Korean J. Chem. Eng., **26**(5), 1259-1264 (2009)
DOI: 10.1007/s11814-009-0223-6

The effect of additive chemicals on the viscosity of coal-petroleum coke-water slurry fuel for a gasification process

Sang Jun Yoon, Young-Chan Choi, and Jae-Goo Lee†

Department of Fossil Energy and Environment Research, Korea Institute of Energy Research,
71-2 Jang-dong, Yuseong-gu, Daejeon 305-343, Korea
(*Received 21 February 2008 • accepted 9 March 2009*)

Abstract−As a preliminary study for the gasification of an anthracite and petroleum coke mixture, viscosity was measured at various temperatures (20-50 °C), slurry concentrations (60-70 wt%) and additive amounts (0-0.8 wt%) by using an LV-II type viscometer. In addition, four types of different additives, sodium naphthalene sulfonate, poly(methyl methacrylate), polypropylene and a polypropylene glycol based additive, were applied to Korean anthracite, petroleum coke and mixtures of these materials, and the viscosity data were compared. Viscosity dependency values for coal, anthracite, bituminous and sub-bituminous coal, were compared, and it was found that a high content of moisture and particularly ash increases CWS viscosity. The four types of additives tested in this research can effectively diminish the viscosity of coal and especially petroleum coke-water slurry by more than 70% to 95%, respectively. Moreover, the sodium naphthalene sulfonate-based additive reduced the viscosity of coal and petroleum coke-water slurry best, especially at concentrations in excess of 65 wt%. Based on these results, highly loaded slurry created by mixing anthracite and petroleum coke with additives was achieved.

Key words: Coal, Petroleum Coke, Slurry, Viscosity, Gasification

INTRODUCTION

Factors such as the continued rise in oil prices, the difficulties associated with a stable supply of crude oil, increased fuel consumption, and the limited oil reserves in recent years have increased interest in and research related to the use of coal, which is relatively cheaper, plentiful, and widely distributed across the globe. Therefore, many studies pertaining to coal water slurry as an alternative fuel replacing petroleum oil in the liquid state have been carried out [1-5]. Coal slurry fuel can be divided into CWS (coal-water slurry), COS (coal-oil slurry), COWS (Coal-oil-water slurry), CMS (coal-methanol slurry), and CMWS (coal-methanol-water slurry) depending on the type of liquid mixed with the solid coal. Among these different types, CWS fuel is considered by some to have the greatest economic feasibility as a fuel source and the greatest potential for commercialization [5,7].

Coal particles are substances with an uneven structure. In general, ash is hydrophilic, whereas the surface of a pure coal particle is hydrophobic. Accordingly, coal particles have poor contact affinity with water, resulting in poor stability, so additives are used to make up for this [8,9]. These additives increase the contact affinity between coal particles and water and decrease interfacial tension. Surfactants used as dispersants are classified into ionic and non-ionic surfactants. Ionic types of matter stick to coal particles; the hydrophilic group of the dispersant is ionized in water and electrically charges the particles, thereby causing electrostatic repulsion between the particles, increasing their dispersibility. With non-ionic substances, the high-molecular absorbent layer formed on the surface of the coal particle causes steric repulsion, thereby promoting dispersion [10].

Gasification refers to a series of processes to produce synthesis gases such as H_2 and CO from all carbonaceous substances, including coal, petroleum coke, heavy residual oil, wastes and biomass [11,12]. Integrated gasification combined cycle (IGCC), which produces synthesis gas for power generation, is known to have higher energy efficiency than existing power generation technologies. It also satisfies current environmental regulations as this gasification process is one of the most promising suppliers of hydrogen for fuel cells, a growing power generation technology. In addition, the gasification process is widely used in the oil refining industry and in the petrochemical industry. Typical examples are the heavy oil gasification process that supplies H_2 in the oil refining process and the coal gasification process that supplies H_2 in ammonia production.

