Physio-Chemical Modeling of Coal and Coal/Biomass Slurries for Gasification and Direct Combustion Applications

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Abstract

Developing appropriate slurry feeds of gasifier feedstocks including coal and biomass derived solids is usually a matter of trial and error, involving laboratory and pilot scale testing. The same holds true for direct combustion applications. In both entrained flow gasifiers and steam generating combustors rheological properties can be critical in determining handling and atomization characteristics of slurry fuels. This becomes critical as more advanced combustors and gasifiers come on line which are designed to have a biomass cofiring option.

In this paper a model is presented which can predict the properties of coal slurries from a few basic physio-chemical properties of the coal. This model is based on an extensive research and development program conducted in conjunction with EPRI. Several applications of the technology are presented and compared with laboratory data. The model is also applied to a variety of coal and/or biosolids slurries. Various application scenarios are presented and the benefits of the model both as a design tool and for feedstock screening are elaborated.

Background and Introduction

Highly concentrated suspensions of coal particles in water or alternate fluids appear to have a wide range of applications for energy production. Since most coal cleaning processes produce coal slurries, it is natural to utilize dense suspensions for transportation and power generation. As a method of utilizing coal fines, coal slurries provide a viable approach. In addition biosolids can be introduced as a component of a fuel slurry considerably widening the application base.

For successful commercial utilization of coal slurries, it is important that a thorough understanding of their properties be developed and applied for a basis for engineering and design. Unlike oils, which are essentially Newtonian fluids fully characterized by a few basic physical parameters, such as viscosity, density, and surface tension, coal and/or biosolids slurries are complex structures with large numbers of internal degrees of freedom and are usually non-Newtonian. Therefore it is necessary either to perform an extensive series of laboratory and scale up tests for each new application of solids/liquids fuel slurries or develop a model based on fundamental principles that can used for predicting relevant design parameters. The model developed in this program can be used for designing slurry applications. The physical basis for the model is discussed next.

Physical Properties of Coal Water Slurries

The study of the deformation and flow of a suspension is the single most important method of characterizing coal slurry.

Viscometric Properties

It has been demonstrated that it is possible to describe viscometric properties of dense coal slurries by treating them as mechanical continua following the rheological behavior of a power law fluid.

(1) $$\tau = k\,\dot{\gamma}^{n}$$

Where

τ = shear stress (Pa)
k = consistency index
$\dot{\gamma}$ = shear rate (s^{-1})
n = power law index

The power law index (n) is a measure of the deviation from Newtonian behavior of the fluid, i.e. n=1 for a Newtonian fluid, n<1 for a pseudo plastic system, and n>1 for a dilatant system.

In some cases a stress must be overcome to obtain fluidity. This yield stress requires a modification of Eq. 1 where:

(2) $$\tau - \tau_o = k\,\dot{\gamma}^{n}$$

The apparent viscosity of the system is obtained by evaluating $d\tau/d\gamma$ at a specific shear rate, $\dot{\gamma}$.

In programs conducted at Adelphi University and other institutions, the rheology of coal slurries tested have been described as power law behavior. It is important to note that the power law is only valid in the shear rate range over which it was measured and cannot generally be extrapolated to other shear rate regions. However as will be shown the model developed in this program is capable of extrapolation.

Coal water slurries are classified as suspension concentrates. Suspension concentrates are solid in liquid dispersions in which the mean particle size exceeds colloidal dimensions, i.e. greater than one micron. , and will settle under the influence of gravity. Suspension concentrates of coal are very complex systems. Van der Waals attractive forces promote flocculation and aggregation of the particles. These attractive forces can be opposed by electrical forces of repulsion caused by a charge structure surrounding individual coal particles and steric effects due to adsorbed macromolecules which lead to an increase in free energy when particles approach each other. The stability of a suspension concentrate against sedimentation of particles is a measure of the structure of the system and has been extensively studied for coal water slurries. The degree of structure formation such as agglomeration, flocculation, and the strength of the interparticle binding forces is manifested by the rheological properties of the system under shearing conditions.

