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Publication Date

2009-04-16

Energy Fuels **2009,** *23,* 4763–4767 · DOI:10.1021/ef9000852
Published on Web 05/26/2009

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Rheological Study of Comingled Biomass and Coal Slurries with Hydrothermal Pretreatment†

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Received January 30, 2009. Revised Manuscript Received April 16, 2009

Gasification of comingled biomass and coal feedstock is an effective means of reducing the net life cycle greenhouse gas emissions in the coal gasification process while maintaining its inherent benefits of abundance and high-energy density. However, feeding a comingled biomass and coal feedstock into a pressurized gasification reactor poses a technical problem. Conventional dry feeding systems, such as lock hoppers and pressurized pneumatic transport, are complex and operationally expensive. A slurry formation of comingled biomass and coal feedstock can be easily fed into the gasification reactor but, in normal conditions, only allows for a small portion of biomass in the mixture. This is a consequence of the hydroscopic and hydrophilic nature of the biomass. The College of Engineering Center for Environmental Research and Technology (CE-CERT) at the University of California, Riverside, has developed a process producing high solid content biomass−water slurry using a hydrothermal pretreatment process. In this paper, the systematic investigation of the rheological properties (e.g., shear rate, shear stress, and viscosity) of coal−water slurries, biomass−water slurries, and comingled biomass and coal−water slurries is reported. The solid particle size distribution in the slurry and the initial solid/water ratio were investigated to determine the impact on shear rate and viscosity. This was determined using a rotational rheometer. The experimental results show that larger particle size offers better pumpability. The presence of a high percentage of biomass in solid form significantly decreases slurry pumpability. It is also shown that the solid loading of the biomass−water slurry can be increased to approximately 35 wt % with viscosity of less than 0.7 Pa·s after the pretreatment process. The solid loading increased to approximately 45 wt % when the biomass is comingled with coal.

1. Introduction

Interest in the development of alternative transportation fuels has increased considerably in recent years, as driven by the surging global oil demand and increasing concerns about energy security. Gasification and subsequent conversion of the gasification products to synthetic liquid fuel from a comingled biomass and coal feedstock have been shown to be a promising alternative resource for transportation fuel production. It can provide clean synthetic liquid fuels while potentially reducing the overall net life cycle greenhouse gas emissions when compared to petroleum-based fuels or coal gasification.[1] The transportation and feeding of comingled biomass and coal feedstock into the gasification reactor is a critical issue. Conventional dry feeding systems, such as lock hoppers and pressurized pneumatic transport, are complex, unreliable, and operationally expensive because extra carrier gas is needed and vibrators are implemented to avoid fluctuations.[2,3] Slurry feeding is a much simpler, reliable, and inexpensive method of transporting and pressurizing the feedstock into gasification reactors and has been successfully demonstrated in commercial-scale application using 100% coal as the feedstock.[4] The College of Engineering Center for Environmental Research and Technology (CE-CERT) has developed a steam hydrogasification process, which has been shown to be very efficient for gasification of both coal and biomass feedstock, either alone or comingled.[5] One unique feature of this process is that it uses water in the feedstock to provide an internal source of hydrogen and to control the synthesis gas ratio of the product gas over a wide range.[5] This requires the formation of pumpable slurries with a high carbon/water ratio. However, the hygroscopic and hydrophilic nature posed by the hydroxyl groups in the polymeric structure of the biomass (e.g., cellulose, hemicellulose, and lignin) only allows for a small portion of solid in the biomass or comingled biomass and coal mixtures.[6] To prepare high solid biomass or comingled biomass and coal slurry, a hydrothermal pretreatment process has been developed.[7] However,

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† Progress in Coal-Based Energy and Fuel Production.

