

Rheological modification of corn stover biomass at high solids concentrations

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Synopsis

Additives were tested for their ability to modify the rheology of lignocellulosic biomass. Additive types included water-soluble polymers (WSPs), surfactants, and fine particles. WSPs were the most effective rheological modifiers, reducing yield stresses of concentrated biomass by 60–80% for additive concentrations of 1–2 wt. % (based on mass of dry biomass solids). Yield stress and plastic viscosity of rheologically modified biomass depended on WSP molecular weight and degree of substitution. The apparent shear stress-shear rate data are represented with the Bingham model. In the absence of WSP, the biomass exhibited a positive yield stress and a negative plastic viscosity, which suggests a nonmonotonic dependence of shear stress on shear rate. When WSP was added, the yield stress decreased and the plastic viscosity increased, becoming positive for sufficiently large WSP concentrations. © 2012 The Society of Rheology. [<http://dx.doi.org/10.1122/1.3702101>]

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I. INTRODUCTION

Liquid fuels derived from lignocellulosic biomass provide renewable energy that has the potential to lessen global demand for petroleum-derived fuels. The National Renewable Energy Laboratory (NREL) has described a process for enzymatic conversion of lignocellulosic biomass to ethanol [Aden *et al.* (2002)]. There are also other viable chemical routes for the catalytic conversion of biomass to transportation fuels [Huber *et al.* (2005); Bond *et al.* (2010)]. These processes must compete economically with less expensive grain-derived ethanol and relatively low cost, petroleum-derived fuels. After the cost of biomass itself, the next most expensive step of the NREL process involves the pretreatment of biomass and water slurry. Much of the pretreatment cost is associated with utilities required to heat and cool biomass streams. Reducing water concentration lowers these utility costs in separation operations because of increased product concentrations. Removing water also reduces capital costs [Wyman (2007)] by allowing for smaller processing equipment.

Increasing the solids content, however, creates problems. Above a few weight percent solids, biomass slurries exhibit yield stresses. The yield stress increases rapidly with solids concentration and results in significant processing challenges. For example, mixing above 20 wt. % solids is very difficult due to high yield stresses and above 15–20 wt. % insoluble solids, inefficient heat and mass transfer make both the dilute-acid hydrolysis and enzymatic hydrolysis operations challenging [Carrasco and Roy (1992); Hodge *et al.* (2008); Viamajala *et al.* (2010)].

Lignocellulosic biomass is a complex, multicomponent suspension of solid fibers, but much of the flow behavior can be understood from work done on simple fiber suspensions. For suspensions of wood and synthetic fibers, yield stresses have been related to suspension mass concentration by

$$\tau_o = aC_m^b, \quad (1)$$

where τ_o is the yield stress, C_m is the mass fraction of insoluble solids, and a and b are empirical parameters [Kerekes (1985); Bennington *et al.* (1990); Dalpke and Kerekes (2005)]. The empirical parameters in Eq. (1), and thus the rheology of the suspension, depend on such properties as particle size distribution, particle aspect ratio and fiber flexibility [Bennington *et al.* (1990); Dalpke and Kerekes (2005)]. Values for b range from 2.3 to 6 and depend on the type of lignocellulosic biomass (e.g., wood pulp, corn stover, and acid hydrolyzed corn stover) [Bennington *et al.* (1990); Knutsen and Liberatore (2009); Derakhshandeh *et al.* (2010); Ehrhardt *et al.* (2010)]. In the processing of biomass, yield stress is a critical rheological property since mixing, pumping, and other processes must be designed to overcome this stress. Thus, efforts to understand the rheology of biomass have focused primarily on yield stress and the factors that affect it.

The solids content of lignocellulosic biomass may in principle be quantified by a variety of measures such as the mass fraction, volume fraction, or particle number density. However, the particles often contain hollow cores which can vary from one anatomical feature to another, e.g., leaf vs stalk fibers, which makes measuring or calculating the volume fraction challenging. The particle size distributions are often quite broad and challenging to measure precisely, which makes estimating the number density challenging. We, therefore, chose to represent solids content with the more easily measured mass fraction.

Measuring the yield stress and other rheological properties can be challenging because of a variety of complicating features including large particle sizes, wall slip, large normal stresses, and ejection. The advantages and disadvantages of a number of rheometric techniques used to obtain rheological data for acid-hydrolyzed corn stover were reported by

[Knutsen and Liberatore \(2009\)](#). The authors used squeeze flows as well as torsional flows in a parallel-disk geometry to study the rheology of acid-hydrolyzed corn stover. Transient flow, stress ramps, creep flow, and oscillatory shear were studied using a vane rheometer. The most successful yield stress measurements were obtained using a vane geometry, but above a solids concentration of 25 wt. % the normal force required to insert the vane into the cup exceeded device limits. Thus, vane data were limited to samples containing less than 25 wt. % solids. An alternate technique capable of obtaining rheometric data for highly concentrated biomass slurries is torque rheometry [[Ehrhardt *et al.* \(2010\)](#); [Samaniuk *et al.* \(2011\)](#)]. Torque rheometry has been used to determine the processability of a range of materials including foods and plastics [[Blyler and Daane \(1967\)](#); [Goodrich and Porter \(1967\)](#)]. In a joint study, the rheological properties of acid-hydrolyzed corn stover were examined using a variety of techniques [[Stickel *et al.* \(2009\)](#)]. Yield stress data obtained using a torque rheometer in our laboratory agreed well with data obtained using other instruments. In addition, the torque rheometer allowed measurement of yield stresses at solids concentrations higher than those accessible via other methods.

The rheology of fiber suspensions can be altered by additives. In the pulp and paper industry, water-soluble polymers (WSPs) such as carboxymethyl cellulose (CMC) and polyethylene oxide (PEO) have been used as adhesives, viscosity modifiers and flocculents [[Batdorf and Rossman \(1973\)](#)]. A large amount of research have been done to determine how these additives improve processability [[Kerekes \(2006\)](#)]. [Zauscher and Klingenberg \(2001\)](#) used colloidal probe microscopy to show that WSPs such as CMC reduce friction between cellulose surfaces. Simulations have shown that reducing friction between fibers in a suspension results in lower suspension viscosity [[Switzer and Klingenberg \(2003\)](#)]. [Zauscher *et al.* \(2000\)](#) were able to extrude a recycled waste paper at 45 wt. % solids with the addition of CMC. [Knutsen and Liberatore \(2010\)](#) examined the effects of a variety of additives, including surfactants and WSPs, on the yield stress and the rate of enzymatic hydrolysis of acid-hydrolyzed corn stover. They found CMC increased the yield stress of this type of biomass, while certain surfactants were able to reduce the yield stress. The authors also show that the rheological modifiers can generate additional economic incentive when they enhance the rate of saccharification during the enzymatic hydrolysis unit operation. In this article, we report different trends for nonhydrolyzed biomass.

