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THE EFFECT OF CHEMICALS ON THE RHEOLOGY OF HIGHLY LOADED COAL WATER SLURRIES (CWS)

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Abstract. In this study the influence of chosen detergents on the rheology of highly loaded coal-water slurries (60$\%_{wt}$) made up from coals of differents degree of carbonization from steam coal rank of 31.2 through 33 to coking coal rank of 35.1 according to Polish Standards were tested. In the experiments the nonionic types of chemicals - Rokwinol 60 (polyoxyethylated sorbite oleate, $C_{64}H_{124}0_{26}$), Rokanol LO18 (RO $(CH_2CH_2O)_n$ H, where R – alkyl radical consisting of 16 to 18 carbon atoms in the carbon chain and "n" is around 18), manufactured by Chemical Factory "ROKITA " in Brzeg Dolny, Poland as well as anionic sodium lignosulphonate LSP, a by-product from cellulose production, were used. The detergents used were of a commercial purity. They were chosen taking into account the structure of molecules. Molecules of the surfactants used differ in space structure. Rokanol LO18 has a linear structure, Rokwinol 60 as a derivative of sorbitol has a branched structure whereas sodium lignosulphonate has complicated space structure. The price and accessibility of the detergents used were also considered.

The test results clearly showed that the rheological properties of the CWS depend significantly on both the type of coal and the type of surfactant. The slurries prepared in this study exhibit pseudoplastic and dilatant properties. The same surfactant, depending on the type of coal, may give the CWS of different rheological behaviour.

It was supposed that besides of electrostatic and dispersing forces the steric affect plays a significant role in the CWSs fluidity.

The coal-water slurries, made up from all tested coals without addition of detergents, had consistency of dense mud and their viscosities were not measured..

keywords: coal-water slurries, CWS, coal-water slurry fuels, CWSF, rheology, surfactants

1. Introduction

In recent years, considerable research has been devoted to producing concentrated coal-water slurries, which can be used as a suitable replacement for oil in several industrial applications. Such slurries, which can be shipped and pipelined, are now commercially providing a convenient way of transporting coal over long distances. Coal slurries can also be stored in tanks, which is beneficial in industrial areas.

Several physical properties have been identified as responsible for controlling the properties of the suspensions. They are: the physicochemical properties of the coal, solids volume fraction and particle size distribution, inter-particle interactions in the suspension which are affected by the nature of the surface groups, pH and the presence of electrolytes and chemical additives as well as the temperature of the suspension (Laskowski, 2001; Dincer et al., 2003; Boylu et al., 2004).

In general, it has been shown, that coal particles that have been rendered mutually repulsive (e.g. through the adsorption of ionic or non-ionic surfactants) form a well-dispersed suspension. These suspensions are characterized by low viscosity but form hard sediments that are difficult to redisperse when left to stand (Tudor et al., 1996).

A state of weak flocculation exists in these suspensions when the attractive forces exceed the repulsive forces, and this results in the particles being held together in loose aggregates or flocs. This flocculated state avoids the formation of hard sediments (Tudor et al.,1996).

The mutual interactions between coal grains in the slurry depend on its surface energy which one is the result of slurry composition and may be the measure of the slurry response (Slaczka et al., 2005; Slaczka and Wasilczyk, 2010).

Due to the calorific value, coal concentration in the slurry should be not less than 55% wt. One of the major requirements to be met in preparing Coal–Water Slurry Fuels is that it must have as high as possible coal concentration and a minimum viscosity, to allow ease of handling during preparation, storage, transfer and atomization. However, it is generally known, that the viscosity of CWS increases with the coal concentration in the slurry, and that the stability of the suspension becomes poor if the viscosity is reduced (Papachristodoulou and Tras, 1987; Henderson et al., 1983). Consequently, the problem is how to maintain the highest possible solid concentration and stability simultaneously, at a given or optimum viscosity. To obtain such properties it is necessary to manipulate essentially two major factors: the concentration of the slurry and the addition of suitable fluidizers and stabilizers.

Accordingly, chemical additives are very important in enhancing the fluidity of the coal-water slurries, and the selection of excellent dispersing additives should be recognized as one of the most essential factors in the preparation of highly loaded CWS fuels with reasonably low viscosities.

The rheological properties of CWSs in relation to different additives were subject of interest of many researchers. They investigated the influence of different factors on the apparent viscosity of CWSs (Turian et al., 2002; Logos, 1996; Slaczka, 2004). Therefore in practical terms, the slurry must have a low viscosity at the moderate shear rates that are characteristic of pumping (10-200 s^{-1}). Also, the slurry should possess low viscosity at shear rates corresponding to the atomization process (5000-30000 s^{-1}), because it has been found that low slurry viscosity leads to small droplet sizes during atomization of CWS and hence an increase in the carbon conversion efficiency in a boiler or furnace. Therefore, it is believed that desirable rheological characteristics of CWS would include the phenomenon of pseudoplastic response to increasing shear rate (Nam-Sun et al., 1995).

