Blending of Residual Oil with Fuel Grade Ethanol: Compatibility, Rheology, and Ignition Characteristics

Kayyani C. Adiga, Arambally N. Sunder Ram,[†] and Dinesh O. Shah*

Departments of Chemical Engineering and Anesthesiology, University of Florida, Gainesville, Florida 32611

Brij M. Moudgil

Department of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611

High viscosity fuel oil no. 6 (petroleum residual) and ethanol are found to be not compatible and they separate out upon blending and storing. A method has been developed to prepare homogeneous and stable blends of no. 6 oil and ethanol in the presence of coupling agents, such as kerosene or *n*-alkanes. A systematic study of compatibility of residual oil and ethanol in the presence of kerosene or *n*-alkanes showed a narrow range of compatible compositions in the ternary diagram. Such compatible blends may be referred to as alcofuels. Rheological properties, stability, and ignition characteristics of alcofuels and coal slurries in these blends have been evaluated and are compared with no. 6 oil slurries. Alcofuels and coal/alcofuel slurries exhibited much lower viscosity and better ignition/combustion characteristics as compared to residual oil. Based upon these results, potential applications of alcofuels as fuel oil extenders and their use in coal slurry fuel technology are discussed.

Introduction

It is well-known that petroleum liquid fuel is depleting rapidly and that coal liquids are not available in large quantities. In addition, fuel grade alcohols are not yet produced in commercial scale to burn alone. Therefore, it is expected that intermediate applications may involve mixing and blending of various fuel components (Adiga et al., 1982a; 1983). However, unfortunately, severe incompatibility problems are anticipated while blending the fuels of various origins because of the dissimilarities in chemical structure and elemental contents of the components. For example, Cabal et al. (1977) describe the compatibility of coal liquids with petroleum liquid and add that various incompatibilities may be encountered in the blending of a full range of coal liquids with petroleum liquids. Furthermore, recent studies indicated severe incompatibility problems while blending petroleum residual (fuel oil no. 6) with fuel grade ethanol (Adiga and Shah, 1982; Shah et al., 1984a). Typical incompatibility problems usually lead to phase separation and formation of sludge at the bottom of the fuel storage tank.

Blending of fuel oils with fuel grade ethanol may be immensely helpful for stretching petroleum liquid fuel stock (Shah et al., 1984b). The well-known blends of gasoline with ethanol (referred to as gasohol) and diesel with ethanol have been reported to exhibit incompatibility problems above a certain maximum concentration of water in ethanol. However, the problem has been overcome by adding additives and surfactants. The incompatibility problem appears to be serious upon blending the residual oils, namely no. 5 and no. 6 fuel oils, with ethanol. Nevertheless, the blends of petroleum residuals with ethanol may have several advantages such as lower viscosity and greater fuel saving capacity. In this report, we present the results of incompatibility problems, the method of blending the residual oil with fuel grade ethanol, the compatibility ranges, and rheological properties of the blends.

†Xidex Magnetics, 305 Soquel Way, Sunnyvale, CA 94086.

Residual oils are highly viscous. Hence, the coal/oil mixture technology based on residual oil often employs elevated temperature during mixing, storing, and pumping (Bienstock and Jamgochian, 1981). As a result it is important to note that these alcofuel blends may find potential applications in coal slurry technology mainly because of the low viscosity of the blends and its oil saving capacity. A few of the coal/residual oil slurry fuels reported earlier are known to contain ethanol as additives (Keller, 1978). For example, Keller (1979) proposed a coal slurry referred to as CFOS (Carbonaceous Fuel-in-Oil Suspensoid) fuel in which coal powder is prior-coated with ethanol vapor. Sakuma et al. (1979) invented coal–oil slurries containing ethanol as additive in primarily distillate + coal slurries. However, there is hardly any approach based on obtaining homogeneous blends of residual oil and ethanol (in the presence of a coupling agent) which can either be burnt directly in oil-fired burners or used in coal–oil slurry technology. Hence, as an another objective of the study, the rheology, stability, and ignition characteristics of the coal slurries in these blends have been investigated and are reported.

Experimental Section

A. Materials. Fuel oil no. 6 employed for blending studies was from Florida Power & Light Co., having a viscisoty of 2 P and a density of 0.98 g/cm³. Denatured ethanol from Fisher Scientific was used in all experiments. Kerosene of commercial grade was employed without further purification. Normal hexane, the coupling agent was Analar grade from Fisher Scientific.

Coal powder of a bimodel mixture of 80% by weight −200 mesh and 20% −325 mesh was used for all slurry preparations (Adiga et al., 1983). The coal sample was from Florida Power & Light Co. The commercial surfactants were used for screening studies of coal slurry rheology and stability.

