

Rheology of coal slurries in no. 2 oil and ethanol blends: effect of water

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Abstract: Rheological properties of coal slurries in No. 2 oil and ethanol blends containing various amounts of water have been investigated in detail. Water is observed to increase the viscosity of the slurries. The slurries exhibited appreciable yield stress in the presence of water. The final subsided volume increased sharply and a decrease in critical solids concentration was observed up to 10% of water, above which these effects leveled off. In the case of low coal concentration slurries, the viscosity and the yield stress increased with increasing amounts of water and a critical shear rate was observed. Depending upon the concentration of water, the slurries behaved as dilatant, Newtonian or pseudoplastic below the critical shear rate, in the lower shear rate region. In the higher shear rate region, they exhibited pseudoplastic behavior. The slurries containing higher coal loading were pseudoplastic at all water concentrations, and viscosity along with yield stress exhibited a maximum around 10% of water. The rheological parameters have been analysed using the power law and Bingham plastic models. The effect of water on the rheological characteristics has been explained on the basis of coal particle bridging by water, which is supported by the measured subsidence volumes and critical solids concentration.

Key words: Coal slurry, flocculation, subsidence, critical solids concentration, oil and ethanol blend

1. Introduction

Coal slurries are considered to be the viable alternative fuels for oil fired burners. Further stretch in fuel oil stock could be achieved by incorporating ethanol and appreciable amounts of water. Recently, it has been shown that low viscosity coal slurries in No. 6 oil and ethanol blends could become the potential boiler fuels [1–3]. The addition of water serves as an effective means of stabilizing coal-oil slurries. Water appears to function as a flocculating agent [4]. Also, water is known to form particle network by bridging the solid particles, as shown in the case of dispersions of glass beads in liquid polybutadiene medium [5]. The dispersions containing small amounts of water as an immiscible third phase is known to exhibit appreciable yield values [6, 7]. Kao et al. [5] have studied the rheological behaviour of suspensions of glass beads in liquid polybutadiene containing water,

in detail. In the case of coal dispersions in oil, Meyer [4] has shown that apart from stabilizing the slurries, the added water influences the rheological behavior to a great extent. While the function of water as a flocculating agent has been reported in literature, a systematic investigation of the influence of concentration of water on rheological behavior has not been carried out. In this paper, we present the results of rheological properties and subsidence behaviour of coal/No. 2 oil and ethanol slurries containing appreciable amount of water at high as well as low solids contents. Also, recently, we have shown that further modification in rheological behavior of these slurries could be achieved by incorporating suitable surfactants, [8, 9]. While the addition of ethanol may improve the ignition properties, the added water may further accelerate the burning efficiency due to microexplosion of the water droplets during atomization [10].

2. Experimental study

2.1 Materials and sample preparation

Coal samples were from a single batch of finely powdered coal obtained from Florida Power & Light Company, Florida. Bimodal mixture of pulverized coal of 80% 200 mesh (i.e. 80% of the coal particles were 75 μ or less in diameter) and 20% 325 mesh (i.e. 20% of the coal particles were 46 μ or less in diameter) was used. The coal density was determined by volume displacement of reagent grade hexane in a specific gravity bottle and was found to be 1.28 g/cm³. Fuel oil No. 2 used in this study was from Gainesville Utility Center, Florida. The characteristics of No. 2 oil are: viscosity 4 cp (ambient temperature), specific gravity 0.876, percent ash and sulfur 0 and 0.5 respectively. Ethanol, both absolute and denatured were obtained from Fisher Scientific Company. The densities of absolute and denatured ethanol are 0.785 and 0.789 gm/cc respectively. Distilled water was used in all our experiments. Coal slurries in No. 2 oil and No. 2 oil and ethanol blends (4:1 by weight) with varying amounts of water were prepared in sample vials. Samples were homogenized by shaking the vials vigorously.

2.2 Methods

Viscometric measurements were carried out using Brookfield cone and plate viscometer having the shear rate from 1.15 to 230 sec⁻¹, at ambient temperature. A small amount of slurry was introduced into the viscometer plate and readings were taken after two minutes of shearing, when the pointer was stable. All subsidence volume measurements were carried out using settling columns of 15 ml capacity at ambient temperature. The wall effect was minimized by keeping the diameter of the column constant. The terminal settled bed volume (TSV) was measured after the subsidence reached the equilibrium value, usually after a week of settling. The relative TSV was calculated using the relation

$$\text{TSV} = V_c/V_t \quad (1)$$

where V_c is the final volume of the settled coal bed and V_t is the volume of the slurry.

