A Characterization of the Rheological Properties of Coal-Fuel Oil Slurries

JAMES M. MUNRO, MARLA M. LEWELLYN, PHILLIP R. CRACKEL, and LARRY G. BAUER

Department of Chemical Engineering
South Dakota School of Mines and Technology
Rapid City, South Dakota 57701

Although several investigators (Barkley et al., 1944; Berrowitz et al., 1963; Gradishar et al., 1943; Moreland, 1963) have addressed the topic of viscosities of coal-fuel oil slurries, consistency of their results appears to be lacking.

Slurries of low solids concentrations are Newtonian fluids according to all of the above investigators. However, the solids concentration level at which non-Newtonian behavior begins has been reported at values from 10 to 50% by volume. Both Berrowitz and Moreland reported non-Newtonian behavior at slurry concentrations $> 10\%$ by volume based on Brookfield viscometer measurements, but in the same investigation, Berrowitz reported Newtonian behavior at all solids concentrations $< 50\%$ by volume from pipeline measurements. Berrowitz attributed this discrepancy to solids settling during the pipeline experiments. Gradishar measured slurry viscosities up to the coal concentration where a yield stress occurred (about 39% by volume). However, as noted by Moreland, it is unclear if Gradishar used kinematic or absolute viscosities in reporting his results.

Gradishar suggested that slurries might behave as Bingham plastics, while Berrowitz and Moreland reported high solids slurries were pseudoplastic because the apparent viscosity decreased as the viscometer speed was increased; such a decrease would also be evident in a Bingham plastic material, however.

In no case did any of the investigators present flow curves for the slurries to accurately show the type of flow behavior. Only apparent viscosities were reported, and those without the corresponding value of shear rate or shear stress. Moreland reported speeds of revolution of the Brookfield viscometer; however, these data are not amenable to shear rate determination because of the complex geometry of the various spindle and guard arrangements.

Of the aforementioned investigators, only Barkley reported experimentally determined settling characteristics of the coal slurries. Unfortunately, Barkley also used a Brookfield viscometer and failed to give any experimental conditions such as spindle number and speed which were shown by Moreland to influence the viscosity reading.

Although the results reported by these investigators are somewhat incomplete, their results do have value in qualitative comparisons with other slurries using identical equipment and experimental conditions. It is recognized that some of the inconsistencies appearing in the literature could arise from differences in coal composition and in the oil used as the continuous phase by the various investigators. The objective of this investigation was to obtain rheological data on coal in fuel oil slurries and to report this information in as complete a manner as possible. Hopefully, then, the data can be used as a basis of comparison for future investigations in this area.

Correspondence concerning this note should be addressed to Larry G. Bauer.

0001-1541-79-1547-0355-$00.75.

EXPERIMENTAL

A subbituminous coal from Northeastern Wyoming was used in this study. The coal was crushed, milled in a ball mill, and screened to three different particle size distributions (PSD):

Number 1.	90-104 μm	(150-170 Tyler mesh)
Number 2.	75-90 μm	(170-200 Tyler mesh)
Number 3.	<75 μm	(minus 200 Tyler mesh)

Specifically, the PSD of number 3 was 34% 63 to 75 μm, 27% 53 to 63 μm, 27% 45 to 53 μm, and 12% < 45 μm. The specific gravity of the coal was 1.30. Number 4 fuel oil was used as the continuous phase, and its specific gravity was 0.9070 at room temperature. Viscosity of the fuel oil at 25°, 40°, and 60°C is shown in Table 1.

Slurries of the proper PSD and solids concentration were prepared just prior to each set of experimental runs; that is, the slurries had no previous history per se.

