



Characterization of changes in viscosity and insoluble solids content during enzymatic saccharification of pretreated corn stover slurries

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ABSTRACT

Viscosity trends in pretreated corn stover slurries undergoing enzymatic saccharification were characterized for a range of initial insoluble solids concentrations from 10% to 25% and correlated with total glucose released and changes in insoluble solids concentration throughout a 7 day period. Viscosity trends are defined in two phases, which coincide with two rate zones observed in the release of sugar during enzymatic hydrolysis. Viscosity rapidly decreased as initial solids concentration decreased in the first phase, and appears to reach a steady value for the lower solids concentrations in the second phase. The first phase is defined as approximately the first 8 h of the reaction based on the rates of glucose release, viscosity changes, and insoluble solids changes. A method for premixing the slurry samples in the viscometer cup prior to viscosity measurements is introduced. The method takes into consideration the need to maintain a uniform solids suspension while ensuring steady-state flow inside the viscometer cup. The slurries exhibit pseudoplastic behavior and are well described by the power law model for non-Newtonian fluids throughout the course of the reaction. Small changes in percent solids concentration lead to order of magnitude differences in viscosity.

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1. Introduction

While current technology's predominant source of fermentable sugars for making ethanol is derived from starchy crops such as corn, the feedstock is relatively expensive because of its value as a foodstuff. The conversion of agricultural residues to ethanol offers a savings when compared to the energy spent on crop production and harvesting. However, technical challenges must be overcome for making the conversion economically competitive to mature and proven grain conversion process. Improving the digestibility of the material's cellulose and hemi-cellulose is a key technological barrier in reducing the cost of producing a sugar stream suitable for fermentation to ethanol.

Saccharification of the cellulose is both the rate and cost limiting step in the overall conversion process; residence times on the order of 7 to 10 days, or more, are required to achieve 80–90% conversion of the cellulose (Dasari et al., 2009; Hodge, 2005). This compares to a residence time scale of hours for the fermentation and minutes for the pretreatment of the raw material. Improving the saccharification process has the most potential for reducing operating and capital costs in the overall conversion process. Reducing enzyme usage and associated energy, processing, and

capital costs of this step are required improvements if this technology is to become economically feasible.

To maximize the amount of ethanol produced per batch, it is desirable to begin with a high solids concentration in the pretreated slurry in order to provide the most potential sugar for fermentation. However, high solids content may result in processing obstacles including high power consumption (Dasari et al., 2009), excessive wear on equipment, and reduced conversion.

High power consumption and equipment wear are related to the viscosity of the fluid being mixed. Corn stover slurries exhibit non-Newtonian properties. Pimenova and Hanley (2004) characterized the viscosity of corn stover suspensions and found that the slurries closely follow a power law model that relates shear stress to impeller shear rate using a consistency index factor. However, they only collected data for un-hydrolyzed corn stover. According to Tayal et al. (1997), enzymatic hydrolysis significantly reduced the viscosity of such solutions over time. They found that, as the starting material is reduced by the enzyme action, substantial viscosity reductions were seen at elevated temperatures. Some lowering of viscosity even occurred at temperatures much lower than common reaction temperatures.

Hodge (2005) found that in simple shake flask trials, solids concentration above 27% significantly decreases the rate of cellulose hydrolysis. However, it has also been reported (Dasari et al., 2009; Hodge et al., 2005) that the use of properly designed reactors could reduce some of the conversion-limiting effects.

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The lower reaction rates in the shake flasks were largely attributed to limited mixing and temperature control. Increased shear in the reactors resulted in better distribution of the enzyme and more even heating, especially in the case of a scraped surface system that kept the heat transfer surface clear of material build-up (Dasari et al., 2009). Their results supported the findings of Mansfield et al. (1999) who related the degree of saccharification to mixing through factors like adsorption. They concluded that more even distribution of enzyme achieved by proper mixing allows for effective interaction between the substrate and enzyme. Kaar and Holtzapfel (1998) also stated that areas of high or low heat in an unmixed or improperly stirred reactor may damage or deactivate temperature-sensitive enzymes.

Designing reactors and processes for the saccharification of biomass solids to a fermentable sugar stream requires knowledge of the characteristics of the fluid to be processed. Highly viscous slurries with high solids content, such as biomass slurries, cause high power consumption and excessive equipment wear in poorly designed systems. This paper aims to characterize viscosity trends throughout the course of saccharification reactions for a range of initial insoluble solids concentrations (from 10% to 25% w/v) of pretreated corn stover slurries (PCS) and correlates the viscosity changes to changes in insoluble solids concentration and glucose concentration throughout a 7 day period. Since obtaining accurate viscosity data is difficult in solids suspensions, a method for measuring viscosity using a standard vane impeller and cup viscometer is introduced. The method determines the amount of time the slurry must be premixed to reach a steady-state flow inside the viscometer cup while also estimating the mixing speed needed to maintain the solids in suspension. The viscosity trends will be useful for establishing reactor design and operating parameters for an eventual large-scale saccharification system.

