1 Rheometry of Coarse Biomass at High Temperature and 2 Pressure

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9 Abstract

We designed, constructed, and tested a new device that can measure the rheological properties of lignocellulosic biomass slurries with high solids concentrations (> 25 %) containing large particles (> 10 mm), and that can operate at high temperatures (> 230°C), high pressures (> 2.8 MPa), and low pH (< 1.0). Rheological properties measured with this Lignocellulosic Biomass Rheometer (LCBR) are consistent with those measured with another instrument. Biomass samples investigated are yield stress materials, consistent with previous reports. For modest temperatures, the viscosity decreases reversibly with increasing temperature. When the biomass is exposed to sufficiently high temperature and low pH, we observe an irreversible decrease in apparent viscosity, consistent with that expected as hydrolysis reactions reduce the concentration of insoluble solids.

10 **Keywords:** Biomass, Rheology, Rheometer, High Temperature, High Solids
11 Concentration

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1. INTRODUCTION

Lignocellulosic biomass processing typically involves numerous steps. In a process developed by the National Renewable Energy Laboratory (NREL) for the conversion of corn stover to ethanol [1, 2, 3], the particle size of the biomass is first reduced, and then the biomass is pretreated using dilute-acid hydrolysis at elevated temperature to make the cellulose more accessible. This biomass is a suspension of natural fibers whose average fiber length starts at several centimeters to inches and decreases through subsequent processing steps. After pretreatment, the cellulose is then enzymatically hydrolyzed to produce glucose. The glucose is subsequently fermented to produce ethanol; the ethanol is then purified in separation steps. Ethanol from biomass has been a principal target fuel that is industrially relevant, but there are numerous proposed processing routes leading to other chemicals and fuels (e.g., hydrocarbons such as gasoline) [3, 4, 5]. Commercialization of such biorefining processes requires reducing the processing costs [6, 7, 8].

Increasing the concentration of insoluble solids can reduce the cost of processing biomass [9, 10, 11, 12, 13]. Decreasing the water content reduces operating costs (e.g., heating, water handling) as well as capital costs. However, concentrated biomass suspensions are very viscous, non-Newtonian, complex fluids, which make mixing reactants and conveying the biomass challenging [12, 14, 15, 16, 17, 18, 19]. It is thus apparent that understanding their rheological properties is essential for designing efficient processes and equipment [13, 16, 20, 21, 22].

Measuring the yield stress and other rheological properties of lignocellulosic biomass in traditional rheometers can be challenging because of a variety of complicating factors, including large particle sizes, wall slip, large normal stresses,

fracture, and ejection. These complications can be attributed to the diverse anatomical features of lignocellulosic biomass, including particle size and shape distributions, chemical composition variations, and compressibility. 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 Liberator [21]. Nonetheless, numerous features of lignocellulosic biomass rheology are well established. Above a low mass fraction of solids, biomass suspensions are viscoplastic, shear thinning materials with a yield stress, τ_0 . The steady-state shear stress (τ) as a function of shear rate ($\dot{\gamma}$) has been represented by the Bingham ($\tau = \tau_0 + \eta_{pl}\dot{\gamma}$), Casson ($\tau^{1/2} = \tau_0^{1/2} + (\eta_{pl}\dot{\gamma})^{1/2}$), and Herschel-Bulkley models ($\tau = \tau_0 + K\dot{\gamma}^n$) [22, 23, 24, 25, 26, 27]. The yield stress of biomass is a rapidly increasing function of solids concentration, often represented by the empirical expression

$$\tau_0 = aC^b, \quad (1)$$

where C is the solids concentration, and a and b are empirical parameters [28, 29, 30, 31]. The parameters depend on such properties as particle size distribution, fiber aspect ratio, stiffness, and additive type and concentration [27, 28, 29]. Values for b vary from about 2.3 to 6, and depend on the type of lignocellulosic biomass (e.g., wood pulp, corn stover, and acid-hydrolyzed corn stover) [21, 25, 28, 32].

The yield stress depends on a variety of other variables. Experimental [26, 28, 29, 33] and particle-level simulation studies [33, 34, 35] both show that the yield stress increases with increasing fiber length. Decreasing fiber stiffness leads to a decrease in fiber network shear strength [28, 36, 37]. The presence of various additives (e.g., rheological modifiers) can also modify the yield stress signifi-

61 cantly [27, 38, 39, 40, 41].

62 A critical element that is missing in our understanding of the rheological prop-
63 erties of biomass is the behavior of the biomass under the relatively extreme re-
64 action conditions often employed in hydrolysis and other catalytic reactions (e.g.,
65 $170 < T < 230^{\circ}\text{C}$ and low pH). Furthermore, these properties change signifi-
66 cantly during processing, so there is a great need to understand this behavior in
67 situ while the reactions are proceeding. It is this information that is necessary for
68 the design of practical processes for the efficient production of biofuels and other
69 chemicals.