The advantage of petroleum coke is that it has a high calorific value and is cheaper than coal; however, its high levels of sulfur and vanadium are a disadvantage from an environmental perspective as compared to coal. In particular, the vanadium oxide (V_2O_5) in the ash causes slagging of the boiler pipes; this accumulates in the SCR NOx removal catalyst and serves as an oxidation catalyst, thereby oxidizing SO_2 into SO_3. SO_3 forms deposits in the downstream process together with ammonia. As the amount of deposited V_2O_5 increases, the quantity of SO_3 produced continues to increase, necessitating frequent replacement of the SCR catalyst. Accordingly, a gasification process that does not emit SOx and NOx and that is capable of generating power and producing chemical raw materials is the best process for utilizing petroleum coke [13,14].

In recent years, various attempts have been made to create a synergic effect through the co-processing of fuels. Kinetic research of polypropylene and oil shale mixtures has been done by Gersten et

†To whom correspondence should be addressed.
E-mail: jaegoo@kier.re.kr

al. [15] and the pyrolytic characteristics of a coal and biomass blend were reported by both Jones et al. [16] and Moghtaderi et al [17]. Suelves et al. [18] studied a synergetic effect of a coal and petroleum residue blend and reported the poor characteristics of the production of aromatic compounds during co-pyrolysis.

If coal, petroleum coke and a coal/petroleum coke mixed fuel are gasified by GE or by using a ConocoPhillips type entrained flow gasifier, they will be rendered into a slurry state. If the concentration of the slurry is low at this time, the combustion inside the gasifier will be thermally unstable, and it will be difficult to maintain the temperature. Alternatively, a high concentration increases the frictional resistance of the fluid in the pipe. This will increase the power consumption and the load of the pump. Therefore, a slurry concentration appropriate for the fuel characteristics must be determined, necessitating the measurement of the viscosity according to the concentration and additives in advance.

This study is a preliminary investigation into the gasification of anthracite with petroleum coke. Anthracite is used sparingly due to its low calorific values and high contents of ash, and petroleum coke has a high calorific value, low ash content, and high level vanadium. The viscosity values of anthracite, petroleum coke and an anthracite/petroleum coke mixed fuel slurry were measured at various temperatures and with different additives and concentration levels.

EXPERIMENTAL

1. Reagents

In this study, one anionic additive and three types of non-ionic additives were used. Among the non-ionic additives, two types of propylene glycol surfactant and one type of polypropylene polymeric surfactant were chosen. Table 1 shows the characteristics of these additives, as used for the manufacturing of the coal, petroleum coke and mixed fuel slurry. The surfactants CWM 1002, ATLOX 4913, Zephrym PD3315 and HIGHCOAL F3120 used in the viscosity measurement were purchased from Dongnam Chemical Ind. (Korea), ICI Co. (Uniqema), and Dai-Ichi Kogyo Seiyaku Co. (Japan) and were used without further purification.

The anthracite, bituminous coal, sub-bituminous coal and petroleum coke were obtained from the Jangseong deposit in Korea, Australia (Drayton), Indonesia (Kideco) and Hyundai Oilbank Co., respectively. All particle sizes ranged from 20 to 50 μm in this study. Table 2 shows the proximate, ultimate and calorific value analysis results of the coals and petroleum coke.

2. Viscosity Measurement

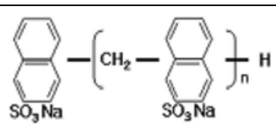
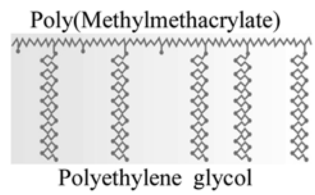
An LV adaptor attached to a Brookfield viscometer (LDVD-II) capable of measuring a wide range of viscosity was used to measure the viscosity of the slurry in this study. In a 600 ml volume jacketed beaker kept at a constant temperature, 400 ml of slurry was used in all experiments. The calculated weight of coal or petroleum coke with additive and water amounts that depended on the desired slurry and additive concentration were obtained by using a balance (Sartorius R120S) with a precision of 0.001 g. These were then poured into a jacketed beaker. A water bath allowing temperature control to 0.1 °C was provided to maintain a constant temperature. The contents of the beaker were then mixed for 15 min by an agitator. Finally, a spindle was dipped in this homogeneously stabilized slurry at the same depth, and a viscosity measurement was done.

