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Coal Slurries in Mixed Liquid Fuels: Rheology and Ignition Characteristics

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ABSTRACT

In the presence of surfactant, coal/No.2 oil + ethanol, slurries containing water exhibited dramatic reduction in Bingham yield stress and plastic viscosity. The observed rheological behavior was explained in terms of coal particle network formation by water bridging mechanism. Lowering of interfacial tension between water and suspension medium in the presence of surfactant was attributed to be responsible for the reduced yield stress and plastic viscosity. In the low heating rate experiments, ignition behavior of slurries containing up to 20 wt.% of water was not appreciably altered. It appears that water vaporizes prior to the ignition/combustion stage, thereby not influencing the overall ignition behavior.

INTRODUCTION

Coal/oil slurries are being rapidly replaced by coal/water slurry technology [1–2]. This is primarily because the coal/water slurries are cost effective and can also completely replace oil burning in the existing liquid fired combustion systems. However, in the intermediate stage, coal slurries in mixed fuels [3–6] (such as oil+alcohol) may play a significant role in composite fuel formulations.

In the mixed fuel slurry technology, stability and rheological properties of the dispersion play an important role in relation to storage, transportation, pumping and atomization. As reported in our previous paper [6], addition of water to slurry formulations containing mixed fuel (diesel+ethanol) resulted in a significant change in the rheological behavior. For example, water was

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observed to increase the subsidence volumes and decrease the critical solids concentration of the slurries. The presence of a critical shear rate region and the viscosity maximum around 10–15% of water in these slurries were suggested to be due to the coal particle network formation (flocculation) by a water bridging mechanism [7]. These observations were similar to the rheological behavior of model systems (glass beads in organic liquids) containing water, as studied by Kao et al. [8], Van den Tempel [9] and Gradishar [10]. The rheological behavior of these slurries in the presence of surfactants has been examined on the basis of water as the bridging medium [11].

The objective of this study was to investigate the rheological properties of mixed fuel systems in the presence of surfactants and analyze the data using an appropriate flow expression. Ignition behavior of the slurry in the presence of added water was also examined. It should be noted that water, being an inert component, can deteriorate ignition properties. On the other hand, it is possible that the added water would accelerate the burning efficiency due to microexplosion of water droplets during atomization [12].

EXPERIMENTAL

The coal powder used in the present study (80%, −200 mesh, density 1280 kg/m^3) was obtained from Florida Power & Light Company, Sanford, Florida. Fuel oil No. 2 was provided by Gainesville Utility Center, Gainesville, Florida. The viscosity of oil was 4 mPa·s and specific gravity 0.876. Ethanol (absolute) was obtained from Fisher Scientific Company. The surfactant TRS 10-80 was a product of WITCO Chemical Co. Distilled water was used in all the experiments. Coal slurries in No. 2 oil, and in No. 2 oil + ethanol blends (4:1 by weight) with varying amounts of water were prepared in sample vials.

Rheological measurements were carried out using a Brookfield cone-and-plate viscometer with a shear rate of 1.15 to 230 s^{-1}.

Ignition temperature of a 25 mg sample was measured by a DuPont thermal analyzer (Model 900) with calorimeter attachment. Identical oxygen flow rates were employed in all experiments.

BACKGROUND

Detailed rheological behavior of coal/No. 2 oil + ethanol slurries containing 1 to 20 wt.% of water at different coal loadings has been discussed elsewhere [6]. It was reported that at higher coal loading (e.g. 40 wt.%) viscosity, and Bingham yield stress were maximum when 10 wt.% water was added to the slurry. Most of the trends in rheological behavior of the mixed fuel slurries containing water were explained on the basis of particle network formation by water bridging mechanism.