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evaluation of the dynamic rheological properties of a slurry, such as shear stress, shear rate, and viscosity, is needed for the determination of pumpability as well as the selection of a pump and pipe system for slurry handling.[8]

Prior studies concluded that the rheological properties of coal—water slurries are dependent upon the type of coal, solid loading, coal particle size and size distribution, temperature, and additives.[9,10] Other studies have addressed biomass suspension and the effect of particle size,[11] temperature, and additives[12] on rheological properties of cellulosic biomass—water slurries. However, rheological studies of the biomass—water slurry and its potential as a gasification feedstock when either alone or comingled with coal have not been reported. This paper presents the results of a series of experiments that systematically examine the rheological properties of various coal—water, biomass—water, and comingled biomass and coal slurries. The correlations between the rheological properties and the pumpability of the slurry are also discussed. The major factors considered are particle size, solid loading, viscosity, and the conditions related to the hydrothermal pretreatment procedure of the biomass.

2. Experimental Procedures

2.1. Preparation of Coal and Biomass Feedstock. Coal particles were prepared using southern Utah sub-bituminous coal. Pine wood sawdust was used as a representative for biomass in this study. Each material was initially ground and then pulverized in a pulverizing grinder. The pulverized particles were then sieved into three particle size ranges: 0—150, 150—250, and 250—500 μm. The particles were then dried in a vacuum oven at 70 °C for 3 h for vaporization of the moisture. Finally, particles were mixed with water to form numerous coal and biomass slurries. The proximate analysis of the coal and biomass feedstock is presented in Table 1. The solid loading for the coal—water slurries ranged from 40 to 65 wt % by every 5%. The biomass—water slurries ranged from 5 to 12.5 wt % by every 2.5%. The mixtures were stored overnight to allow for complete mixing of the particles and water. The mixtures were gently stirred just before the rheological tests to avoid particle settlement. Harsh stirring was avoided to prevent generating small air bubbles in slurries, which would impact the rheological tests.

2.2. Pretreatment of Biomass Slurry. A portion of the prepared biomass particles in the particle size of 0—150 μm was pretreated using a hydrothermal pretreatment method. In the pretreatment process, the biomass particles were mixed with water at solid weight percentages of 20, 30, and 40 wt %. The mixtures were then heated to 230 °C in 690 kPa of hydrogen for 30 min. The process was carried out in a sealed batch reactor to conserve the total mass after the pretreatment. The difference in the solid content before and after the pretreatment was negligible and further confirmed by the elemental analysis of the biomass slurry after pretreatment. The 20 wt % pretreated biomass slurry was then mixed with up to 35 wt % of the 0—150 μm coal particles to form the comingled biomass and coal slurries.

Table 1. Proximate Analysis of the Coal and Biomass Particles

	coal particles	biomass (pine wood) particles
ash content (wt %)	7.6	0.4
moisture content (wt %)	4.0	10.7
volatile matter (wt %)	36.2	74.5
fixed carbon (wt %)	52.2	13.6
total (wt %)	100	100

2.3. Determination of the Slurry Rheological Properties. Rheological properties of slurries were determined using an Anton Paar Reolab QC rotational rheometer. The rotational rheometer is a coaxial-cylinder rheometer with a center rotor rotating at a defined speed or torque. A six-blade vane spinner with 1 in. outside diameter was used as the rotor. The reason for employing a vane spinner as the rotor is that the vane-cup system causes much less error when testing large particles, has less impact on the slurry structure, and therefore, offers more consistent results.[13]

Pump selection for handling slurries for industry applications is based on rheological data that are obtained from slurry rheology tests. The crucial parameters for pump selection are shear stress at certain shear rates, viscosity of the slurry, yield point, and settlement rate of the slurry. Other physical properties, such as attrition and the friction of particles inside the slurry, may also need to be considered for pump selection. The shear rate and shear stress curve of coal—water and biomass—water slurry coordinates can be characterized by the generalized Bingham plastic model,[14] as shown in eq 1, where τ is shear stress applied to the system when the shear rate of γ is maintained. τ_y is the yield stress of the starting slurry. K and n are empirical parameters determined by fitting the equation with experimental data. The correlation between shear rate and shear stress corresponds to a power law with a constant coefficient of K. Thus, the viscosity of the slurry is defined as the slope of change in the shear rate with a change in shear stress, as given by eq 2. A change in viscosity can be obtained by either shear thinning or shear thickening. In a shear thinning flow, the viscosity decreases with an increasing shear rate, while in a shear thickening flow, viscosity increases with increasing shear rate.

$$\tau = \tau_y + K\gamma^n \tag{1}$$

$$\mu = \frac{\Delta\tau}{\Delta\gamma} \tag{2}$$

3. Results and Discussion

3.1. Effect of the Shear Rate on Viscosity. The effect of an increase in the shear rate on slurry viscosity was evaluated for different particle sizes and solid loading for both coal—water and biomass—water slurries. The relationship between shear rate and viscosity was obtained, and the results are shown in Figures 1 and 2, respectively. The solid loading in the coal—water and biomass—water slurries was fixed at 60 and 10 wt %, respectively.

