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Research paper

Rheometry of coarse biomass at high temperature and pressure

Daniel J. Klingenberg [a], [*], Thatcher W. Root [a], Shalaka Burlawar [a], C. Tim Scott [b], Keith J. Bourne [b], Roland Gleisner [b], Carl Houtman [b], Vish Subramaniam [c]

[a] Department of Chemical and Biological Engineering, and Rheology Research Center, University of Wisconsin, Madison, WI, 53706, United States
[b] U.S. Forest Service Forest Products Lab, Madison, WI 53726, United States
[c] Subsea Surveillance, Shell Exploration & Production Co., New Orleans, LA 70139, United States

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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.

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 [1–3], 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) [3–5]. Commercialization of such biorefining processes requires reducing the processing costs [6–8].

Increasing the concentration of insoluble solids can reduce the cost of processing biomass [9–13]. 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 [12,14–19]. It is thus apparent that understanding their rheological properties is essential for designing efficient processes and equipment [13,16,20–22].

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 Liberatore [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

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[*] Corresponding author.
E-mail addresses: dan.klingenberg@wisc.edu (D.J. Klingenberg), twroot@wisc.edu (T.W. Root), burlawar@wisc.edu (S. Burlawar), tscott@fs.fed.us (C.T. Scott), kjbourne@fs.fed.us (K.J. Bourne), rgleisner@fs.fed.us (R. Gleisner), choutman@fs.fed.us (C. Houtman), Vish.Subramaniam@shell.com (V. Subramaniam).

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($\tau = \tau_0 + K\dot{\gamma}^n$) [22–27]. The yield stress of biomass is a rapidly increasing function of solids concentration, often represented by the empirical expression

$$\tau_0 = aC^b, \tag{1}$$

where C is the solids concentration, and a and b are empirical parameters [28–31]. The parameters depend on such properties as particle size distribution, fiber aspect ratio, stiffness, and additive type and concentration [27–29]. 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 [33–35] 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 significantly [27,38–41].

A critical element that is missing in our understanding of the rheological properties of biomass is the behavior of the biomass under the relatively extreme reaction conditions often employed in hydrolysis and other catalytic reactions (e.g., $170 < T < 230\,^\circ$C and low pH). Furthermore, these properties change significantly during processing, so there is a great need to understand this behavior in situ while the reactions are proceeding. It is this information that is necessary for the design of practical processes for the efficient production of biofuels and other chemicals.

In this paper, we describe a new rheometer that is capable of measuring apparent rheological properties of lignocellulosic biomass at high temperatures (>230 °C), high pressures (>2.8 MPa), low pH (<1.0), very high solids concentrations, and for large particles (>10 mm). We show that rheological properties measured with this Lignocellulosic Biomass Rheometer (LCBR) are consistent with those measured with a torque rheometer. Biomass samples investigated show that these materials are yield stress fluids whose yield stress decreases with increasing temperature. Changes in apparent rheological properties with temperature are reversible at low temperatures, but apparent viscosities decrease dramatically and irreversibly at high temperatures, or when a sufficient amount of mineral acid is present. Irreversible changes in rheological properties appear to arise from the acid-catalyzed hydrolysis of the biomass solids.

2. Materials and methods

2.1. Equipment

The Lignocellulosic Biomass Rheometer (LCBR) comprises an impeller and insert that are placed inside a 2 L Parr reactor (Model 4530, 2-L Floor Stand Reactor, Parr Instrument Co., Moline, IL). The temperature of the reactor vessel is increased or decreased with an external heating/cooling jacket. The reactor head has ports for injecting liquids, inserting a thermocouple, pressure gauges (we do not report pressures in this paper), pressure relief devices. The impeller, insert, and Parr vessel and head (shown schematically in Fig. 1) are constructed from Hastelloy B2 and B3 alloys in order to resist corrosion under harsh reaction conditions (B2 was used for the Parr vessel and head, and B3 was used for the insert and impeller).

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

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

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

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

The rotating shaft contains an array of blades that are pitched at a 30° angle from horizontal and cut with a 1.905 cm radius on the leading and trailing edges. The top pair of blades is oriented to produce a downward flow of biomass from the feed zone into the mixing zone. The bottom pair of blades is oriented upward to scrape the biomass up off the insert base. The middle two tiers of blades are alternately pitched to cycle the biomass flow upward and downward (see Fig. 2). This blade configuration is designed to produce zero net motion of sheared material in the axial direction.

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

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

The insert and impeller were used in a Parr Model 4530, 2 L Floor Stand Reactor. Several modifications of the Parr reactor head were required to accommodate the insert and impeller shaft. Blind openings were drilled to receive the locating pins. The thermowell was reduced to 0.635 cm diameter and relocated inward on the same radius for insertion into the bore in the guide bar. The Parr