Based on the data fitting method, at higher coal loading, a Bingham plastic model represented by the relationship given below was found to adequately describe the rheological behavior of coal mixed fuel slurries [8].

$$\tau_0 = C(W_B^{0.324}/W_S), \tag{1}$$

$$\text{where } C = \left(\frac{2.51\,\sigma\,\phi^2}{\pi\,\gamma^2}\right)\left[\frac{0.86\,\pi\rho_S^3\,(1-\phi^*)^{0.324}}{\rho_B}\right], \tag{2}$$

and where τ_0=Bingham yield stress, γ=radius of the primary particles, ϕ=volume fraction of solid particles in the suspension, ϕ^*=volume fraction of particles in the agglomerates, W_B=weight of the bridging liquid, W_S=weight of solid particles, ρ_B=density of bridging liquid, ρ_S=density of solids, and σ=interfacial tension.

Using the above flow expression, a semiquantitative analysis of the effect of the concentration of water on the observed yield stress in terms of the ratio of W_B and W_S and relevant packing density ϕ^* of the agglomerates may be achieved. Furthermore, the effect of added surfactants on yield stress may be examined in terms of the lowering of interfacial tension, σ, and packing density, ϕ^*.

The following flow models were used to analyze the results:

(a) Bingham plastic model

$$\tau = \tau_0 + \eta_p\gamma \tag{3}$$

(b) Power-law model

$$\tau = k\gamma^n \tag{4}$$

where τ=yield stress, τ_0=Bingham yield stress, η_p=plastic viscosity, γ=shear rate, k=pseudo-viscosity, and n=power-law index.

RESULTS AND DISCUSSION

Rheological behavior

Model calculations (eqns. 1 and 2) of the rheological behavior of coal/mixed liquid fuels containing 0–20 wt.% of water are presented in Fig. 1 along with the experimental results from our previous study. Various input parameters used for computing Bingham yield stress are given in Table 1. It is realized that the physical constants of oil and coal are sufficiently accurate, the value used for interfacial tension σ, and packing density ϕ^*, however, have to be considered as of only relative importance. From the results presented in Fig. 1, similar trends between the rheological behavior predicted by theory and the experimental results are noted. The experimental data indicate a maximum in yield stress around 10 wt.% of water. Moreover, the yield stress maximum predicted by theory is shifted slightly toward higher water content. It appears therefore,

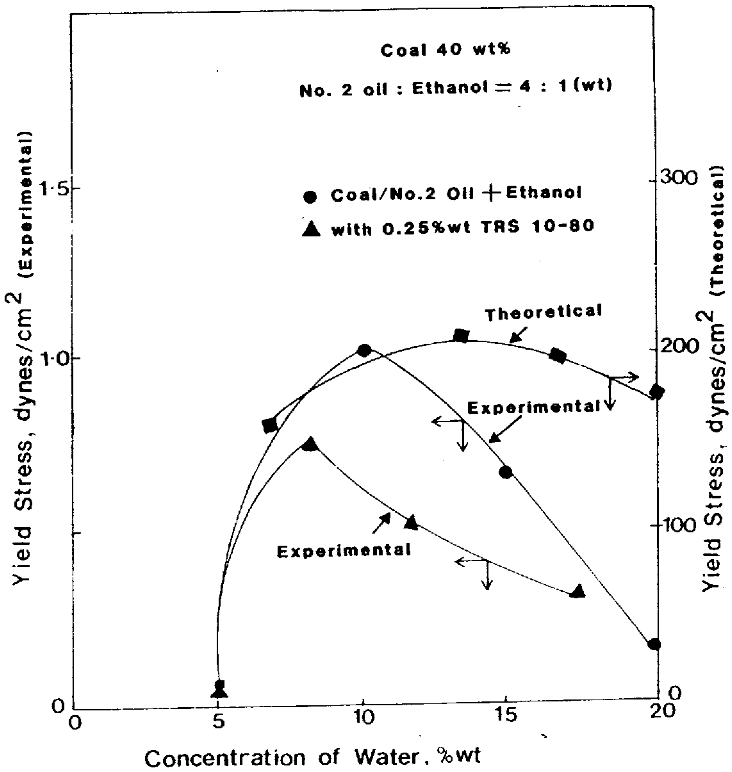

Fig. 1. Effect of water content on the predicted and experimental Bingham yield stress of the coal/mixed fuel slurry.

that the flow behavior of the coal/mixed liquid fuel slurries in the presence of water can be explained semiquantitatively, by the model proposed by Kao et al. [8].