70 In this paper, we describe a new rheometer that is capable of measuring ap-
71 parent rheological properties of lignocellulosic biomass at high temperatures ($>$
72 230°C), high pressures ($> 2.8\text{ MPa}$), low pH (< 1.0), very high solids concentra-
73 tions, and for large particles ($> 10\text{ mm}$). We show that rheological properties mea-
74 sured with this Lignocellulosic Biomass Rheometer (LCBR) are consistent with
75 those measured with a torque rheometer. Biomass samples investigated show that
76 these materials are yield stress fluids whose yield stress decreases with increas-
77 ing temperature. Changes in apparent rheological properties with temperature are
78 reversible at low temperatures, but apparent viscosities decrease dramatically and
79 irreversibly at high temperatures, or when a sufficient amount of mineral acid is
80 present. Irreversible changes in rheological properties appear to arise from the
81 acid-catalyzed hydrolysis of the biomass solids.

82 **2. Materials and Methods**

83 *2.1. Equipment*

84 The Lignocellulosic Biomass Rheometer (LCBR) comprises an impeller and
85 insert that are placed inside a 2 L Parr reactor (**Model 4530, 2-liter Floor Stand**

86 **Reactor, Parr Instrument Co., Moline, IL). The temperature of the reactor ves-**
87 **sel is increased or decreased with an external heating/cooling jacket. The**
88 **reactor head has ports for injecting liquids, inserting a thermocouple, pres-**
89 **sure gauges (we do not report pressures in this paper), pressure relief devices.**
90 The impeller, insert, and Parr vessel and head (shown schematically in Fig. 1) are
91 constructed from Hastelloy B2 and B3 alloys in order to resist corrosion under
92 harsh reaction conditions (B2 was used for the Parr vessel and head, and B3 was
93 used for the insert and impeller).

94 (PLACE FIGURE 1 HERE)

95 The impeller and insert were designed to allow for biomass with large parti-
96 cles and high solids concentrations to be well-mixed during hydrolysis reactions
97 so that rheological properties can be measured. A photograph of the insert and
98 impeller is shown in Fig. 2. The rheometer insert consists of a feed zone above
99 a mixing zone. The feed zone was designed to provide sufficient pressure on the
100 biomass to insure that the mixing zone is fully loaded during operation. The mix-
101 ing zone has a capacity of 1 L and was designed to mix the biomass in a consistent,
102 repeatable manner. The insert was made from a thin sheet (31.000 cm $\times$ 25.718
103 cm, with a thickness of 0.1588 cm) of Hastelloy B3 that was drilled with pilot
104 holes, and then rolled into a cylinder (OD = 10.058 cm) providing a clearance of
105 0.0508 cm to the inner diameter of the 2 L Parr vessel. Four windowed openings
106 were cut out of the cylindrical insert to expose the sheared biomass to the Parr
107 vessel wall for improved heat transfer.

108 (PLACE FIGURE 2 HERE)

109 In the mixing zone (**the space below the bottom of the guide bars**), an array
110 of static pins (also made from Hastelloy B3; 0.635 cm diameter, 3.810 cm long
111 shouldered leaving a 0.152 cm stub) were welded into the pilot holes of the rolled
112 cylinder at strategic locations to prevent the sheared biomass from rotating with
113 the impeller as a rigid body. Four pins were placed in each of three horizontal
114 planes to allow a sufficient gap (0.953 cm) for clearance of the rotating impeller.

115 In the feed zone (**the space above the bottom of the guide bars**), four ver-
116 tical guide bars were welded onto the interior of the rolled cylinder for multiple
117 purposes. Two of the guide bars incorporated locating pins (0.635 cm diameter,
118 1.588 cm long) which were used to engage blind holes drilled into the Parr reactor
119 head to keep the insert from rotating. A hole was drilled through one of the guide
120 bars (Fig. 1) so that a thermowell attached to the Parr head could be inserted and
121 protected from the rotating impeller and sheared biomass. The thermowell ex-
122 tends approximately 0.953 cm below the base of the guide bar into the mixing
123 zone to measure the temperature of the biomass during operation. The guide bars
124 also keep the weights (described below) from rotating.

125 The base of the LCBR insert was machined with a counter-bore recess for
126 the placement of an impeller shaft centering/bearing pin. The lower end of the
127 impeller shaft was bored and beveled to receive the pin and center the shaft.

128 The rotating shaft contains an array of blades that are pitched at a 30° angle
129 from horizontal and cut with a 1.905 cm radius on the leading and trailing edges.
130 The top pair of blades is oriented to produce a downward flow of biomass from the
131 feed zone into the mixing zone. The bottom pair of blades is oriented upward to
132 scrape the biomass up off the insert base. The middle two tiers of blades are alter-
133 nately pitched to cycle the biomass flow upward and downward (see Fig. 2). This

134 blade configuration is designed to produce zero net motion of sheared material in
135 the axial direction.