Relative settling reduction was calculated according to Meyer [4] as follows:

$$\text{settling reduction} = V_0 - V_w/V_0 \quad (2)$$

where V_0 is the volume of the supernatant liquid above the coal bed in the case of slurries not containing water. V_w is

the volume of the liquid layer separated above the coal bed in the case of slurries containing water.

Critical solids concentrations (C_{SC}) was calculated using the relation [11],

$$C_{SC} = C_0 h_0/h_\infty \quad (3)$$

where C_0 is the initial coal concentration, h_0 is the height of the coal slurry and h_∞ is the final settled bed volume of coal¹.

The rheological data obtained were fitted into the following two models,

$$\text{Power-Law Model: } \tau = K\dot{\gamma}^C \quad (4)$$

and

$$\text{Bingham Plastic Model: } \tau = \tau_0 + \eta_p \dot{\gamma} \quad (5)$$

where τ is the shear stress, $\dot{\gamma}$ is the shear rate, K is the pseudo-viscosity, C is the power-law index, τ_0 is the Bingham yield stress and η_p is the plastic viscosity. The correlation coefficients upon fitting the data to these models were 0.98 or better.

3. Results and discussion

3.1 Rheology of coal slurries in No. 2 oil and blends of No. 2 oil and ethanol

Figure 1 shows the viscosities of various coal slurries as a function of coal concentration. It is seen that the viscosities increase sharply above 40–50% coal for various slurries. Also, the slurries of coal in No. 2 oil containing ethanol (curves B and C) and water (curves D and E) show higher viscosities compared to the coal/No. 2 oil slurries (curve A), at all coal concentrations. For reasons not clear, slurries in No. 2 oil and absolute ethanol were not very stable. While the increase in viscosity upon the addition of ethanol could be due to coal-alcohol interactions [12], further increase observed in the case of slurries containing water may be the result of flocculation [4].

In figure 2 are shown the flow curves of coal/No. 2 oil slurries at various coal loadings. From the curves it is seen that the No. 2 oil slurries above 40% coal loading are non-Newtonian. Also at higher loadings, slurries showed appreciable Bingham yield stress. At 40% coal loading the data can be fitted to the following expression,

$$\tau = 0.598 + 0.01 \dot{\gamma} \quad (6)$$

¹ The critical solids concentration (C_{SC}) as expressed in eq. (3) refers to the maximum amount of coal that can be loaded (still keeping the solid-liquid dispersion property) in a given oil and coal slurry. For example C_{SC} of typical coal/No. 2 oil slurries is $\approx 50\%$ (see fig. 9).

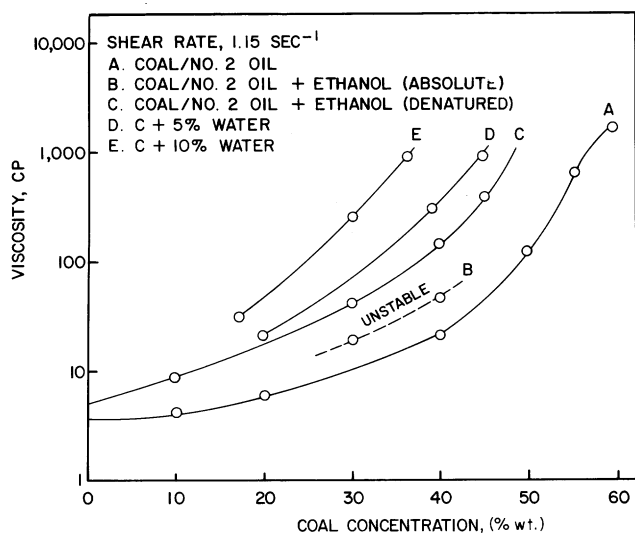


Fig. 1. Viscosity as a function of coal concentration for various coal slurries

using Bingham plastic model. Further, the flow curves of slurries in No. 2 oil and ethanol blends are shown in figure 3. Absolute ethanol was used to prepare the blends in all these studies. It is seen that, upon the addition of ethanol, the slurries become pseudoplastic at coal loadings as low as 20%. The slurries showed appreciable yield values at higher coal loadings.