The experiments were generally conducted at a constant temperature of 25 °C, and triple distilled water was used as the solvent. To check the viscosity characteristics according to the temperature and concentration, the experiments were conducted at various levels of temperature and slurry concentration: 20-50 °C and 60-70 wt%. In addition, the characteristics and effects of additives with diverse functional groups were compared while varying their contents in the slurry: 0-0.8 wt%. Fig. 1 illustrates a schematic diagram of the viscosity measurement apparatus used in this work. The measured viscosity value was the apparent viscosity.

RESULTS AND DISCUSSION

Various attempts to improve the fluidity and combustion characteristics of CWS have been made involving ultrasonic irradiation, organic solvents and new types of additive [19,20]. In the present study, in an effort to develop the most feasible additive for a type of slurry consisting of water with anthracite, petroleum coke or an anthracite/petroleum coke mixed fuel, four different types of addi-

Table 1. Characteristics of additives

Name	Component	Formula	Ionic	Purpose
CWM 1002	Formaldehyde condensate of sodium naphthalene sulfonate	 n = 4 ~ 5	Anionic	Dispersant
ATLOX 4913	Methyl methacrylate graft copolymer		Non-ionic	Emulsifier Dispersant
Zephrym PD3315	Propylene glycol based polymeric surfactant	-	Non-ionic	Emulsifier Dispersant
HIGHCOAL F3120	Polypropylene based polymeric surfactant	-	Non-ionic	Emulsifier

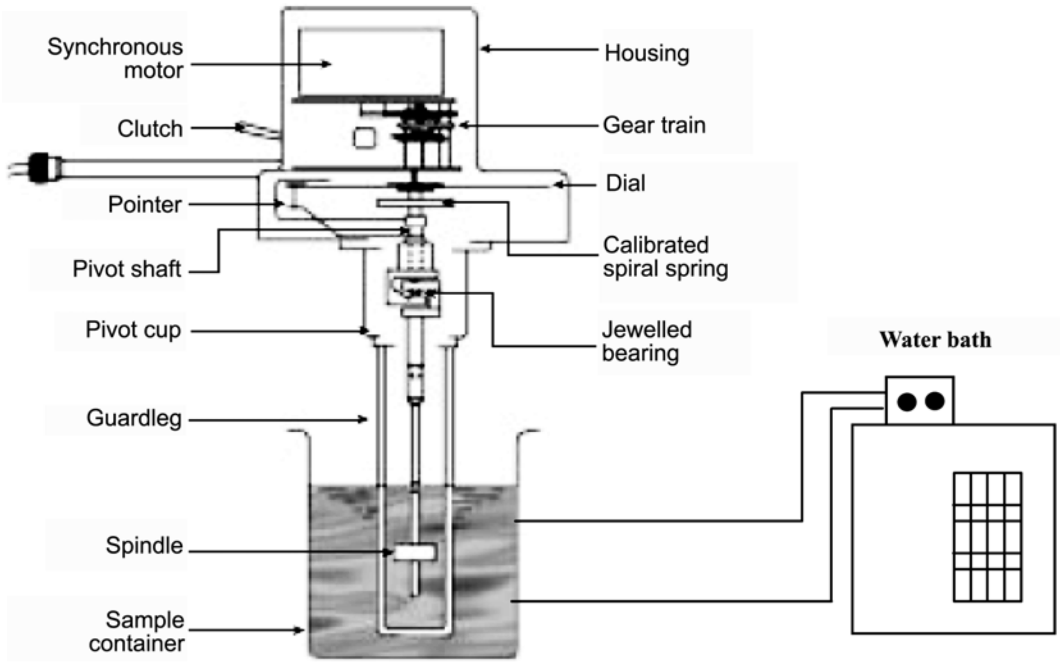


Fig. 1. Schematic diagram of viscosity measurement apparatus.

tives were selected. These were grouped into ionic, non-ionic and high-molecular additives.