A key parameter in describing a suspension concentrate is the particle concentration or the volume fraction of solid particles, ϕ. For very dilute systems, ($\phi < 0.1$) particle-particle interactions can be neglected and it is possible to develop a theory describing *the relative viscosity*, ?, by treating the interactions between the fluid and the individual particles. The result is

$$\eta = 1 + K_1 \phi \qquad (3)$$

where K_1 is a constant dependent upon particle shape and is equal to 2.5 for hard spheres. As concentration (ϕ) increases, particle-particle interactions become important and the simple linear relation does not obtain.

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For highly concentrated suspensions which are the main focus in the study of coal water fuels the shear viscosity will be infinite at some value called the maximum packing, ϕ_m. At this volume density of particles, the suspension will not flow under the stresses typical in pumping and flow of the suspensions. Therefore,

$$\eta = F(\phi, \phi_m) \qquad (4)$$

such that

$$\eta \to \infty \text{ as } \phi \to \phi_m$$

The maximum packing, ϕ_m, includes structural information such as the geometric placement of particles which maximizes ϕ_m by smaller particle filling voids present in the loose packing structure of larger particles.

In this program a well-defined method of computing ϕ_m from a given particle size distribution of suspended particles has been developed. In addition, this theory allows the development of particle size distribution functions which can increase ϕ_m to a value

greater than 0.90. This model has been applied to the analyses of hundreds of coal slurries including an extensive development program for the Electric Power Research Institute. This model has the potential of describing non-Newtonian rheological behavior of suspension concentrates and the effect of coal surface properties by incorporating structural information in the maximum packing density. Increasing the shear rate will decrease agglomerate formation thereby decreasing the volume occupied by the particles *and the viscosity.*
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An important property for atomization of a slurry in combustion systems is the change in viscosity from pumping shear rates (~100 s^{-1}) to atomization shear rate (~5000 s^{-1} or higher). Therefore, in determining whether a coal water slurry is acceptable for a combustion application such as gasifier feedstock, the entire range of shear rates must be evaluated and any model must take this into account. The model that has been developed utilizes algorithms that can be applied over a wide range of shear rates. This model has been developed over the last decade and has been verified on *hundreds* of coal and other settling slurries.

Description of model

The model is most easily understood by analyzing the flow diagram shown in Figure 1

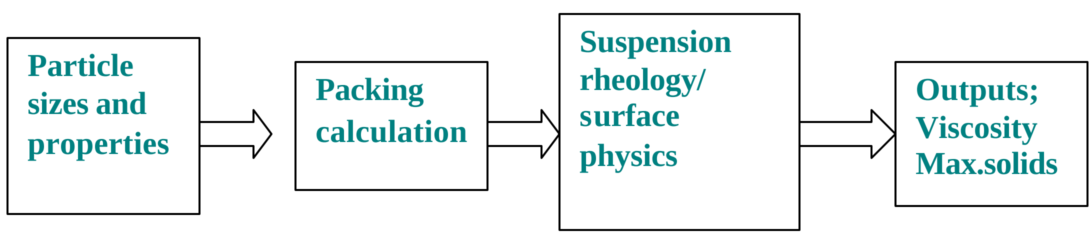


Figure 1 Slurry Model Operation

The basic inputs to the model are the particle size distribution and material bulk and surface properties as determined by chemical analyses (for coal –ultimate and proximate analyses). The model can be refined by inputting some surface properties such as % C-O bonds as determined by ESCA. For most applications such refinements are not necessary. The maximum packing is then determined with the given particle size distribution or a particle size distribution can be generated that will yield the highest maximum packing. The model can then predict the viscosity as a function of solids content, determine the maximum solids that can be pumped, the degree of agglomeration of the particles, the expected high shear behavior, and the type and concentrations of any dispersants and Ph adjusters required subject to an add on cost limitation of less than .10$/millionBtu. Algorithms based on suspension rheology and particle surface physics are used to accomplish these tasks and the program can be formatted for easy lap top use.

Applications

Some important applications of the model are discussed below.