Recent research efforts on the rheology of biomass have focused on acid-hydrolyzed corn stover in the hopes of improving process economics during the relatively expensive dilute-acid prehydrolysis and enzymatic-hydrolysis unit operations. New chemical conversion process routes [[Bond *et al.* \(2010\)](#)] will require more attention to the rheology of upstream process feeds like untreated corn stover. Currently, there are few studies on the rheology of untreated lignocellulosics. In this report, we describe the effects of additives on the rheological properties of untreated, i.e., nonhydrolyzed, corn stover. In the absence of additives, untreated corn stover at high solids concentration behaves as a Bingham fluid with a negative plastic viscosity. We show that for this type of material, WSPs like CMC can dramatically reduce the yield stress, whereas surfactants have little impact at similar concentrations. Additives such as CMC also increase the plastic viscosity, making it positive for sufficiently large additive concentrations.

II. MATERIALS AND METHODS

A. Biomass

The lignocellulosic biomass used in this study was baled corn stover obtained from the Arlington Research Station at the University of Wisconsin-Madison. Before rheological

measurements, the corn stover was hammermilled, washed by mixing approximately 1 kg dry biomass in 100 l of water, and then bladder-pressed to an insoluble solids concentration of 30 wt. %. Soluble solids concentration was estimated by measuring the difference in dry solid mass before and after washing 200 g samples of bladder-pressed corn stover in a Buchner filter with 20 l of reverse osmosis (RO) water. Three such measurements resulted in a fraction of soluble solids of 0 wt. % within the uncertainty of the solid mass measurements. Unless otherwise stated, all rheological measurements were made with corn stover at an insoluble solids concentration of 25 wt. %, obtained by addition of the appropriate amount of RO water. The *pH* of all experiments was 5.5 and was measured with *pH* paper with a precision of 0.5. From visual inspection, hammermilled corn stover [see Fig. 1(a)] contained particles which ranged in size from a fraction of a millimeter to several centimeters.

B. Rheological modifiers

Additives examined included polymers, surfactants, and particles, which are listed in Table I. All of the additives were powders except for liquid polysorbate 80. Additives were used as received from the manufacturer.

C. Torque rheometer

The torque rheometer consists of a stainless steel mixing chamber with two equally sized cylindrical chambers (each approximately 50 ml) where chrome-plated steel impellers are rotated to impose shear. A schematic diagram of the torque rheometer used here is shown in Fig. 2. The left impeller rotates at the input shaft rotation rate, Ω , while the other rotates in the opposite direction at $2\Omega/3$. As the impellers are rotated, biomass can pass from one side to the other. The temperature of the biomass in the mixing chamber is controlled by flowing water through a channel around the chamber. Both water temperature and chamber internal temperature are measured using thermocouples, with the internal chamber thermocouple enclosed in a thermowell inserted into the top of the chamber. Total shaft torque, Γ , is measured with a magnetoelastic sleeve torque transducer connected to the motor shaft and is recorded at 5 Hz. Additional details about the torque rheometer and data analysis methods used here can be found elsewhere [Monz (2007); Ehrhardt (2008); Ehrhardt *et al.* (2010); Samaniuk *et al.* (2011)].

Calibration of the rheometer was accomplished using the procedure developed by Goodrich and Porter (1967). The torque rheometer is modeled as two sets of concentric cylinders. The objective of the calibration procedure is to obtain a value for the effective inner radius of the idealized geometry, R_i . The outer radius, R_o , is equated with the actual

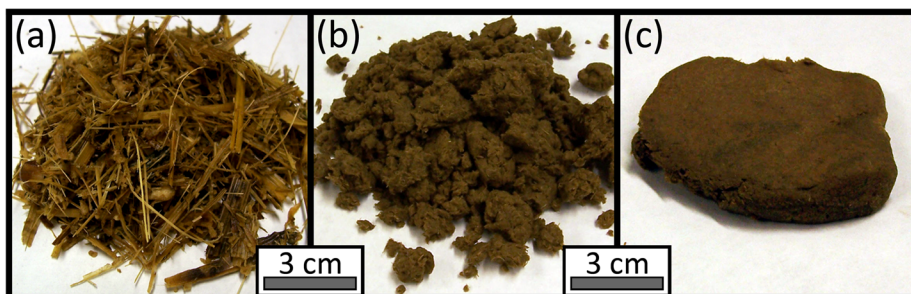


FIG. 1. Hammermilled corn stover at 25 wt. % solids concentration (a) before being run in a torque rheometer, (b) after the loading and no additive phase (corresponding to 3400 s in Fig. 3) and (c) after WSP addition.

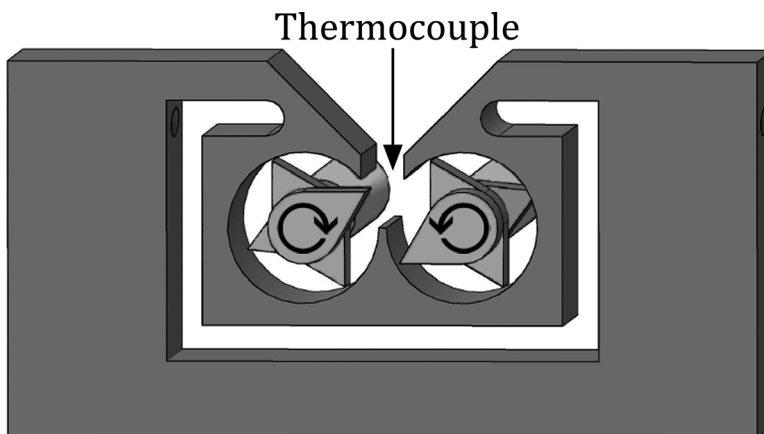
TABLE I. Relevant information about the additives used in this study.

