conditions, such as storage temperature, pH and the size of milled coal particles.

Third, the performance of manufactured CWM as a fuel may depend on the temperature in the storage tank of the plant. Considering the seasonal effect according to the storage of CWM, the effect of storage temperature on viscosity of CWMs should be determined. Therefore, experiments were performed with the variation of storage temperature between 5 °C and 65 °C in increments of 10 °C under amount of coal of 58 wt% (Shenhua coal, as received basis), 56 wt% (Kideco coal, as received basis) and surfactant of 0.4 wt% in the initial CWM.

Fourth, all surfactants have their inherent pH value. In other words, the viscosity characteristics of CWM added with surfactant may be changed by the pH of surfactant. It is important to decide the optimum pH with regard to each surfactant. Herein, with increasing pH value (from 1 to 10) by addition of 98% NaOH (Samchun Pure Chemical) and 99% citric acid (Sigma Aldrich), the influence of pH value for the variation of CWMs viscosity was also investigated.

Finally, the viscosity characteristics of CWMs made by three different sizes of two coals, A: ≥75 μm (200 mesh), B: 45-75 μm (325-200 mesh), and C: ≤45 μm (325 mesh), were evaluated. Additionally, three categories of coal particles were mixed at a three determined ratios (A : B : C=80% : 20% : 10%, 10% : 80% : 20%, 20% : 10% : 80%) based on mass fraction and their viscosities were evaluated.

RESULTS AND DISCUSSION

1. The Influence of the Surfactant Type

To observe the effect of surfactants on the viscosity characteristics of CWM, experiments were conducted in which the coal weight ratio was fixed as 58 wt% (Shenhua coal, as received basis), 56 wt%

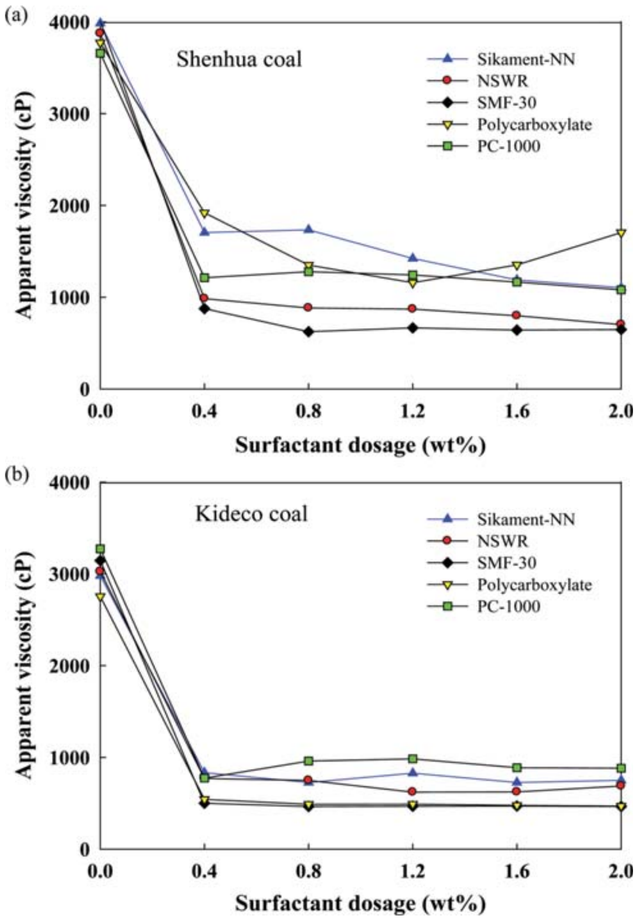

Fig. 3. The viscosity of CWMs using (a) Shenhua coal and (b) Kideco coal with the variation of type and addition amount of five surfactants.

(Kideco coal, as received basis) and the addition ratio of each surfactant was incrementally changed from 0 wt% to 2.0 wt%. Fig. 3(a) and (b) show the viscosity variation of the CWM according to the type and amount of surfactant added to CWM using Shenhua coal and Kideco coal, respectively.