136 The shaft coupling was designed to combine a direct couple (threaded) to the
137 Parr drive shaft and a snug-fit spline coupling to the LCBR impeller shaft such
138 that the impeller shaft is not directly coupled to the Parr drive shaft and can be
139 easily separated.

140 For most operating conditions, a weight is required to apply downward pres-
141 sure on the biomass in the feed zone to keep the mixing zone fully packed. An
142 optional spring-loaded system was designed to increase this downward pressure if
143 needed. **The spring was not used in the experiments reported here, and thus**
144 **the normal force exerted on the biomass was limited by that of the weight**
145 **(1.326 kg).** Retention pins were placed as shown in Fig. 1 to limit the movement
146 of the loading weight and restrict the displacement of the compression spring
147 (made from coiled B3 welding wire). With a hole in the center, the weight also
148 serves to center the impeller shaft for ease of coupling to the Parr drive shaft.

149 The insert and impeller were used in a Parr Model 4530, 2 L Floor Stand Reac-
150 tor. Several modifications of the Parr reactor head were required to accommodate
151 the insert and impeller shaft. Blind openings were drilled to receive the locating
152 pins. The thermowell was reduced to 0.635 cm diameter and relocated inward
153 on the same radius for insertion into the bore in the guide bar. The Parr drive
154 shaft (internally coupled through the Mag Drive) was shortened to extend 1.613
155 cm below the surface of the reactor head, and was threaded ($1/2-20 \times 0.953$ cm)
156 to receive the shaft coupling. Standard cooling ports were not used and were not
157 provided.

158 The LCBR reactor system is controlled by a Parr 4848B controller that has
159 been modified. The 4848B controller as received from Parr has five modules that
160 monitor and control the motor speed, reactor temperature, heater temperature, and
161 pressure. The system also came with an MTM module that measured the voltage
162 supplied to the motor controller by a signal isolator board. This module was not
163 useful for measuring motor torque, and thus was repurposed as described below.
164 These modules communicate via RS 485 serial communications with a PC with
165 SpecView data logging software supplied by Parr. The SpecView software can
166 control all of the settings on the 4848B controller remotely, as well as record and
167 plot the data received from the modules (limited to a 1 Hz data acquisition rate).
168 To measure the power consumed by the motor so that the shaft torque on the
169 rheometer could be determined, an external power meter was built that measures
170 the motor voltage with an NK Technologies (San Jose, CA) voltage transducer
171 and the motor current with a CR Magnetics (St. Louis, MO) Hall effect current
172 transducer. This power meter is plugged into the motor power cord between the
173 4848B controller and the motor. The output of the voltage transducer is attached to
174 the repurposed MTM module, and an additional module was added to the 4848B
175 controller to measure the output from the current transducer. These modules are
176 connected to the serial communications in the 4848B controller so that SpecView
177 can read the voltage and current data in addition to the temperature, pressure, and
178 speed data.

179 *2.1.1. Motor Torque Calibration*

180 The motor current is directly proportional to the torque delivered to the biomass.
181 To determine the quantitative relationship between the motor current and torque,
182 a Futek torque sensor (Irvine, CA, 50 Nm capacity) was coupled to the Parr im-

183 peller drive shaft. An independent A/D system utilizing LabView software was
 184 configured to acquire sensor signals. A large helical coupling was attached and
 185 manually restrained to provide variable torque resistance at selected motor speeds.
 186 The measured torque delivered through the Mag Drive (Γ) is related to the motor
 187 current (I) and impeller speed (Ω) by

$$\Gamma = aI + b\Omega + c \quad (2)$$

188 where $a = 4.420 \pm 0.008 \text{ N}\cdot\text{m}\cdot\text{A}^{-1}$, $b = -0.0638 \pm 0.0013 \text{ N}\cdot\text{m}\cdot\text{s}\cdot\text{rad}^{-1}$, and
 189 $c = -1.508 \pm 0.013 \text{ N}\cdot\text{m}$. Note that the torque is essentially a linear function of
 190 motor current and is only slightly affected by rotation speed. This is typical for
 191 the type of motor used in the Parr reactor (180 VDC, 0.75 hp (559 W) permanent
 192 magnet motor). The loss term (-1.508 N·m) was determined with the gear reducer
 193 running warm at steady state. (The torque predicted by Eq. 2 is plotted against the
 194 torque measured with the Futek torque transducer in Fig. S1 of the Supplementary
 195 Online Material.)