3.2 Rheology of slurries containing various amounts of water

3.2.1 Low coal concentration

Use of water as an effective means of stabilizing coal oil mixtures (COM) involve different approaches. Water-in-oil emulsion can reduce settling by the thickening of the suspension medium and/or water can also function as a polar flocculating third phase (water bridging) forming a network structure throughout the suspension medium, thereby reducing the settling [4]. The rheological behavior of the flocculated suspensions containing appreciable amounts of water is shown in figures 4 and 5. It is seen that, with increasing water content, up to a certain shear rate (say, critical shear rate, $\dot{\gamma}_c$), slurries show shear-thickening, Newtonian and shear-thinning behavior. Above this critical shear rate, at all water contents, slurries were shear-thinning. The initial dilatant behavior of the slurries containing lower concentrations of water could be attributed to the large number of agglomerates formed by the water bridging of the coal particles. The transition from dilatant to Newtonian behavior may be due to the dilution of the suspension by the added water, after a maximum bridging. At sufficiently higher water content, the formation of water/oil emulsion (suspension medium) may contribute to shear-thinning behavior of the diluted system. At shear rates high enough (above $\dot{\gamma}_c$) the agglomerates are broken

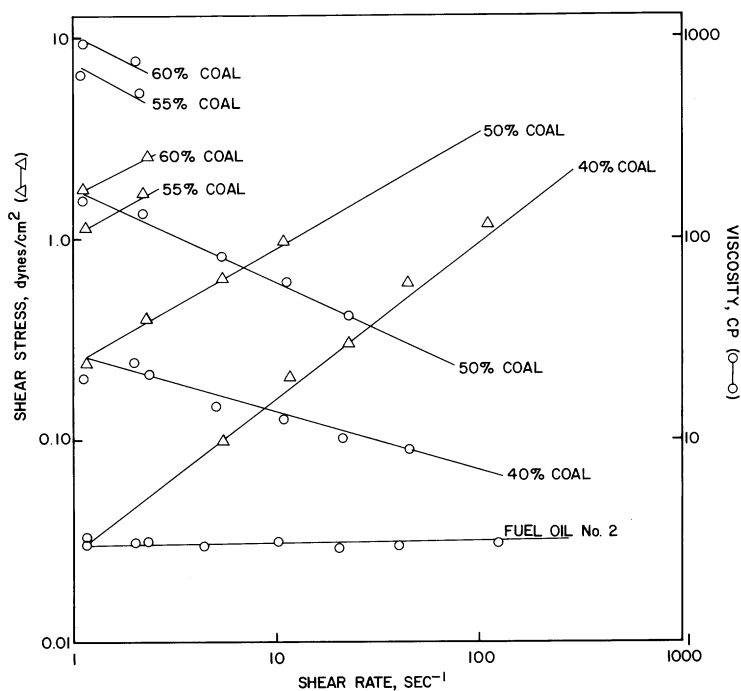


Fig. 2. Viscosity and shear stress as a function of shear rate for coal slurries in No. 2 oil at various coal loadings

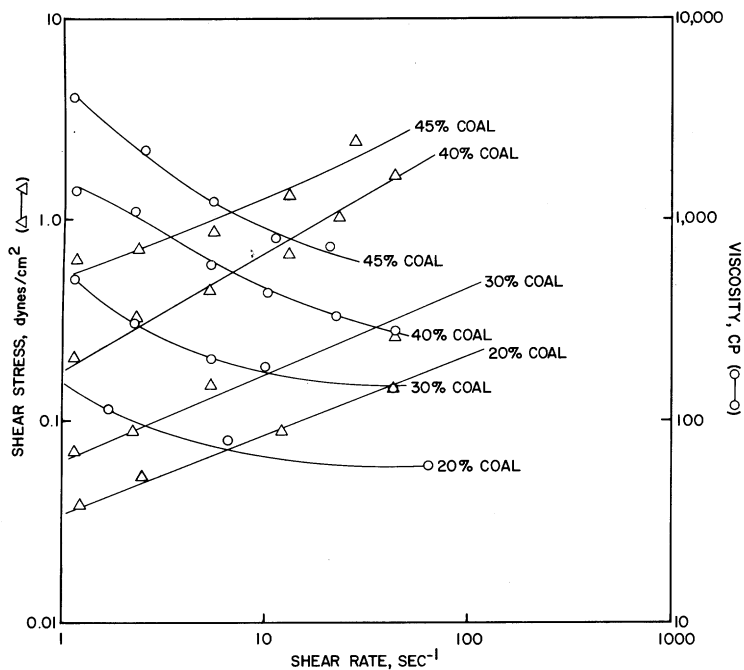


Fig. 3. Viscosity and shear stress as a function of shear rate for coal slurries in No. 2 oil and ethanol at various coal loadings