B. Blending of Fuel Oil No. 6 and Ethanol. Fuel oil no. 6 and ethanol were weighed into sample vials and kerosene was added. The samples were vigorously shaken
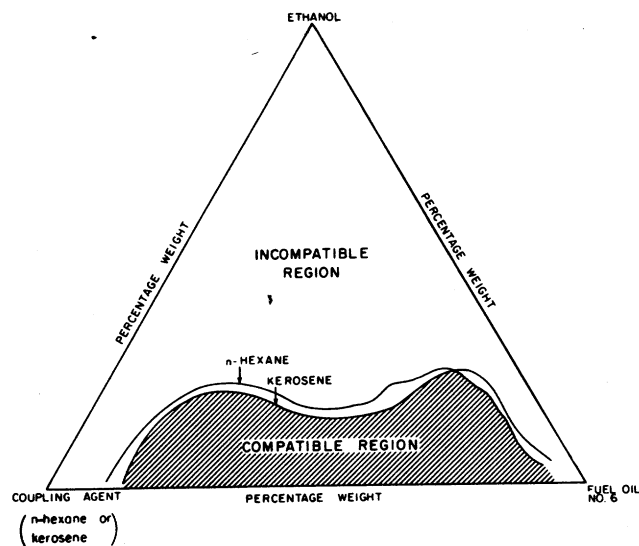
Figure 1. Compatibility of fuel oil no. 6 and ethanol in the presence of kerosene; ternary diagram.

Figure 2. Viscosity as a function of shear rate for fuel oil no. 6 and various alcofuel blends.

Table I. Compatible Blends of Fuel Oil No. 6 and Ethanol Containing Kerosene–Alcofuels

sample blend	compn, % wt		
	fuel oil no. 6	ethanol	kerosene
alcofuel A	65	25	10
alcofuel B	65	20	15
alcofuel C	65	10	25

to obtain homogeneous blends. The compatibility of the blends was tested by centrifuging the samples for 20–30 min and measuring the volume of the incompatible liquid separated at the top of the column. The most compatible blend did not show any supernatant liquid layer at the top. The percentage incompatibility of blends for various ratios of fuel oil and ethanol in the presence of kerosene was carried out and percentage incompatible ($V_{\%incomp.}$) was calculated by

$$V_{\%incomp.} = \frac{V_l}{V_t} \times 100 \qquad (1)$$

where V_l is the volume of supernatant incompatible liquid and V_t is the total volume of the blend. The incompatibility/compatibility regions of ethanol and fuel oil no. 6 in the presence of kerosene was represented in the form of a ternary diagram.

C. Rheology. The viscosity of the blends and slurry made out of coal/alcofuel was measured with a Brookfield cone and plate viscometer (Adiga et al., 1983). The viscometer has a shear rate range from 1.15 to 213 s^{-1}. The viscosity dependence on temperature was determined by passing water at different temperatures through the viscometer jacket.

The alcofuel blends were prepared in larger quantities (1 to 2 kg), sonicated, and tested for compatibility by aging for months. Such blends were used to prepare coal/oil slurries. All coal slurries with alcofuels were prepared at ambient temperature, unlike the ones with fuel oil no. 6 which require elevated temperatures. Mixing and transferring of alcofuel coal slurry were easy even at ambient temperature due to its low viscosity.

D. Settling Tests. All the settling tests were carried out in 150-mL graduated cylinders at ambient temperature over a time interval of 150 h. The samples were drawn from the top of the column at regular intervals and analyzed for coal content by the gravimetric method, i.e., by extracting the weighed amount of sample using n-hexane and weighing the dried coal. Typical commercial surfactants such as Triton X-15, Span 20, Tergetol (nonionic), and TRS 10-80 have been screened for the effectiveness in reducing the settling of coal in the slurry.

E. Ignition Studies. Ignition temperature measurement was carried out by a differential thermal analysis (DTA) technique (DuPont Model 900) using a calorimetric cell attachment. A small amount (20–30 mg) of the slurry
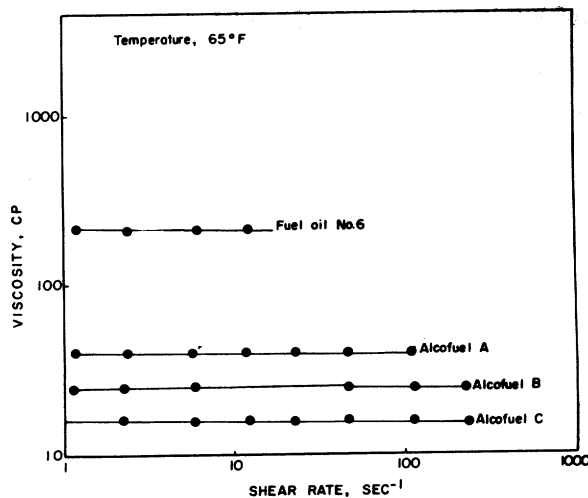
was taken in the sample cup made of aluminum and oxygen was flushed at a constant rate during the linear heating. In the present study, the DTA experiments were carried out only up to 500 °C. DTA curves with sharp ignition peaks were obtained for alcofuel/coal slurries and fuel oil no. 6/coal slurries at different heating rates such as 15, 25, 45, 90 °C/min. The sample weight and oxygen flow rates were kept constant in all the experiments.