To compare the dependency of the coal characteristics and classifications, the apparent viscosity levels of anthracite, bituminous and sub-bituminous coal-water slurry with 0.6 wt% of CWM 1002 were measured at slurry concentrations of 60 to 70 wt%. This is shown in Fig. 2. The bituminous coal (Drayton) reached the lowest viscosity over the slurry loading range in this research. This implies

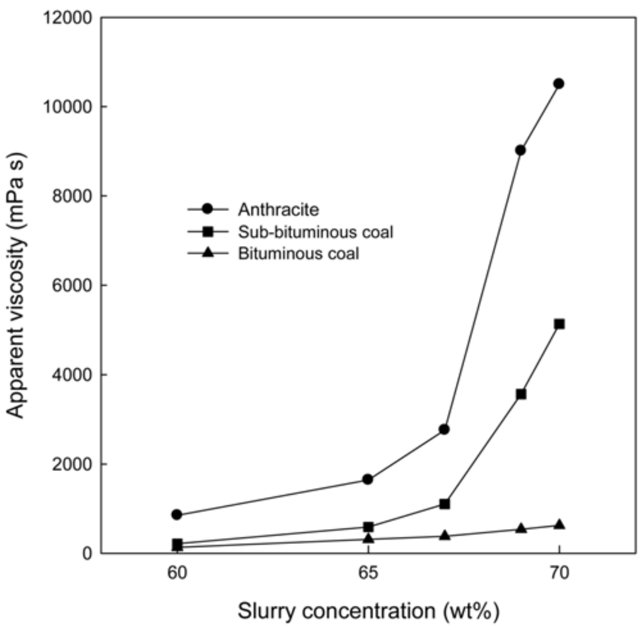


Fig. 2. Comparison of apparent viscosity of anthracite, bituminous (Drayton) and sub-bituminous (Kideco) coal as a function of slurry concentration (0.6 wt% additives concentration, 25 °C).

that the Drayton coal containing CWS, which shows an apparent viscosity of less than 700 mPa·s at a concentration of 70 wt%, is feasible for use with a high content of coal. The anthracite reached a much higher viscosity than either the bituminous (Drayton) or the sub-bituminous coal (Kideco), especially at a high coal concentration, due to the different contents of moisture and ash, as shown in Table 2. The anthracite and sub-bituminous coal contain higher amounts of ash or moisture relative to the others. Therefore, the ash content is the predominant factor in the dependency of the CWS viscosity compared to the moisture content. Consequently, coal containing low ash and moisture levels, such as bituminous coal, is proper for use with CWS at a high concentration. Moreover, with anthracite, it is difficult to make highly loaded CWS independently.

Fig. 3 illustrates the measurement result of the apparent viscosity of the 60 wt% anthracite-water slurry (AWS) at different concentration levels and additive types. In general, as the concentration of the additives increased, the apparent viscosity of the slurry decreased. However, except for CWM 1002, if an additive concentration of 0.6 wt% or higher was added, the apparent viscosity increased. Therefore, the minimum viscosity was achieved at an additive loading of 0.6 wt%, except for the case of CWM 1002. These characteristics depend mostly on the additive properties, and they can be found in other surface active agents [21,22]. In the case of AWS, the Zephrym PD3315 additive performed the best in lowering the apparent viscosity, followed by CWM 1002, ATLOX 4913, and HIGHCOAL F3120 in that order. That is, non-ionic additives, in particular propylene glycol polymeric surfactants, proved to be effective in lowering the viscosity of AWS. Compared to a case in which no additive was added, the apparent viscosity was reduced by more than 70%. Naphthalene sulfonate formaldehyde functionalized additives such as CWM 1002 usually reduce the viscosity of various types of coal containing CWS well [23].