196 2.1.2. Rheometer Operation

197 First the impeller shaft is placed inside the insert with the bottom of the shaft
 198 engaged with the centering pin. The weight is then aligned with the guidebars
 199 and placed on the shaft to properly align it. The insert containing the impeller and
 200 weight is then placed in the cylindrical vessel. A “dry-fit” is first made to orient
 201 the impeller shaft, thermowell, and locating pins before biomass is added.

202 To load the mixing zone, the assembly is decoupled from the Parr head and
 203 the weight is removed. For the calibration described below, a high viscosity New-
 204 tonian fluid was heated and poured into the vessel. For comparison with mea-
 205 surements made with a torque rheometer, modeling clay was pushed into the mix-
 206 ing zone. For most experiments with biomass, a dry, granulated biomass is first

207 poured into the mixing zone and lightly tamped. Once the mixing zone is filled,
 208 excess biomass is added in the feed zone and the weight is installed. Liquid (pure
 209 water or acid solution) is then added to obtain the desired pH and mass fraction
 210 of biomass solids (typically 20 %). Once the assembly is filled, it is recoupled
 211 to the Parr head for the start of a test. After a run, the vessel is cooled and any
 212 residual head pressure released. The vessel is then decoupled from the Parr head
 213 and placed in a sufficient containment receptacle. The LCBR insert can then be
 214 removed and the insoluble biomass and liquor recovered. The LCBR components
 215 can then be cleaned and re-assembled for the next test.

216 Apparent rheological properties measured using the LCBR were compared
 217 with those measured using a torque rheometer. **The torque rheometer consists**
 218 **of two counter-rotating impellers within a chamber. The material is held**
 219 **within the chamber with a plunger that is held in place with a weight.** Meth-
 220 ods for measuring rheological properties of biomass with a torque rheometer are
 221 described **in more detail** elsewhere [22, 26].

222 2.2. Materials

223 The LCBR was calibrated using a standard Newtonian fluid (polybutene, Can-
 224 non). The viscosity values reported by Cannon at **four** different temperatures are
 225 **plotted in Fig. 3** and tabulated in Table S1 of the Online Supplementary Ma-
 226 **terial. To obtain “known” viscosities at other intermediate temperatures for**
 227 **calibration purposes, the tabulated** viscosities were fit with the equation

$$\eta(T) = A \exp\left(\frac{B}{T}\right), \quad (3)$$

228 where T is the absolute temperature. The best-fit parameter values are $A =$
 229 1.80237×10^{-9} Pa·s and $B = 7858.5$ K. The data are compared with the fit
 230 in Fig. 3.

(PLACE FIGURE 3 HERE)

A modeling clay was used to compare rheological properties measured in the LCBR and a torque rheometer. The modeling clay was obtained from a local craft store (Polyform ModelAir manufactured by Polyform Products Company).

Corn plants were harvested in a forage/silage chopping operation using a John Deere Model 3950 Forage Harvester. The corn variety selected was Golden Harvest G05T82 (Syngenta) and was planted in mid-May, 2012. The harvest occurred in early October, 2012. The approximate growing location is in the northern region of the United States at latitude 42° 49' N, longitude 89° 53' W (about 65 km southwest of Madison, WI). In the harvesting operation, whole stalks (including ears) were severed 20-25 cm above the ground and chopped into particles approximately 2.5 cm x 2.5 cm. **This material contains numerous particles with linear dimensions larger than 10 mm.** The kernels remained relatively intact and were later manually removed. The remaining “corn stover” was subsequently air dried to approximately 8% moisture content and stored in sealed bags. For preliminary experiments, the corn stover was tested in **this condition, specifically for comparing rheological properties measured with the LCBR and the torque rheometer. We will refer to this material as “chopped corn stover.”** However, the cob particles proved difficult to process so the corn stover was further size-reduced in a Wiley mill using a 5 mm screen and collected with a custom-designed vacuum collection system. This material is shown in Fig. 4, **and was employed in other rheological experiments. We refer to this material as “chopped and milled corn stover.”**

A second supply of corn stover was obtained by manually harvesting corn plants (Northrup King N45P, planted in mid-May of 2016 and harvested in

256 **October of 2016 at latitude 42° 49' N, longitude 89° 53' W, about 65 miles**
257 **southwest of Madison, Wisconsin), removing the kernel and hammermilling**
258 **the rest of the harvested plants. The hammermilled material was further**
259 **size-reduced in a Wiley mill using a 3 mm screen and air dried. The mois-**
260 **ture content was approximately 5%. We refer to this material as “milled**
261 **corn stover,” which was also used to compare rheological properties mea-**
262 **sured with the LCBR and the torque rheometer.**

263 (PLACE FIGURE 4 HERE)