TABLE 1

Input parameters used in the analysis of rheological behavior of slurries[a]

Physical constants	Values of constants
γ, cm	0.0076
ϕ	0.48
W_S, g	40.0
ρ_B, g/cc	1.00
ρ_S, g/cc	1.28
σ, dynes/cm^2	10.00

[a] ϕ^* was varied from 0.36 to 0.71 in the range of W_B from 5 to 20 wt.%.

Based on the liquid bridging mechanism proposed by Kao and coworkers, the attractive force caused by liquid bridges is a function of interfacial tension between oil and water. Since interfacial tension can be varied by adding a surfactant, it is expected that the flow behavior of these suspensions could be modified using a suitable surfactant such as TRS 10-80 (petroleum sulfonate).

Effect of TRS 10-80 on coal/mixed fuel slurry rheology

The Bingham yield stress of a slurry containing 0.25% of TRS 10-80, as a function of concentration of water, is plotted in Fig. 1. It is observed that in the presence of surfactant, yield stress is lower, particularly above 10 to 15 wt.% of water. However, similar trends in rheological behavior with and without the surfactant are observed.

The effect of concentration of surfactant on rheological behavior of a given slurry is illustrated in Fig. 2. It can be seen that flow curves of slurries containing surfactant are dramatically different from the original slurry (without surfactant). For example, the shear stress in the low shear rate region clearly indicates an order of magnitude reduction (qualitatively) in extrapolated yield stress values. Furthermore, it appears that in the very low shear rate region, similar reduction in yield stress occurs at 0.25 and 0.50 wt.% surfactant addition. In other words, changes in yield stress beyond 0.25 wt.% surfactant are not significant.

Detailed analysis of rheological parameters using the Bingham plastic model was carried out for coal/mixed fuel slurries containing increasing concentrations of TRS 10-80 (0.1 to 1 wt.%). The yield stress as well as plastic viscosity as a function of the concentration of the surfactant are plotted in Fig. 3. It is observed that the yield stress is reduced from 1 dyne/cm^2 (0.1 Pa) to as low as 0.34 dynes/cm^2 around 0.25% of surfactant. This is followed by a reduction in plastic viscosity of the slurries. Based on the flow equation proposed in the previous section (eqns. 1 and 2), changes in the yield stress as a function of added surfactant can be explained on the basis of a lowering of interfacial tension (σ) of the oil/water system.

Further analysis of rheological data was carried out by the Power-law model. Power-law index, n, and pseudo-viscosity k of slurries are plotted in Fig. 4 as a function of the concentration of surfactant. It is to be noted that the power-law index reaches a maximum value at 0.25% of surfactant indicating that, upon increasing the concentration of surfactant, slurries become less shear thinning and finally approach Newtonian behavior (constant viscosity). In other words, the flow units appear to undergo dramatic change with respect to their shape and size in the presence of added surfactant.