Results and Discussion

Compatibility of No. 6 Oil + Ethanol Blends. A ternary diagram illustrating the compatible/incompatible regions for the fuel oil no. 6, ethanol, and kerosene/n-hexane system is shown in Figure 1. The blends are seen to be compatible over a very narrow range of compositions. It is seen from the ternary diagram that a maximum of 25% by weight of ethanol could be incorporated into fuel oil no. 6 in the presence of 10 to 15% by weight of kerosene to obtain a compatible (homogeneous) blend. The other interesting observations are that (1) the blends are not compatible below 65% of fuel oil no. 6 even at higher concentration of coupling agent (kerosene); (2) the concentration of coupling agent is usually low, 5 to 10% wt of the blend; (3) kerosene or n-hexane were found to have similar effects on blend compatibility; and (4) the range of compositions such as 65 to 90% of fuel oil no. 6, 25 to 5% of ethanol, and 10 to 5% wt of kerosene appear to be practically important.

The origin of incompatibility and particle or molecular nature of the blend is not clear so far. The miscibility of kerosene with ethanol as well as fuel oil no. 6 suggests that kerosene may function as a coupling agent between the two major components, oil and alcohol. Further, at reasonably higher concentrations (above 25% by weight) of ethanol, the molecular/particle interaction may result in phase separation caused by the presence of relatively polar alcohol molecules. This is further supported by the increase in the viscosity of the blends upon increasing ethanol concentration as shown later in this paper. On a similar basis, the decrease in compatible liquid volume separated when the kerosene proportion is increased also emphasizes
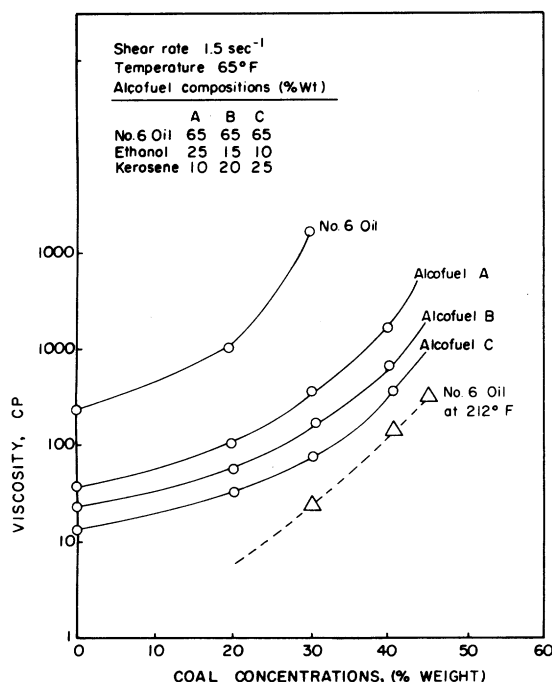
Figure 3. Viscosity as a function of coal concentration for fuel oil no. 6 and various alcofuels.

the role of a coupling agent in imparting compatibility.

Rheology of Blends. Figure 2 shows viscosity vs. shear rate curves for no. 6 oil and various alcofuels (Table I) with decreasing ethanol concentration from alcofuel A to C. The flow curves indicate that similar to no. 6 oil, various alcofuel blends exhibit shear independent viscosity (Newtonian behavior). The alcofuel containing 65% no. 6 oil and varying proportions of ethanol and kerosene shows increasing viscosities with increased alcohol concentration. The rheological behavior is quantitatively summarized by fitting the shear stress (τ) vs. shear rate ($\dot{\gamma}$) data into power law model.