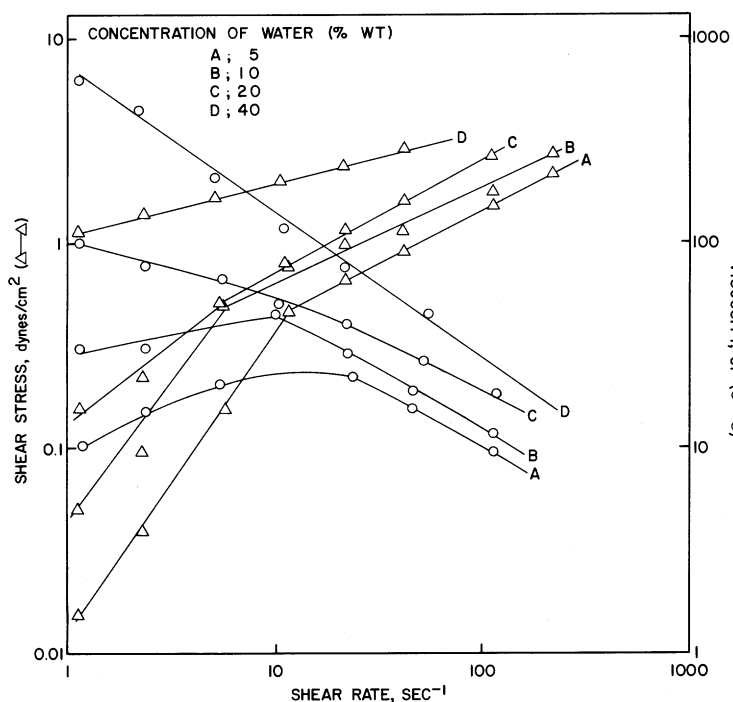


Fig. 4. Viscosity as a function of shear rate for coal slurries in No. 2 oil and ethanol blends in presence of various amounts of water at 20% coal loadings

up and the reduced number of flocs may result in shear-thinning behavior of the slurries at all water contents. In the low shear rate region (below $\dot{\gamma}_c$) the equilibrium agglomerate radius R could be related to the square root of the shear rate [5] by the following expression

$$R = (r^2 \dot{\gamma}_c / \dot{\gamma})^{1/2} \tag{7}$$

where r is the radius of primary coal particles¹⁾.

The Bingham plastic and power-law model parameters as a function of concentration of water for both low and

¹⁾ Eq. (7) is referred only for a qualitative assessment of the observed effect. However, quantitative aspects of this derivation are found in Kao et al. [5].

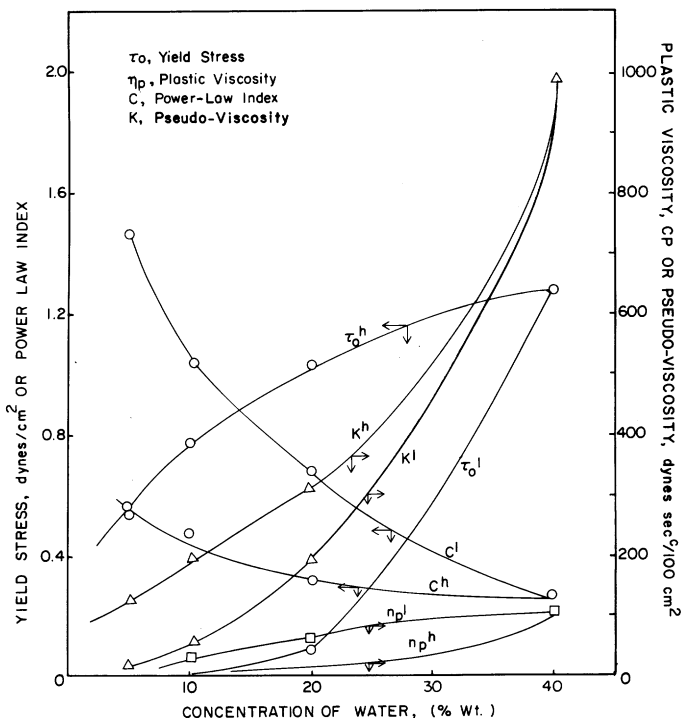


Fig. 5. Effect of concentration of water on rheological parameters of coal slurries in No. 2 oil and ethanol blends at 20% coal loading