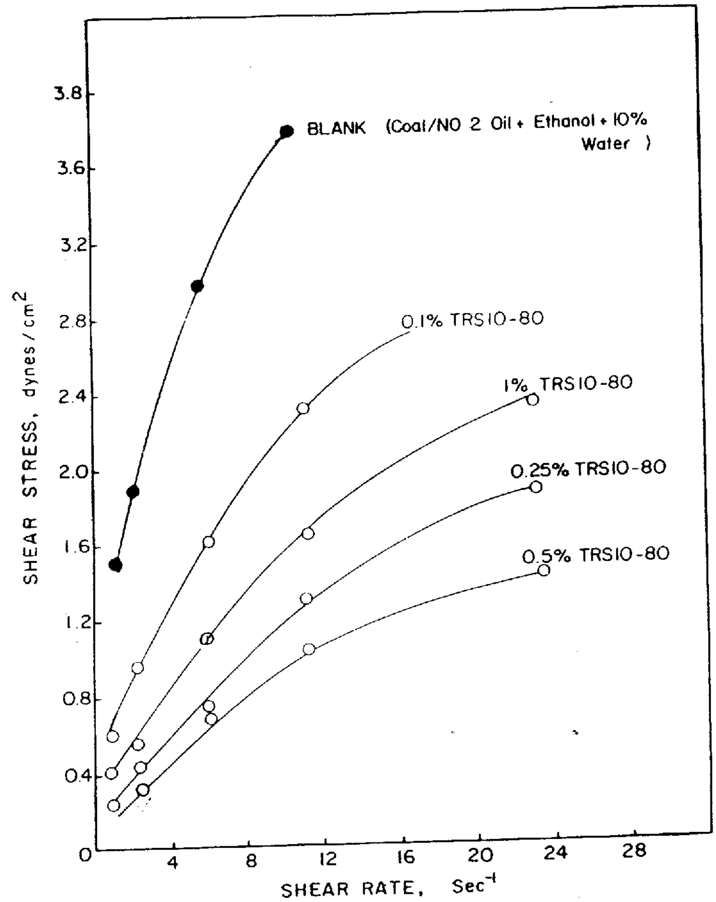

Fig. 2. Effect of surfactant concentration on rheological behavior of coal/mixed fuel slurry containing 10% water.

Ignition behavior

Coal slurries in No. 2 oil and ethanol blends containing various amounts of water were characterized for their ignition behavior using differential thermal analysis (DTA) technique. The DTA traces (or burning profiles) of mixtures of coal (40%) and 4:1 by weight of oil and ethanol (COEM) containing increasing amounts of water are shown in Fig. 5. An analysis of various peak temperatures indicates that No. 2 oil ignites around 250°C. The coal slurries also ignited around the same temperature. It is seen that upon increasing the amount of water in the slurry the ignition temperature was not appreciably altered. It should also be noted that proceeding the initial ignition peak, the entire burning profile exhibits a number of exothermic peaks. It is possible that the most reactive components of the slurry being No. 2 oil and ethanol