In this study, the effects of different chemicals used as dispersing agents on the viscosity of CWS were investigated. The coal samples used were Polish coals of different ranks. Two types of surfactant, nonionic and anionic, were used as dispersing agents.

2. Experimental

2.1. Materials

2.1.1. Coals

CWS were made up from coal samples of different degrees of carbonification from steam coal rank of 31.2 through 33 to coking coal rank of 35.1 according to Polish Standards.

The proximate analysis of the coal samples and their ranks are given in Table 1.

Table 1. Proximate analysis of investigated coals

Coal	Ash [%]	Sulphur [%]	Higher calorific value [MJ/kg]	Volatile matter [%]	Rank	
					Polish Standard	ECC Geneva
A	6.9	0.6	27.8	32.3	31.2	06 0 1 3 0 38 07 06 33
B	3.4	0.4	33.1	30.1	33	09 0 3 2 6 30 03 04 35
C	4.7	0.4	34.2	23.8	35.1	11 0 2 1 8 24 04 04 36

2.1.2 Detergents

Additives, which are mainly surfactants and potentially may be used as fluidizers and stabilizes in CWSF technology are numerous.

This work is focused on three of them belonging to three different groups of chemicals: Rokanol LO18 (nonionic surfactant, RO $(CH_2\ CH_2\ O)_n$ H, where R means unsaturated alkyl radical consists of 16 to 18 carbon atoms in the chain and *n* equal to around 18), Rokwinol 60 (nonionic surfactant being polyoxyethylated sorbitol stearate, $C_{64}H_{124}O_{26}$, molecular weight of around 1300), and sodium lignosulphonate LSP (anionic compound which is a by-product of cellulose production. It was of commercial purity grade). The detergents were chosen taking the structure of molecules into account. The price and accessibility of the detergent used were also considered. Rokanol LO18 has a linear structure, while Rokwinol 60, as a derivative of sorbitol, has a branched structure, whereas sodium lignosulphonate has a complicated space structure.

2.2. Slurry preparation

The grain size of the coal sample was reduced below 1 mm using laboratory scale jaw crusher, cone mill and disintegrator. Then, the coal samples were rubbed in an agate mortar for 30 minutes together with water and proper additive to get a slurry of coal concentration equal to 60 wt% and 1.0 wt% of dispersant (based on dry coal). The slurries obtained in this way contained 95% grains below 0.1 mm.

The frequency distribution of the grain size in the slurries were very similar. For example Fig. 1 provides the frequency distribution of the slurry prepared from coal B.

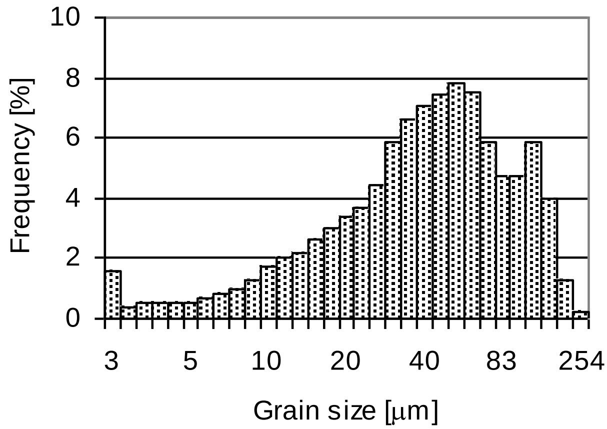

Fig. 1. Grain size distribution of coal B in the slurry

2.3. Rheology measurements

The rheological curves were obtained using a Rheotest 2 viscometer with the vane spindle at 25 to 500 rev/min. The pH value of the slurry varied between 5.8 and 6.0 in all the experiments. The temperature was kept constant within 20 and 21^{o}C. The shear stress-shear rate curves obtained from the experiments were fitted to the Ostwald-de Waele or power law model

$$\tau = K\gamma^{n}$$

where *K* and *n* are rheological constants referred to a fluid consistency coefficient and flow behavior index, respectively. For $n = 1$ this equation reduces to Newton's law of viscosity with $K = \tau/\gamma$, hence the departure of *n* from unity indicates the degree of deviation from the Newtonian behaviour. Rheograms of shear stress versus shear rate as well as apparent viscosity versus shear rate are presented in Fig. 2.