Compound	Commercial name	MW (kDa)	DS	Supplier
CMC	Aqualon 7H4F	700	0.7	Ashland, Inc.
	Aqualon 7MF	250	0.7	
	Aqualon 9M8F	250	0.9	
	Aqualon 12M8F	250	1.2	
PEO	Polyox	8	—	Dow Chemical
		600		
		2000		
		7000		
Guar gum	—	200	—	Aldrich Chemical Company
Xanthan gum	—	15 000	—	
HPMC	Methocel 240	180	Unknown	Dow Chemical
PAM	—	8	—	Polysciences, Inc.
		6000		
Potato starch	Penplus 2000	—	—	Penford Food Ingredients Company
Carboxymethyl starch (CMS)	—	*	Unknown	Multi-Kem Corporation
Polysorbate 80	Tween 80	1.3	—	Fischer
MCC	Avicel	—	—	FMC Corporation

Note: “*” Signifies potato starch MW and carboxymethyl starch MW are unknown—product was used as received from the manufacturer.

radius of the chambers. The effective inner radius is determined by equating the torque measured for a Newtonian fluid of known viscosity with the torque predicted from the solution of the Navier–Stokes equation for the two cylinders. Although non-Newtonian fluids can be used in this calibration procedure, [Bousmina *et al.* \(1999\)](#) showed that R_i is independent of the nature of the fluid.

Once the effective inner radius is determined for a Newtonian reference fluid, there are several ways in which torque-rotation rate data for non-Newtonian fluids may be represented or analyzed. An apparent shear stress, τ , and an apparent shear rate, $\dot{\gamma}$, can be

**FIG. 2.** Schematic diagram of a torque rheometer.

calculated for the faster (left) impeller in a torque rheometer with a 3:2 drive-to-driven gear ratio using

$$\tau = \frac{9}{13} \frac{\Gamma}{2\pi R_a^2 h}, \quad (2)$$

$$\dot{\gamma} = \frac{2R_i R_o \Omega}{\left(\frac{1}{\kappa} - \kappa\right) R_a^2}, \quad (3)$$

where $R_a \equiv (R_i + R_o)/2$ is the midpoint radius, h is the impeller depth, $\kappa \equiv R_i/R_o$, Ω is the input shaft rotation rate, and Γ is the total shaft torque. Evaluation of the apparent shear stress and shear rate at the midpoint radius, R_a , follows [Bousmina *et al.* \(1999\)](#) and is consistent with transformations employed in software for commercial rheometers [[Bohlin VOR Users Manual \(1991\)](#)].

Extraction of rheological parameters such as yield stress and plastic viscosity can be accomplished by fitting torque-rotation rate data with a constitutive model. For example, the Bingham model can be applied to the concentric cylinders of the model torque rheometer geometry. The Bingham model may be written as

$$\tau_{\text{loc}} = \tau_o + \eta_{pl} \dot{\gamma}_{\text{loc}}, \quad (4)$$

where τ_{loc} is the local shear stress, $\dot{\gamma}_{\text{loc}}$ is the local shear rate, τ_o is the yield stress, and η_{pl} is the plastic viscosity. Shaft torque from the left concentric cylinder, Γ_1 , and right concentric cylinder, Γ_2 , are related by conservation of energy, $\Gamma\Omega = \Gamma_1\Omega + \Gamma_2\Omega_2$, and the rotation rate of the right shaft (Ω_2) is related to that of the left by $\Omega_2 = 2\Omega/3$. The total shaft torque is then

$$\Gamma = \Gamma_1 + \frac{2}{3}\Gamma_2, \quad (5)$$

where the relationship between torque and rotation rate in each set of concentric cylinders ($k = 1, 2$) is

$$\Gamma_k = 4\pi R_i^2 h \left[\frac{\Omega_k + \frac{\tau_o}{\eta_{pl}} \ln\left(\frac{r_o}{R_i}\right)}{1 - \frac{R_i^2}{r_o^2}} \right], \quad (6)$$

where r_o is the location where fluid velocity approaches zero. For Bingham fluids, $R_i < r_o < R_o$ for certain rotation rates, and r_o can have a different value in each set of concentric cylinders. At high rotation rates, r_o approaches R_o , and at low rotation rates, r_o approaches R_i . In the regime where r_o is between R_i and R_o , r_o can be found by combining Eq. (6) with $\Gamma_k = 2\pi r_o^2 h \tau_o$, which gives

$$\left(\frac{r_o}{R_i}\right)^2 - 1 = \frac{2\eta_{pl}\Omega_k}{\tau_o} + \ln\left[\left(\frac{r_o}{R_i}\right)^2\right]. \quad (7)$$

The Bingham parameters, τ_o and η_{pl} , are thus determined by fitting Eq. (5) to the measured torque-rotation rate data, where the individual shaft torques are given by Eq. (6), and r_o is given by Eq. (7) [[Monz \(2007\)](#); [Ehrhardt \(2008\)](#); [Ehrhardt *et al.* \(2010\)](#)].

For some conditions, the measured torque decreases with increasing rotation rate. If the data are represented by a Bingham model, this implies that the plastic viscosity is

negative. For these situations, a yield stress is obtained by first linearly extrapolating the torque-rotation rate data to zero rotation rate to obtain the “yield torque,” Γ_o . The yield stress is then obtained by noting that the torque on each impeller at zero rotation rate will be $2\pi R_i^2 h \tau_o$. Equation (5) for the total torque can then be rearranged to give

$$\tau_o = \frac{3}{10} \frac{\Gamma_o}{\pi R_i^2 h}. \quad (8)$$

D. Rheological measurement procedure

Before obtaining rheological measurements with the torque rheometer, the impellers are removed and cleaned. Teflon O-rings are installed on the base of the impeller shafts and a Teflon shim is placed behind the chamber housing to prevent water leakage from the mixing chamber. The O-rings are conditioned by operating the rheometer empty at 55, 110, and 220 rpm for 60 s at each speed. The baseline torque is measured while operating the empty rheometer at 55 rpm for 60 s and is subtracted from the raw data to obtain the net torque transmitted to the sample.

Torque rheometry with biomass can alter particle size distribution as illustrated in Fig. 1. Figure 1(a) is a photograph of hammermilled corn stover before being loaded into the torque rheometer, and Fig. 1(b) is a photograph of hammermilled corn stover after it has been mixed in a torque rheometer for 3400 s. It is apparent from a comparison of the images that the mean particle size has been reduced by the torque rheometer operation. Consequently, the procedure employed to measure the rheological properties of biomass with different conditions and modifiers must be followed precisely to control for expected mechanical damage and particle size changes during measurements. The procedure followed for particle size measurements is described in Sec. II E; and the quantitative results from those measurements are discussed in Sec. III C. The procedure we employed for measuring rheological properties and the effects of rheological modifiers using the torque rheometer consists of several steps, as illustrated in Fig. 3, where the torque and rotation rate are plotted as functions of time for a corn stover sample at 25 wt. % solids. All experiments described here were done at 35 °C. This temperature was chosen