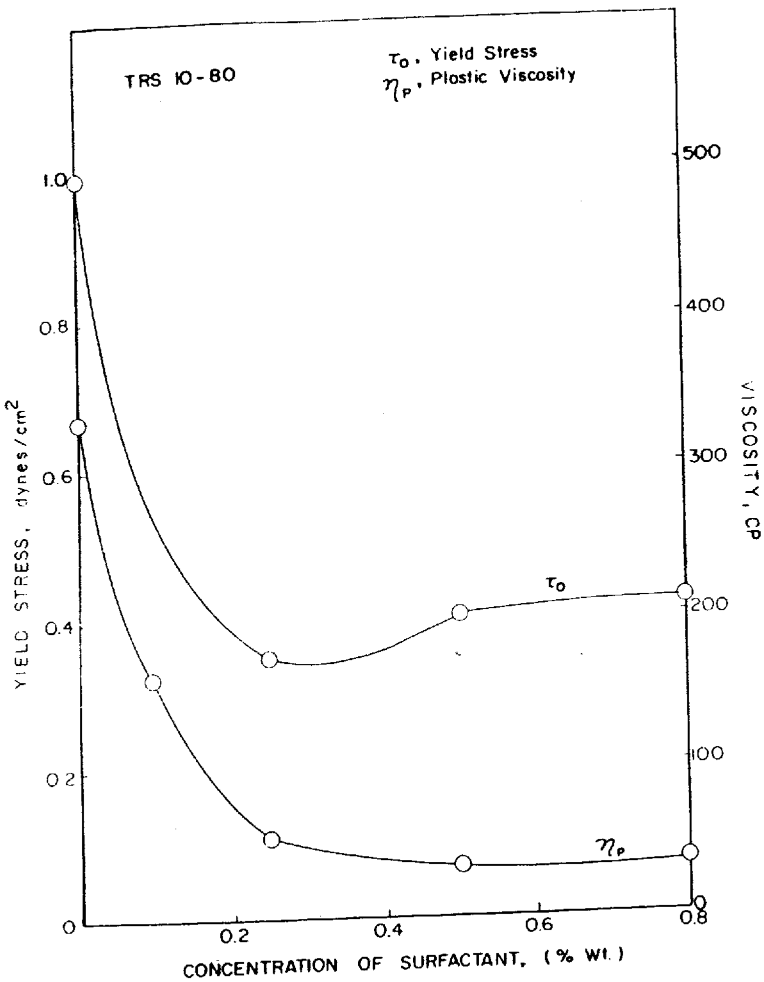

Fig. 3. Effect of surfactant concentration (TRS 10-80) on rheological behavior of coal/mixed fuel slurry (Bingham plastic model)

blends, the overall ignition is controlled by the ignition of oil itself. The heat generated during this step appears to accelerate subsequent ignition/combustion of coal particles.

The fact that water did not increase the ignition temperature (lower the reactivity) may imply that addition of water does not result in the deterioration of ignition reactivity. On the other hand, it is possible that, in the slow heating rate experiments water may evaporate completely prior to the ignition stage without affecting the ignition process. Under high heating rate conditions, overlapping (simultaneous) evaporation, and oxygen diffusion can result in lowering of ignition reactivity.