$$\tau = k_p \dot{\gamma}^c \tag{2}$$

The flow curves for various alcofuels and fuel oil no. 6 are as follows

$$\tau = 0.0155 \dot{\gamma}^1 \text{ (alcofuel C)} \tag{3}$$

$$\tau = 0.033 \dot{\gamma}^{0.99} \text{ (alcofuel B)} \tag{4}$$

$$\tau = 0.053 \dot{\gamma}^{1.01} \text{ (alcofuel A)} \tag{5}$$

$$\tau = 0.201 \dot{\gamma}^1 \text{ (fuel oil no. 6)} \tag{6}$$

It is seen that power law index (c) is nearly unity and pseudo-viscosity k_p is the highest for no. 6 oil. Within the alcofuels, as seen from flow curves (3) through (5), pseudo-viscosity increased with increasing proportions of ethanol (or decreasing kerosene concentration). This effect can be attributed to the presence of ethanol as polar molecules in the hydrocarbon component mixtures. Further, it is interesting to note that such interactions did not appreciably alter the Newtonian behavior of no. 6 oil.

Fuel Blend Application in Coal Slurry Technology

Coal/Alcofuel Slurries vs. Coal/No. 6 Slurries. Viscosities of coal slurries in alcofuel and no. 6 oil, as a function of coal concentration, are shown in Figure 3. It is seen that alcofuel slurries exhibit far lower viscosities (at all coal loadings) as compared to no. 6 oil slurries. However, at appreciably higher temperature, namely at
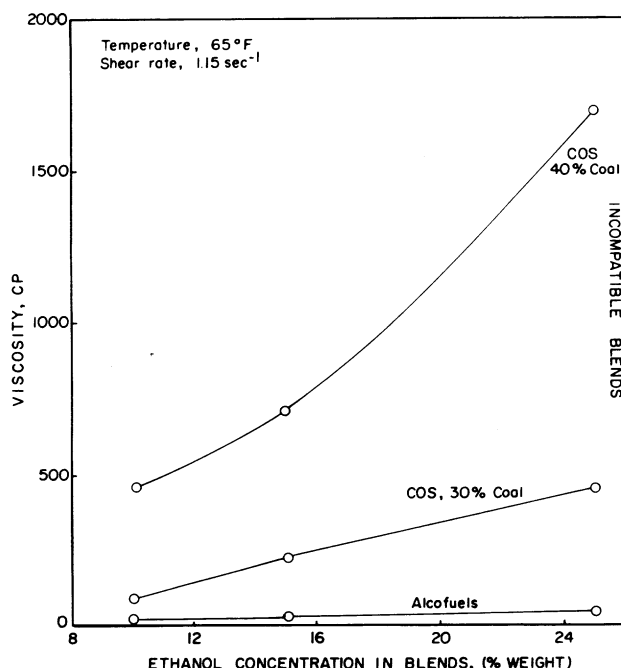

Figure 4. Effect of ethanol concentration in the blend on viscosity of alcofuels and coal oil slurries (COS) containing alcofuel.
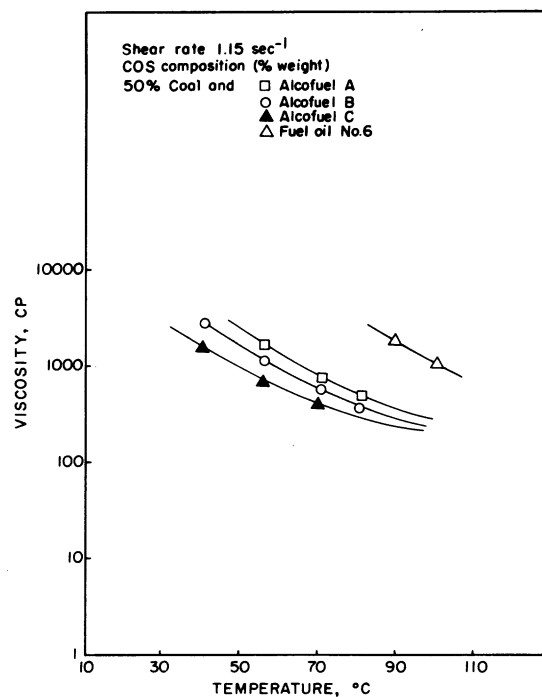

Figure 5. Effect of temperature on viscosity of fuel oil no. 6 and alcofuel slurries containing 50% wt of coal.

212 °F, viscosities of no. 6 oil slurries are comparable (or lower) to alcofuel slurries at ambient temperature. The curves also indicate that within the series of alcofuels, the viscosity of the slurry increased with increasing proportions of ethanol. Further, results on the effect of ethanol on viscosity of pure blends and coal + blends slurries are shown in Figure 4 for typical coal loadings such as 30 and 40% by weight. While the increase in viscosity is marginal (but definite) in the case of pure blends, increasing the coal loading appears to magnify the effect. This probably suggests that an additional factor, namely coal–alcohol interaction, seems to contribute to the observed increase in the viscosity of slurries. Similar mechanisms have been proposed earlier in coal–methanol (methacoal) and coal–

Table II. Activation Energy of Viscosity of Various Slurry Fuels

COS containing 50% coal and 50% wt of	act. energy, E, kcal/g-mol
alcofuel A	10.5
alcofuel B	7.5
alcofuel C	8.8
fuel oil no. 6	7.2

ethanol systems (Keller, 1978).