In Fig. 4, the apparent viscosity of 60 wt% petroleum coke-

Table 2. Proximate, ultimate and calorific value analysis of coals and petroleum coke on air dried basis

	Anthracite	Kideco coal	Drayton coal	Petroleum coke
Proximate analysis (wt%)				
Moisture	9.36	18.23	5.75	7.59
Volatile matter	7.22	38.99	31.27	10.46
Ash	47.26	2.28	11.73	0.25
Fixed carbon	36.16	40.49	51.21	81.70
Ultimate analysis (wt%)				
Carbon	50.05	59.22	70.65	87.16
Hydrogen	1.31	4.91	4.87	3.75
Nitrogen	0.52	0.48	1.28	0.98
Oxygen	0.25	25.98	11.46	0.02
Sulfur	0.61	0.15	0.49	7.84
Calorific value (kcal/kg)	4,060	5,776	6,435	8,550

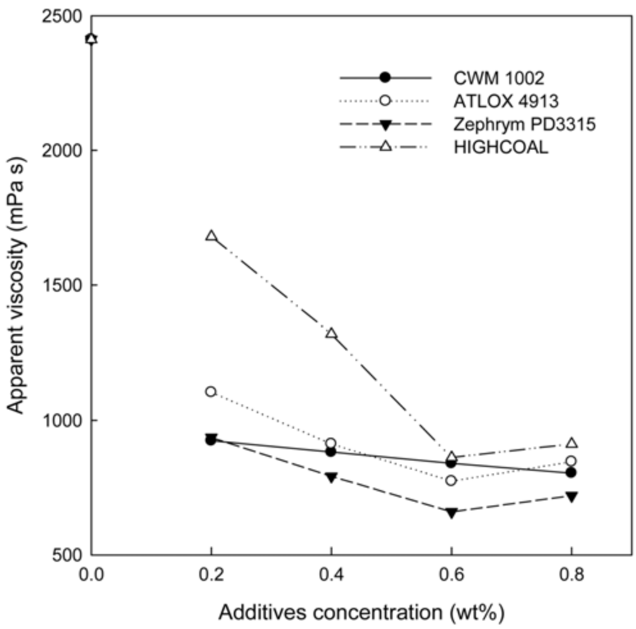


Fig. 3. Apparent viscosity of 60 wt% anthracite slurry as a function of additives concentration at 25 °C.

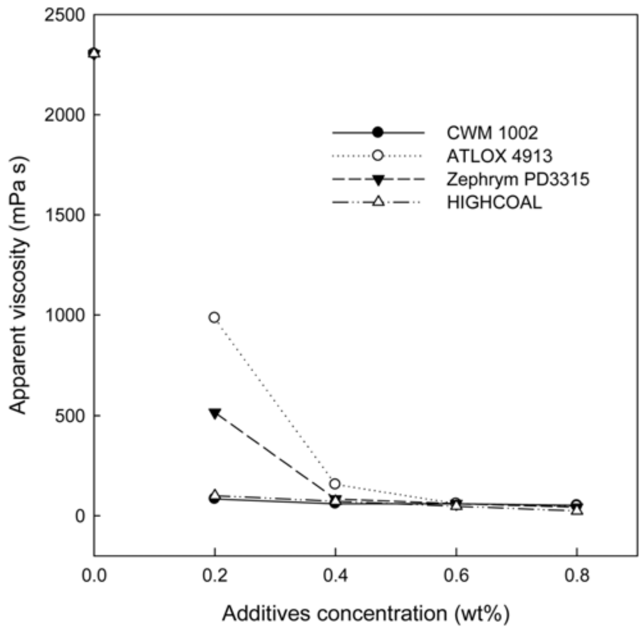


Fig. 4. Apparent viscosity of 60 wt% petroleum coke slurry as a function of additives concentration at 25 °C.

