Chemical and Morphological Structure of Solubilized Lignin Extracted via Ethanol, Tetrahydrofuran, and γ-Valerolactone Pretreatments from Wild Type and Transgenic Switchgrass

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https://cmb.ornl.gov/dynamic-visualization-of-lignocellulose/

Project Goals: The development of renewable biofuels is a key mission of the DOE Genomic Science program. Lignocellulosic biomass has the potential to be an abundant, renewable source material for production of biofuels and other bioproducts. The use of organic solvents to optimize biomass pretreatment has shown considerable promise, but their disruption of microbial membranes is key to toxic effects limiting fermentation titers. The Oak Ridge National Laboratory (ORNL) Scientific Focus Area (SFA) Biofuels Program utilizes multi-length scale imaging with neutron scattering complemented by high performance computer simulations, NMR, biochemistry and targeted deuteration to provide fundamental knowledge about the molecular forces that drive solvent disruption of the critical assemblies of biomolecules that comprise plant cell walls and microbial biomembranes.

The recalcitrance of lignocellulosic biomass remains a challenge in the biofuels and bioenergy process due to its complex physical and chemical structures of plant cell walls. To overcome the biomass recalcitrance, pretreatment and genetic modification are two techniques in the biological conversion of biomass to change or modify structures of biomass components in the plant cell wall. In this study, three organosolv pretreatments using ethanol (EtOH), tetrahydrofuran (THF), and γ-valerolactone (GVL) were applied on wild type and transgenic switchgrass including down-regulation of caffeic acid/5-hydroxyconiferyl aldehyde *O*-methyltransferase gene (COMT) and over-expression of MYB4 gene (MYB) (see Figure). The physicochemical properties of fractionated lignin precipitated from EtOH, THF, and GVL pretreatments were analyzed by gel permeation chromatography (GPC), small angle X-ray scattering (SAXS), nuclear magnetic resonance (NMR) techniques including ^{31}P and two-dimensional ^{13}C-^{1}H heteronuclear single quantum coherence (HSQC). In addition, molecular dynamics simulation was used to provide the molecular modes of lignin molecules in the pretreatment solvents of EtOH, THF and GVL. The pretreated solubilized lignins revealed a significant decrease in molecular weight compared to the untreated native lignin, especially in EtOH pretreatment. A near complete removal of β-O-4 interunit linkages was also observed in EtOH pretreated lignin. Furthermore, THF pretreated lignin presented the highest molecular weight, $\beta - 0 - 4$ linkages and aliphatic hydroxyl contents among the three organosolv lignin streams.

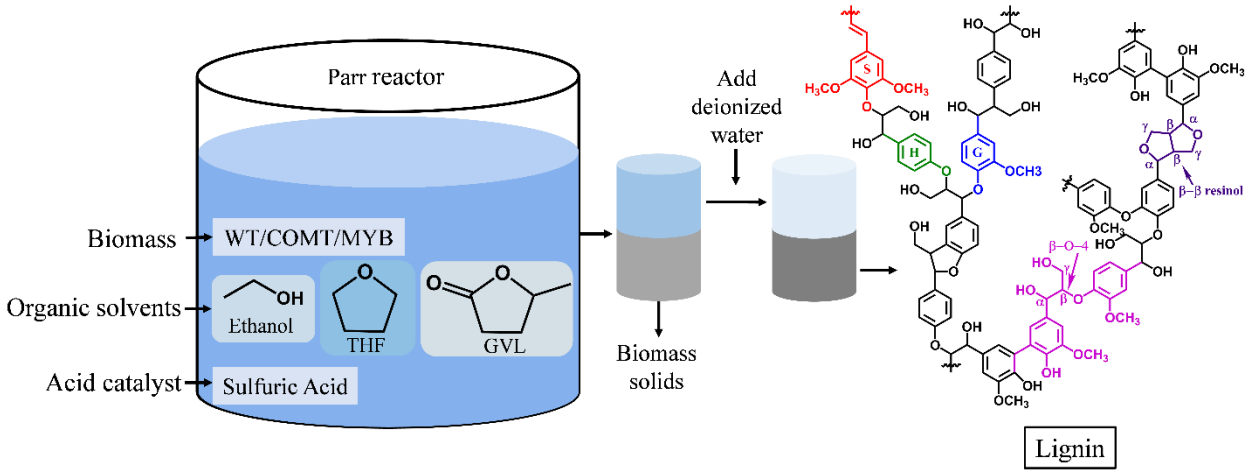

Figure: Pretreatment processes of WT, COMT, and MYB switchgrass.

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