CWS Rheology: The Role of the Coal Particle

Dean C. Marvin & Theodore C. Frankiewicz

Occidental Research Corporation
2100 S.E. Main Street
Irvine, California 92713

Introduction

The rheological properties of concentrated suspensions are important in a number of industries, particularly paints and coatings. The work of Chang et al (1) mentions some of the early experimental work in this area, but theoretical work on concentrated systems is quite limited(1-5). The reason for this is clear--the assumption of independent particles interacting only with fluid surroundings is not valid under these conditions, and the coupled motions of particles can be treated only empirically. The current research activity in coal slurry fuels has caused a renewed interest in this problem because the rheological properties of these fuels are of primary importance. Typically, one desires a liquid fuel with 65-70 weight percent solids, viscosity on the order of 10^3 centipoise, and resistance to sedimentation and shear degradation. These properties can be manipulated by the use of different particle size distributions of the powdered coal, surfactants or wetting agents, and water soluble polymers which act as stabilizers.

However, the wide variety of choices for these three compounding variables makes the task of finding the optimal formulation quite tedious and unsure. For this reason the work described below was undertaken. it represents an attempt to isolate the effect of particle size distribution (PSD) on the resulting slurry viscosity given that all other variables, i.e., the additive package, remain fixed. Comparison of theoretical predictions of relative viscosities of slurries with different PSD with experimental results show that the theory can be useful in optimizing the PSD.

Theory

There are two steps in the development of a model for predicting relative viscosity for particle size distribution. The first is to compute the maximum packing efficiency (volume fraction) $\emptyset_p$ possible for a given PSD. At this loading the viscosity of a slurry at realistic shear rates is assumed to be infinite, since it represents a random dense packing. Another way of viewing this limit is to consier the flow of a slurry as motion of the larger particles over one another as being "lubricated" by the motion of the smaller particles in the interstices. At $\emptyset_p$ no motion of these smaller particles is possible and hence the viscosity becomes very high. Thus it is expected that the viscosity of a slurry will increase rapidly as the actual particle loading $\emptyset$ approaches the value $\emptyset_p$. The second step of the model is to quantify this behavior.

In order to calculate $\emptyset_p$ for a given PSD the method of Lee (7) has been used. A brief description of this procedure will be given here, but for a detailed discussion the reader is referred to the original work. Consider a binary PSD, that is one which consists of only two sizes of spherical particles, and ask how the maximum packing fraction can be determined. One procedure is to fill a volume with the dense random packed larger spheres giving a packing fraction $\emptyset_{max,L}$ and then filling the remaining volume with the smaller spheres. The final packing fraction is

$$\emptyset_{max} = \emptyset_{max,L} + (1-\emptyset_{max,L})\cdot\emptyset_{max,S}$$

It is assumed that $\emptyset_{max,L} = \emptyset_{max,S}$, that is that monodisperse spheres all pack with the same efficiency in dense random packings. The value assigned is determined by experiment to be .639. The composition of this mixture is $X_{max,L} = \emptyset_{max,L}/\emptyset_{max} = .735$. An assumption which is implicit in the above is that the large and small particles are sufficiently different in diameter ($D_L/D_S > 100$) that the interstitial volumes between the large spheres can be summed and treated as a bulk void for purposes of packing the smaller spheres. The experimental work of McGeary (8) is used to determine the $\emptyset_{max}$ for diameter ratios $1 < D_L/D_S < 20$. Thus far this process gives the $\emptyset_{max}$ for binary mixtures of arbitrary sized spheres. The next extension is to compute the packing fraction $\emptyset_p$ for binary mixtures with a specified composition. Lee has given an analytical procedure for doing this under the assumption that the $X_{max,L}$ is independent of the diameter ratio of the spheres. This reasonable assumption is based on the premise that any optimal packing will contain a dense, random packing of the largest spheres in the system, which is then filled in with any available smaller spheres. Clearly the replacement of a large sphere in such a packing arrangement with the maximum number of inscribed smaller spheres will produce a less efficient packing. Finally, Lee has given an algorithm for computing the packing fraction $\emptyset_p$ for mixtures which contain an arbitrary distribution of spherical particles. The algorithm, which is based on a geometrical construction, is given below.

