EFFECTIVE METAL CATALYZED OXIDATIVE PRETREATMENT OF WOODY BIOMASS

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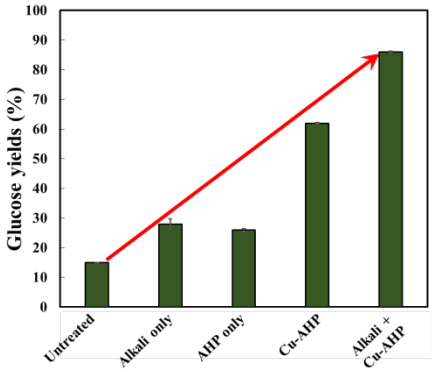
Woody biomass represents a vast source of fermentable carbohydrates and offers significant advantages relative to other potential lignocellulosic feedstocks. It also presents special challenges, however, due to its thicker cell walls, denser vascular structure, and higher lignin content. We recently discovered that alkaline hydrogen peroxide pretreatment catalyzed by copper(II) 2,2'-bipyridine complexes (Cu-AHP) significantly increases the enzymatic digestibility of woody feedstocks, including hybrid poplar. Significantly, this pretreatment is performed under relatively modest conditions (i.e. room temperature and ambient pressure) and is complete within 24 hours. Subsequent optimization of Cu-AHP has led to decreased catalyst utilization, copper recycling, lower enzyme concentrations, and more efficient H_2O_2 utilization. Utilizing our new, modified pretreatment method we are currently achieving glucose and xylose yields of up to 90%, and the resulting hydrolysate can be readily fermented to achieve high titers of ethanol.



Mechanistic studies of the catalytic oxidation process revealed disruption of the cell wall layers, which is associated with lignin removal and cellulose oxidation. Interestingly, preliminary transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), and electron energy loss spectroscopy (EELS) experiments reveal the presence of copper nanoparticles at the site of cell wall disruption following Cu-AHP pretreatment. Detailed analysis of the solubilized lignin via 2D-NMR in collaboration with John Ralph at the University of Wisconsin revealed the formation of oxidized syringyl and guaiacyl units as well as the presence of aldehydes groups conjugated to aromatic rings. These results are consistent with our analysis via liquid chromatography – mass spectrometry (LCMS), which demonstrated the presence of monomeric lignin fragments including vanillin, vanillic acid, syringic acid, syringaldehyde, acetosyringone, azelaic acid, and p-hydroxybenzoic acid. Together these results provide additional insight into the oxidative reaction mechanism. Intriguingly, a relatively large portion of both the solubilized and unsolubilized lignin appears to be unmodified, indicating that Cu-AHP pretreatment of woody biomass may also provide a convenient source of clean lignin amenable to subsequent valorization.