A Stormer viscometer (Van Wazer et al.,1963) was modified to a concentric cylinder, rotary viscometer while maintaining the Stormer drive mechanism. The standard Stormer rotor and cup were unacceptable because they were designed to create turbulence which makes it impossible to analytically determine rate of shear and thus express the results in standard flow curve format (shear stress vs. rate of shear). The modified Stormer viscometer was composed of a stainless steel cup with an inside radius of 1.41 cm and depth of 5.72 cm. The bob was solid aluminum with a radius of 1.27 cm and a length of 5.08 cm. During experimental runs, the bob was centered in the cup so that it was always 1.27 cm above the cup bottom; slurry was added until the submerged length of the bob was always 3.81 cm. Temperature control was maintained at ± 0.5°C by circulating tempered water around the outside of the cup.

In the determination of each flow curve, weights were added to the modified Stormer drive mechanism to give a variation in the applied shear stress. These weights were varied from ones just large enough to rotate the bob to weights large enough to cause turbulence or to reach the capacity of the instrument. These weights, along with the time for a given number of revolutions of the bob, were the data obtained from the viscometer. From these data one can obtain the desired components of the flow curve—shear stress and rate of shear, both at the bob surface.

Each datum measurement must be taken when the fluid in the annulus is in laminar flow, since in the event of turbulence, accurate calculation of the rate of shear is impossible. To insure that the flow was laminar under the test conditions, the data were checked for Taylor instability (Taylor, 1923) using the expressions developed by Kaye and Elgar (1958). This analysis indicated the existence of laminar flow for all the results reported here. Details of these calculations can be obtained from the authors.

TABLE 1. VISCOSITY (NEWTONIAN, μ, OR PLASTIC η_{pl}) · 10^3 AND YIELD STRESS ψ · 10

PSD No.	Temp., °C	Wt% coal: 0 μ	10 μ	20 μ	30 μ	30 ψ	40 η_{pl}	40 ψ	55 η_{pl}	55 ψ
1	25	48.6	84.2	154	206	15	428	22	10 400	530
	40	24.6	40.4	70.5	90.6		208	9.8	4 340	405
	60	11.8	22.1	34.2	42.5		125	0	909	529
2	25	48.6	61.8	150	214		481	60	6 500	760
	40	24.6	31.0	64.4	89.5		215	37	1 720	332
	60	11.8	22.4	30.2	48		97	11	594	305
3	25	48.6	74.1	138	192		376	28	4 474	664
	40	24.6	44.5	72.9	107		224	14.8	3 630	371
	60	11.8	23.8	33.7	49.5		94.4	19.8	746	537

The weight added to the string of the instrument, less the weight needed to overcome the internal friction of the drive mechanism, is proportional to the torque applied to the bob per Van Wazer et al. (1963):

$$T = \frac{R_d g(W - f)}{R} \tag{1}$$

The shear stress and shear rate at the bob surface are given by (Skelland, 1967)

$$\tau_b = \frac{T}{2\pi R_b^2 l_e} \tag{2}$$

and

$$\left(\frac{du}{dR}\right)_b = \frac{4\pi N C_r}{1 - S^{-2}} \tag{3}$$

where

$$C_r = 1 + \frac{S^2 - 1}{2S^2}\left(\frac{1}{n''} - 1\right)$$

$$\left[1 + \frac{2}{3}\ln(S) + \frac{1}{3}\gamma - \frac{1}{45}\gamma^3 + \frac{2}{945}\gamma^5 + \ldots\right] \tag{4}$$

and

$$\gamma = \left(\frac{1}{n''} - 1\right)\ln(S) \tag{5}$$

A plot of τ_b vs. $(du/dR)_b$ represents the flow curve for a particular slurry. If the plot is linear and passes through the origin, the Newtonian viscosity is given by