high shear rate regimes are shown in figure 5¹). The pseudo-viscosity K and the plastic viscosity η_p increased with increasing water content. The initial increase in the viscosity may be due to the formation of coal particle network and the further increase may be the result of the thickening of the suspension medium (formation of emulsion). The power-law index C decreased upon increasing the concentration of water in both the low and high shear-rate region. In the low shear-rate region, the power-law index (C^l in figure 5) shows that the slurries were dilatant ($C^l > 1$) at low water content and become shear thinning ($C^l < 1$) upon the addition of appreciable amount of water. Also, at all water concentrations, the power-law index is appreciably lower in the high shear-rate region. The Bingham yield stress increased with increasing water content in the entire shear rate region. However, the magnitude of yield values in the high shear-rate region (τ_0^h in figure 5) is much higher compared to low shear-rate yield values. The presence of yield values in a slurry indicates flocculation or network formation by the particle-particle interactions [5–7, 13]. Further, the yield

¹) These model parameters were obtained by fitting shear stress–shear rate data into power-law and Bingham plastic models, using least square analysis for various concentrations of water.

stress is a measure of interaction energy between particles [13] which in the present case is determined from the linear extrapolation at high shear rates and/or at low shear rates to the shear stress axis. The low shear-rate Bingham yield stress would however reflect more realistically the interaction energy associated with structural or network flocculation [4]. A quantitative increase in the extent of network formation appears as increased yield values. This is further supported by the larger subsidence volumes and lower critical solids concentration of slurries containing increasing amounts of water as discussed later.

3.2.2 Higher coal concentration

The flow curves of higher coal loaded (40% coal) slurries with various amounts of water are shown in figure 6. The slurries exhibit typical pseudoplastic behaviour at all water concentration. However, the absence of a critical shear rate is probably due to the limited shear-rate region scanned.

The rheological parameters obtained from power-law and Bingham plastic models are shown as a function of concentration of water in figure 7. The shear-thinning behavior of the slurries appears to be pronounced around 10% water as shown in figure 7. The pseudo-viscosity and the plastic viscosity along with the Bingham yield stress show a maximum around 10% of water. The increase in viscosity as well as yield value up to 10% of water could be attributed to the increase in the extent of bridging by the added water. However, after a maximum bridging, probably decided by the ratio of weight of water to that of coal, additional water may go into the suspension medium. In this concentrated system, the dilution of the suspension by the additional water may decrease the number or may reduce the size of the flocs which in turn results in the reduction of viscosity and yield value. In the case of low coal concentration slurries, as discussed earlier, the thickening of the suspension by the additional water (after the bridging) may predominate over the reduction in the number or size of agglomerates in contributing to viscosity and yield value.

3.3 Subsidence and critical solids concentration of coal slurries

Figure 8 shows terminal sedimentation volume (subsidence volume) of slurries as a function of coal concentration. It is seen that the measured subsidence volumes of slurries increase upon the addition of ethanol