Effect of Temperature on Viscosity of Slurries.
Figure 5 shows the viscosity vs. temperature relation for no. 6 oil and alcofuels containing 50% by wt of coal. An analysis for temperature dependence of viscosity can be carried out by Arrhenius plots, namely

$$\eta = A \exp(-E/RT) \tag{7}$$

Activation energies calculated with the above expression are shown in Table II. Though marginal, an increase in activation energy of alcofuel slurries may be attributed to the presence of coal–alcohol interaction.

Residual oil slurry technology often employs elevated temperatures for mixing, storing, and pumping of slurry. Hence, a limited number of measurements have been carried out for evaluating the high-temperature rheology of conventional coal/no. 6 oil slurries. Figure 6 shows viscosity vs. shear rate curves for coal/no. 6 oil slurries containing various concentrations of coal at 212 °F. It is seen that the slurries are of the shear-thinning type. Such non-Newtonian behavior of coal/oil slurries at ambient temperature have been reported by various other authors, for example, Benstock and Jamgochian (1981).

Effect of Surfactants on Rheology of Slurries

A selected number of surfactants have been screened for further reducing the viscosity of alcofuel–coal slurries. Typical coal loading in the slurry was 30% by wt. The surfactants which are employed in the present study are: TRS 10-80, Span 20, Tergetol (nonionic) and Triton X-15. The flow curves of alcofuel COS (30% wt coal) containing various surfactants, based on power law model, are as follows

$$\tau = 0.226\dot\gamma^{0.98} \text{ (no surfactant)} \tag{8}$$

$$\tau = 0.213\dot\gamma^{0.99} \text{ (0.25\% Triton X-15)} \tag{9}$$

$$\tau = 0.186\dot\gamma^{0.99} \text{ (0.25\% Tergetol)} \tag{10}$$

$$\tau = 0.160\dot\gamma^{0.99} \text{ (0.25\% Span 20)} \tag{11}$$

$$\tau = 0.146\dot\gamma^{0.99} \text{ (0.25\% TRS 10-80)} \tag{12}$$

Among these surfactants, TRS 10-80 is found to be very effective in reducing the viscosity; namely, pseudo-viscosity decreased from 226 cP to 146 cP upon the addition of 0.25% of TRS 10-80. The flow curves indicate that though surfactants, in general, decreased viscosity of slurries, there is marginal effect on the power law index. Hence, it appears that rheological behavior is not appreciably altered in the presence of surfactants in the case of low coal concentration slurries.

Stability of Slurries. Since the viscosities and densities of alcofuels are lower as compared to fuel oil no. 6, we may anticipate that the stability of coal slurries in alcofuels will be appreciably lower than that of no. 6 oil slurries. On the other hand, the presence of coal–alcohol interaction may impart considerable stability as well. Hence, studies have been carried out on the stability of slurries in the presence of a selected number of commercial
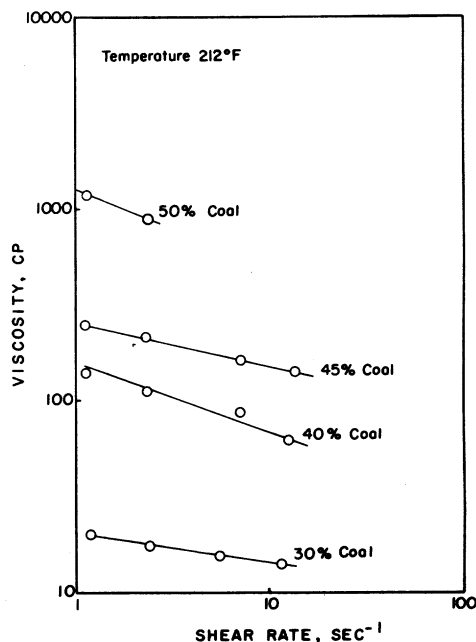