$$\mu = \frac{\tau_b}{\left(\frac{du}{dR}\right)_b} \tag{6}$$

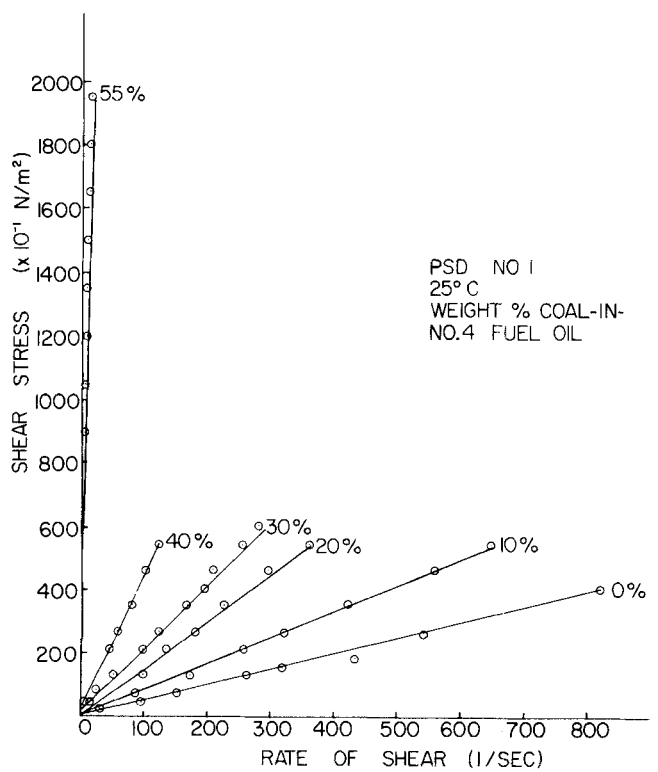

Fig. 1. Flow curves for subbituminous coal of PSD number 1 in number 4 fuel oil.

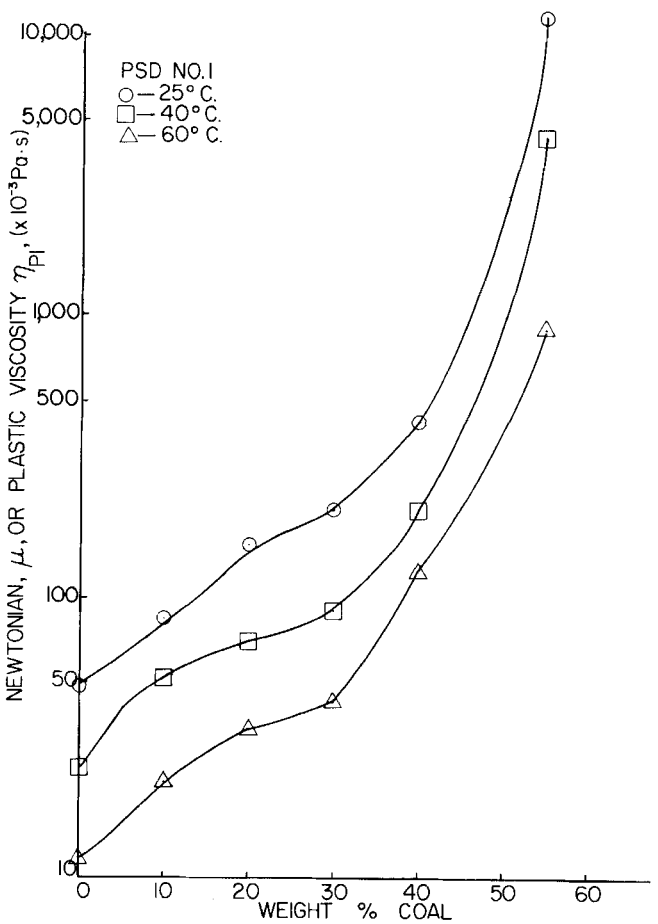

Fig. 2. Effect of temperature and solids concentration on the viscosity of subbituminous coal slurries of PSD number 1.

If the plot is linear but has a finite yield value (shear stress intercept), the plastic viscosity is given by

$$\eta_{pl} = \frac{(\tau_b - \psi)}{\left(\frac{du}{dR}\right)_b} \tag{7}$$

Correction of the immersed bob length for the end effect was accomplished by obtaining viscometer data for standard viscosity silicone fluids having viscosities from 0.100 to 0.540 Pa · s and for a high molecular weight organic oil having a viscosity of 3.670 Pa · s. Since the viscosity of the standard fluid would be known, the flow equations [Equations (1) to (6)] could be solved for the effective length of the bob. For the viscosity range investigated, the effective length was nearly constant at 4.51 cm.

