Investigating the changing rheology of high-solids biomass slurries during enzymatic saccharification

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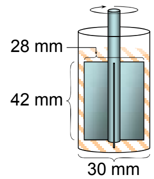
Introduction

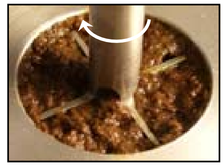
Processing of high-solids slurries will be necessary for the economic operation of lignocellulosic biorefineries. In this work, we examine the changing yield stress and viscosity of high-solids dilute acid pretreated corn stover (PCS) during enzymatic saccharification. PCS slurries containing 20% (w/w) insoluble solids were observed to liquefy to the point of being pourable after about two days, at a biomass conversion of about 40%. Mass balance and semi-empirical relationships were developed to connect the progress of enzymatic hydrolysis with particle concentration and yield stress, and the rheological properties of unsaccharified and saccharified PCS agree well when compared at equivalent volume fractions of insoluble particles.

Because the yield stress drops with conversion, indicating when a suspension becomes "pumpable", this work will help the process designer identify an optimal residence time during saccharification. In this light, we also present preliminary results suggesting that viscosity-modification / flow-assurance additives may significantly reduce the yield stress and viscosity of PCS slurries, ensuring their downstream processability.

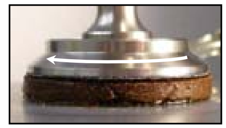
Rheometry

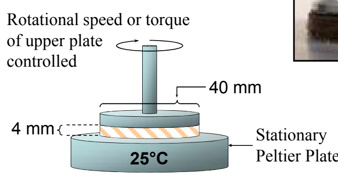
Vane-in-cup geometry:





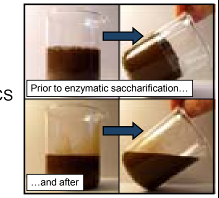
Parallel plate geometry:



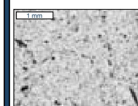


Enzymatic Saccharification

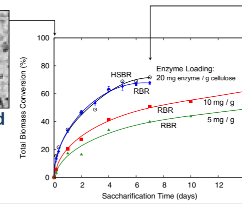
- High-solids bioreactor (HSBR)
  - Horizontal reactor with impellors to mix PCS and enzymes at 48°C
- Roller bottle reactor (RBR)
  - 2 L roller bottles containing 1000 g PCS
  - Incubated at 48°C
  - Rotated at 2 – 20 rotations / minute
  - 20% (w/w) washed PCS
  - 5 - 20 mg cellulase / g cellulose
- Samples of suspension
  - Collected at various time points
  - Boiled / refrigerated to deactivate enzyme

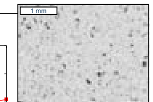


Liquefaction of PCS After 1 – 2 days



Unsaccharified PCS





After Saccharification
7 days / 70% Conversion

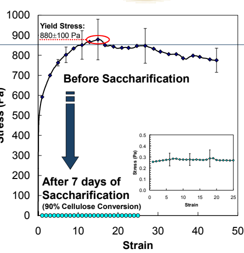
Determination of Yield Stress

A yield stress is the applied stress at which yield-stress fluids begin to flow. At imposed stresses below their yield stress, such materials act much like a solid. For example, while water and honey, both Newtonian fluids, form a smooth surface over time, mayonnaise, a yield-stress fluid, remains deformed after mixing with a spatula.

Honey
No Yield Stress
(Newtonian Fluid)

Mayonnaise
Yield Stress = 100 Pa

Freshly Poured Concrete
Yield Stress = 1,000 Pa

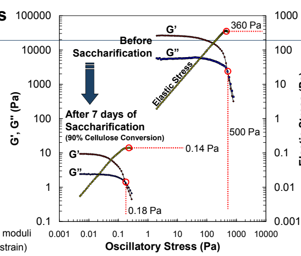


Transient Flow experiments

- Rheometer vane rotates steadily (15 min/revolution)
- Early saccharification times: Maximum stress interpreted as yield stress
- Later saccharification times: Yield behavior not obvious

Oscillatory experiments

- Stress oscillated sinusoidally (1 Hz)
- Yield Stress defined by:
  1. Crossover of elastic (G') and viscous (G") moduli
  2. Maximum of the elastic stress (G' × peak strain)



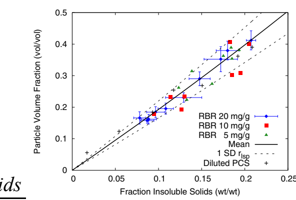
Solids Characterization of PCS Suspensions

- **Weight fraction of insoluble solids:** f_{is}, estimated by quantitatively drying samples of the whole suspension and interstitial fluid.