As shown in Fig. 3(a) and 3(b), the SMF-30, anionic surfactant shows the best performance surfactant for the decrease in viscosity of both CMWs with two different coals. When an anionic surfactant is added to CWM, the lipophilic alkyl group in the surfactant molecule is adsorbed onto the hydrophobic surface of the coal particles; hence, it is negatively charged. As a result, an electrical double layer is formed on the surface of the coal particle by countercations. The repulsive force of this electrical double layer surpasses the aggregation of coal particles due to the van der Waals force, resulting in reduced viscosity. When the addition amount of surfactant is more than 0.4 wt%, the viscosity is maintained at a certain level or somewhat increased in all experiments. This result is attributed to the fact that the surface area of a coal particle is limited, and if more surfactant as compared to the amount that can be adsorbed onto the surface of the coal particles is added, the remaining surfactant ions form micelles in the aqueous solution, resulting in increased viscosity, attributed to the interaction between the hydrophobic parts of the micelles and coal particles [12]. Viscosity of CWM depends on the pH of coal and surfactant. Shenhua coal and Kideco coal used for this experiment have pH values of 6.4 and 3.6, respectively. Since Kideco coal has acid characteristics, during making CWM, Kideco coal with polycarboxylate surfactant might be decreased viscosity of CWM. In summary, from this experiment, the optimum addition amount of a surfactant was determined 0.4 wt%; therefore, the concentration of coal is fixed as 58 wt% (Shenhua coal, as received basis), 56 wt% (Kideco coal, as received basis) and the content of distilled water is 41.6 wt% and 43.6 wt%.

2. The Influence of the Coal Concentration

Generally, high solid concentration of CWM is one of the most important factors to determine the quality of CWM in terms of high energy density. The viscosity characteristics of CWMs with increasing coal concentration from 54 wt%, 56 wt%, 58 wt% to 60 wt% (as received basis) were evaluated under the same amount of 0.4 wt% of a surfactant in all experiments. The viscosity results are presented in Fig. 4(a) and 4(b).

From Fig. 4(a) and 4(b), CWM without surfactant (blank case) had the highest viscosity. In all experiments, the increase in coal concentration in CWMs has the increase in coal concentration of CWMs resulting in increase in the viscosity of CWMs, and hence, it leads to the bad fluidity of CWMs. In addition, at the range of 54-60 wt% of coal concentration, CWMs using Shenhua coal and either PC-1000 or polycarboxylate shows viscosity value of less than 2,000 cP, which can be used as CMW fuel. On the other hand, CWMs produced with Kideco coal and either polycarboxylate or NSWR had under 2,000 cP at the whole coal concentration even at 60 wt%. As depicted in Fig. 4(b), the viscosity of CWMs with each surfactant decreased by about 4,000 cP compared to CWM without surfactant (blank case), which indicated that the reduction trends of viscosity is higher than that of CWM from Shenhua coal.

High inherent moisture content of coal has an adverse effect to decrease in coal concentration of CWM. The inherent moisture content of Kideco coal was higher than that of Shenhua coal. Therefore, coal concentration of CWM produced with Shenhua coal was higher than that with Kideco coal. Considering inherent moisture content as dry basis, the coal concentration of 58 wt%, as received for each CWM produced by Shenhua coal and Kideco coal in Fig. 4(a) and (b) means that Shenhua coal has 53.5 wt% coal concentration while Kideco coal has 46.1% on the dry basis due to inherent moisture content of each coal. Therefore, apparent viscosity of CWM made by Shenhua coal is higher than that of Kideco coal.

3. The Influence of Temperature and pH

The effects of storage temperature and pH on the viscosity characteristics of CWMs were investigated using two surfactants, which were found to be most effective in terms of low viscosity: SMF-30 and NSWR for Shenhua coal, SMF-30 and Polycarboxylate for Kideco coal.