RESULTS AND DISCUSSION

Figure 1 shows the flow curves for coal of PSD number 1 in fuel oil at 25°C with solids concentration as a parameter. The curves shown are the result of a linear, least-squares fit.

Inspection of this figure indicates that for solids concentrations up to about 30 wt %, the flow curves are straight lines which pass through the origin. Hence, one can conclude that for these experimental conditions, the coal slurries are Newtonian in nature. The corresponding Newtonian viscosities, that is, the slope of these straight line curves passing through the origin, are given in Table 1.

If turbulence had been present in the annular region of the viscometer, the flow curves would bend towards the shear stress axis. The fact that the curves are linear serves as a check that the flow in the viscometer was laminar.

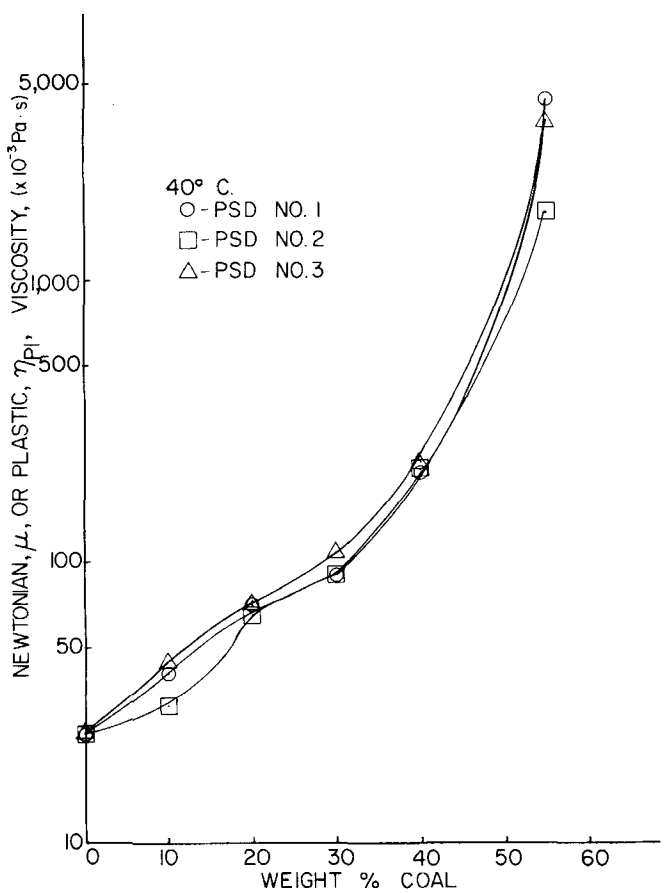

Fig. 3. Effect of PSD and solids concentration on the viscosity of subbituminous coal slurries at 40°C.

Figures 2 and 3 illustrate typical slurry viscosity (plastic viscosity for Bingham plastics) vs. coal concentration plots with temperature and PSD as parameters, respectively. These figures indicate a gradual increase in slurry viscosity with an increase in solids concentration up to approximately 30 wt %. The viscosity increases dramatically between 40 and 50 wt %. Qualitatively, this is in agreement with the results of Moreland (1963) and Barkley et al. (1944). A significant variation of the slurry viscosity with temperature is also noted in Figure 2.

Figure 3 indicates essentially no variation of viscosity with the coal PSD. Although this is not in agreement with the results of Moreland (1963) and Barkley et al. (1944), it should be pointed out that the PSD used in the current investigation was much more narrow than the PSD range used by either Moreland or by Barkley et al.

A combination of experimental variables was used that resulted in little or no solids settling during the time required for data determination. Details on these conditions can be obtained from the authors.