Non-Newtonian shear thinning property was observed for both coal—water and biomass—water slurries. The viscosity of the coal—water slurries, shown in Figure 1, decreased rapidly with an increased shear rate of up to 200 s^{-1} but then reduced at a slower rate beyond 200 s^{-1}. Also, larger particle sizes had lower slurry viscosity. A similar trend was observed

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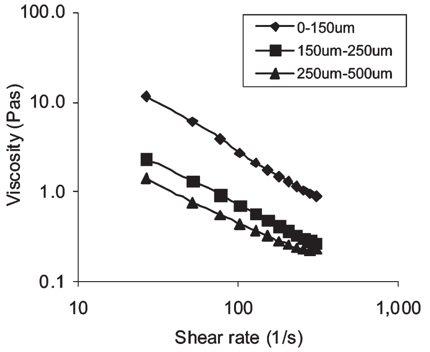

Figure 1. Effect of the particle size on the shear rate to viscosity profile in coal−water slurries (solid loading of 60 wt %).

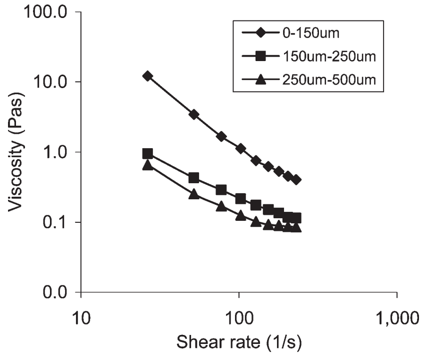

Figure 2. Effect of the particle size on the shear rate to viscosity profile in biomass−water slurries (solid loading of 10 wt %).

in biomass−water slurry tests, as seen in Figure 2. The viscosity of biomass−water slurries decreased rapidly with increased shear rates of up to 100 s^{-1} but decreased at a slower rate beyond 100 s^{-1}. The viscosity decreased with an increasing particle size, similar to that observed for the coal−water slurries. Fine particles give rise to their population and hence the interparticle interaction, which resulted in an increase of viscosity.[15] A comparison of these two figures shows that much higher shear thinning properties were observed for biomass−water slurries. Possible reasons may be that water is highly bonded with biomass particles because of the hydroscopic and hydrophilic nature of biomass and much more force is required to deform the biomass slurry. While on the other hand, bituminous and anthracitic coals have rather hydrophobic properties and the particles are more stable and can be more concentrated in comparison to lignite biomass slurries.[16]

3.2. Effect of the Solid Content. The maximum solid loading in coal−water and biomass−water slurries varied for different particle sizes. When the maximum solid loading was exceeded, the mixture was not uniform because small particles bound together to form larger particles and water was swelled and trapped inside the formed large particles. Table 2 shows the maximum solid loading for coal−water and biomass−water slurries.

Table 2. Maximum Solid Loading in Biomass−Water and Coal−Water Slurries

	maximum biomass loading in slurry (wt %)	maximum coal loading in slurry (wt %)
0−150 μm	13	65
150−250 μm	13.5	66.5
250−500 μm	15	68

It can be seen from Figure 3 that the coal−water slurries changed from a shear thinning property to a shear thickening property as the coal-loading decreased from 50 to 45 wt %. The shear thickening property of coal−water slurry was rarely observed by other studies. Majumder et al.[17] reported that the reason for the shear thickening behavior was due to the emulsion solids exhibiting dilatants flow behavior with a low solid loading range. It is also seen that the viscosity of coal−water slurries increased with increasing solid loading. There was not much difference between slurries with solid loading of less than 55 wt % for shear rates over 150 s^{-1}. Similar to the coal−water slurries, the viscosity of biomass−water slurries also increased with increasing solid loading. However, at a shear rate over 100 s^{-1}, Newtonian fluid properties were observed at solid loading less than 7.5 wt % and the viscosity increased slightly with increasing shear rate, as shown in Figure 4.