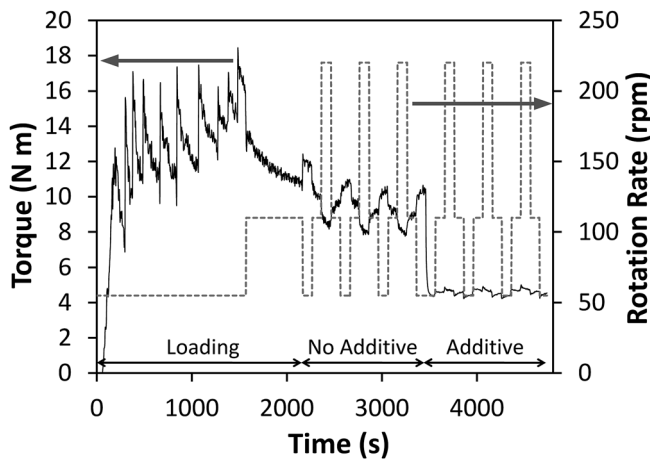


FIG. 3. Torque rheometer data illustrating a typical experiment to obtain rheological parameters from both unmodified and rheologically modified biomass. The solid curve is the measured torque, Γ , and the dashed curve is the input shaft rotation rate, Ω . The biomass is hammermilled corn stover at 25 wt. % solids.

because daily fluctuations in the temperature of the cool-water stream in the torque rheometer occasionally resulted in a minimum controllable temperature between 25 °C and 30 °C. Beginning at 0 s, 105 g of hammermilled corn stover was added in stages to the rheometer chamber while maintaining a rotation rate of 55 rpm. Approximately 10 g of stover was added every 2 min during the loading phase to prevent overloading the torque transducer. Once fully loaded (after 1500 s in Fig. 3), the rotation rate was increased to 110 rpm for 600 s, which concluded the loading phase of the experiment. In the “no additive” phase, the rotation rate was held for 100 s at each of 55, 110, 220, 110, and then 55 rpm. Three such cycles were performed in all experiments, which were sufficient to obtain torque measurements that no longer varied with time.

Rheological modifier was added at the end of the no additive phase (at 3400 s in Fig. 3) by pouring the liquid or powder into the chamber. The torque was then measured for three additional rotation-rate cycles. The torque-rotation rate data from the final rotation-rate cycle for both the “no additive” and “additive” stages were fit with the Bingham model as described above.

E. Particle size measurements

Particle size distributions were measured using a Bauer-McNett screen classifier. Material flows down a cascade of increasingly finer screens (16, 28, 48, 100, and 200 meshes) in order to separate particles into size fractions. Each fraction was dried and weighed to determine the particle size distribution. Hammermilled corn stover, such as that shown in Fig. 1(a), typically contains numerous particles with length greater than 1 cm, which are much too large to be effectively analyzed using this technique. However, after running the samples in the torque rheometer using the procedure described above, the particle sizes were sufficiently reduced [as illustrated in Figs. 1(b) and 1(c)] such that particle size distributions could be measured with the Bauer-McNett classifier. All particle size distributions were measured after running biomass through a TAPPI T 205 sp-95 compliant standard pulp disintegrator [TAPPI (2006)] for 60 s to break up any fiber aggregates that may have formed. All measurements were performed using 10 g of dry biomass. Particles smaller than 90 μm were not retained by the finest screen (200 mesh) and were lost.

III. RESULTS AND DISCUSSION

A. Effects of WSP properties

The yield stress of 25 wt. % insoluble-solids corn stover is plotted as a function of added polymer concentration in Fig. 4 for three different WSPs: polyacrylamide (PAM), PEO, and CMC. The biomass prior to WSP addition exhibited a yield stress of 55 kPa with a standard deviation of 4 kPa based on six replicate runs. The yield stress decreased with increasing WSP concentration for all WSPs. However, the yield stress decreased more slowly with increasing WSP concentration. For example, adding 2 wt. % CMC decreased the yield stress by 67% (from 55 to 18 kPa), while an additional 2 wt. % CMC (4 wt. % total) decreased the yield stress a total of 75% (to 14 kPa). In all cases, the yield stress asymptotically approaches a lower limit value which depends on the type of WSP and represents a substantial decrease of the yield stress of the biomass. If one was interested in small yield stress changes that might occur at polymer concentrations less than 2 wt. %, more data in this regime are required.

The yield stress of 25 wt. % corn stover is plotted as a function of added PEO concentration for several different PEO molecular weights in Fig. 5. The yield stress decreases

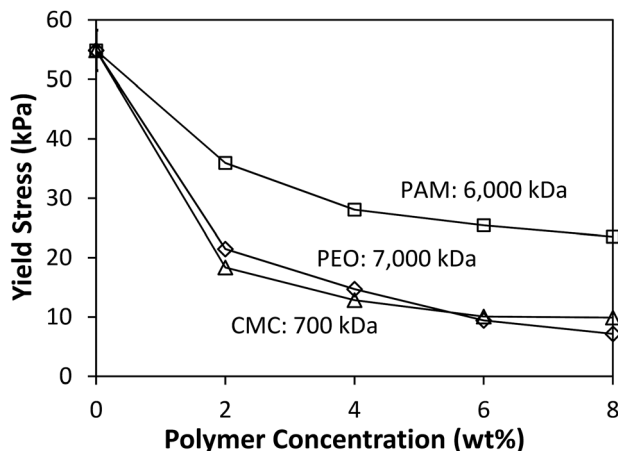


FIG. 4. Yield stress of hammermilled corn stover at 25 wt. % solids as a function of WSP concentration and WSP type.

monotonically with increasing molecular weight, becoming independent of molecular weight for large values. Similar trends were also observed for CMC and PAM. [Knutsen and Liberatore \(2010\)](#) reported that for a PEO molecular weight of 4 kDa, which is smaller than those represented in Fig. 5, a relatively large PEO concentration of 10 wt. % (based on the dry biomass weight) was required to achieve only a modest 16% decrease in the yield stress of 20 wt. % dilute-acid hydrolyzed corn stover. This is consistent with the results in Fig. 5 where the largest decreases in yield stress for small additive concentrations are achieved with large WSP molecular weights.

CMC is a derivative of cellulose where some hydroxyl groups have been replaced with carboxylic acid groups [[Batdorf and Rossman \(1973\)](#)]. The degree of substitution (DS) of CMC is the average number of hydroxyl groups that have been replaced per glucose repeat unit ($0 < DS < 3$). In Fig. 6, the yield stress of 25 wt. % corn stover samples is plotted as a function of DS for three addition levels of CMC. Increasing the DS of CMC made the polymer less effective at decreasing yield stress.