$$(\emptyset_p)_i = \sum_{j=1}^{N} \emptyset_{ij} X_j \qquad\qquad 1 = \sum_{j=1}^{N} X_j$$

where $\emptyset_{ii} = .639$

$\emptyset_{ij} = .639 + (\emptyset_{max}(D_i/D_j)-.639)/.265$

$\emptyset_{ji} = .639 + (\emptyset_{max}(D_i/D_j)-.639)/.735$

$D_i/D_j \geq 1$ or $i \geq j$

X_j = volume fraction of particles of diameter D_j

N = number of discrete diameters present in mixture

$\emptyset_{max}(D_i/D_j)$ = maximum packing fraction of binary mixture consisting of spheres of diameter D_i and D_j.

The set of $(\emptyset_p)$ values has N members and the smallest one is chosen as the packing fraction $\emptyset_p$. The algorithm is not easily understood by inspection because it is graphical in nature, but is developed in a straightforward way in Reference 7. In order to use this technique to predict $\emptyset_p$ for a coal grind, one simply performs a particle size analysis, discretizes the distribution into N bins, and then computes $\emptyset p$.

There are several equations available for obtaining the relative viscosity of concentrated slurries from a knowledge of the packing fraction $\emptyset_p$ and the actual volume fraction solids $\emptyset$. The Mooney equation (9)

$$\eta = \eta_o \exp[2.5\emptyset/1-\emptyset/\emptyset_p] \qquad (1)$$

expresses the hydrodynamic viscosity of the suspension in the limit of high shear rate, relative to the viscosity of the pure suspending medium η_o. This expression is valid in the range where $\emptyset \approx \emptyset_p$, and where the double layer thickness surrounding particles in aqueous solution is small compared to the particle diameter. Both of these criteria are satisfied by the coal slurries described here.

However, the justification for this form is clear only for monodisperse or slightly polydisperse systems. An alternative is the empirical equation (1,10)

$$\eta = \eta_0 \left[1 + .75 \frac{\phi/\phi_p}{1-\phi/\phi_p}\right]^2 \qquad (2)$$

which has been successful in describing results obtained with suspensions of glass beads in polyisobutylene.

Experiments

The theory presented above has been used in two different ways to predict the viscosity of coal water slurries. One application involved mixing a fine grind of coal with a coarse grind in varying proportions to produce bimodal particle size distributions. It was found by experiment that there always existed an optimum blending proportion which produced a slurry of minimum viscosity (with the additive package remaining fixed). The theory was tested to see if it could successfully predict this optimum blend given the PSD for the two starting grinds and the total weight fraction of coal to be used. The procedure was simply to compute the packing fraction ϕ_p using the above algorithm, convert the weight fraction coal to a volume fraction ϕ in the slurry, and use equation (1) or (2) to evaluate the relative viscosity η/η_0. The value of η_0 was then selected to scale the data at one point (usually the minimum viscosity). The results of this procedure are shown in Figures 1 and 2. The data in the former utilized two different grinds of the same coal which had median diameters of 5μ and 35μ. Although the viscosities are not predicted quantitatively, the shapes of the curves are similar and the location of the minimum is given correctly. In Figure 2 the data was obtained from mixtures of two different coals with median sizes 15μ and 40 μ. Again the blend composition giving the minimum viscosity is given correctly. Both of these coal slurries were 65% coal by weight. Also equation (2) was used to compute the theory points in both cases but equation (1) was equally suitable, the difference being in the width of the curves rather than in the location of the minima.

A second application was to predict the change in viscosity with coal loading in coal water slurries. Figures 3 shows viscosity data for a coal subjected to different grinding conditions which resulted in different size distributions, A and B. The volume median (or equivalently, weight) sizes were 50μ and 25μ, respectively. The ϕ_p corresponding to each of these PSD's were computed, and theoretical curves drawn using equation (2) with ϕ being the independent variable. Note that the x axis in the figure is the more familiar weight percent coal while the ϕ_p in equation (2) is the volume fraction coal (conversion was made assuming a coal density of 1.34 g/cm^3). The theory is quite successful in fitting these results, but substantially less so when equation (1) is used.