2. Methods

2.1. Biomass slurry preparation

Corn stover slurry pretreated with dilute sulfuric acid (190 °C, 1.6% acid, 30% solids, 5 min residence time) was provided by the National Renewable Energy Laboratory. The pretreated corn stover is comprised of 60% cellulose, 32% lignin, and 5% hemicelluloses as reported by NREL. To prepare a slurry for the enzymatic reaction, liquid hydrolysate and solids were first separated by vacuum filtration. Vacuum dried solids were then washed with 10 times dilution of de-ionized water in a large beaker with stirring, then vacuum dried through filter paper. This washing and drying procedure was repeated two more times to ensure that pre-existing sugars, organics, and other residues from the pretreatment process were removed from the solids.

A set of 11 beakers with identical initial contents constituted one test. The contents of one beaker were used per sample point and disposed of following measurement, with samples taken at 2, 4, 6, 8, 24, 48, 72, 96, 120, 144, and 168 h from the start of incubation. A policy of one sample per beaker was used since the viscosity measurements required 30 mL samples. This prevented both a significant reduction in volume throughout the duration of each test and prevented the returning of material that had been removed for measurement to be re-mixed with un-sampled test material. The solids loadings were calculated on a weight per volume basis taking into account the water present in the vacuum filtered solids. To prepare a batch of PCS slurry, washed solids and 0.05 M citrate buffer at 4.8 pH were added to autoclaved shake flasks. To prevent bacterial growth, 3 µL/mL of cycloheximide and 4 µL/mL of tetracycline were added to the slurry. Total operating volume per test was 50 mL: the washed solids were added to

two-thirds of the total liquid volume, and enzyme was mixed into the remaining one-third of the liquid volume. The enzyme dosage was 15 FPU/g of cellulose. The enzyme was Spezyme CP (Lot # 301-05021-011) from Genencor International. Enzyme addition and all further handling and sampling occurred in a laminar flow hood. The beaker containing the slurry was covered in parafilm and aluminum foil, and tests run in a shaker incubator operating at 55 °C and 250 rpm. Each test was run in duplicate and two samples were measured from each test so each data point represents the average of four measurements.

2.2. Glucose measurements

The liquid was tested for dissolved sugar content using a YSI 2700 Select Biochemistry Analyzer. For sampling, the slurry was stirred in the laminar flow hood and three 1.5 mL aliquots were removed and loaded in micro-centrifuge tubes which were centrifuged to separate the liquid from the remaining solids. The liquid was diluted to a glucose concentration between 2 and 10 gm/L, the recommended range of the YSI.

2.3. Viscosity measurements

For measuring viscosity, a 30 mL slurry sample was transferred to the sample cup of a Physica MCR 300 Modular Compact Rheometer from Anton Paar. The rheometer used a vane impeller with a diameter of 2.1 cm which provided a clearance of 0.6 cm from the cup wall and 2.48 cm from the bottom. Prior to recording measurements, the rheometer stirred the slurry sample for 6 min at a shear rate of 170 s⁻¹ while the sample was maintained at the reaction temperature (55 °C) in a peltier environmental chamber. Measuring the viscosity of solids slurries presented difficulties due to the need for a homogeneous solids suspension. Accurate measurements of the viscosity of corn stover slurries required a period of premixing to suspend the solids and to achieve a steady-state. The change in viscosity during premixing is attributed to the alignment of fibers with the direction of flow, which works to lower the viscosity in a way similar to the effect described by Ebeling et al. (1999) who reported that cellulose microcrystal orientation is dependent on the direction of shear. Eventually the particles reach a steady alignment and the viscosity stopped decreasing over time. The solids tended to stay suspended at the higher solids concentrations due to the higher viscosities, but the premixing was more of a necessity for the 10% solids concentration where the particles were more likely to settle out without the aid of the impeller. To determine the time required to reach steady-state, viscosity was measured as a function of time at 170 s⁻¹ shear for slurries of 10%, 15%, 20% and 25% PCS. The time to reach steady-state varied somewhat with initial solids concentration, but minimal viscosity changes occurred in all of the slurries by 6 min (Fig. 1). The 170 s⁻¹ shear rate corresponds to the impeller speed that was 30% higher than the speed necessary to suspend all particles (130 s⁻¹) as estimated using Zweitering's equation, Eq. (1), for suspension of solid particles in liquid in baffled tanks (Zweitering, 1958). In this equation, n is the stirrer speed, s is a dimensionless number defined in the paper, ν is the kinematic viscosity, x is the particle size, g is the acceleration due to gravity, $\Delta\rho$ is the difference between liquid and solid density, ρ_L is the liquid density, B is the weight of solids per weight of liquid, and D is the stirrer diameter.

$$n = \frac{sv^{0.1}x^{0.2}(g\Delta\rho/\rho_L)^{0.45}B^{0.13}}{D^{0.85}} \quad (1)$$

The higher shear rate was used to account for a higher rotational speed that is expected to be needed to suspend particles in an unbaffled viscometer cup. Following the 6 min of pre-shear,

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