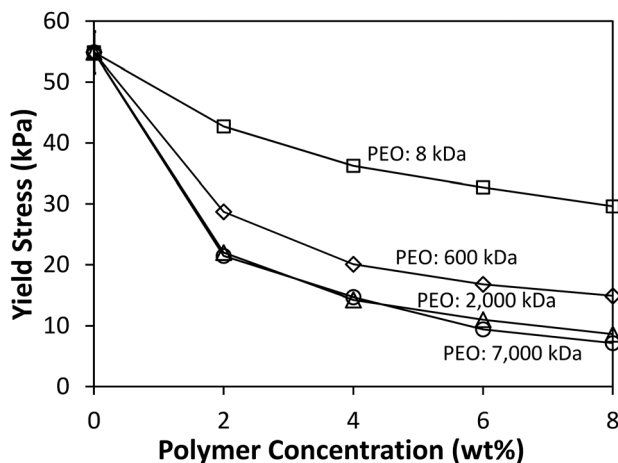


FIG. 5. Yield stress of hammermilled corn stover at 25 wt. % solids as a function of the concentration and the molecular weight of PEO.

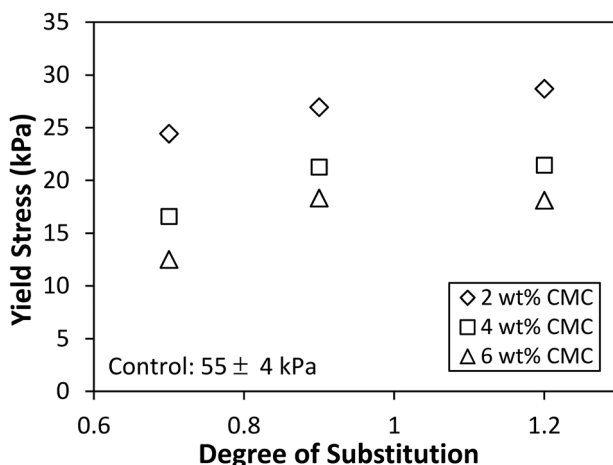


FIG. 6. Yield stress of hammermilled corn stover at 25 wt. % solids as a function of the DS for three addition levels of CMC (250 kDa). The yield stress of the corn stover with no WSP is 55 ± 4 kPa.

The observed trends in yield stress with WSP addition are consistent with the theory that WSPs reduce network strength in fiber suspensions by reducing friction between fibers [Zauscher and Klingenberg (2001); Switzer and Klingenberg (2003)]. The lower limit of yield stress observed in Fig. 4 is consistent with the theory that WSP chains adsorb to fiber surfaces, since a maximum level of interfiber friction reduction is expected as fiber surface area becomes saturated with WSP. The reason for the molecular weight trend observed in Fig. 5 is unknown, but low molecular weight WSPs hydrate more readily than high molecular weight WSPs [Wang *et al.* (2003)] and may, as a consequence, have less affinity for fiber surfaces. Increasing the DS of CMC is expected to decrease the affinity of WSPs for fiber surfaces. Thus, the results in Fig. 6 are also consistent with the theory that WSPs reduce friction in networked fiber suspensions.

The changes reported here to biomass yield stress with the addition of CMC differ significantly from those reported by Knutsen and Liberatore (2010). They found an increase in yield stress with the addition of CMC, while our results show a decrease. The different results might be attributed to the differing ways that CMC adsorbs on the hydrolyzed corn stover they used vs the nonhydrolyzed corn stover used here. All experiments in this study were carried out at a pH of 5.5, so it is also plausible that the low pH of their hydrolyzed corn stover may have a significant impact on the rheological-modifying abilities of CMC. Above a pH of approximately 4, CMC is deprotonated. Below a pH of approximately 4, the free-acid form of CMC predominates and below a pH of 2, CMC becomes unstable in solution and precipitates [Hercules (1999)]. We, indeed, have found that rheology modification with CMC behaves differently with acid hydrolyzed corn stover than with nonhydrolyzed corn stover. Those results will be described in more detail in a future publication on the dependence of rheological modification on biomass type. Although our results for CMC differ from those reported by Knutsen and Liberatore, the results for PEO and polysorbate 80 are in agreement.

B. Negative plastic viscosity

In most experiments with untreated corn stover, the apparent shear stress decreased with increasing shear rate. In Fig. 7, apparent shear stress is plotted as a function of apparent shear rate for 20 wt. % corn stover with 0, 1, and 2 wt. % CMC added. The solid

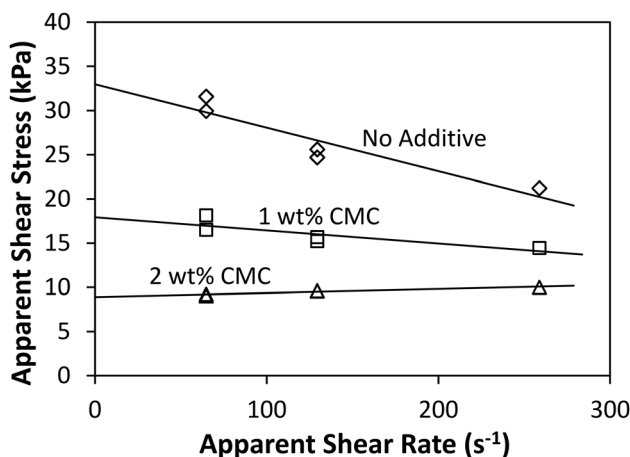


FIG. 7. Apparent shear stress as a function of apparent shear rate for corn stover at 20 wt. % solids. The CMC is high molecular weight (700 kDa).

lines in Fig. 7 are linear fits of data. This negative slope (negative plastic viscosity) is reproducible (and is also exhibited in Fig. 3 between 2100 and 3400 s). The negative plastic viscosity suggests a nonmonotonic shear stress-shear rate relationship, as we expect the shear stress to increase with shear rate at sufficiently large shear rates. The stress may also decrease to zero as the shear rate approaches zero, i.e., below shear rates accessible with the torque rheometer, if the materials are pseudoplastic rather than true yield stress fluids. Figure 7 shows that the addition of 1 wt. % CMC decreases the yield stress, as expected, while increasing the plastic viscosity. With a second addition of CMC, 2 wt. % total, the yield stress decreases further and the plastic viscosity increases to a positive value. Similar behavior was observed when CMC was replaced with PAM or PEO.

The linear fits to the data in Fig. 7 should not be construed as meaningful representations of the rheological behavior of these materials. The linear fits are used here only to estimate the yield stress and to quantify the negative slope averaged over this range of deformation rates. As illustrated by the data for the material with no polymer, the actual behavior over this range of deformation rates appears to be nonlinear. Furthermore, if nonmonotonic behavior is observed as anticipated for rates beyond this range, a more complicated constitutive model will be required. Choosing the appropriate model will have to wait until more data are obtained.