Experimental results for different solid loading on coal−water and biomass−water slurries are shown in Figures 3 and 4, respectively.

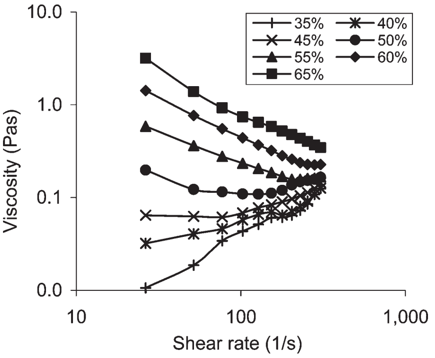

Figure 3. Effect of the solid loading on the shear rate to viscosity profile in coal−water slurries (particle size of 250−500 μm).

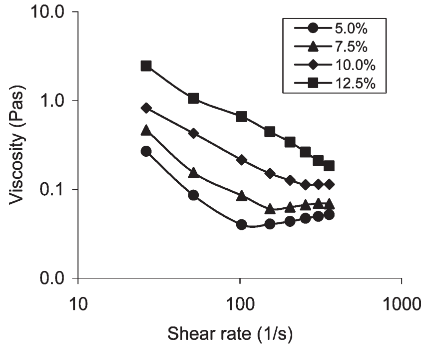

Figure 4. Effect of the solid loading on the shear rate to viscosity profile in biomass−water slurries (particle size of 0−150 μm).

3.3. Rheological Properties of Pretreated Biomass−Water and Comingled Biomass and Coal Slurries. The effect of the

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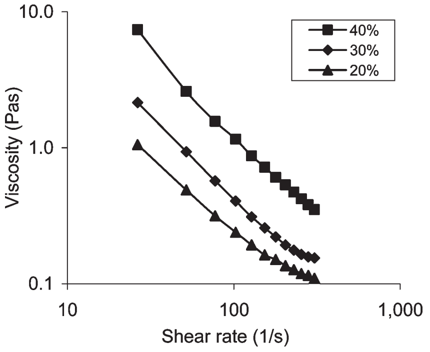

Figure 5. Shear rate to viscosity profile of the pretreated biomass–water slurry with a solid loading range from 20 to 40 wt %.

shear rate on viscosity in the pretreated biomass–water slurry was also evaluated. Figure 5 shows the shear rate to viscosity profile of pretreated biomass slurries with solid loading of 20, 30, and 40 wt %. Unlike the biomass–water slurry before pretreatment, the viscosity profile of pretreated biomass–water slurry dropped rapidly as the shear rate increased from 10 to 200 s^{-1} and then decreased slightly beyond 200 s^{-1}. The viscosity increased with increasing solid loading, which is consistent with a biomass–water slurry before pretreatment. The important result is that with pretreatment there is an increase in the solid loading of a biomass–water slurry to 40 wt % as compared to 12.5 wt % before pretreatment. It is believed that the treatment in the presence of hydrogen under 230 °C and 690 kPa help break down the cellulose and hemicellulose structure of biomass, which resulted in breaking the hydrogen bond between the biomass and water. However, no analytical experiments were performed to confirm this but will be performed in the future.

Figure 6 shows the comparison of viscosity of slurries at increasing solid loading. It is obvious that the pretreatment process greatly helped increase the solid content in the biomass–water slurry at a similar viscosity. The coal–water slurry had the higher solid content at the same viscosity, followed by comingled biomass and coal slurry. The pretreated biomass–water slurry had significantly higher solid content at the same viscosity than the biomass–water mixture without pretreatment. A total of 20 wt % of pretreated biomass comingled with 35 wt % of coal produces a biomass and coal slurry with solid loading of 55 wt %.