264 **3. Results**

265 *3.1. Calibration*

266 Torque-rotation rate data can be converted to conventional rheological quan-
267 tities using a calibration procedure that involves representing the actual geometry
268 with an idealized geometry. Torque-rotation rate data obtained for fluids with
269 known rheological properties can then be used to determine the dimensions of the
270 idealized geometry. Such a calibration for the idealized geometry of concentric
271 cylinders is shown below (and illustrated in Fig. S2 of the Online Supplementary
272 Material). **A calibration employing an idealized geometry of parallel disks**
273 **leads to essentially equivalent results, as described in the Online Supplemen-**
274 **tary Material.**

275 Here we describe a calibration approach analogous to that developed for torque
276 rheometers by Goodrich and Porter [42], where the rheometer is represented by
277 a set of concentric cylinders (as illustrated in Fig. S2). The outer cylinder ra-
278 dius, R_o , is equated with the insert inner radius. The effective inner radius,
279 R_i , is determined by equating the measured torque for a Newtonian fluid with

known viscosity with that calculated from the solution of the Navier-Stokes equation [43]. Bousmina *et al.* [44] showed that such a calibration with a Newtonian fluid gives equivalent results to those obtained using a more sophisticated analysis with power-law fluids.

The torque (Γ) and rotation rate (Ω) for tangential flow between concentric cylinders are related to the apparent shear stress (τ_{app}) and apparent shear rate ($\dot{\gamma}_{\text{app}}$) via

$$\tau_{\text{app}} = K_{\tau} \Gamma, \quad (4)$$

$$\dot{\gamma}_{\text{app}} = K_{\dot{\gamma}} \Omega, \quad (5)$$

where

$$K_{\tau} = \frac{1}{2\pi R_i^2 h}, \quad (6)$$

$$K_{\dot{\gamma}} = \frac{2R_i R_o}{\left(\frac{1}{\kappa} - \kappa\right) R_a^2}, \quad (7)$$

and where $R_a \equiv (R_i + R_o)/2$ is the midpoint radius, h is the impeller height, and $\kappa \equiv R_i/R_o$. This approach is consistent with that employed in commercial rheometers [45]. Note that Eq. 6 is obtained from a momentum balance that is valid for any type of fluid, whereas Eq. 7 is obtained from the equation of motion for incompressible Newtonian fluids, and thus is only strictly valid for Newtonian fluids.

To calibrate the rheometer, we note that the ratio of Eqs. 4 and 5 gives

$$\frac{\tau_{\text{app}}}{\dot{\gamma}_{\text{app}}} \equiv \eta_{\text{app}} = \left[\frac{(1 - (R_i/R_o)^2) R_a^2}{4\pi R_i^4 h} \right] \frac{\Gamma}{\Omega} \quad (8)$$

where η_{app} is the apparent viscosity of the material in the rheometer. Thus a plot of $\eta\Omega$ vs. Γ for a Newtonian fluid with known viscosity η should yield a straight

line with a slope given by the quantity in square brackets in Eq. 8; from this slope, one can extract the effective inner radius R_i .

The calibration experiments were performed by first heating the polybutene in the Parr cylinder to above 60°C. The fluid was allowed to cool slowly within the LCBR. At several temperatures, the torque was measured for a variety of rotation rates. For each rotation rate, the data were collected over 50 s (1 Hz acquisition rate), and then averaged. This provided data for Γ as a function of Ω for **each temperature. For each temperature, the viscosity $\eta(T)$ is known via Eq. 3, and thus we are able to construct a set of data for $\Omega\eta$ as a function of Γ .** The results are **presented** in Fig. S3 of the Online Supplementary Material, where $\Omega\eta$ is plotted as a function Γ . The slope obtained from a least-squares fit of the data to a straight line passing through the origin is **$173 \pm 5 \text{ m}^{-3}$** . The value of R_i obtained by equating the slope with the term in square brackets in Eq. 8 (using $R_o = 0.04864 \text{ m}$ and $h = 0.141 \text{ m}$) is $R_i = 0.038790 \pm 0.00018 \text{ m}$ (or $\kappa = R_i/R_o = \mathbf{0.798 \pm 0.004}$).

Once the effective inner radius is known, torque-rotation rate data can be converted to apparent shear stress-shear rate data using Eqs. 4 and 5. Using the value of R_i determined from the calibration, as well as the known values of R_o and h specified above, we obtain the values of K_τ and $K_{\dot{\gamma}}$ from Eqs. 6 and 7 as

$$K_\tau = \mathbf{750 \pm 7 \text{ m}^{-3}}, \quad (9)$$

$$K_{\dot{\gamma}} = \mathbf{4.33 \pm 0.09 \text{ rad}^{-1}}. \quad (10)$$

3.2. Modeling the Torque-Rotation Rate Data

Torque-rotation data can also be fit with a convenient rheological model to obtain model parameters. For biomass, we have fit such data with the Bingham