In order to investigate this effect, the ignition temperature of slurries have

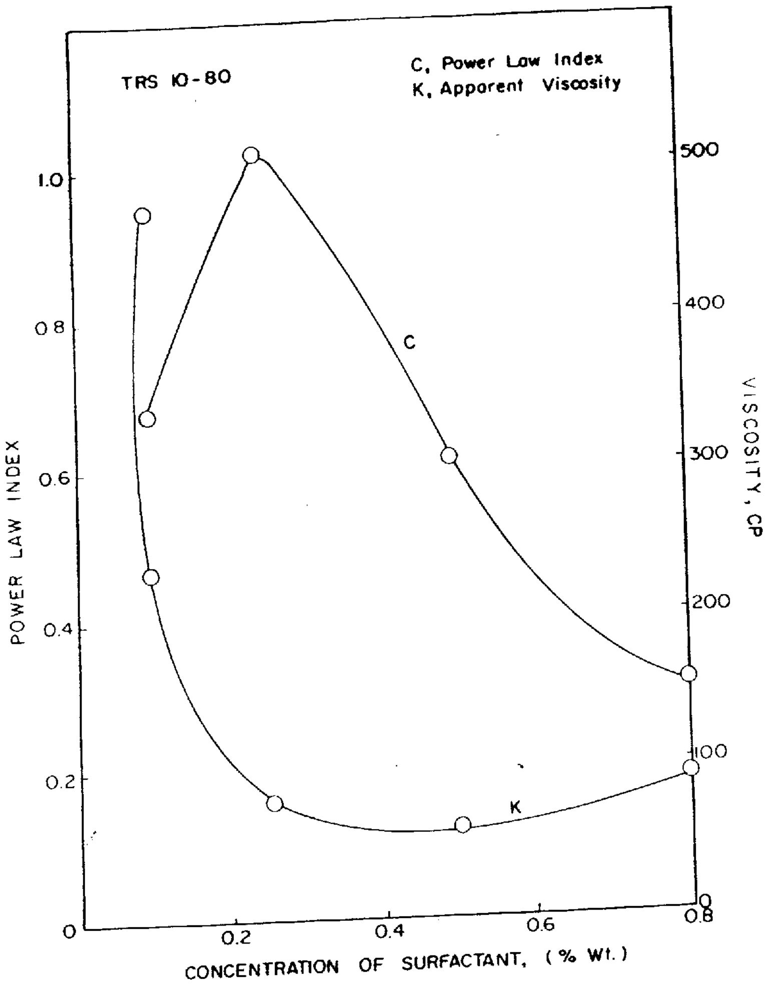

Fig. 4. Effect of surfactant concentration (TRS 10-80) on rheological behavior of coal/mixed fuel slurry (Power-law model).

been determined as a function of heating rate. Heating rate was varied from 10 °C/min to 60 °C/min. The DTA data is plotted in Fig. 6 for coal/No. 2 oil and ethanol slurries. At 10 °C/min heating rate, it can be seen that the slurry shows a predominant exothermic peak only around 390 °C, indicating slow oxidation rather than ignition. Upon increasing the heating rate to 25 °C/min, initial peaks appear around 255 °C, and at 60 °C/min these peaks are observed at 210 °C. This implies that the ignition behavior is dramatically affected by the rate of heating. It is, therefore, possible that at sufficiently high heating rate the ignition and vaporization of water may occur simultaneously. Under these conditions there may be an appreciable influence of added water on ignition behavior.

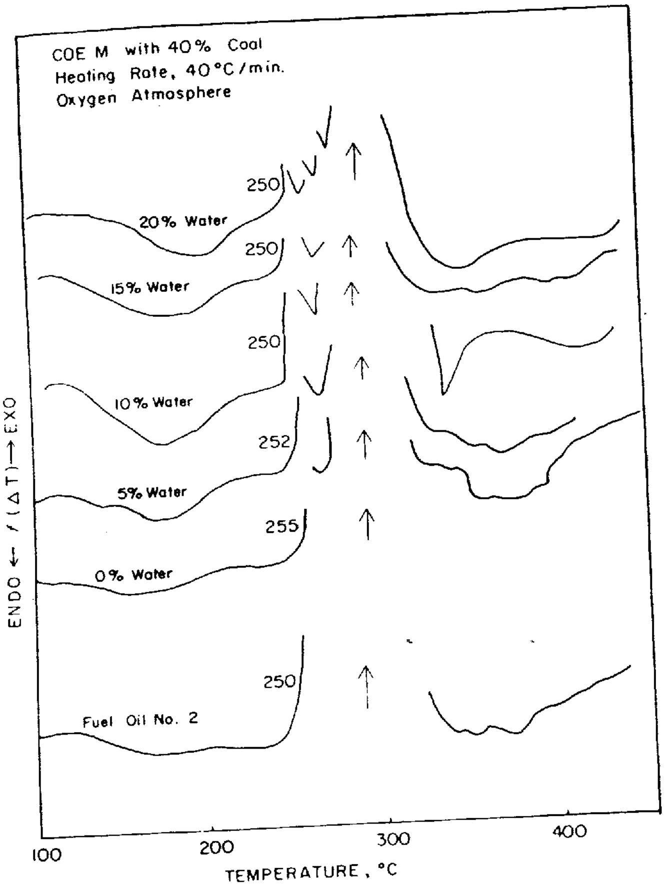

Fig. 5. DTA traces showing the ignition behavior of coal/mixed fuel slurry containing 0–20% water.