Coal Slurries for Combustion, Gasification, and Transportation

Coal slurry fed entrained flow gasifiers(e.g. Texaco gasifiers) are an obvious application of the model. The model was initially developed for this application. For the gasifiers it is important to maximize the coal content of the slurry to reduce energy losses and excess oxygen use. The model can predict the maximum pump able coal concentrations in a slurry(the slurriability) as a function of a few basis coal properties. Because of this capability it can be used as a design tool for gasifiers, as a quality control and trouble shooting tool by plant engineers, and as a coal screening system by fuel purchasing agents. For example when coal supply bids are screened for gasifier applications the slurriability can be used to asses the coals effectiveness as a gasifier feed stock.. In addition the slurry atomization can be evaluated from the predicted rheological properties.

For combustion applications the coal concentration, low shear rheology($100s^{-1}$), and high shear rheology($>1000s^{-1}$) are important for handling, thermal efficiency, and spray atomization effectiveness. For example NO_x reduction techniques including reburning applications can be effected by water content and spray properties of slurries. For pipeline transportation the cost is determined by pressure drop requirements and maximum allowable coal throughput which can be analyzed with the model thereby avoiding extensive pilot scale testing.

Biomass Slurries for Energy Production

A new application for slurries that has emerged in the past few years is for the transport and combustion of biosolids. Biosolids can incude agicultural wastes, switch grass, wheat straw, wood chips and saw dust, paper waste, hydrothermally treated sewage sludge,et. All these materials can be transported and burned in the form of slurries. In some cases, such as gasification or co-gasification with coal the slurry is the simplest approach. Slurries also present a good coal co-firing option. In many of these applications it is critical to have a good understanding of the expected handling and atomization properties(e.g. reburning and entrained flow gasification). The model has been successfully applied to biosolids slurries. Some results are presented in the following sections.

Particulate and Slurry Waste Mobilization and Transport

There are many potential applications for slurry waste retrieval and transport. Coal ponds provide an obvious application where the ability to predict slurry flow properties can be very important. The clean up of coal pond spills is a clear application where the model could provide useful guidance.

Between 1944 and 1986, 177 underground storage tanks were constructed at Hanford in Washington State to contain the byproducts / waste resulting from the production of plutonium. There are 149 SSTs(single shell tanks) and 26 DSTs(double shell tanks). These tanks contain approximately 54 million gallons of radioactive, hazardous, and mixed waste. The SSTs are the oldest tanks at Hanford. The SSTs contained mixtures of liquid, salt cake, salt slurry, and sludge waste forms. Because some of the SSTs have leaked and DST space is limited, sluicing the SST tanks with water to obtain a more pumpable mixture is not a desirable practice. Therefore, removal of the saltcake and sludge wastes will require robotic / remote handling technology coupled with systems capable of transporting highly loaded slurries. The model can be successfully applied to this program as discussed below.