The source of the nonmonotonic behavior is not understood but may be related to the observation that untreated biomass becomes reversibly heterogeneous during deformation. At low shear rates, the solids concentration varies from one location to another, while interstitial fluid reversibly migrates throughout the sample. At higher shear rates, the spatial variations in solids concentration are less apparent. For all shear rates, the biomass deforms throughout the visible volume, i.e., there are no stagnant regions observed. Because stresses in fiber networks increase more rapidly than linearly in concentration [Bennington *et al.* (1990); Carrasco and Roy (1992); Dalpke and Kerekes (2005)], the more heterogeneous systems observed at lower deformation rates are capable of transmitting larger stresses. When WSP was added, spatial variations of solids concentration were no longer visible at any rotation speed, and the stress was observed to increase with increasing speed, e.g., 2 wt. % CMC data in Fig. 7. In the future, a quantitative analysis of local concentration variations within the flow may be possible with image analysis.

C. Polymer addition and particle size

Untreated corn stover samples initially contained particles with lengths on the order of centimeters. Operation of the torque rheometer resulted in particle size reduction, as is evident in Figs. 1(a) and 1(b). Particle size distributions obtained using a Bauer-McNett screen classifier are presented in Fig. 8 for two, 25 wt. % corn stover samples. Both samples were subject to the experimental technique depicted in Fig. 3 up to 3400 s, i.e., the same rotation-rate history. One sample contained 4 wt. % CMC (added prior to loading in the torque rheometer), while the other sample contained no polymer. The distributions in Fig. 8 show that the sample with CMC underwent less particle size reduction than the sample without CMC. The coarsest screen, which retained particles larger than 1360 μm , retained 240% more material for the sample containing CMC than the sample without CMC. The finest screen, which retained particles between 90 and 165 μm , retained 30% less material for the sample containing CMC. Overall retention was 11% greater for the sample containing CMC, indicating that more material was able to pass through the finest screen for the sample without CMC. Similar trends were observed for samples containing PEO and PAM.

Models that include the effects of friction on network stress predict that a decrease in friction should result in a decrease in network stress [Schmid and Klingenberg (2000); Switzer and Klingenberg (2003)]. Lower stresses in fiber suspensions should result in less particle size reduction during mixing while higher stresses should result in greater size reduction. The particle size data in Fig. 8 are consistent with the theory that WSPs reduce friction between fibers in networked fiber suspensions.

D. Polymer rapid screening

Making a single yield stress measurement with the torque rheometer using the experimental procedure illustrated in Fig. 3 takes approximately 2 h, including set-up time, run time, and clean-up time. To reduce the time required to test many types of rheological modifiers, a more rapid screening method was developed. The method employs an experimental procedure similar to that described above with two major changes: the torque rheometer is only half filled with biomass (50 g) and repeated step changes in rotation rate like those illustrated in Fig. 3 are not employed. Biomass was loaded into the

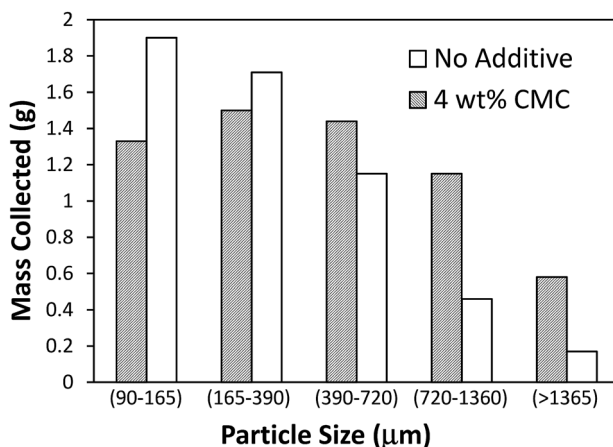


FIG. 8. Particle size distributions obtained from a Bauer-McNett screen classifier for hammermilled corn stover at 25 wt. % solids. The CMC is high molecular weight (700 kDa).

rheometer and then immediately mixed for 600 s at 110 rpm. The rotation rate was then decreased to 55 rpm for 100 s before additive was introduced. Three metrics of rheological modifier efficacy were recorded: the torque reduction, defined as the percent decrease in the torque upon addition of modifier, the drop time, t_d , defined as the time required for the torque to decrease to 80% of the total torque drop, and the rate of torque decrease. Utilizing the labels in the torque-time trace in Fig. 9, the drop time can also be defined as the time following the addition of modifier at which the torque at point B in Fig. 9, $\Gamma_B(t_d)$, satisfies $(\Gamma_A - \Gamma_B)/(\Gamma_A - \Gamma_C) = 0.8$. The rate of torque decrease, or drop rate, is defined as the absolute value of the slope of a linear fit between points A and B in Fig. 9. These measures are illustrated on the torque-time trace in Fig. 9 where the torque reduction is 80%, the drop time is 25 s, and the drop rate is 0.29 Nm/s. Using this screening technique, up to five different additives can be tested in 2 h.

Torque reduction as a function of additive concentration is shown in Fig. 10. Of the additives tested, WSPs were the only class of additive to effect significant change in the measured torque at concentrations as low as 1 wt. %. The results for fly ash are not shown, since it had no measurable effect on torque at concentrations as high as 10 wt. %. A torque reduction of only 5% was measured with the addition of 3 wt. % microcrystalline cellulose (MCC). The surfactant polysorbate 80 decreased torque 11% at a 5 wt. % concentration and 36% at a 10 wt. % concentration. These results for polysorbate 80 are consistent with results obtained by Knutsen and Liberatore (2010). They observed a 30–40% decrease in yield stress of acid hydrolyzed corn stover with a 10 wt. % (on a dry-solids basis) addition of polysorbate 20.

The torque reductions in Fig. 10 show that WSPs were the most effective class of rheological modifiers at decreasing mixing stress. The trends in torque reduction for WSPs are similar to those observed in the yield stress measurements: the yield stress and torque decrease with increasing WSP concentration. Guar gum, hydroxypropyl methyl cellulose (HPMC), a guar gum–xanthan gum mixture, and a guar gum–HPMC mixture all reduced torque more effectively than CMC. Considering the dependence of yield stress on molecular weight (Fig. 5), it is surprising that guar gum, with 1/3 the molecular weight of the CMC used here, is more effective than CMC at torque reduction. It is, therefore, possible, if not likely, that there are more effective WSPs than those examined here. It is also apparent in Fig. 10 that mixtures of WSPs can be more effective

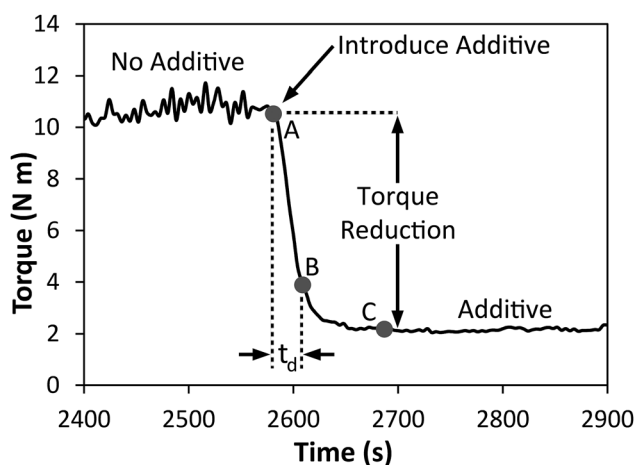


FIG. 9. Torque rheometer data illustrating how torque reduction and drop time, t_d , are obtained from the screening technique. Drop rate is the absolute value of the slope of a linear fit between points A and B.