Conclusion

The effect of coal particle size distribution on the viscosity of coal water slurries has been analyzed using a particle packing model due to Lee in conjunction with an empirical relationship between packing efficiency and viscosity. The technique is able to predict the optimum PSD when one degree of freedom is present, such as the blending ratio between a coarse and a fine grind of coal. The results presented here illustrate this for the cases where the two grinds are the same coal and where they are different coals. In addition data has been presented which shows that one can predict the behavior of viscosity vs. coal loading curves as the PSD of the coal is varied. Both of these achievements are quite useful in the development of coal water slurry formulations in that they allow the value of specific coal

grinds to be assessed without extensive slurry preparation and measurement. The method can also be used to assess the relative merits of unimodal and bimodal size distributions.

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FIGURE 1

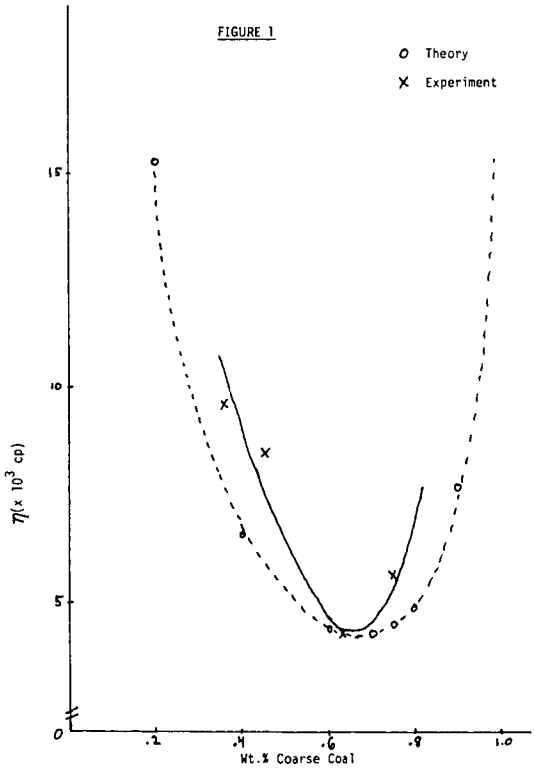

FIGURE 2

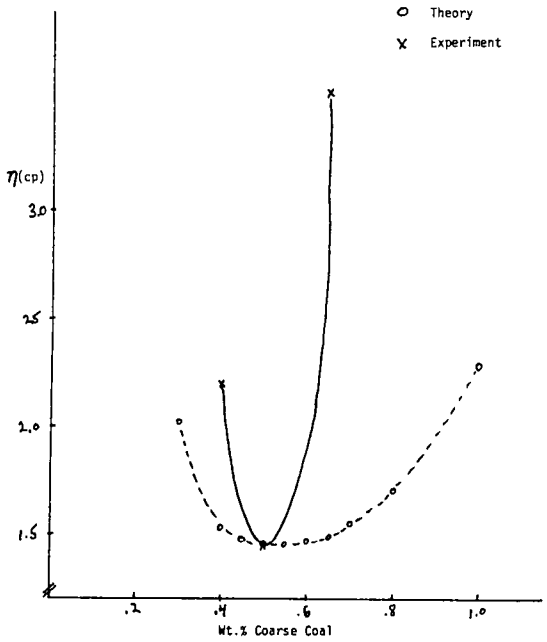
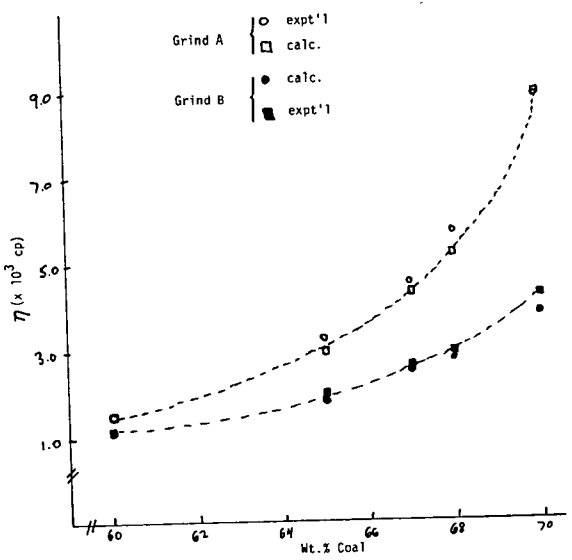
FIGURE 3