Coal-water slurries made up from the all tested coals without addition detergents had consistency of a dense mud. Therefore, their rheological curves were not determined.

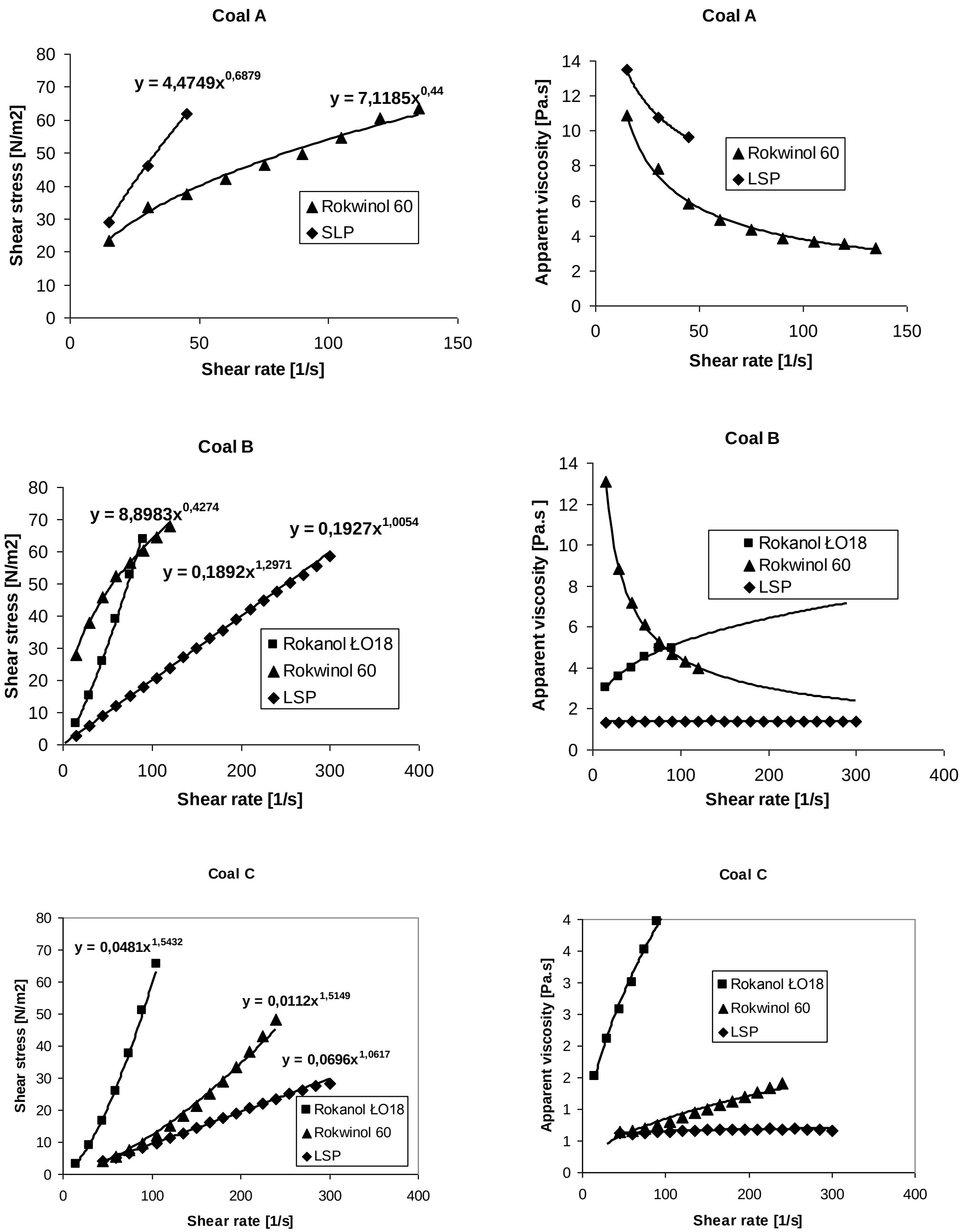

Fig. 2. Effect of surfactant on the rheological behavior of the slurries tested

In the Figures there are also given the best fit power law equations describing the rheological properties of the slurries tested.

The flow behavior indices *n* taken from the best fit power low model formulas are given in the Table 1.

Table 1. Effect of surfactant addition on flow behavior index of the slurries tested

Coal	Flow behavior index (n)		
	LSP	Rokwinol 60	Rokanol LO18
A	0.688	0.440	--
B	1.005	0.427	1.297
C	1.062	1.514	1.542

3. Results and discussion

From Figure 2 it is visible, that the rheological behavior of all the tested slurries fits the Ostwald-de Waele model. Nevertheless, Fig. 2 and Table 1 also show large differences in slurry rheological responses between different kinds of coal and surfactant used.