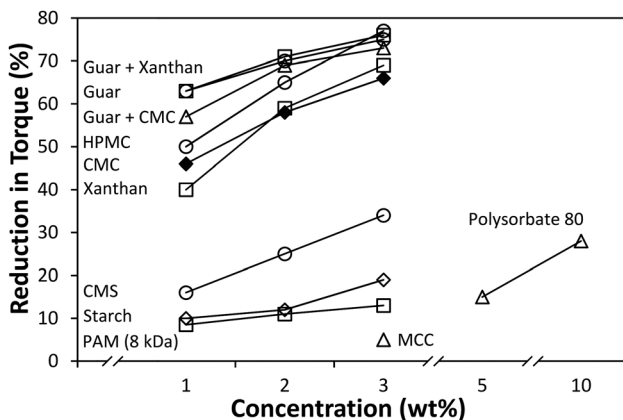


FIG. 10. Torque reduction for hammermilled corn stover at 25 wt. % solids as a function of rheological modifier concentration. The CMC is high molecular weight (700 kDa).

rheological modifiers than either of the pure WSPs. The 50/50 (by mass) mixture of guar gum and xanthan gum resulted in torque reduction values exceeding those of either pure WSP. Thus, mixtures of WSPs need not result in a linear combination of their individual rheological-modifying capabilities.

The drop time, a measure of how rapidly the rheological modifier acts, was recorded for each screening test. This information will be valuable when WSPs are needed in unit operations where rapid mixing is desired. The drop times in Fig. 11 were recorded after a 1 wt. % addition of WSP. The drop times varied with the WSP, but in all cases were on the order of seconds to tens of seconds. The drop time for the guar gum–xanthan gum mixture (22 s) was the largest, an order of magnitude larger than the drop time for starch. We also note that drop time for each WSP is correlated with the torque reductions shown in Fig. 10.

In Fig. 12, the torque drop rates are presented for the various WSPs. The torque drop rates are negatively correlated with drop times.

The time required for WSPs to take effect is potentially controlled by many different factors including, but not limited to, the nature of the mixing, polymer chemistry,

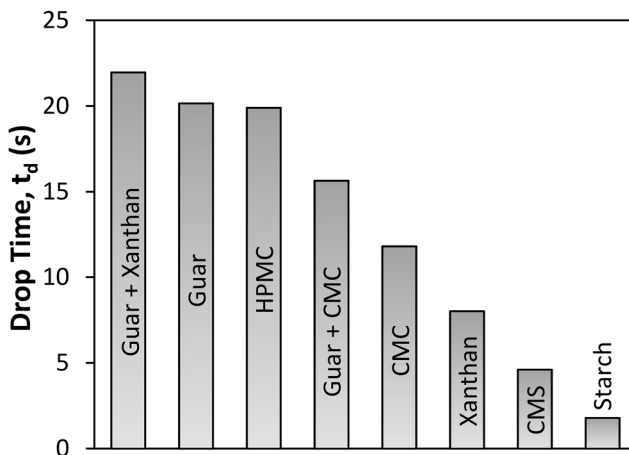


FIG. 11. Drop time for hammermilled corn stover at 25 wt. % solids with a 1 wt. % addition of rheological modifier. The CMC is high molecular weight (700 kDa).

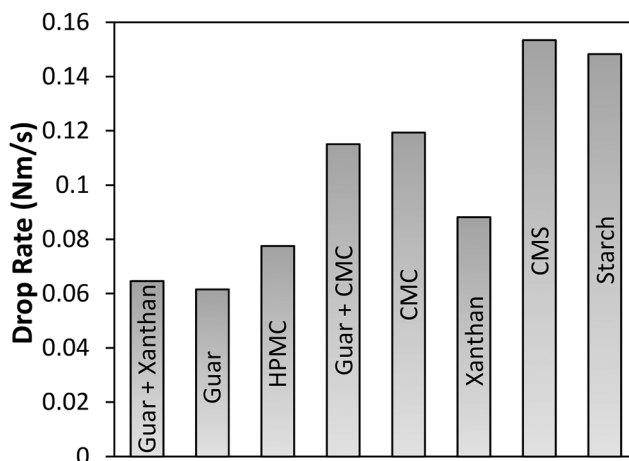


FIG. 12. Drop rate for hammermilled corn stover at 25 wt. % solids with a 1 wt. % addition of rheological modifier. The CMC is high molecular weight (700 kDa).

granular size of the WSP powder, biomass properties, and operating conditions such as temperature and pH . Thus, a better understanding of the factors that affect this kinetic behavior is required before predictions about the efficacy of WSPs in any particular application can be made.

IV. CONCLUSIONS

The effects of different additives on the rheology of lignocellulosic biomass were investigated. Torque rheometry was used to characterize the rheology of corn stover samples before and after the addition of rheological modifier. The most effective rheological modifiers tested were the WSPs. Yield stress in corn stover samples decreased 60–80% with the addition 1–2 wt. % WSP. Other additives such as polysorbate 80, MCC, and fly ash effected little or no change in the biomass rheology at the addition levels tested. We show that the effectiveness of WSPs depends on WSP concentration, molecular weight and WSP chemistry and that all of the results are consistent with the theory that WSPs reduce yield stress by reducing interfiber friction. A nonmonotonic shear stress dependence on shear rate was found for all of the untreated biomass samples prior to WSP addition. The addition of WSPs increased biomass plastic viscosity, decreased yield stress, and at high enough concentrations resulted in a monotonically increasing shear stress with shear rate. Particle size analysis shows that the addition of WSPs retards particle size reduction during mixing.