Densely Packed Materials

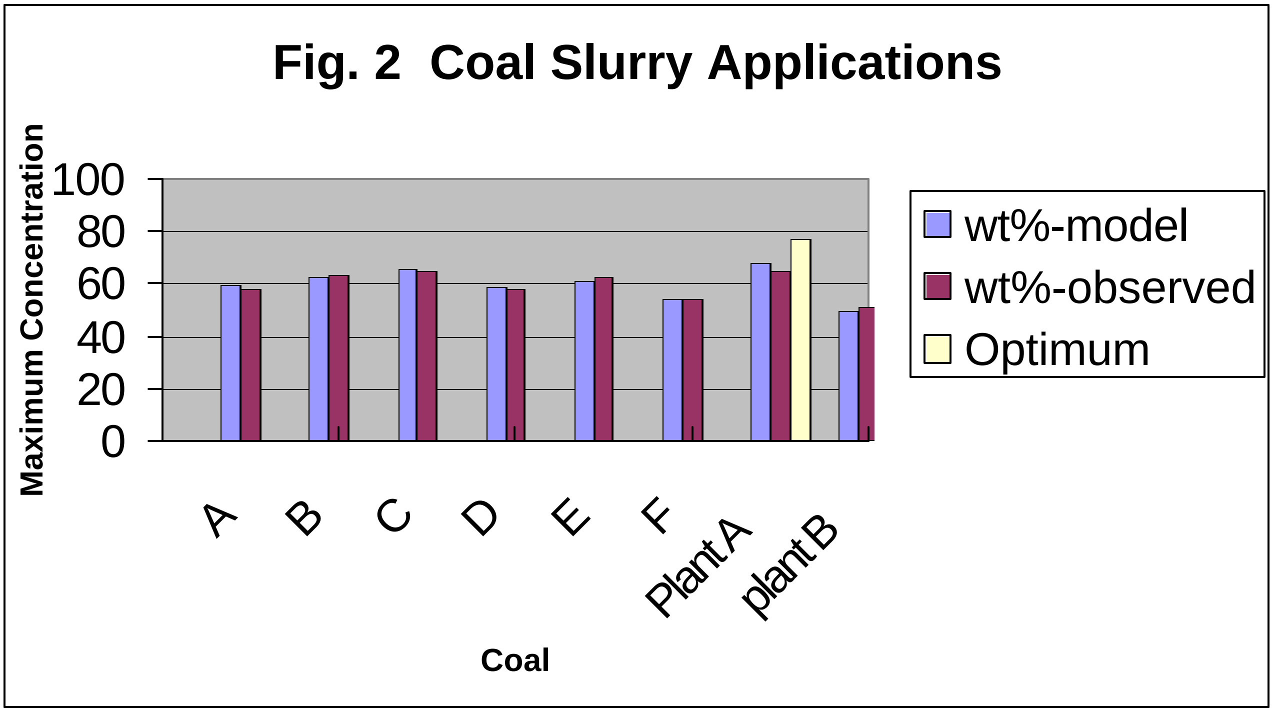
Because the model can accurately predict the packing and agglomerating properties of solid particles independent of scale it can be useful in determining properties such as porosity and mechanical strength of materials

Applications Results and Model Verification

In the following the results of several applications are reviewed.

Applications to Coal Gasification

In Figure 2 the results of applying the model for slurry fed gasifiers are presented. A variety of potential gasifier coals were analyzed, including two coals being used by existing plants(demo). Ultimate and proximate analyses were done and the ESCA analysis on the % C-O bonds performed. The maximum pumpable coal concentration was determined by the model and the measured in the laboratory. The coal properties varied widely but in all cases the predicted and measured results agreed within a few percent. In the case of the two existing plants the model demonstrated that that these plants could operate with higher concentration slurries by adjusting the coal particle size distributions.



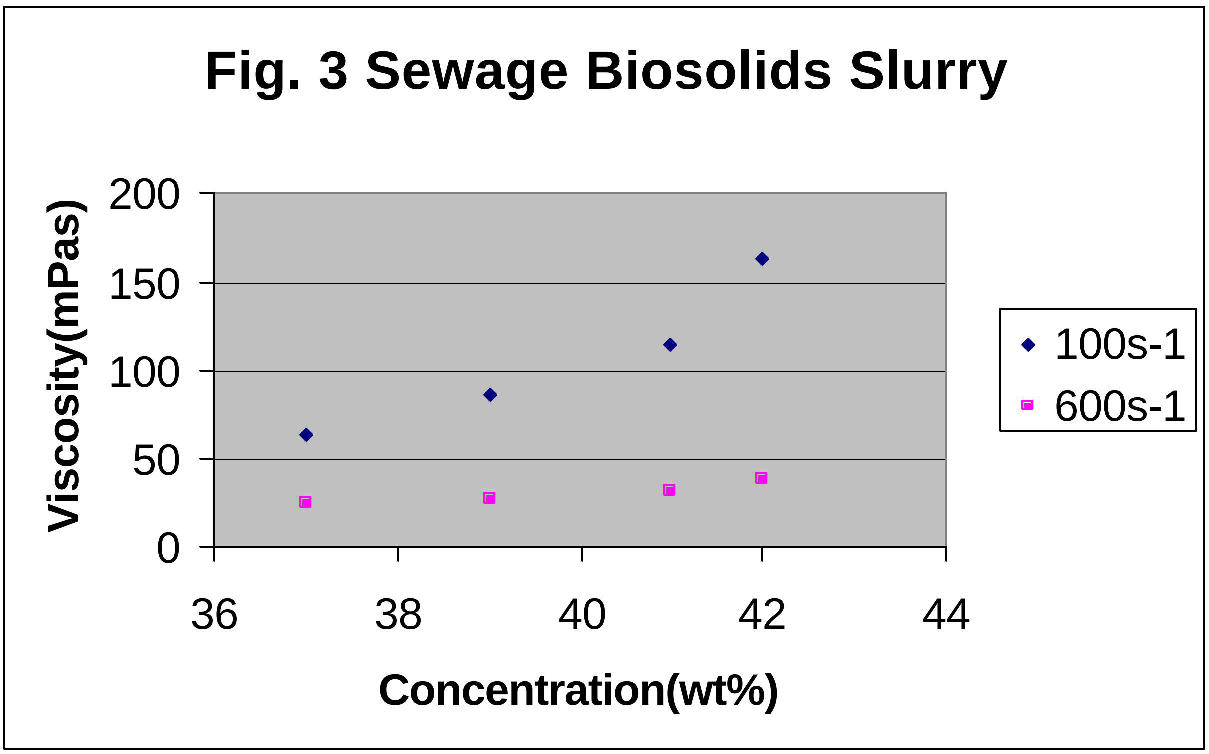
Biosolids Slurries
There have been several applications , but only one will be discussed here.