water slurry (PWS) was measured with the aforementioned different amounts (0-0.8 wt%) of additives. Compared to the case in which no additive was added, the viscosity was reduced by more than 95% when 0.8 wt% of additive was added. In the case of PWS, the ionic additive (CWM 1002) and the non-ionic additive (HIGHCOAL F3120) showed similar performance levels. Particularly, the viscosity was not greatly reduced when a small amount of 0.2 wt% was mixed with the polymeric surfactants of ATOLX 4913 and Zephrym PD3315; however, when 0.4 wt% or more was added, the viscosity of the slurry was as lowered as effectively as by the two other types of additives. In addition, when compared to AWS of the same concentration, if no additive was added, the viscosity was similar; in contrast, if an additive was added, the viscosity of the PWS was found to be very low at the same concentration. In other words, the additives used in this study were more effective in lowering the viscosity of PWS than they were that of AWS.

The apparent viscosity levels of four types of additives using 60 wt% mixed fuel slurry formulated by mixing anthracite and petroleum coke at a mass ratio of 1 : 1 were measured with various additives concentrations. This result is shown in Fig. 5. The apparent viscosity of anthracite/petroleum coke-water mixed slurry (APWS) tended to decrease as the concentration of the additive increased to 0.2-0.8 wt%. In general, HIGHCOAL F3120, a non-ionic polypropylene additive, performed at the highest level. This was followed by CWM 1002, Zephrym PD3315 and ATOLX 4913 in that order. This result indicates that propylene glycol polymeric surfactants are not appropriate for APWS. The petroleum coke-containing AWS shows a much lower viscosity than AWS in a comparison of the results shown in Figs. 2 and 4. This indicates that the rheological properties of AWS are improved by the addition of petroleum coke. Therefore, it makes mild usage of AWS and gives an alternative way to utilizing this refinery residue [24]. Moreover, a synergic ef-

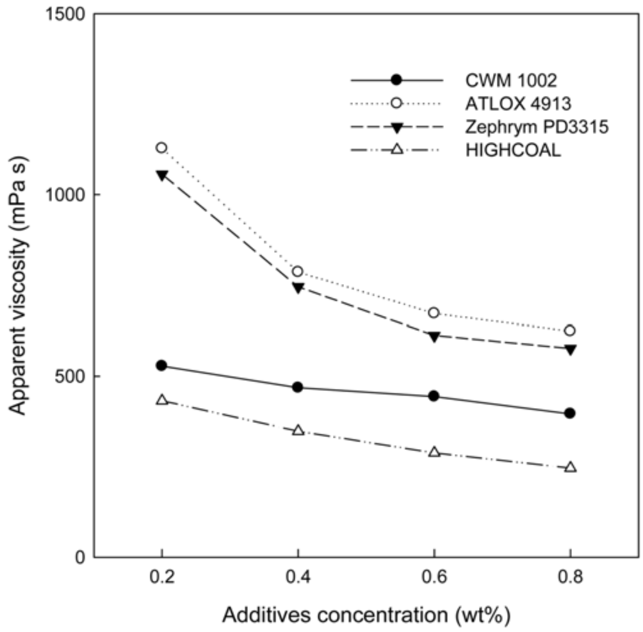


Fig. 5. Apparent viscosity of 60 wt% anthracite/petroleum coke mixed slurry at the mass ratio of 1 : 1 (25 °C).