ACKNOWLEDGMENT

The authors wish to acknowledge John D. Osnes, Brant C. Grote, James E. Slichter, and James P. Swyter for preliminary work on this project; the National Science Foundation Office of Experimental Projects and Programs, and in particular the Undergraduate Research Program (NSF Grant No. EPP75-04172); the Tesoro Petroleum Corporation; The Black Hills Power and Light Company; and Dr. Robert L. Sandvig of the Chemical Engineering Department at the South Dakota School of Mines and Technology for supporting this investigation.

NOTATION

$(du/dR)_b$ = shear rate at bob surface, s^{-1}
f = weight needed to overcome friction in viscometer, 2.5×10^{-3} kg
g = acceleration due to gravity, m/s^2
l_e = effective immersed length of bob, m
n'' = slope of a plot of log T vs. log N
N = rotational speed of bob, rev/s
R = viscometer gear ratio, drum to rotor, 11:1
R_b = bob radius, m
R_c = cup radius, m
R_d = viscometer drum radius, 1.425×10^{-2} m
S = R_c/R_b, dimensionless
T = torque applied to bob, N · m
W = weight applied to viscometer, kg

Greek Letters

γ = dimensionless constant for calculation of rate of shear per Equation (5)
η_{pl} = plastic viscosity, Pa · s
τ_b = shear stress at bob surface, N/m^2
μ = Newtonian viscosity, Pa · s
ψ = yield stress for Bingham plastic, N/m^2

LITERATURE CITED

Barkley, J. F., A. B. Hersberger, and L. R. Burdick, "Laboratory and Field Tests on Coal-in-Oil Fuels," *Trans. ASME*, 185 (Apr., 1944).

Berrowitz, N., C. Moreland, and G. F. Round, "The Pipeline Flow of Coal-in-Oil Suspensions," *Can. J. Chem. Eng.*, 116 (June, 1963).

Gradishar, F. J., W. L. Faith, and J. E. Hedrick, "Laminar Flow of Oil-Coal Suspensions," *Trans. Am. Inst. Chem. Engrs.*, **39**, 201 (1943).

Kaye, J., and E. C. Elgar, "Modes of Adiabatic and Diabatic Fluid Flow in an Inner Rotating Cylinder," *Trans. ASME*, 753 (Apr., 1958).

Moreland, C., "Viscosity of Suspensions of Coal in Mineral Oil," *Can. J. Chem. Eng.*, 41 (Feb. 24, 1963).
Skelland, A. H. P., *Non-Newtonian Flow and Heat Transfer*, Wiley, New York (1967).
Taylor, G. I., "Stability of a Viscous Liquid Contained Between Two Rotating Cylinders," *Phil. Trans. Royal Soc. London Series A*, **223**, 283-93 (1923).
Van Wazer, J. R., J. W. Lyons, K. Y. Kim, and R. E. Colwell, *Viscosity and Flow Measurement*, Interscience, New York (1963).

Manuscript received November 29, 1977; revision received February 13, and accepted March 6, 1978.

On Comparing NMR and Adsorption Rate Diffusion Coefficients

DAVID GELBIN

**Central Institute of Physical Chemistry
Academy of Sciences
of the German Democratic Republic
Berlin.**

In a recent publication, (Ruthven and Doetsch, 1976), and in a further study (Ruthven, 1977), it has been mentioned that large discrepancies are observed between diffusion coefficients in identical systems measured by NMR and by adsorption rate experiments. Although he did not support the view, Ruthven commented in detail on one proposal to explain the observed differences. Kärger et al. (1976) assume that NMR determines the true mobility of adsorbed molecules within the body of adsorbent, whereas for certain types of zeolites, the limiting resistance in the adsorption rate experiment is a barrier resistance at the outer crystal surface.

With the NMR method, the average displacement of magnetically tabbed molecules is measured during a known period of time under equilibrium conditions, and from these data the diffusivity is calculated according to Einstein's law.