Figure 6. Viscosity as a function of shear rate for coal/fuel oil no. 6 slurries, with different coal loadings at 212 °F.
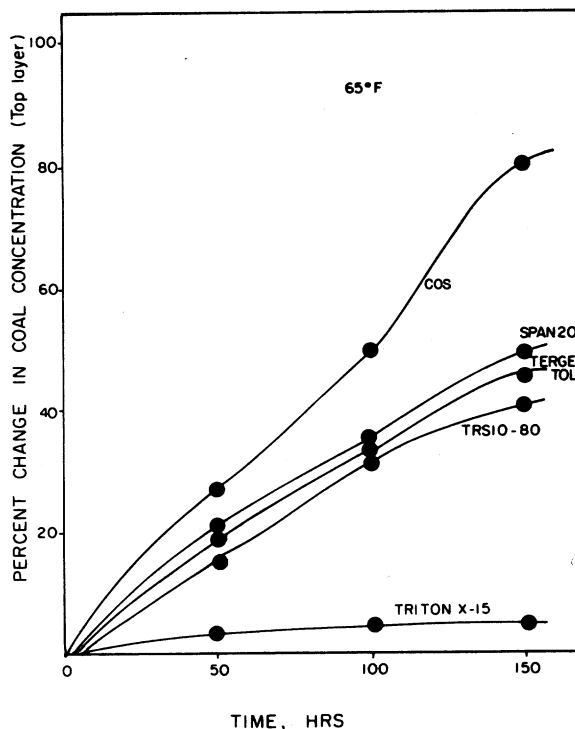

Figure 7. Effect of surfactants on stability of coal/alcofuel A slurries containing 30% wt of coal and 0.25% wt of surfactant at ambient temperature.

surfactants. Figure 7 shows the stability of coal/alcofuel slurries expressed in terms of percentage change in coal concentration of the top layer vs. time at 65 °F. It is seen that of all the surfactants, Triton X-15 is the most effective in stabilizing the slurry. However, the other surfactants which also impart stability (in the decreasing order) are TRS 10-80, Tergetol (non-ionic), and Sapn-20. While TRS 10-80 was the most effective in reducing the viscosity of the slurries, Triton X-15 appears to be the best stabilizing agent for these slurries. As a result, it appears that a judicious choice of suitable surfactants for stability as well as for modification of rheological behavior may require screening of several other surfactants.
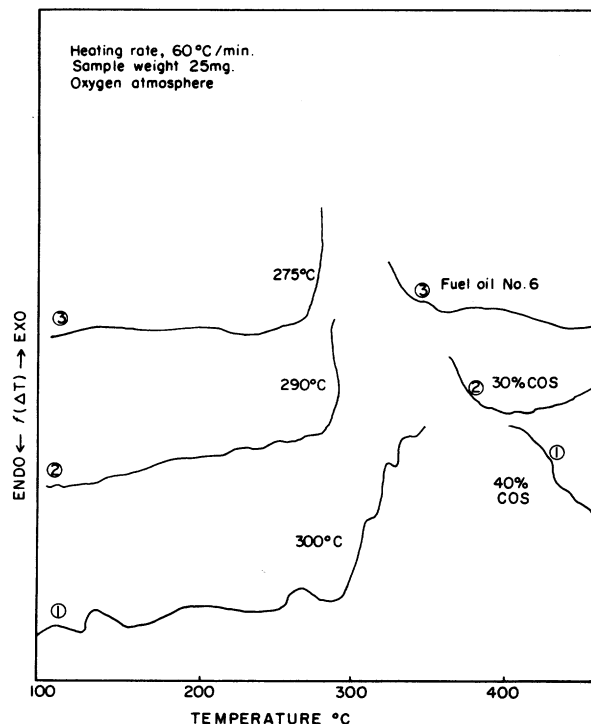
Figure 8. DTA traces of fuel oil no. 6 and coal slurries, in oxygen atmosphere-burning profiles.
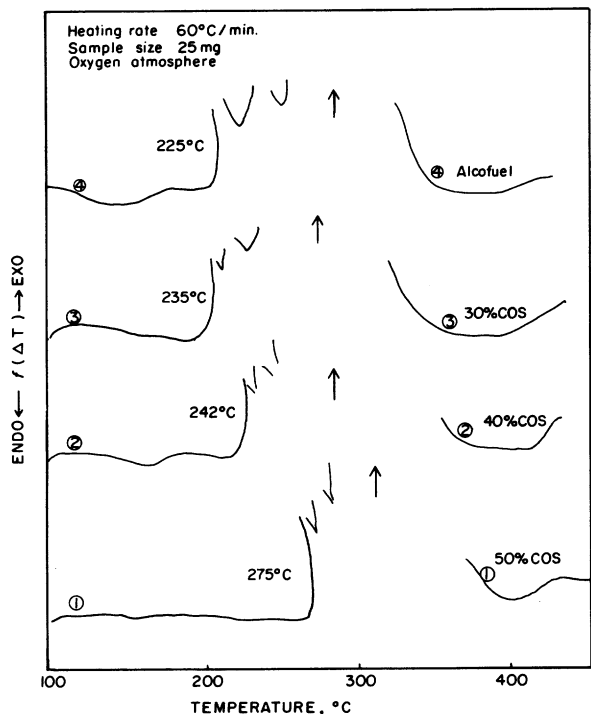

Figure 9. DTA traces of alcofuel A and coal slurries, in oxygen atmosphere-burning profiles.