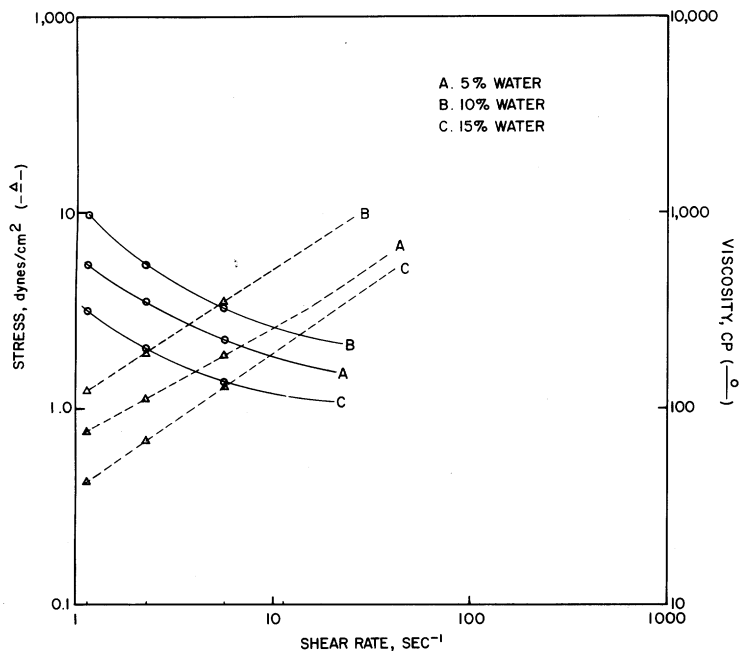


Fig. 6. Viscosity as a function of shear rate for coal slurries in No. 2 oil and ethanol blends in the presence of various amounts of water at 40% coal loading

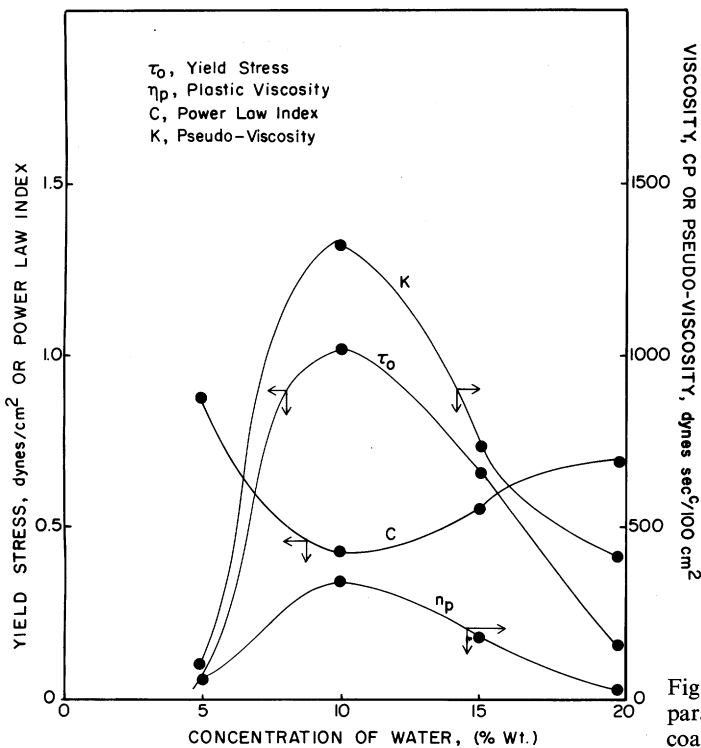


Fig. 7. Effect of concentration of water on rheological parameters of coal slurries in No. 2 oil and ethanol blends at 40% coal loading

or water at all coal concentrations. Figure 9 shows the subsidence behavior and critical solids concentration of 20% and 40% coal-loaded slurries containing various amounts of water. A considerable increase in subsidence

volumes (proportional to relative reduction in settling) observed up to 10% of water in the case of high and low coal-loaded slurries (figure 9), may indicate initial bridging. This is further supported by the decrease in

critical solids concentration as shown in figure 9. However, at high concentration of water, subsidence volumes and critical solids concentrations did not exhibit

significant change, which could be attributed to the completion of the bridging. The observed rheological behavior, thus, could be explained on the basis of coal particle bridging by water as reflected by the subsidence behavior.

4. Conclusions

- (i) Viscosities of coal slurries in the blends of No. 2 oil and ethanol are higher than in No. 2 oil. Addition of water results in further increase in the viscosity of the slurries.
- (ii). At lower coal loading, depending on the concentration of water and below 15% of water, the slurries are pseudoplastic, Newtonian or dilatant up to a critical shear rate ($\dot{\gamma}_c$). Above $\dot{\gamma}_c$, the slurries are typical pseudoplastic. The presence of critical shear rate suggests that the slurries may contain large number of agglomerates below $\dot{\gamma}_c$ and reduced floc sizes at higher shear rates.
- (iii). The slurry viscosity, yield stress and power-law index show a maximum around 10% of water in the case of higher coal loaded slurries (40% coal loading). Water may function as the bridging agent between coal particles up to a particular ratio of weight of water/weight of coal,