In several publications (Kärger and Walter, 1974; Pfeifer, 1972; Caro, 1977) Arrhenius plots of NMR diffusivities have been presented as in Figure 1. The solid line represents the measured results and may be divided into three regions: at lower temperatures intracrystalline diffusion coefficients D_z are measured with low activation energy, at intermediate temperatures there is a plateau, and at higher temperatures effective intercrystalline diffusivities D_a/K_A are measured with higher apparent activation energy. With increasing temperature, the plateau is reached when the average displacement of an adsorbed molecule during the NMR experiment is about equal to the crystal radius; this is documented for several systems and for different crystal radius in the literature cited. It is evident that the adsorbed molecules are not able to leave the crystals to enter the intercrystalline space over a range of temperatures, and some authors interpret this as meaning that a special barrier resistance exists at the outer crystal surface. However, we extrapolate the measured intercrystalline diffusivity (the dashed line, Figure 1). Adsorbed molecules moving within the crystals reach the outer surface (the low temperature end of the plateau) at a temperature where the intercrystalline diffusivity is an order of magnitude lower than the intracrystalline diffusivity; the system is macropore limited. Average molecular displacement increases only when the effective macropore diffusion coefficient becomes larger than the coefficient calculated from displacement equal to the crystal radius. Results are thus readily interpreted in terms of the common macropore-micropore model, and there is no need for introducing a third resistance. If such a third resistance exists and is greater than the macropore resistance, one should expect the measurements to follow the dotted line, lying below the effective intercrystalline diffusivity for some range of temperatures. No system in the literature to our knowledge shows this behavior; the plateau always ends near the intersection with the intercrystalline diffusion line. NMR measurements therefore prove conclusively that any barrier resistance is appreciably lower than the intercrystalline resistance. The barrier can by no means explain the three to four orders of magnitude by which NMR and adsorption rate results differ in the intracrystalline region.

Kärger et al. (1976) have attempted to prove the existence of the barrier by varying crystal size in adsorption rate experiments. Since the time parameter for the diffusion model is D_z/R^2 and for the barrier model $\mathcal{B}/R$, apparent diffusion coefficients should increase directly proportional to R if the barrier resistance theory applies. Figure 2 shows data presented by Kärger et al. (1976) for three systems with crystal sizes varying from 1 to 50 μ. The ordinate axis has been adjusted to permit representation of all systems in one figure, so that the D_z values are not given. All systems show an initial rise in D_z at a rate much faster than proportional to R and a gradual transition to a constant value at crystal sizes around 50 μ. Evaluation of the experiments according to the barrier model as done by Caro (1977) leads to barrier transfer coefficients varying with crystal size. It is evident that the diffusion coefficients measured by Kärger et al. (1976) and Caro (1977) are not invariant to size, but replacing them with size dependent barrier transfer coefficients is no solution to the problem.

As has been pointed out by Ruthven (1977), both NMR and adsorption rate diffusivities show similar trends with respect to increasing hydrocarbon chain length in

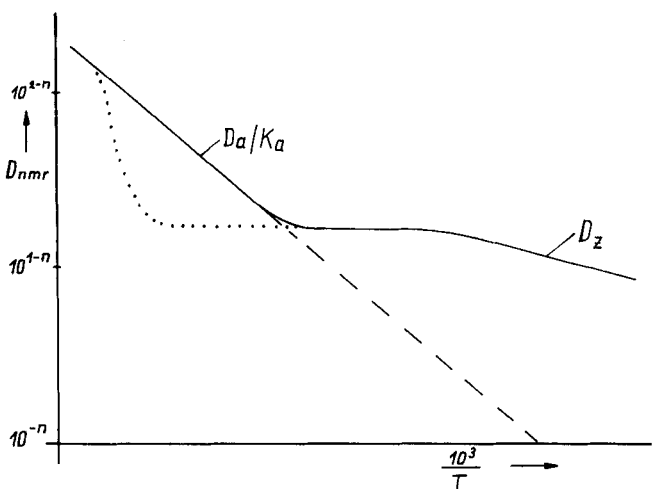

Fig. 1. Sketch of Arrhenius plot of NMR diffusivities.