Ignition and Combustion Characteristics

Figures 8 and 9 show DTA traces of fuel coal/oil no. 6 slurries and coal/alcofuel slurries, respectively. It is seen that the curves essentially represent an initial exothermic peak which may be attributed to the onset of ignition. The multiple peaks proceeding the ignition may represent the entire burning profiles of the slurry fuel. These multiple exothermic peaks may arise due to the complicated reactions of oxygen with fuel oil and fuel oil + coal and various other fuel fragments of residual oil. A detailed analysis has not been carried out for individual peaks. However,
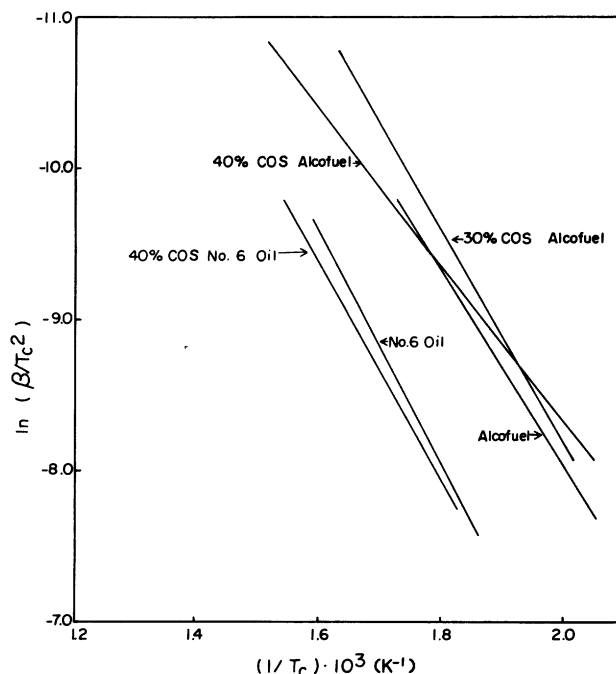

Figure 10. Arrhenius plot for ignition of fuel oil no. 6 alcofuel A and various coal slurries.

Table III. Activation Energy of Ignition of Various Slurry Fuels

fuels	act. energy, E, kcal/g-mol
alcofuel	17.60
fuel oil no. 6	16.63
30% alcofuel COS	16.41
40% alcofuel COS	16.43
40% fuel oil no. 6 COS	15.00

assuming that the initial sharp exothermic peak is due to the onset of ignition (and subsequent peaks can overlap with it at sufficiently high heating rate), ignition peak temperatures for fuel oil and alcofuels can be summarized as follows: fuel oil no. 6 ignites at $\simeq 275$ °C and subsequent slurries at 290–400 °C, depending on the concentration of coal in the slurry. Ignition temperatures increased with coal concentration (Figure 8, 30% and 40% slurry). In the case of alcofuel, ignition occurred at a much lower temperature, namely 225 °C, and ignition peak temperatures increased with increasing coal concentration. It is worth noting that the ignition temperatures of alcofuel slurries are far lower than the corresponding no. 6 oil slurries.

Kinetic parameters of ignition of different fuels have been carried out using dynamic DTA curves obtained at different heating rates under similar experimental conditions such as sample weight and oxygen flow rate. We employed the Kissinger method (1957) of fitting the data into a kinetic equation irrespective of the order of reaction. Kissinger showed that the activation energy, E, and the "order of reaction", n, obeying the Arrhenius equation, irrespective of the order of reaction, can be expressed as

$$\frac{dx}{dt} = A(1 - X)^n \exp(-E/RT_s) \tag{13}$$

A plot of $\ln (\beta/T_c^2)$ vs $1/T_c$ for various fuels is shown in Figure 10. Activation energies calculated using the least square fitting technique are shown in Table III. It is seen that alcofuel and coal/alcofuel slurries up to 40% coal loading have similar activation energies, assuming the difference of 1–5 kcal as error involved in the method of analysis. The alcofuels being more reactive as compared to coal, the rate-determining steps may be the ignition of

alcofuel itself (as seen from similar activation energies). However, at very high coal loadings, the activation energy may involve the breaking of coal structure as well; probably the values may be higher. Similar explanation appears to be true for fuel oil no. 6 and coal/fuel oil no. 6 slurries. The comparison of ignition behavior of fuel oil, alcofuels, and coal slurries in these fuels suggests that ignition of the liquid fuel appears to control the overall ignition process and the mechanism of ignition of alcofuel and no. 6 oil slurries appears to be similar (as shown by similar activation energy values).