322 model. For flow of a Bingham fluid between concentric cylinders, the relationship
 323 between torque and rotation rate is

$$\Gamma = 4\pi R_i^2 h \eta_{pl} \left[\frac{\Omega + \frac{\tau_0}{\eta_{pl}} \ln \left(\frac{r_0}{R_i} \right)}{1 - \frac{R_i^2}{r_0^2}} \right] \quad (11)$$

324 where τ_0 is the yield stress, η_{pl} is the plastic viscosity, and r_0 is the yield surface,
 325 which is the minimum of R_o and the solution to equation

$$\left(\frac{r_0}{R_i} \right)^2 - 1 = \frac{2\eta_{pl}\Omega_k}{\tau_0} + \ln \left[\left(\frac{r_0}{R_i} \right)^2 \right]. \quad (12)$$

326 Torque-rotation data obtained with the LCBR were fit with Eq. 11 to obtain yield
 327 stresses and plastic viscosities. When the plastic viscosity is positive, the fit is
 328 performed with a nonlinear, least-squares algorithm. When the plastic viscosity
 329 is negative, the torque is simply fit as a linear function of rotation rate, with the y
 330 intercept equated with $2\pi R^2 h \tau_0$.

331 3.3. Modeling Clay

332 Apparent rheological properties of modeling clay were measured at 65°C us-
 333 ing both the LCBR and the torque rheometer. Data obtained using the LCBR were
 334 acquired at 1 Hz, and data obtained with the torque rheometer were acquired at 5
 335 Hz; all data were averaged over at least 100 s. **The data are presented in Fig. 5.**
 336 The apparent viscosity is plotted as a function of apparent shear rate for both ap-
 337 paratuses in Fig. 5(a). The two rheometers accessed different shear rate ranges,
 338 but the two sets of data are consistent with nearly identical viscosities in the re-
 339 gion where the shear rate ranges overlap. **The inset shows the viscosity plotted**
 340 **as a function of shear stress. The data fall on a nearly vertical line, consistent**
 341 **with a yield stress material. The shear stress is plotted as a function of shear**

342 rate in Fig. 5(b). The apparent nonzero intercept illustrates the existence of
343 a yield stress, which is similar for the two data sets. The data are replotted in
344 the inset with the shear rate on a log scale. Here the yield stress appears as a
345 plateau at low shear rates.

346 (PLACE FIGURE 5 HERE)

347 The flow behavior of the modeling clay in the LCBR was investigated at the
348 end of the test. The LCBR insert containing the clay and the impeller were re-
349 moved from the 2 L vessel. **The impeller blade ends travel close to the insert**
350 **radius, leaving only a small amount of clay beyond the end the impeller.** A
351 pick was used to **remove this small amount of clay to** expose an impeller blade,
352 which revealed a cavity behind the impeller blade (Fig. 6). Such a situation is
353 expected when an object translates through a Bingham plastic material, “carving”
354 a channel along its path. More importantly, however, the space in front of the im-
355 peller blade is completely filled with clay. The absence of a cavity in front of the
356 advancing impeller blade arises because an impeller blade below the one in ques-
357 tion is pitched so that it will push material into the cavity created by the first blade.
358 In fact, the pitches of all of the blades were designed to push material into all cav-
359 ities created by blades above or below. This feature is essential to the operation
360 of the device as a rheometer. If the cavities were not filled but became permanent
361 during the impeller rotation, the material would exert no torque on the impeller.
362 Designing appropriate pitches on the blades creates only temporary cavities, and
363 thus allows the material to exert a torque on the impeller at all times.

364 (PLACE FIGURE 6 HERE)

365 3.4. *Lignocellulosic biomass*

366 Rheological properties of chopped corn stover suspensions, as well as
367 milled corn stover suspensions, were measured using both the LCBR and
368 the torque rheometer. For the chopped corn stover, only one sample was ex-
369 amined in each rheometer at an insoluble solids mass fraction of 15%. The
370 material was loaded into each rheometer, and properties at several appar-
371 ent shear rates were measured at room temperature. For the milled corn
372 stover, three replicate runs were performed at each shear rate—that is, be-
373 tween replicate runs, the rheometers were emptied and then reloaded with
374 new biomass from the same source and at the same concentration (insoluble
375 mass fraction = 20 %). In each experiment, the temperature was first in-
376 creased to 90°C, then decreased to $33.0 \pm 0.5^\circ\text{C}$, while shearing at moderate
377 rotation rate the entire time. Data were then collected at various apparent
378 shear rates. For the LCBR, data were collected for 60 s at each rotation rate
379 and averaged. For the torque rheometer, data were collected for 100 s at each
380 rotation rate and averaged. For each rheometer, the averages from the repli-
381 cate runs were used to obtain overall averages and uncertainties. The results
382 for both materials are presented in several ways in Fig. 7. In Fig. 7(a), the
383 apparent viscosity is plotted as a function of apparent shear rate, with the
384 apparent viscosity plotted as a function of shear stress in the inset. The data
385 from the two rheometers agree qualitatively for both stover materials, with a
386 pronounced shear thinning viscosity as the shear rate is increased. The ap-
387 parent viscosities obtained with the torque rheometer are larger than those
388 obtained with the LCBR. The slope of the log-log plot of apparent viscosity
389 vs apparent shear rate is approximately -1, indicative of fluids with a yield

