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Improving stability of concentrated coal–water slurry using mixture of a natural and synthetic surfactants

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ABSTRACT

The use of a surfactant mixture of natural and synthetic surfactants as additives in stabilizing coal-water slurry (CWS) formed from low rank Indian coals has been explored. The surface activities of the synthetic surfactants, hexadecyltrimethyl ammonium bromide (CTAB, cationic surfactant) and sodium dodecyl sulphate (SDS, anionic surfactant) are found to alter when various concentrations of natural surfactant, saponin (non-ionic surfactant) extracted from the fruits of *Sapindous laurifolia* are added to them independently. A considerable decrease in viscosity of CWS has been observed on the addition of saponin to the synthetic surfactants, CTAB/SDS (at 50:50 (w/w) for saponin:CTAB; 60:40 (w/w) for saponin:SDS systems). The mixture of anionic-nonionic is however, found to be more effective than the mixture of cationic-nonionic surfactants in reducing the apparent viscosity of the mixtures. The surface tension and contact angle data of the mixtures in solution suggest the high surface activity of the mixtures at these ratios. The rheological behaviors of CWS at weight concentrations varying from 55% to 65% wt.%, the static stability test, effect of pH, temperature, etc. have been studied. The slurries follow Bingham plastic behavior within these ranges of concentrations. A qualitative model of interaction of additive with a coal particle at the interface has been suggested.

1. Introduction

There is an acute shortage of petroleum products around the globe due to the remarkable depletion of the oil layer as a result of environmental effect as well as indiscriminate use of oil due to industrialization and urbanization [1]. The alternative energy fuels such as hydrogen fuel [2], fuel from biomass [3], biodiesel [4], and coal water slurry [5] are appearing as promising sources due to their ability to replace fossil fuel efficiently. Coal–water slurry (CWS), in particular has been adopted in many industries for power generation due to its low cost and ease in handling and therefore, has been receiving intensive research in Science and Technology since 1980 [1]. The maximum efficiency of CWS as fuel lies on volume fraction of coal in the slurry which should be high and on its viscosity which should be moderately low [6]. Such concentrated slurries are however, not stable ordinarily due to increased inter-particle interactions among the coal particles at higher coal concentrations [7]. The viscosity of the concentrated slurries also exceeds the permissible range needed for its storage as well as transport through pipeline [8]. To minimize the inter-particle interactions and improve rheological behaviors of the slurries, the surfaces of the parent coals are modulated by a number of physical [9–12] and chemical [13–16] modification techniques. There is also a general consciousness-raising that the additive improves the stability of coal–water slurry effectively [17,18]. The sole aim of adding additive is to minimize the coal–coal interaction and to improve the suspension stability by introducing several factors like electrostatic or steric repulsions or increasing the steric wettability of coal as suggested by DLVO theory [19]. As pointed out in a number of articles [20,21], surfactants and polymers in particular, have been found to be effective additives in stabilizing the coal–water slurry. Such additives due to their amphiphilic nature, have the tendency to adsorb strongly on coal through their nonpolar moieties [22,23] leading thereby the exposure of their polar head groups to interact with surrounding bulk water molecules. This orientation of additives leads to a thermodynamically more favorable situation since the wettability of the coal is increased through interaction of the polar groups of the additives with water and inter-particle attraction decreases due to steric or electrostatic repulsion offered by their head groups. Consequently coal agglomeration is inhibited to a substantial extent [6]. Gurses et al. [16] have studied the effect of various parameters like coal loading, rheology of coal water slurry using sodium dodecyl sulfate (SDS), cetyltrimethyl ammonium bromide (CTAB) as additives. They have observed that both CTAB and SDS effectively reduce the viscosity of coal–water slurry. Aktas et al. [15] have studied the stabilization of slurry by adding a commercial nonionic surfactant, Triton X-100. Natural surface active agent like saponins from *Sapindus laurifolia* [24], *Acacia concinna* [6] have also been reported to be effective additives for concentrated coal–water slurry stabilization.

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In continuation to our earlier works [6,24,25] in developing natural as well as biodegradable additives, the present paper is an attempt to explore the possibility of developing the mixture of synthetic surfactants available commercially with natural surfactant, used by us elsewhere [6]. Surfactant mixtures rather than pure species are more preferably used as they are naturally prevalent, less expensive, eco-friendly and often perform better than single surfactants in several applications [26–28]. This improved performance often arises through synergetic interactions between two surfactants. Such synergistic behavior of surfactant mixtures reduces the total amount of surfactant used, thereby reducing both the cost and the environmental impact. It is well known that mixture of nonionic surfactant shows ideal behavior in respect of their mixing [29,30], while mixture of ionic–nonionic, anionic–cationic and fluorocarbon surfactants exhibit significant departure from the ideal behavior and hence may lead to synergism [31–35] or antagonism [36–38]. The synergism leads to enhanced surface activity of the mixtures and hence more interfacial adsorption is inducted on coal surface resulting in stabilization of the suspension through steric/electrostatic repulsions [39–42]. But synergism stimulates in early micelle formation leading to increased viscosity of slurry [43–46] which would therefore, disfavor pipeline transport. On the contrary, the antagonism results in decrease of the surface activity of the mixture [47], which would therefore, lead to not only a decrease in the viscosity but also a reduction in the adsorption density of the mixture on coal surface. It is therefore, essential to maintain a proper balance of viscosity and interfacial adsorption and hence to set the protocol for optimizing the efficiency of a surfactant mixture in stabilizing concentrated coal–water slurry. A proper combination of the surfactant mixture coupled with non-coking coals (cheap coal) may reduce specific cost and energy during the transportation, storage and shipping of the slurry.