The results showed that the slurry based on coal A (rank of 31.2) exhibits shear thinning, i.e. pseudoplastic behaviour ($n<1$). That means it has lower apparent viscosity at higher shear rates both for Rokwinol 60 and LSP used as additives. In that case, one can observe rapidly decreasing of apparent viscosity when the shear rate grows. However, in the case of the Rokanol LO18 used as the additive, the slurry was devoid of the fluidity at all (there is no proper curves in Figure 2).

The slurries made up from coal B (rank of 33) and coal C (rank of 35.1) exhibit different rheological response, depending on the additive used. Namely, it was found that the slurry based on coal B with Rokwinol 60 reveals pseudoplastic behaviour ($n<1$), whereas with Rokanol LO18 it is shear-thickening or dilatant fluid ($n>1$). This means that it increases its apparent viscosity at higher shear rates. The same slurry with the LSP reveals almost Newtonian behavior ($n=1.005$) and rather low apparent viscosity.

The slurries made up from coal C (rank of 35.1) with Rokanol LO18 and Rokwinol 60 exhibits dilatant behaviour ($n>1$), whereas with the LSP the slurry becomes practically Newtonian fluid of low apparent viscosity.

Typically, SLP as the anionic surfactant in a CWS adsorbs on hydrophobic sites of the coal and consequently impart a negative charge to the coal particles. Since the counter-cations are strongly attracted to the interfaces, and electrical double layer is formed. These counter-cations are usually distributed in the diffuse layer when there is no specific adsorption. Alternatively, some of the counter-cations are associated with the surface in the Stern layer. This electrical double layer creates repulsive interaction forces caused by the overlap of the double layers, preventing the aggregation of the coal particles. It leads to increase in fluidity of the slurry in the presence of the SLP (coals B and C).

One should notice that the detergents used differ in the space structure. Molecules of Rokanol LO18 has a linear structure, Rokwinol 60 has branched molecules whereas LSP molecules has complex and space structure. Experiments showed that introducing SLP to the CWSs based on coals B and C leads to almost Newtonian fluids of low viscosities. It indicates that besides of electrostatic and dispersing forces, the space structure of detergents molecules used as fluidizers in CWSs preparation, plays the significant role.

Adsorption on coal grains molecules of the SLP, branched in space, creates large distances between coal grains in the slurry. Water fills these spaces and acts as a lubricant which leads to a decrease in apparent viscosity.

In the case of coals A and B with nonionic Rokwinol 60 (molecular weight about 1300) one can suppose that the large molecular chains adsorbed on the coal surface tumble at random and affect large volumes of fluid under low shear, but that they gradually align themselves in the direction of increasing shear and produce less resistance. The decrease in apparent viscosity of CWSs influenced by Rokwinol 60 may be explained also by another mechanism. Hydrophilic spots on the coal surface attach hydrophilic poles of the surfactant. The hydrophobic poles of the surfactant will thus orient itself towards the aqueous phase. In this case, water acts as a lubricating material between the coal particles. In contrast, if the hydrophilic part orients itself towards the aqueous phase, the amount of water at the surface of the coal particle will be increased by hydrogen bonding with the polyethoxy chain. This will produce a hydration layer or solvation shell of water around the coal particles and prevent agglomeration by eliminating preference between other coal particles and water. This might decrease the viscosity if the hydrophilic chains act to separate the coal particles by cushioning them and allowing them to slip against one another.

It is obvious, that slurries of dilatant properties are not useful as slurry fuels. Such properties make impossible pumping them and atomization in burners as well.

Summarizing, one can say that among tested systems for preparation of Coal-Water Slurry fuels the best are these composed of coal C and LSP and of coal B with LSP or Rokwinol 60 as the additives.

4. Conclusions

The test results clearly show that the rheological properties of CWSs depend significantly on both the type of coal and surfactant. The slurries prepared in this study exhibit pseudoplastic as well as dilatant properties. The same surfactant, depending on the type of coal, may give the CWS of different rheological behavior.

The experiments showed that LSP has a considerable influence on the rheological properties of the coal-water slurries. The slurries of coals B and C in which LSP used as the additive reveal almost newtonian behavior and its apparent viscosity was diminished significantly.

It was supposed that besides of electrostatic and dispersing forces, the steric effects play a significant role in the CWSs fluidity.

The coal-water slurries made up from all the tested coals without addition of detergents had consistency of dense mud and their viscosities were not measured.

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