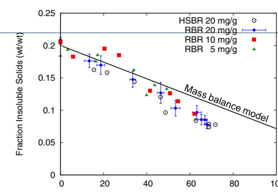
$$f_{is} = \frac{\text{Mass of Insoluble Solids}}{\text{Mass of Suspension}}$$

- **Particle volume fraction:** ϕ, measured by quantifying the fraction of liquid volume passing through a centrifuge filter.

$$\phi = \frac{\text{Volume of Particles}}{\text{Volume of Suspension}}$$



- The particle volume fraction is roughly proportional to the fraction of insoluble solids.



- The fraction of insoluble solids, and therefore the particle volume fraction, decrease as the biomass is hydrolyzed.
- These trends were independent of reactor configuration and enzyme loading.

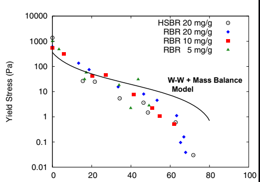
Enzo-rheology:

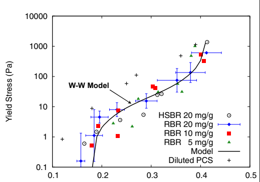
Rheology of Saccharified Corn Stover[1]

- The yield stress of PCS suspensions decreases with biomass conversion.
- A rheological model developed by Wildemuth and Williams[2,3] adequately correlates yield stress with particle volume fraction for both saccharified and un-saccharified PCS:

$$\tau_y(\phi) = \left[A \left(\frac{\phi/\phi_{m0}}{1-\phi/\phi_{m\infty}} \right) \right]^{1/m}$$

- Parameters with 95% CI:
  - $m = 1$
  - $A = 9 \pm 5$ Pa
  - $\phi_{m0} = 0.18 \pm 0.02$ Pa
  - $\phi_{m\infty} = 0.41 \pm 0.01$ Pa





[1]Roche, CM, CJ Dibble, JS Knutsen, JJ Stickel, and MW Liberatore (2009) "Particle concentration and yield stress of biomass slurries during enzymatic hydrolysis at high-solids loadings" In Press: *Biotechnology and Bioengineering*.
[2]Wildemuth, C. R., and M. C. Williams (1984) "Viscosity of Suspensions Modeled with a Shear-Dependent Maximum Packing Fraction," *Rheologica Acta* 23:627-635.
[3]Wildemuth, C. R., and M. C. Williams (1985) "A New Interpretation of Viscosity and Yield Stress in Dense Slurries - Coal and Other Irregular Particles," *Rheologica Acta* 24:75-91.

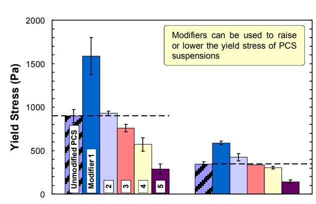
Current and Future Research:

Viscosity Modification

Numerous studies have been conducted to assess how surfactants and other chemical additives can be used to modify the binding properties of cellulase enzymes, resulting in enhanced saccharification kinetics and biomass conversions.

Additionally, "drag reducing" polymers have long been known to lower the viscosity of water and petroleum, reducing pumping power and transport costs in pipelines.

In this work, we explore chemical additives to both enhance enzymatic saccharification and effect a reduction in the suspensions' yield stress, a desirable synergy.



Summary

- A clear relationship between biomass conversion, fraction insoluble solids, and particle volume fraction was defined.
- At an insoluble solids concentration of 20% (w/w), as little as 30% cellulose conversion is necessary to achieve a "pumpable" suspension with a yield stress below 10 Pa.
- A semi-empirical rheological model was used to relate volume fraction with yield stress.
  - A single set of model parameters is capable of characterizing yield stresses of suspensions in a number of enzymatic hydrolysis experiments across a range of enzyme concentrations.
  - It provides a good prediction of yield stress determined from particle volume fraction.

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