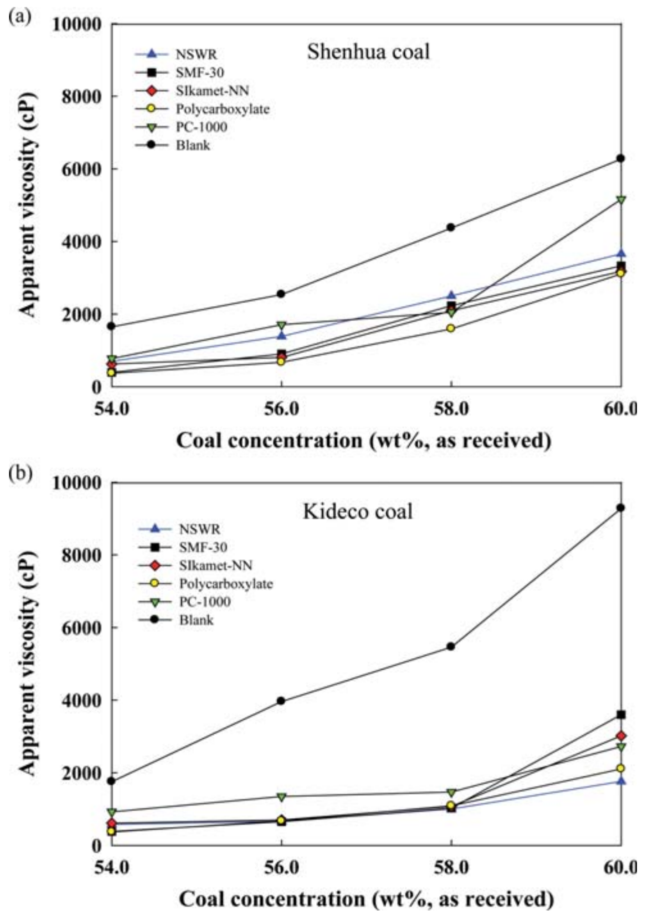

Fig. 4. The viscosity of CWMs using (a) Shenhua coal and (b) Kideco coal with the variation of coal concentration.

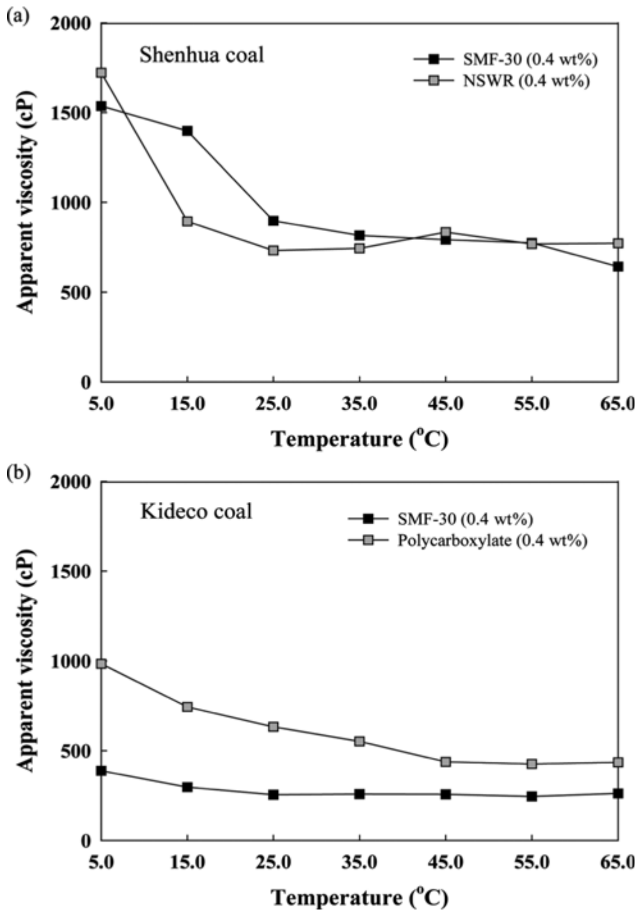

Fig. 5. The viscosity of CWMs using (a) Shenhua coal and (b) Kideco coal with increasing temperature.

The viscosity of a liquid proportionally decreases with increasing temperature. A temperature of below 25 °C (5 and 15 °C) means the temperature of CWM storage tank for the winter season and above 25 °C (35 to 65 °C) indicates the temperature of CWM storage tank for the summer season. As shown in Fig. 5(a) and 5(b), the viscosity of CWMs decreased with temperature increasing in the range of 5 °C-65 °C.

The viscosity of CWM is not only affected by water, but also more significantly by the surfactant adsorbed on the surface of the particles, depending on the temperature. With increasing temperature of CWM, the particles in CWM are considered to become active, increasing the repulsive force of the electrically charged parts, expanding the distance between the particles causing steric hindrance, and increasing dispersibility [13].

In addition to temperature, Fig. 6(a) and 6(b) present the viscosity measured at various pH values of CWM adjusted by the addition of basic (NaOH) and acidic (citric acid) solution.

As can be seen in Fig. 6(a) and 6(b), the CWM having higher pH using NaOH (base) leads to the lower viscosity of CWM, because OH^- ion on the coal surface increases with increasing pH, leading to increase in the repulsive force between negatively charged coal particles. On the other hand, at lower pH using citric acid (an acid), H^+ is adsorbed on the coal surface, thereby decreasing the number of anions and increasing viscosity [14,15]. The increase (high alkalinity) in pH of CWM was favorable for the decrease in viscosity of CWM. But high alkalinity will cause damage to the equipment (Pump, Pipe Line), because alkali is corrosive. The optimum pH for CWM preparation was found to be in the range of 4-9.