The kinetic analysis of different fuels was carried out using dynamic heating DTA curves at different heating rates. The Kissinger [13] method of fitting data in to kinetic equation (irrespective of the order of reacton) was employed. Kissinger showed that the activation energy E, of the reaction obeying the Arrhenius equation could be determined by DTA peak temperatures obtained at different heating rates,

$$\frac{dx}{dt}=A(1-x)\exp(-E/RT) \quad (1)$$

where x is the fraction reacted; A, pre-exponential factor; T, the temperature; and R, universal gas constant. It was shown that a plot of $\ln(h/T_C^2)$ versus $1/T_C$ yields a slope of $-E/R$, where h is the heating rate and T_C is the peak temperature. The activation energy calculated by this method corresponded to 8.5 kcal/mol for coal slurry in mixed fuel and 18 kcal/mol for slurry containing

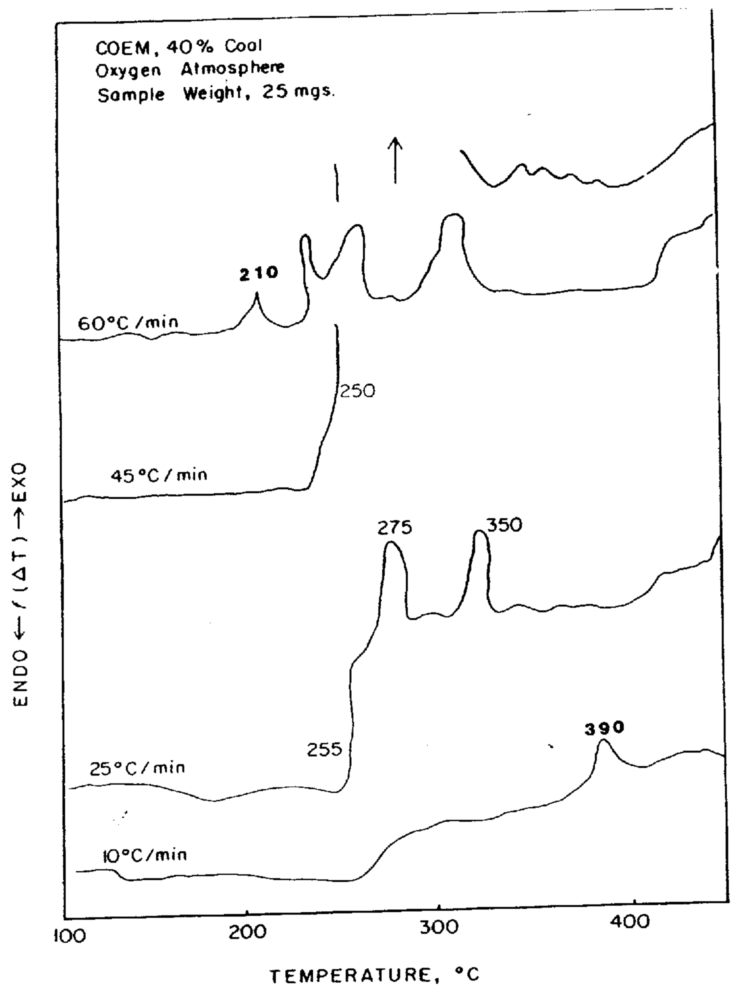

Fig. 6. Effect of heating rate on ignition behavior of coal/mixed fuel slurries.

water. An increase in the activation energy upon addition of water is expected on the basis of opposing transport processes of vaporization and diffusion of oxygen on to the coal surface.

CONCLUSIONS

A maximum in Bingham yield stress is exhibited by coal/No.2 oil and ethanol slurry when 10% water is added to it. A significant decrease in the yield stress is observed upon addition of a surfactant which possibly reduces the oil/water interfacial tension, thereby reducing the attractive force caused by the bridging liquid. Analysis of the rheological model by applying the Power-law model indicated that at 0.25% surfactant concentration, slurries become less shear thinning and approach Newtonian behavior. This can probably be attributed to changes in the size and shape of the flow units upon surfactant addition.

Ignition behavior of slurries containing up to 20 wt.% of water was found to be similar to those without added water. It is suggested that in the low heating rate experiments, water evaporates prior to the ignition process thereby leaving the overall ignition process unchanged.

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