390 stress. When the apparent viscosity is plotted as a function of apparent shear
391 stress (inset), the data illustrate a rapid change of viscosity with shear rate,
392 as expected for yield stress materials with stresses near the yield stress. In
393 Fig. 7(b) we have plotted the apparent shear stress as a function of apparent
394 shear rate. For the torque rheometer, the apparent shear stress decreases
395 with increasing shear rate. Such negative plastic viscosities have been re-
396 ported previously for suspensions of untreated lignocellulosic biomass near
397 room temperature [27]. For the LCBR, the chopped corn stover also exhibits
398 a decrease in stress with increasing shear rate. For the milled stover, lin-
399 ear regression also gives a negative slope, but the magnitude of the slope is
400 smaller than the uncertainty (slope = -7 ± 14 Pa·s). A negative slope may
401 become more pronounced if a wider range of rotation rates were employed.

402 (PLACE FIGURE 7 HERE)

403 The mechanisms that produce a negative plastic viscosity, and the condi-
404 tions for which they are observed are unclear (except that we do not observe
405 negative plastic viscosities for measurements with clay or Newtonian fluids).
406 Further investigation and discussion of negative plastic viscosities is the sub-
407 ject of future work.

408 While the rheological data for lignocellulosic biomass suspensions measured
409 with the LCBR and torque rheometer agree qualitatively, the quantitative agree-
410 ment is not as good as for the data obtained for modeling clay. We note that the
411 stresses measured for lignocellulosic biomass on different instruments can differ
412 by more than a factor of two, with stresses measured using the torque rheometer
413 typically larger than those measured with other devices [22].

414 Typical raw data for **chopped and milled** corn stover (insoluble solids mass
415 fraction = 20 %, without acid) are presented in Fig. 8, where the torque, rotation
416 rate, and temperature are plotted as a function of time. **There are several note-**
417 **worthy features of the temperature dependence of the rheological behavior**
418 **of the biomass. First, the torque (and thus apparent shear stress and vis-**
419 **cosity) decrease significantly as the temperature is increased to 155°C. Sec-**
420 **ond, the temperature dependence is largely reversible under these conditions**
421 **(i.e., maximum temperature $\leq 155^{\circ}\text{C}$, no added acid)—the torque increases**
422 **again as the temperature is subsequently decreased. Third, the torque fluc-**
423 **tuates, but the fluctuations decrease significantly as the temperature is in-**
424 **creased. The fluctuations then increase when the temperature is subsequently**
425 **decreased.**

426 Most of the data in Fig. 8 were obtained for a rotation rate of $1.57 \text{ rad}\cdot\text{s}^{-1}$. At
427 certain times, the rotation rate was cycled to 4.71, 9.42, 4.71, and back to 1.57
428 $\text{rad}\cdot\text{s}^{-1}$. The duration of each intermediate rotation rate step was 50 s. For tem-
429 peratures above approximately 80°C , the torque tends to increase as the rotation
430 rate is increased.

431 (PLACE FIGURE 8 HERE)

432 The torque values obtained during each of the rotation rate steps were averaged
433 over the 50 s steps. The average torque and rotation rate values obtained during the
434 first four rotation rate cycles in Fig. 8 were converted to apparent shear stress and
435 apparent shear rate using Eqs. 4 and 5, and these transformed data are presented
436 in Fig. 9. The symbols represent the experimental data, and the solid curves rep-
437 resent fits of the torque-rotation rate data with the Bingham model (Eq. 11), with

438 results converted to stress as a function of shear rate using Eqs. 4 and 5. **The**
439 **values of the best fit parameters (the yield stress and plastic viscosity) at the**
440 **different temperatures are tabulated in Table 1.** The data are well described by
441 the Bingham model as commonly observed for biomass and other suspensions of
442 synthetic and natural fibers [22, 23, 24, 25, 26, 27]. Figure 9 also illustrates that
443 the stresses decrease with increasing temperature.