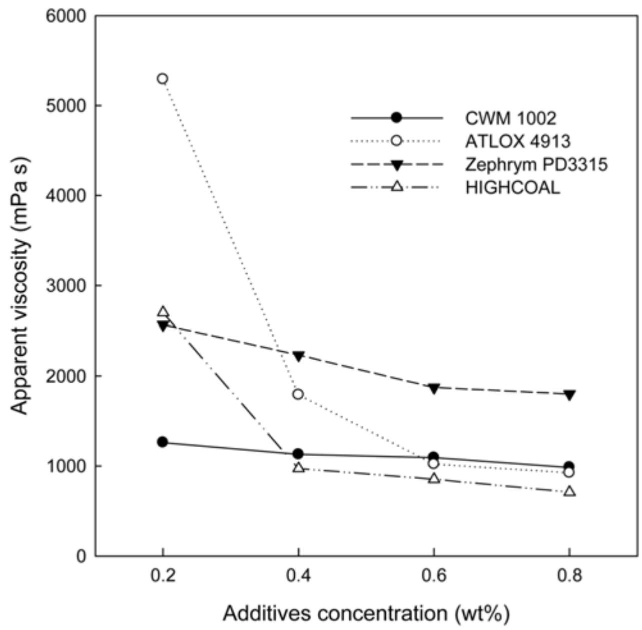


Fig. 6. Apparent viscosity of 65 wt% anthracite/petroleum coke mixed slurry at the mass ratio of 1 : 1 (25 °C).

fect of improved combustibility, lower activation energy and a shortened reaction time was obtained by the mixing or co-processing of coal with other fuels [16-18,25].

In Fig. 6, the apparent viscosity of 65 wt% APWS with a mixing mass ratio of 1 : 1 is depicted as a function of the additive concentration for four different additives. As in the result shown in Fig. 5, the minimum viscosity was obtained with an addition of HIGHCOAL F3120, except at a low additive concentration of 0.2 wt%. CWM 1002 showed the second most effective performance, followed by ATLOX 4913 and Zephrym PD3315. Notably, ATOLX 4913 and HIGHCOAL F3120 did not significantly lower the viscosity of a high concentration of APWS under the conditions of a low additive concentration of 0.2 wt%, whereas the other two additives showed a steadily decreasing tendency with an additive concentration similar to the result shown in Fig. 5. ATLOX 4913, which shows the lowest viscosity-decreasing efficiency at a low APWS concentration of 60 wt%, showed good performance at a level similar to that of CWM 1002 when the additive concentration exceeded 0.6 wt%. This shows that ATLOX 4913 is viable at high APWS and additive concentrations.

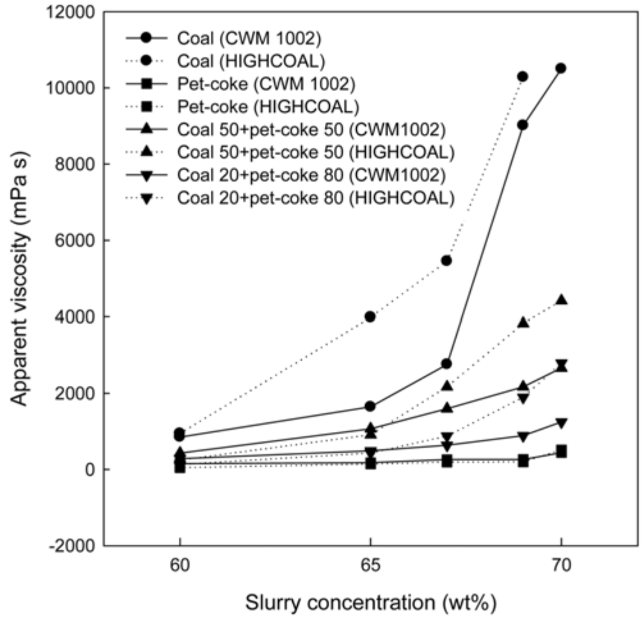


Fig. 7. Apparent viscosity of anthracite, petroleum coke and mixed fuel as a function of slurry concentration (0.6 wt% additives concentration, 25 °C).

The results show that, in general, CWM 1002 and HIGHCOAL F3120 were effective in lowering the viscosity of the coal, petroleum coke and water mixed fuel slurry, whereas the propylene glycol polymeric surfactant was less effective. Accordingly, two additives, 0.6 wt% CWM 1002 and HIGHCOAL F3120, were used to measure the viscosity of 60-70 wt% slurry at various concentrations and mixture ratios. These results are shown in Fig. 7. The viscosity of PWS was lower than that of AWS at all levels of slurry concentration. As the concentration of the slurry increased, the difference in the viscosity increased considerably; at 70 wt%, the viscosity of the AWS was 20 times higher than that of PWS. When coal and petroleum coke were mixed at ratios of 1 : 1 and 1 : 4, the viscosity level was close to the middle of the viscosity levels of the samples. As the proportion of petroleum coke increased, the viscosity decreased. Regarding the viscosity according to the concentration of the slurry, as the concentration of the slurry increased, the viscosity increased. At a level higher than 65 or 67 wt%, the viscosity increased rapidly. According to this result, petroleum coke can make highly concentrated slurry better than if coal is used; upon the formulation of slurry of the same concentration, PWS has the advantage of lower power consumption during the injection flow to the gasifier. In addition, petroleum coke can make slurry of the same viscosity made by AWS