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References

- Aden, A., M. Ruth, K. Ibsen, J. Jechura, K. Neeves, J. Sheehan, B. Wallace, L. Montague, A. Slayton, and J. Lukas, "Lignocellulosic biomass to ethanol process design and economics utilizing co-current dilute acid prehydrolysis and enzymatic hydrolysis for corn stover," NREL, Report No. TP-510-32438, 2002.

- Batdorf, J. B., and J. M. Rossman, "Sodium carboxymethylcellulose," in *Industrial Gums: Polysaccharides and Their Derivatives*, 2nd ed., edited by R. L. Whistler and J. N. BeMiller (Academic Press, New York, 1973), pp. 695–729.
- Bennington, C. P. J., R. J. Kerekes, and J. R. Grace, "The yield stress of fiber suspensions," *Can. J. Chem. Eng.* **68**, 748–757 (1990).
- Blyler, L. L., and J. H. Daane, "An analysis of Brabender torque rheometer data," *Polym. Eng. Sci.* **7**, 178–181 (1967).
- Bohlin VOR Users Manual* (Malvern Instruments, Westborough, MA, 1991).
- Bond, J. Q., D. M. Alonso, D. Wang, R. M. West, and J. A. Dumesic, "Integrated catalytic conversion of gamma-valerolactone to liquid alkenes for transportation fuels," *Science* **327**, 1110–1114 (2010).
- Bousmina, M., A. Ait-Kadi, and J. B. Faisant, "Determination of shear rate and viscosity from batch mixer data," *J. Rheol.* **43**, 415–433 (1999).
- Carrasco, F., and C. Roy, "Kinetic study of dilute-acid prehydrolysis of xylan-containing biomass," *Wood Sci. Technol.* **26**, 189–208 (1992).
- Dalpkke, B., and R. Kerekes, "The influence of fibre properties on the apparent yield stress of flocculated pulp suspensions," *J. Pulp Pap. Sci.* **31**, 39–43 (2005).
- Derakhshandeh, B., S. G. Hatzikiriakos, and C. P. J. Bennington, "The apparent yield stress of pulp fiber suspensions," *J. Rheol.* **54**, 1137–1154 (2010).
- Ehrhardt, M., "Rheology of biomass," M.S. thesis, University of Wisconsin-Madison, Madison, 2008.
- Ehrhardt, M. R., T. O. Monz, T. W. Root, R. K. Connelly, C. T. Scott, and D. J. Klingenberg, "Rheology of dilute acid hydrolyzed corn stover at high solids concentration," *Appl. Biochem. Biotechnol.* **160**, 1102–1115 (2010).
- Goodrich, J., and R. Porter, "A rheological interpretation of torque-rheometer data," *Polym. Eng. Sci.* **7**, 45–51 (1967).
- Hercules Incorporated, "Aqualon sodium carboxymethylcellulose—Physical and chemical properties," Product Brochure, 1999.
- Hodge, D. B., M. N. Karim, D. J. Schell, and J. D. McMillan, "Soluble and insoluble solids contributions to high-solids enzymatic hydrolysis of lignocellulose," *Bioresour. Technol.* **99**, 8940–8948 (2008).
- Huber, G. W., J. N. Chheda, C. J. Barrett, and J. A. Dumesic, "Production of liquid alkanes by aqueous-phase processing of biomass-derived carbohydrates," *Science* **308**, 1446–1450 (2005).
- Kerekes, R. J., "Rheology of suspensions—Rheology of fibre suspensions in papermaking: An overview of recent research," *Nord. Pulp Pap. Res. J.* **21**, 598–612 (2006).
- Kerekes, R. J., R. M. Soszynski, and P. A. Tam Doo, "The flocculation of pulp fibres," in *Papermaking Raw Materials*, Transactions of the Eighth Fundamental Research Symposium, Oxford, edited by V. Punton (Mechanical Engineering Publications Limited, London, 1985), pp. 265–310.
- Knutsen, J. S., and M. W. Liberatore, "Rheology of high-solids biomass slurries for biorefinery applications," *J. Rheol.* **53**, 877–892 (2009).
- Knutsen, J. S., and M. W. Liberatore, "Rheology modification and enzyme kinetics of high solids cellulosic slurries: An economic analysis," *Energy Fuels* **24**, 6506–6512 (2010).
- Monz, T. O., "Investigation of biomass rheology in different geometries," M.S. thesis, University of Wisconsin-Madison, Madison, 2007.
- Samaniuk, J. R., C. T. Scott, T. W. Root, and D. J. Klingenberg, "The effect of high intensity mixing on the enzymatic hydrolysis of concentrated cellulose fiber suspensions," *Bioresour. Technol.* **102**, 4489–4494 (2011).
- Schmid, C. F., and D. J. Klingenberg, "Mechanical flocculation in flowing fiber suspensions," *Phys. Rev. Lett.* **84**, 290–293 (2000).
- Stickel, J. J., J. S. Knutsen, M. W. Liberatore, W. Luu, D. W. Bousfield, D. J. Klingenberg, C. T. Scott, T. W. Root, M. R. Ehrhardt, and T. O. Monz, "Rheology measurements of a biomass slurry: An inter-laboratory study," *Rheol. Acta* **48**, 1005–1015 (2009).
- Switzer, L. H., and D. J. Klingenberg, "Rheology of sheared flexible fiber suspensions via fiber-level simulations," *J. Rheol.* **47**, 759–778 (2003).
- TAPPI: Pulp Properties Committee of the Process and Product Quality Division, "Forming handsheets for physical tests of pulp: T 205 sp-06," TAPPI Test Method Standards (2006).

- Viamajala, S., B. S. Donohoe, S. R. Decker, T. B. Vinzant, M. J. Selig, M. E. Himmel, and M. P. Tucker, "Heat and mass transport in processing of lignocellulosic biomass for fuels and chemicals," in *Sustainable Biotechnology*, edited by O. M. Singh and S. P. Harvey (Springer, New York, 2010), pp. 1–18.
- Wang, Q., P. R. Ellis, and S. B. Ross-Murphy, "Dissolution kinetics of guar gum powders—II. Effects of concentration and molecular weight," *Carbohydr. Polym.* **53**, 75–83 (2003).
- Wyman, C. E., "What is (and is not) vital to advancing cellulosic ethanol," *Trends Biotechnol.* **25**, 153–157 (2007).
- Zauscher, S., and D. J. Klingenberg, "Friction between cellulose surfaces measured with colloidal probe microscopy," *Colloids Surf., A* **178**, 213–229 (2001).
- Zauscher, S., C. T. Scott, J. L. Willet, and D. J. Klingenberg, "Pulp extrusion at ultra-high consistencies: A new processing method for recycling wastepaper and papermill sludges," *Tappi J.* **83**, 62 (2000).