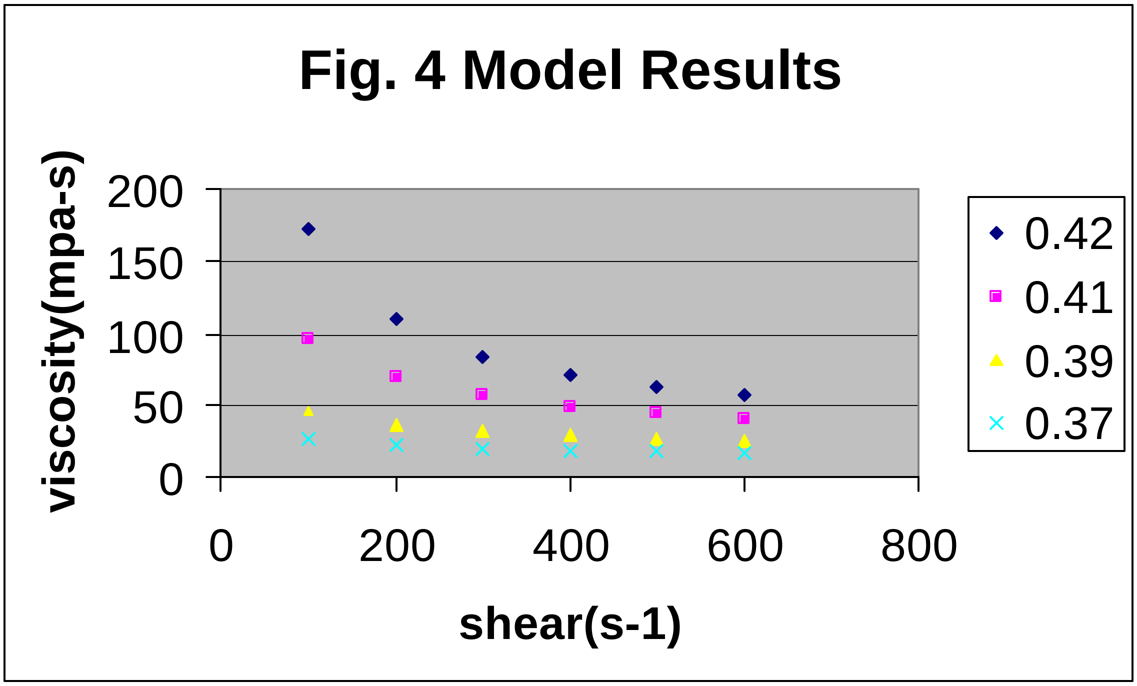
Concentrated Thermally Treated Sewage Sludge

In this application sewage sludge from the Johnstown Sewage treatment plant was hydrothermally treated by the EnerTech process and the slurry rheology analyzed.