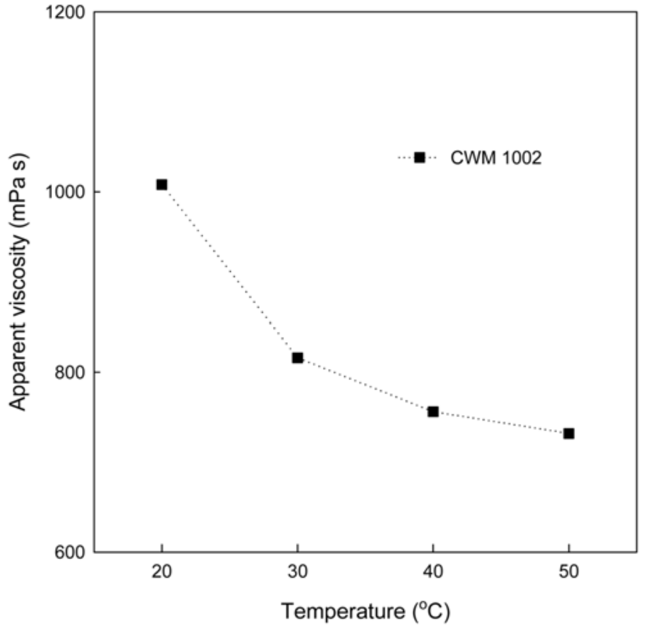


Fig. 8. Apparent viscosity of 65 wt% anthracite/petroleum coke 1 : 1 mixed slurry as a function of temperature (0.6 wt% additives concentration, 25 °C).

with a smaller amount of additive. Comparing the two additives used in this study, CWM 1002 shows better viscosity-decreasing performance for AWS and slightly lower performance for PWS compared to HIGHCOAL F3120. For the case of APWS, at low slurry concentration levels, the viscosity was low when HIGHCOAL F3120 was added, whereas the CWM 1002 additive performed better at high slurry concentration levels (>65 wt%).

Fig. 8 shows the apparent viscosity variation of 65 wt% anthracite/petroleum coke (1 : 1)-water mixed slurry, with 0.6 wt% additive, with the temperature. As the temperature of the APWS increased from 20 °C to 50 °C, the apparent viscosity of the slurry was reduced by approximately 30%. However, the rate of the decrease in the viscosity was diminished as a consequence of desorption of the additive from the surface of the coal and petroleum coke [24].

CONCLUSIONS

As a preliminary investigation of the co-gasification of an anthracite and petroleum coke mixed fuel using a slurry-feeding entrained flow gasifier, viscosity measurements of different slurries were performed. The inherent ash content of anthracite leads to a much higher viscosity of CWS compared to bituminous and sub-bituminous coal and makes the usage as CWS by itself difficult. Four different types of additives were used to measure the apparent viscosity at various concentration levels of slurry and additives. All of the additives used in this study effectively decreased the viscosity of AWS and especially PWS. If the slurry concentration is 65 wt% or higher, the viscosity rapidly increases. Additionally, CWM 1002, an anionic additive, was effective in lowering the viscosity of the anthracite and petroleum coke-water slurry under most of the tested conditions. Highly loaded anthracite-water slurry could be prepared with viscosities of nearly 1,000 mPa·s through mixing with petroleum coke.

ACKNOWLEDGMENT

This work was supported by New and Renewable Energy Center of Korea Energy Management Corporation.

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