

BIOMASS

The Biochemical Process Integration Task focuses on integrating the processing steps in enzyme-based lignocellulose conversion technology. This project supports the U.S. Department of Energy's efforts to foster development, demonstration, and deployment of "biochemical platform" biorefineries that economically produce ethanol or other fuels, as well as commodity sugars and a variety of other chemical products, from renewable lignocellulosic biomass.

The National Renewable Energy Laboratory manages this project for DOE's Office of the [Biomass Program](#).

To discuss the contents of this update, or for further information on the Biochemical Process Integration Task, contact Dan Schell at NREL, phone 303-384-6869, email dan.schell@nrel.gov.

R&D Progress

Evaluating New Analytical Techniques for Measuring Sugars

Soluble sugars in the liquid portion of biomass hydrolysates are typically measured by High Performance Liquid Chromatography (HPLC). Currently, we use a Shodex Sugars SP0810 lead cation column with a water mobile phase and refractive index detection (Pb/RI) using the procedure described in the following document: <http://www.nrel.gov/biomass/pdfs/42618.pdf>. We recently evaluated two other techniques for measuring biomass-derived sugars: a Shodex SZ5532 zinc cation column using an acetonitrile/water gradient and charged aerosol detection (Zn/CAD), and an ion chromatography method using a Dionex SA-10 column with pulsed amperometric detection (IC-PAD).

Both techniques have advantages and disadvantages compared to the current method. Zn/CAD may be able to resolve and quantitate oligomeric sugars with further method development, but the gradient-based technique requires using a CAD detector whose non-linear response is less accurate and has a smaller dynamic range than RI detection. The IC/PAD system produced better separation of the sugars, but the PAD system was not stable and again the analytical results were less accurate than the Pb/RI method. While both of the new techniques resolved sugars with shorter run times, neither system was able to match the accuracy and precision of the Pb/RI method.

Measuring Fraction Insoluble Solids in Biomass Slurries

The fraction of insoluble solids (f_{is}) in biomass slurries is defined as the dry mass of insoluble solids divided by the total mass of the slurry. It differs from the total solids of the slurry because it excludes all compounds that are soluble in the aqueous phase. This measurement is required to calculate the mass of sugars in the liquid phase of these slurries, which is necessary to determine conversion yields during pretreatment or enzymatic hydrolysis. Historically, we have measured f_{is} by repeated washing and centrifugation of the biomass slurry solids to obtain washed solids. This technique is laborious; some of the solids are lost during decanting of the liquid and it is assumed that all of the soluble solids are removed by repeated washing. We have also published a report on a "no wash" method to determine f_{is} based on a measurement of the slurry's total solids content and the solids content of the liquid phase.¹ Although less laborious than the wash method, there are concerns with loss of volatile compounds and chemical reactions that might occur during drying of acidic biomass slurries.

The first problem in characterizing the f_{is} of a biomass slurry is obtaining a sample that accurately represents the original slurry. But it can be extremely difficult to representatively sample a biomass slurry depending on the amount of material to be sampled and its solids content. For example, for pretreated biomass slurries, the liquid fraction may separate from the solids over time and vigorous mixing may be required to obtain a uniform solid suspension that usually resembles a paste. In some cases, sampling at multiple locations throughout the slurry is required to characterize a large lot of material. Enzymatically hydrolyzed slurries consist of solids suspended in an excess of water. There can be large errors in accurately sampling these slurries; for example, the material may dewater during the sampling process. Ultimately, some level of uncertainty in the sample's ability to represent the original slurry must be accepted.

Once a sample of slurry is obtained, the f_{is} must be accurately measured. To test the accuracy of the no-wash method, MIT Practice School students and NREL researchers prepared synthetic pretreated biomass slurries by combining thoroughly washed pretreated solids and a liquid solution with known concentrations of sugars and acids (sulfuric and acetic). Total solids measurements were performed by drying (oven at 105°C and 40°C with vacuum) and by lyophilization on both the whole slurry and liquid fraction. Both 40°C vacuum drying and lyophilization accurately measured the slurry's total solids content, but the 105°C drying method underestimated the total solids content, presumably due to creation and loss of volatile compounds during drying. Measurements of the liquid phase total solids content were less accurate, but the 40°C vacuum drying method produced the best results (see Figure 1). Nevertheless, the variability is higher than desired and we are continuing to improve the technique with the goal of eventually issuing an improved procedure.

¹Weiss, N. D.; Stickel, J. J.; Wolfe, J. L.; Nguyen, Q. A. 2009. "A Simplified Method for the Measurement of Insoluble Solids in Pretreated Biomass Slurries." *Appl. Biochem. Biotechnol.* 162, 975-987.

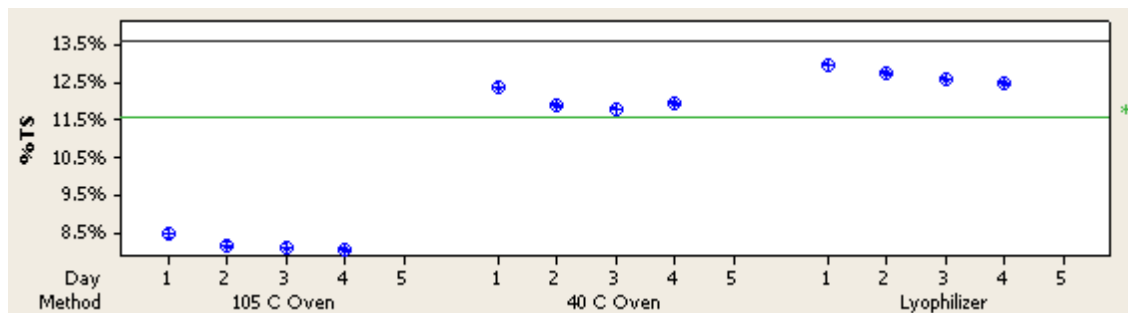


Figure 1. Multiple measurements of the total solids content of a synthetic hydrolysate liquor (at 11.5% total or dissolved solids (TS), w/w) using three drying techniques.

Biochemical Process Integration Task Information

Web-based information on the biochemical process integration project, including presentations made at past review meetings, is available at the following links: <http://www.obpreview07.govtools.us/biochem/> and <http://www.obpreview2009.govtools.us/biochem>. The latest project review meeting was held February 14-17, 2011, in Denver, Colorado. Information is available at the following website: <http://obpreview2011.govtools.us/>.

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