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Water sorption in pretreated grasses as a predictor of enzymatic hydrolysis yields

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ABSTRACT

This work investigated the impact of two alkaline pretreatments, ammonia fiber expansion (AFEX) and alkaline hydrogen peroxide (AHP) delignification performed over a range of conditions on the properties of corn stover and switchgrass. Changes in feedstock properties resulting from pretreatment were subsequently compared to enzymatic hydrolysis yields to examine the relationship between enzymatic hydrolysis and cell wall properties. The pretreatments function to increase enzymatic hydrolysis yields through different mechanisms; AFEX pretreatment through lignin relocalization and some xylan solubilization and AHP primarily through lignin solubilization. An important outcome of this work demonstrated that while changes in lignin content in AHP-delignified biomass could be clearly correlated to improved response to hydrolysis, compositional changes alone in AFEX-pretreated biomass could not explain differences in hydrolysis yields. We determined the water retention value, which characterizes the association of water with the cell wall of the pretreated biomass, can be used to predict hydrolysis yields for all pretreated biomass within this study.

1. Introduction

Lignocellulosic biomass can serve as an environmentally beneficial feedstock for the production of petroleum-displacing renewable biofuels and biochemicals (Souza et al., 2015). One promising route to produce liquid transportation fuels from lignocellulosic biomass utilizes thermochemical pretreatment coupled to enzymatically-catalyzed deconstruction of plant cell wall structural polysaccharides followed by microbial conversion of the sugars to metabolites such as ethanol (Qureshi et al., 2014). The pretreatment step is necessary to overcome cell wall recalcitrance, which is a consequence of the complex secondary cell wall matrix comprised of cellulose, hemicelluloses, and lignin (Himmel et al., 2007). A diverse range of pretreatments have been studied that act through a variety of chemistries and mechanisms to achieve improved polysaccharide accessibility to cellulolytic enzymes. Greater accessibility can be manifested through a number changes to the cell wall, typically involving reorganization, solubilization, and modification of lignin and hemicelluloses (Chundawat et al., 2011a; Ong et al., 2014). For dilute acid or hydrothermal pretreatments, one of the primary quantifiable outcomes is xylan removal and depolymerization (Schell et al., 2003), while lignin relocalization is also important, yet more difficult to quantify (Donohoe et al., 2008). For delignifying pretreatments such as alkaline (Stoklosa and Hodge, 2015), alkaline-oxidative (Yu et al., 2011), and organosolv (Nitsos et al., 2016), lignin removal (as well as some hemicellulose) is one of the primary outcomes, with lignin content subsequently resulting as a strong predictor of hydrolysis yields (Li et al., 2012). AFEX pretreatment has been extensively studied since the 1980s as a route for the production of cellulosic sugars and animal feed (Balan et al., 2009). While it is known that lignin and hemicellulose relocalization impact the cell wall nanoscale porosity and its susceptibility to enzymatic depolymerization (Chundawat et al., 2011b), there is no significant change in composition following AFEX pretreatment. However, like the other alkaline pretreatments, lignin content has also been negatively correlated to hydrolysis yields from AFEX-pretreated biomass (Garlock et al., 2012).

Increased enzyme accessibility following cell wall reorganization can be considered a function of surface area, surface composition and chemistry, and cell wall porosity (i.e., pore volume and pore size distribution). Furthermore, cell wall porosity is a complex function of both polymer properties and solvent environment during porosity measurement. Consequently, characterization approaches that yield

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information about these properties can be useful for assessing the cell wall's susceptibility to enzymatic hydrolysis. Porosimetry techniques for solid porous materials such as mercury intrusion and BET porosimetry, are unsuitable for plant cell walls as these methods require dry samples and drying modified lignocellulosic fibers can result in "hornification" or irreversible collapse of pores (Fernandes Diniz et al., 2004). Nanoscale imaging techniques that have been applied to modified plant cell walls include SEM (Chinga et al., 2002), AFM (Fahlén and Salmén, 2004), and TEM tomography (Chundawat et al., 2011b), although these require careful sample preparation that preserves the pore structure. A number of methods relate water-cell wall interactions to pore and surface properties and include assessing water constraint in pores or surfaces by proton NMR (Meng et al., 2013), T_2 NMR relaxometry (Felby et al., 2008), freezing point depression of constrained water in plant cell walls by differential scanning calorimetry (DSC) (Park et al., 2006), and drainability of biomass fibers when subjected to centrifugation (water retention value or WRV) (Grethlein, 1985; Weise et al., 1996). Recently, we and others have investigated how quantitative metrics for cell wall-water association (e.g., WRV) can be used as a descriptor of cell wall porosity and the cell wall's response to enzymatic hydrolysis, with the potential for these techniques to be employed as high-throughput screening tools to assess biomass response to enzymatic hydrolysis. Our previous work has shown a positive, linear correlation between WRV and glucose hydrolysis yields for corn stover and switchgrass subjected to a range of alkaline-oxidative delignification and liquid hot water pretreatment conditions (Williams and Hodge, 2014) and for untreated diverse maize cultivars (Li et al., 2015).

