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**Improving alkaline-oxidative pretreatment in hardwoods**

Improving alkaline hydrogen peroxide pretreatment of woody biomass via transition metals.

**The Science**

As a feedstock for biomass-to-biofuel processes, woody biomass exhibits several advantages that facilitate logistics relative to herbaceous feedstocks, including year-round availability and high bulk density. As we envision biomass-to-biofuel processes that include diverse biomass feedstocks, the physical and chemical properties of said biomass will have an important impact on the conversion process.

**The Impact**

The pretreatment of lignocellulosic biomass to reduce recalcitrance prior to enzymatic hydrolysis is a critical step required for the conversion of cell wall polysaccharides into biofuels, with the overall conversion efficiency of the process depending heavily on the pretreatment employed. Various approaches have been used to pretreat hardwoods, including soda pulping, dilute acid, dilute acid sulfite, alkali-buffered sulfate, acidic ethanol organosolv, and liquid water pretreatments, as well as pretreatments that decrystallize cellulose (e.g. ionic liquids). Additionally, oxidative pretreatments have been used by the pulp and paper industry for bleaching and delignification, and recently, have also been examined for the biofuels industry with lignin solubilization as the route for reducing biomass recalcitrance. The amount of redox-active metals in woody plants has been shown to exhibit substantial variability, and these metals can dramatically affect the pretreatment process, in part because they can catalyze the formation of reactive oxygen species and thereby contribute to the oxidative scission of polysaccharides.

**Summary**

Previously, researchers in the Great Lakes Bioenergy Research Center demonstrated that the Cu-catalyzed alkaline hydrogen peroxide pretreatment of hybrid poplar resulted in substantial improvement of sugar yields after enzymatic hydrolysis; in this research, they focused on correlating biomass properties to pretreatment efficacy by comparing enzymatic hydrolysis yields after alkaline hydrogen peroxide (AHP) pretreatment of four different hardwoods (silver birch, a hybrid aspen, a hybrid poplar, and sugar maple) and correlating these results with various cell wall properties. The primary outcome of the pretreatment was the solubilization and removal of cell wall lignin and xylan. Lignin removal was correlated with an increase in enzymatic hydrolysis yields, possibly due to the increased accessibility of cell wall polysaccharides to hydrolytic enzymes. They also demonstrated the important role of cell wall-associated redox-active transition metals in impacting the effectiveness of AHP pretreatment by finding that the metals intrinsically present in the biomass correlated with increasing hydrolysis yields and delignification. Addition of Cu 2,2 bipyridine [Cu(bpy)] complexes to transition metal-deficient poplar (total of 7 ppm transition metals) resulted in substantial improvement of hydrolysis yields while providing only minimal improvement for the other three hardwoods which all had transition metal content ranging from 45-111 ppm. Researchers also showed, via glycome profiling, that increased delignification during the pretreatment process resulted in an increase in the extractability of epitopes for xylan, xyloglucan, and pectin backbone epitopes. The implications of their work are that cell wall-associated transition metals can play a positive role in oxidative cell wall deconstruction, and that this property can also be altered to optimize the outcome of the pretreatment.

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**Publications**

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