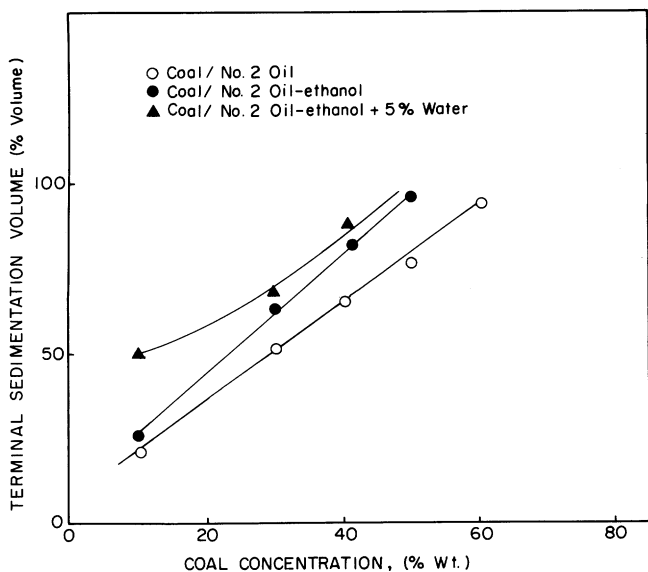


Fig. 8. Effect of ethanol and water on terminal sedimentation volumes of coal/No. 2 oil slurries

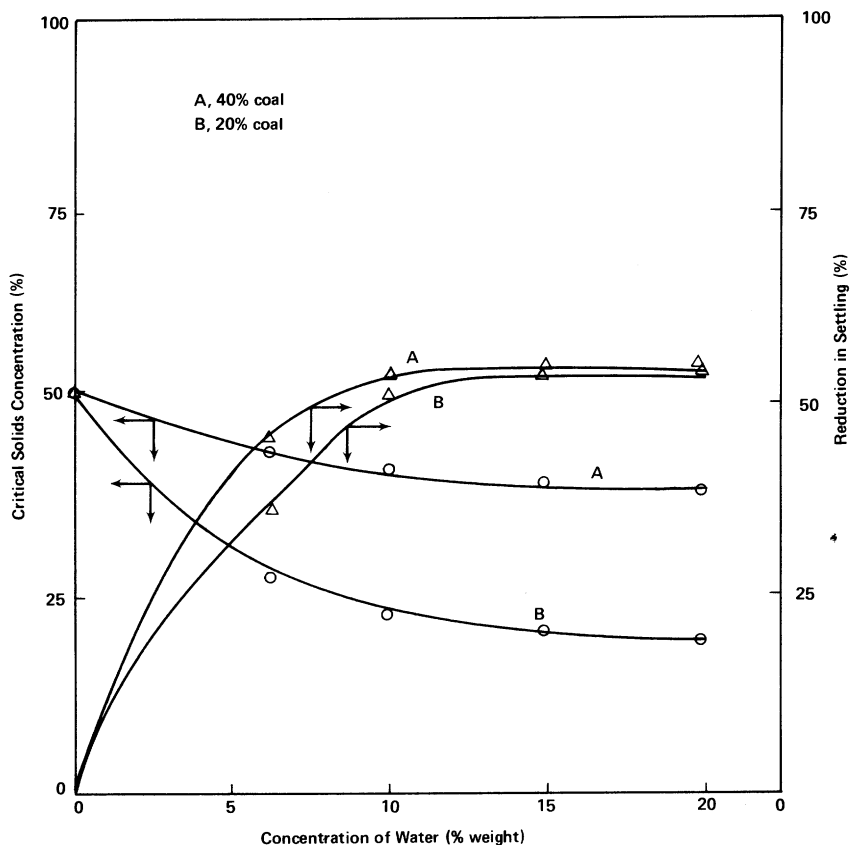


Fig. 9. Effect of water on reduction in settling and critical solids concentration of coal/No. 2 oil slurries

the additional water may go into suspension medium to form emulsion.

(iv). The subsidence volume increases considerably and critical solids concentration decreases with increasing amounts of water (up to 10–15% water) probably indicating a formation of coal particle network.

(v). The observed rheological behavior to a great extent, appears to be influenced by the coal particle agglomeration by water bridging mechanism which is also supported by the measured subsidence volumes and critical solid concentrations.

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