The significant technical advantage of the hydrothermal treatment of the sludge is the dramatic improvement in flow properties due to expulsion of trapped water from the suspended solids. Application of hydrothermal treatment to sewage sludge changes a mixture, which is essentially a filter cake at 20% solids into a pumpable slurry at higher solids concentrations. The ability to pump high concentration sludge slurries is of particular importance because of operational problems in transporting a wet filter cake. Whether the sludge is to be incinerated or fed to a boiler furnace or gasification system (e.g.with coal cofiring), the liquid flow properties reduce the operational and environmental problems.

Figure 3 provides the effect of sludge solids concentration of the treated Johnstown sample. All samples tested displayed pseudoplastic (shear thinning) rheology which became more dramatic at increasing sludge concentrations, i.e. n=0.69 @ 36.8% solids and n=0.37 @ 42.2% solids. In Figure 4 the model predictions are shown. These calculations are based on a calculated maximum packing of .72(from the PSD) and an estimate that the volume of solids bound in agglomerates is between 40-50% at a shear rate of 100 s^{-1}(based on the observed maximum concentration). As can be seen the model correctly predicts the magnitudes and shear dependencies of the viscosities over a range of concentrations. In addition the model can be extrapolated to high shear(>5000s^{-1}) , for atomization applications, showing a limiting viscosity of 25mPas at .42 weight fraction of solids.





Nuclear Waste Mobilization and Transport

This technology can be applied to the tank sludge in the Hanford SST's. This is most simply treated by computing the maximum volumetric packing from the measured particle size distribution. For a sample tank using the most recent particle size distribution the geometric packing volume fraction was determined to be .82. . If there were no agglomeration this would be the concentration at which the slurry would cease to flow. From the viscosity data the maximum solids volume fraction above which the slurry loses fluidity is then determined. For the material in the sample tank this appears to be around 0.30. The difference between these two numbers is due mainly to the void volume fraction in the agglomerates(or average porosity). Using the agglomeration model this would occur if 90-100% of the particles were bound in agglomerates. The ratio .3/.82 yields an average porosity of agglomerates of .634. This approach can be used for all slurries. Based on this result the average density of the agglomerates, which is useful for considerations of in line settling is computed to be 1.83.

Though the suspensions exhibit non-Newtonian behavior thru the existence of a yield point the rheology data indicates that the agglomerates are not broken up further at shear rates in the 300-400 s^{-1}, which is the transport region. This has implications for the tank extraction operation. The option of providing for some minimal dilution (2-3% additional water) is important in order to fluidize any hard pack. For example, if hard pack occurs at a volume fraction of 0.28 and a 2% dilution is applied the material becomes fluid with a viscosity of 200cp using the viscosity model. Since the line velocity would be well above the critical settling velocity there should be little chance of deposits building up in the transport lines when the material is extracted.

Applications to Dense Packed Materials.

The important parameter for the study of dense packed materials is the volumetric packing fraction. From an analysis of the packing the void fraction can be determined and an estimate of the strength of the material can be developed from an analysis of interparticle forces. In table I a comparison of the model predictions of the packing of non agglomerating glass beads of known particle size distributions and measurements of the packing both dry and suspended in a fluid is presented. The model predicts the packing very accurately and can be used as an analysis tool for dense packed materials.

Table 1

Volumetric Packing for Glass Beads(vol%)

	ϕ_m(theoretical)	ϕ_m(dry packing)	ϕ_m(high shear)
PSD#1	63.9	63.0	63.8
PSD#2	68.1	69.0	69.7

Conclusions

The model has been demonstrated to be reliable in predicting a wide range of difficult to measure properties of dense slurries and materials. The are many other possible applications. In summary is is useful to highlight the major areas where the model can be used and the advantages.

Advantages of Model

- **Reduces Need for Extensive Development and Testing**
- **Provides Method for Continuing Quality Control**

- **Allows Screening of Coal Supplies for Slurry fed Coal Combustion Systems**
- **Allows Inexpensive Slurry Design for Coal and Biomass Fuels**
- **Can be Applied to Hard to Test Systems Such as Nuclear Waste Slurries**
- **Can be Used for Property Determinations of Dense Packed Materials**

The model will continue to be applied to a variety of slurry design problems and can be modified to incorporate paste flow and three phase flow such as suspensions and emulsions of several materials