For this work, we propose that quantifiable cell wall-water interactions, such as the WRV, may be a more useful indicator of enzymatic hydrolysis yields than any individual biomass property, such as cell wall composition, porosity and hydrophilicity, as the WRV is dependent upon both structural and compositional factors. This work expands on our previous findings to include a wider range of pretreatment chemistries and conditions. Specifically, we subjected corn stover and switchgrass to AFEX pretreatment and alkaline hydrogen peroxide (AHP) delignification at multiple conditions, with the goal of identifying the predictive capability of WRV alone or in combination with other quantifiable properties. Furthermore, select conditions were tested using DSC to find the freezing point depression of cell wall-associated water, and T_2 NMR relaxometry was tested to assess water constraint.

2. Materials and methods

2.1. Biomass feedstock

The untreated biomass feedstocks used in this work include switchgrass (*Panicum virgatum* L., cv. Cave-in-Rock) and corn stover (*Zea mays* L., Pioneer hybrid 36H56). The biomass was milled with a Wiley Mini-Mill (Thomas Scientific) to pass a 5 mm screen and air-dried to a moisture content of approximately 5% prior to any treatments. The structural carbohydrate and lignin composition of all materials were determined by the NREL/TP 510-42618 protocol (Sluiter et al., 2008) with minor modifications (Li et al., 2012).

2.2. Pretreatment

AFEX pretreatment was run in duplicate for each sample in 22 mL Parr reactors (Garlock et al., 2009). AFEX was run for each sample at two different ammonia/water combinations (1.5 g NH_3 and 2.0 g H_2O/g dry biomass or 2.0 g NH_3 and 0.5 g H_2O/g dry biomass) and four different temperatures (60, 90, 120, and 150 °C). Prior to loading the biomass in the reactors, the moisture was adjusted to the appropriate water loading and then 3 g (dry weight) of sample was loaded in the reactor. Vacuum was applied to the reactors for 20 s. For the 120 and 150 °C samples the reactors were preheated to 40 °C using an aluminum heating block. The appropriate mass of ammonia was added based on a previously determined volume-to-mass calibration using a high-pressure syringe pump (PHD 4400, Harvard Apparatus). After the ammonia was added, the reactors were heated in an aluminum heating mantle for 30 min, including the ramping time. At the end of the residence time, the reactors were vented to release the majority of the ammonia after which the biomass was unloaded and allowed to air dry in the fume hood overnight to allow the residual ammonia to evaporate. Once dry, duplicate batches were combined prior to performing subsequent experiments.

AHP delignification of corn stover and switchgrass was performed using four different conditions of H_2O_2 to biomass loadings, 0%, 6%, 12.5%, and 25% (g H_2O_2 /g biomass). Both conditions were performed in duplicate using 8 g of biomass (dry basis) at 15% (w/v). Samples were prepared in 250 mL Erlenmeyer flasks and placed in an incubator at 30 °C with shaking at 180 rpm. The flasks were sealed with parafilm to prevent evaporation but also to allow for some expansion as the pressure in the flasks increased with O_2 evolution. To counter the drop in pH over the course of the reaction, 5 M NaOH was added at 3, 6, and 9 h to bring the pH back up to 11.5. Delignification was stopped after 24 h by diluting the sample with 25 mL of water to 10% (w/w) solids and adjusting the pH to approximately 4.8 using concentrated sulfuric acid.

2.3. Enzymatic hydrolysis

AFEX pretreated biomass was loaded with water in sample flasks at 10% (w/v) solids. For both the AHP slurries mentioned previously and the AFEX pretreated biomass, 1 M citrate buffer was added to give a concentration of 50 mM buffer in the sample flasks. To prevent contamination of hydrolysate, tetracycline and cyclohexamine were added at a concentration of 10 mg/L each. An enzyme mixture of Cellic CTec2 and HTec2 (Novozymes A/S, Bagsværd, Denmark) was added in a protein mass ratio of 2:1, respectively, at an enzyme loading of 30 mg enzyme/g glucan. The protein contents of the enzymes were based on the Bradford assay (Sigma-Aldrich). Samples were then mixed by hand and placed in a shaking incubator at 50 °C and 180 rpm for either 24 or 72 h. Sugar concentrations in the hydrolysate were determined by HPLC using the method described in the NREL/TP 510-42618 protocol and converted to glucose yields based on the solids content in the reaction vessel and the untreated glucan contents for AHP samples or post-treatment glucan content for AFEX samples.

2.4. Water retention value

Water retention values (WRV) were determined according to a modified version of TAPPI UM 256 (TAPPI, 2015) as described in our previous work (Williams and Hodge, 2014). Briefly, the biomass samples were filter-washed using a Buchner funnel containing a 200 mesh stainless steel screen. The solids remaining after pretreatment and delignification were washed with approximately 700 mL of deionized water and vacuum-filtered to a moisture content of approximately 80%. Next, ~2.5 g of wet biomass was inserted into a spin-column (Handee Spin Column Cs4, Thermo Scientific) modified to have a 200 mesh stainless steel screen as the membrane directly under the biomass. The spin columns were then centrifuged at 900 × *g* for 15 min. The drained biomass was then weighed in an aluminum tray and placed in an oven at 105 °C for 3 h, and then weighed again. The WRV is the ratio of the mass of water remaining in the biomass after centrifuging divided by the mass of dry biomass. Samples were measured in triplicate and error bars represent standard deviations.

2.5. Differential scanning calorimetry

Solid residue after AHP pretreatment was washed with 500 mL of water using a Buchner funnel with a 200 mesh porous base and drained

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