444 (PLACE FIGURE 9 HERE)

445 The effect of sulfuric acid on the rheological properties of biomass are illus-
446 trated in Fig. 10, where the apparent viscosity is plotted as a function of temper-
447 ature for **a single sample of** corn stover (insoluble solids mass fraction = 20 %) **with**
448 **1.0 % H₂SO₄.** The first data point at 55°C shows that the viscosity is large,
449 consistent with previous data. As the temperature is increased, the viscosity de-
450 creases. **The heating rate was 6°C/min for the first two data points, and then**
451 **reduced to less than 1°C/min.** When the temperature reached 166°C, the LCBR
452 was then cooled (**cooling rate less than 1°C/min**). In this case, the viscosity sub-
453 sequently remained small, much less than that measured before the sample was
454 heated to 166°C. Visual inspection of the biomass after the experiment revealed
455 that the biomass solids average particle size and overall concentration had de-
456 creased significantly because of the acid-catalyzed hydrolysis of the solids. The
457 conditions that produce reversible and irreversible rheological changes with in-
458 creased temperature, **and the associated changes in other material properties,**
459 will be discussed further in a future publication.

460 (PLACE FIGURE 10 HERE)

461 4. CONCLUSIONS

462 In this report, we have demonstrated that the LCBR is capable of measur-
463 ing apparent rheological properties that are consistent with those measured with
464 another instrument. The range of torques accessible are appropriate for investigat-
465 ing the rheology of concentrated lignocellulosic biomass. The device is capable of
466 measuring properties at high temperature, high pressure, low pH, and high solids
467 concentrations. The impeller design provides sufficient mixing to measure rheo-
468 logical properties as a function of time.

469 Preliminary tests reveal a number of interesting phenomena. Changing the
470 temperature results in dramatic changes in the apparent suspension viscosity. When
471 the temperature remains below approximately 150°C (no acid added), the appar-
472 ent viscosity decreases reversibly with increasing temperature. In the presence of
473 sulfuric acid, rheological changes are irreversible as the biomass is hydrolyzed.
474 There are temporal torque fluctuations whose magnitude tends to decrease with
475 increasing temperature.

476 **Some conditions produced a negative plastic viscosity, that is, a decrease**
477 **in apparent shear stress with an increase in apparent shear rate. This phe-**
478 **nomenon was observed in both rheometers, and has been reported previously**
479 **for biomass suspensions [27]. The existence of a negative plastic viscosity ap-**
480 **pears to depend on particle size, concentration, and temperature, and per-**
481 **haps other variables. The mechanisms that produce this behavior are un-**
482 **clear, and will be discussed further in future publications.**

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Table 1: Best fit Bingham model parameters for the data presented in Fig. 9. Uncertainties are only estimated for data sets with three or more data points.

T (°C)	τ_0 (Pa)	η_{pl} (Pa·s)
95	1940	19
125	1400	14
140	900 ± 200	12 ± 8
150	510 ± 30	16 ± 2

FIGURE CAPTIONS

Figure 1: Schematic diagram of the Lignocellulosic Biomass Rheometer (LCBR).

Figure 2: Photograph of the LCBR insert and impeller, designed to fit in a 2 L Parr reactor. Left: the cylindrical insert with interior static pin array. Right: the bladed impeller shaft with the slotted weight and Parr shaft coupling.

Figure 3: Viscosity as a function of temperature for the standard Newtonian fluid (polybutene) obtained from Cannon, along with the fit with Eq. 3.

Figure 4: (a) Chopped corn stover. (b) Chopped and milled corn stover (bar = 2.54 cm).

Figure 5: (a) Apparent viscosity as a function of apparent shear rate for modeling clay measured with the LCBR and the torque rheometer at 65°C. Inset: Apparent viscosity as a function of shear stress. (b) Apparent shear stress as a function of apparent shear rate. Inset: Apparent shear stress as a function of apparent shear rate on a log scale. Error bars are smaller than the symbols.

Figure 6: Photograph of the clay following the LCBR operation. The exposed impeller blade was moving right to left. A cavity is apparent behind the blade. The space in front of the blade is filled with clay because an impeller blade below (not visible) pushed material into the previously formed cavity.

Figure 7: (a) Apparent viscosity as a function of apparent shear rate for chopped corn stover (insoluble solids mass fraction = 15 %) and milled corn stover (insoluble solids mass fraction = 20 %) measured using the LCBR and the torque rheometer (TR). Inset: Apparent viscosity as a function of apparent shear stress (b) Apparent shear stress as a function of apparent shear rate. Inset: Apparent shear stress as a function of apparent shear rate on a log scale.

Figure 8: Raw data obtained using the LCBR with chopped and milled corn stover (insoluble solids mass fraction = 20 %) without acid.

Figure 9: (a) Apparent viscosity as a function of apparent shear rate at different temperatures for chopped and milled corn stover (insoluble solids mass fraction = 20 %) without acid, as the biomass is heated from 95 to 150°C. The solid curves are fits with the Bingham model. (b) Apparent shear stress as a function of apparent shear rate. The error bars are smaller than the symbols.

Figure 10: Apparent viscosity vs. temperature for chopped and milled corn stover (insoluble solids mass fraction = 20 %) with acid (1.0 % H_2SO_4).

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