Based upon the much lower viscosity of alcofuel blends at ambient temperature (30–40 cP) as compared to residual oil (200 cP), the coal slurry technology may be proposed which does not involve elevated temperature mixing, storing, or pumping. It can be further emphasized that, in addition to the elimination of preheating steps, the proposed alcofuel technology provides a potential method for residual oil saving by making use of commercial ethanol.

Conclusions

It was shown that alcofuels are homogeneous (compatible) blends of fuel oil no. 6 and ethanol in the presence of coupling agent, kerosene. The typical alcofuel may contain fuel oil no. 6, 65%, ethanol 25%, and kerosene 10% by weight.

Alcofuels exhibit far lower viscosities (40 cP) as compared to no. 6 oil (200 cP). The viscosity of alcofuel increased upon increasing ethanol concentration. These blends are Newtonian fluids.

The viscosities of coal–alcofuel slurries are considerably lower than coal/no. 6 oil slurries, and the ambient viscosities of the alcofuel slurries are comparable to coal/no. 6 oil mixture at 212 °F.

Coal/alcofuel slurries are typical Newtonian fluids below 30% by wt of coal loading and above this concentration are seen to be non-Newtonian. Viscosity of the slurries decreased upon the addition of certain commercial surfactants and stability was enhanced.

A marked increase in viscosity of the slurries is observed at higher coal loading upon increasing the concentration of ethanol in the blends. This may be attributed to the coal–alcohol interaction in the coal/oil + ethanol slurries.

Ignition temperatures of alcofuels are lower than those of coal–alcofuel slurries, implying that the alcofuel COS are more reactive than no. 6 oil COS as seen from lower ignition temperatures of the former under similar experimental conditions. In the burning profile, multiple flames

are observed. The ignition peak temperature increased with coal concentration and decreased with heating rate.

Activation energy of ignition of alcofuels and coal/alcofuel mixtures are similar up to 40% coal loading. This probably suggests that the oil burning controls the ignition process. A similar mechanism appears to be true in the case of the coal/no. 6 oil system.

Based upon the results, the advantages of alcofuel as compared to no. 6 oil are emphasized in relation to coal slurry fuel technology.

Nomenclature

COS = coal/oil slurry
A = preexponential factor
C = power-law index
E = activation energy, cal/g-mol
k_p = pseudo viscosity, (dyn s)/100 cm^2
R = universal gas constant, g-cal/(g-mol K)
T = temperature, K
T_c = ignition temperature, K (or °C)
x = fraction reacted at time t
η = apparent viscosity, cP
τ = shear stress, dyn/cm^2
$\dot{\gamma}$ = shear rate, s^{-1}
β = heating rate, °C/s

Registry No. Ethanol, 64-17-5; hexane, 110-54-3.

Literature Cited

Adiga, K. C.; Shah, D. O. *Colloids Surf*. **1982**, *4*, 271.
Adiga, K. C.; Pithapurrwala, Y. K.; Shah, D. O.; Moudgil, B. M. *Rheol. Acta* **1983**, *22*, 402.
Bienstock, D.; Jamgochian, E. M. *Fuel* **1981**, *60*, 851.
Cabal, A. V.; Voltz, S. E.; Stein, T. R. *Ind. Eng. Chem. Prod. Res. Dev.* **1971**, *16*, 58.
Keller, L. J. "Carbonaceous Fuel-In-Oil Suspensoids", Proceedings of 2nd International Symposium on Coal–Oil Mixture Combustion, CONF 79-1160, Danvers, MA, Nov 27–29, 1979.
Keller, L. J. U.S. Patent 4 089 657, 1978.
Kissinger, H. E. *Anal. Chem.* **1957**, *29*, 1702.
Sakuma, K.; Ukigai, T.; Yamashita, T., Yamaki, O. U.S. Patent 4 177 039, 1979.
Shah, D. O.; Adiga, K. C.; Sunder Ram, A. N. U.S. Patent application allowed on "Low Viscosity Stable Mixtures of Coal and Fuel Oil Containing Alcohol", Serial No. 355 372, 1984a.
Shah, D. O.; Adiga, K. C.; Sunder Ram, A. N. U.S. Patent 4 453 947, 1984b.
Veal, C. J.; Wall, D. R. *Fuel* **1981**, *60*, 873.