4. The Influence of Particle Size Distribution

To minimize the porosity between particles during CWM making process, the particle size distribution (PSD) of coal has to be controlled. It can maximize packing density as well as increase the CWM concentration. To verify it, the viscosities of three kinds of each mono-granular CWM (A: ≥75 μm, B: 45-75 μm, and C: ≤545 μm) and each multi-granular CWM using (A : B : C=80% : 20% : 10%, 10% : 80% : 20%, 20% : 10% : 80%, based on the mass fraction) of Shenhua coal were investigated, and the results are shown in Figs. 7 and 8. As shown, the highest viscosity was observed for CWM produced with the smallest particle size (C: ≤45 μm, a size of less than or equal to 325 mesh) at the same coal concentration. Thus, the smaller the mean grain size of coal, the higher the apparent viscosity of CWM: the smaller the size of the particles, greater is the porosity between them and more water is required to fill the porosity between particles of CWM at the same coal concentration. On the other hand, for multi-granular CWMs pro-

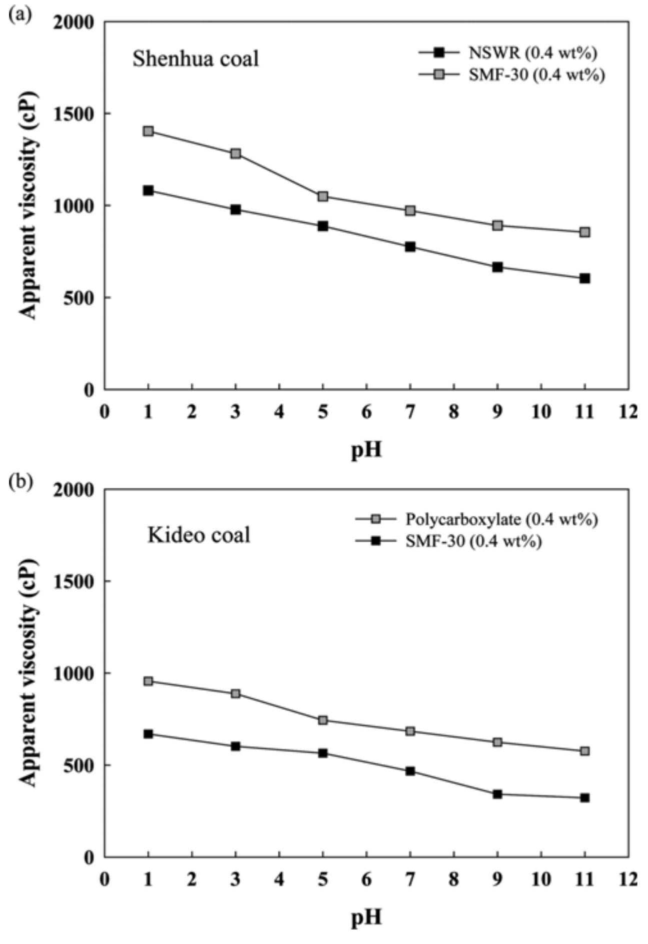

Fig. 6. The viscosity of CWMs using (a) Shenhua coal and (b) Kideco coal with the variation of pH value.