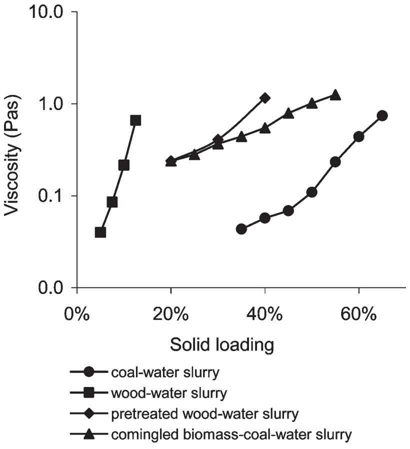

Figure 6. Comparison of viscosity of slurries at increasing solid loading (shear rate of 102 s^{-1}).

Table 3. Mass-Based Water/Carbon Ratio of Slurries (under 0.7 Pa·s)

	coal–water slurry	biomass–water slurry	pretreated biomass–water slurry	comingled biomass and coal slurry
ratio	0.78	13.82	3.67	2.01

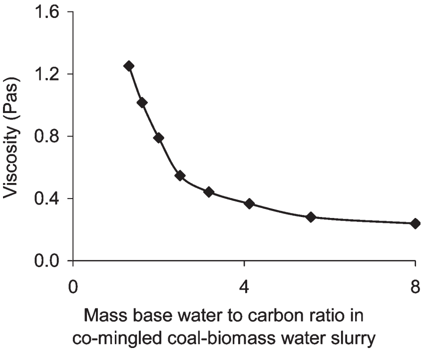

Figure 7. Viscosity of comingled biomass and coal slurries with different water/carbon ratios.

3.4. Solid Loading of Pumpable Slurries. An earlier study suggested that the maximum viscosity of a pumpable slurry is 1.0 Pa·s.[18] Thus, a viscosity of less than 0.7 Pa·s was set for safely pumping slurries into a pressurized gasification reactor. The solid loading in the biomass–water slurry was successfully increased using the pretreatment method while maintaining the same viscosity. The solid loading of pretreated biomass–water slurry under 0.7 Pa·s was less than 35 wt %. The pretreated biomass–water slurry was further comingled with coal to increase its solid loading and carbon content. The results of the change of viscosity with increased solid loading of coal–water, biomass–water, pretreated biomass–water, and comingled biomass and coal slurries are shown in Figure 6. It is shown that, at 0.7 Pa·s viscosity, the coal–water slurry had the highest solid loading of up to 65 wt % and biomass–water slurry before pretreatment had the lowest solid loading of less than 12.5 wt %. After pretreatment, the solid loading in the biomass–water slurry of 0.7 Pa·s increased to nearly 35 wt %, and when comingled with coal, the solid loading increased to nearly 45 wt %. Closer investigation of the water/carbon ratio of these slurries further suggested that the comingled biomass and coal slurry provided a water/carbon ratio of 2:1. The optimized water/carbon ratio is 3:1 when using our gasification process. Thus, with pretreatment, the rheological properties of the comingled biomass and coal slurry are improved for use as a feedstock for gasification. Table 3 shows the results of a mass-based water/carbon ratio of different slurries at a viscosity of 0.7 Pa·s.

The viscosity plot of different water/carbon ratios in comingled biomass and coal slurry is shown in Figure 7. Under the optimized water/carbon feed ratio of 3:1 preferred in our gasification process, slurry viscosity is less than 0.45 Pa·s and offers good pumpability.

4. Conclusion

A rheological study of coal–water, biomass–water, and comingled biomass and coal slurries has been performed.

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Results showed non-Newtonian properties of slurries and shear thinning behavior for most cases, except the coal–water slurries with a solid content below 45 wt %. A comparison of the viscosity of slurries under a shear rate of 100 s^{-1} shows that solid loading of biomass–water and comingled biomass and coal slurries increased after pretreatment for the same viscosity values. The important result is that pretreatment of the comingled biomass and coal slurries provided a pumpable slurry with a solid carbon content for optimum feed to the steam hydrogasification process.

Acknowledgment. The authors thank the W. Ruel Johnson Endowment, Viresco Energy, LLC, and the City of Riverside, CA, for funding support.