Literature survey reveals that the use of surfactant mixture in coal–water research is scanty. Most importantly, very little is known about the mechanism by which the surfactant mixtures stabilize the coal–water slurry. In this paper we have explored the possibility of using the mixture of natural surfactant, saponin isolated from *S. laurifolia* with two conventional synthetic surfactants, sodium dodecyl sulfonate (SDS) and hexadeceyltrimethyl ammonium bromide (CTAB) at different ratios. The established techniques [22] have been used to test the efficiency of stabilizing the concentrated coal–water slurry. The qualitative interaction models have also been proposed.

2. Experimental section

2.1. Materials

2.1.1. Natural surfactant:saponin

Saponin was isolated from drupes of *S. laurifolia* collected from Paralakhemundi, the forest zone of southern Odisha, India in the manner described in literature [24,48]. Saponin is a white powder with melting point of 145 °C. It is a complicated mixture of saccharin derivatives and belongs to a class of naturally occurring nonionic surfactants, having a critical micellar concentration of about 0.8 wt.% [6]. The hydrophilic part of the molecule called glycon, consists of saccharides such as glucose, galactose, rhamnose, xylose, pentose, etc. and the hydrophobic part called aglycone, consists of steroids and triterpene. The hydrophobic part is bonded through oxygen to the hemiketal or hemiacetal carbon of the saccharide residue which in turn is linked through oxygen linkages to other saccharide residues. The saponin has antibiotic activity and is toxic to fish and insects, but it is practically non-toxic to man with expanding applications in food, cosmetics, and pharmaceutical sectors. It is important in human diets to reduce the risk of coronary heart disease. It has been successfully used in obtaining concentrated water slurries [6]. Details of the structure, properties and applications of the saponins have been documented [6,49,50].

2.1.2. Commercial surfactant

SDS (Merck) and CTAB (Merck) are commercial samples and are used after purifying by standard methods reported in literature [51,52].

2.1.3. Procurement of the coal sample

Coal samples were collected from main coal seam of Talcher Coal Field, Talcher, Odisha (Eastern part of India). The coals were beneficiated employing controlled crushing and de-ashing to obtain cleans. Cleans were first crushed in jaw crusher and subsequently in double roll crusher to obtain sample with particle size below 100 μm. Three types of coal samples designated as Coal A, Coal B and Coal C with ash content of 8.02% (low ash coal), 18.14% (medium ash coal), 39.06% (high ash coal), respectively were selected for preparation of high concentration slurry in distilled water. The particle size distribution of the coal samples, measured by a Malvern particle size analyzer are mentioned in Table 1. The log–log plots for the particle size distribution of the three coals are given in Fig. 1. Physico-chemical characteristics of coal particle surfaces vary depending on the source of coal and its treatment. The proximate and ultimate analyses data are given in Table 2.

2.1.4. Surface tension measurement

The surface tension and contact angle of different solutions were measured with the help of an ST-500MAN surface tensiometer (Nima Tech, England) by Wilhelmy plate method.

2.1.5. IR studies

The IR spectral data of the coals have been obtained on a KBr disk in the region 400–4000 cm^{-1} using a Schimadzu IR Prestige-21 FTIR spectrophotometer (Germany). The frequencies and assignment of the bands are given in Table 3.

2.1.6. Preparation of the coal water slurry

About 100 mL of slurry was prepared by adding 55 to 65 wt.% of coal to 45 to 35 wt.% of water containing 1 wt.% of the surfactant mixture (saponin + CTAB/SDS) and agitating the mixture in a helical ribbon mixer at 50–150 rpm(to avoid particle disintegration) by using a variable frequency drive. The suspension has fair stability during the measurement for at least 48 h. The weight fraction of saponin in 1 wt.% of mixture was varied from 0.1 to 1 wt.% in steps of 0.1 wt.% for different weight concentrations of coal in CWS.

2.1.7. Viscosity measurement

The rheological studies of the CWS were carried out using a HAAKE rotational viscometer (Model RV 30), consisting of a measuring drive unit, temperature vessel with circulator, sensor system, and a data logger. A sensor system MV I was chosen for the rheological measurements. The sensor and the cup were cleaned and air-dried. The variation in temperature was 0.1 °C, controlled through a constant temperature circulator bath connected to a viscometer. All experiments were conducted at room temperature of 30 °C. The rheological measurement was controlled by a software rotation version 3.0. The best-fit model was fitted to the shear stress–shear rate data to obtain the nature of coal–water slurry. The various parameters such as shear stress, shear rate, apparent viscosity, and temperature along with the curve were displayed on a computer screen.

Table 1
Particle size parameters of coal samples.

Coal type	Particle size, in μm		
	d_{10}	d_{50}	d_{90}
Coal A	3.894	27.318	95.70
Coal B	3.222	23.949	100.789
Coal C	3.337	33.131	109.531

d_{10}, d_{50}, d_{90} are the diameter percentage points 10%, 50% and 90%, respectively.