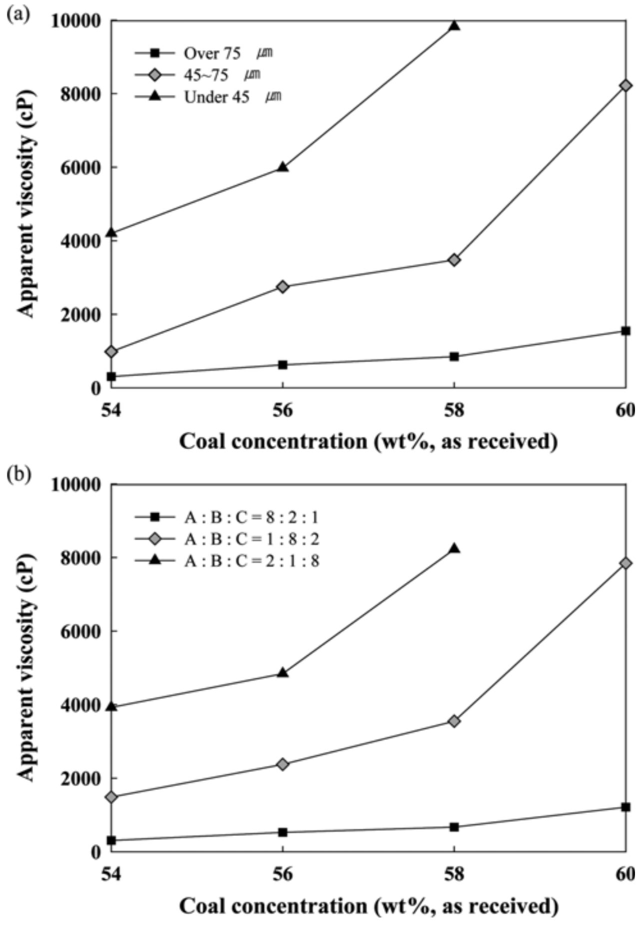

Fig. 7. The viscosity of (a) mono-granular CWMs and (b) multi-granular CWMs according to particle size distribution of Shenhua coal using NSWR as a surfactant (A: ≥75 μm, B: 45-75 μm, and C: ≤45 μm).

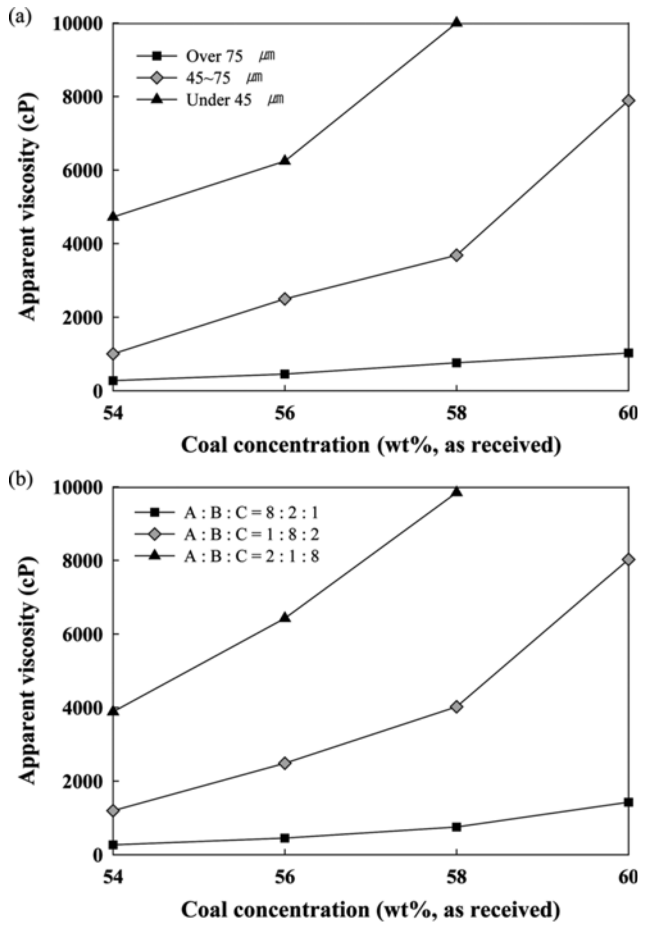

Fig. 8. The viscosity of (a) mono-granular CWMs and (b) multi-granular CWMs according to particle size distribution of Shenhua coal using SMF-30 as a surfactant (A: ≥75 μm, B: 45-75 μm, and C: ≤45 μm).

duced using mixed particle size distributions, the viscosity considerably decreased with increasing coal grain size, which is the same result obtained for mono-granular CWMs. These trends were similar to the results of them [16,17].

CONCLUSION

The viscosity characteristics of CWMs on the effect of relatively economical surfactants, two kinds of coals and the experimental conditions, temperature, pH and coal particle size distribution, have been investigated. The best performing surfactant was SMF-30, both two different coals-based CWM exhibited low viscosity. Additionally, the optimum amount of surfactant required for increasing the fluidity of CWM was estimated to be 0.4 wt% under 58 wt% of coal and 41.6 wt% of water.

The variation of coal concentrations in CWMs, the viscosities of CWM made by each coal were lower by approximately 2,000 cP and 4,000 cP, respectively, at a coal concentration of 58 wt% compared to the result obtained from a CWM without surfactant.

Furthermore, the viscosity of CWM decreased because of the activation of particle motion by water and change of temperature. The increase (high alkalinity) in pH of CWM was favorable for the decrease in viscosity of CWM. Finally, the very fine particles (≤45 μm) of coals should be removed before making CWMs,since it revealed the increase in viscosity of CWMs. These findings will contribute to adding surfactant and determining operating conditions for CWM manufacture process.

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