Understanding Lignin Fractions of Biomass during Dilute Acid Pretreatment Using a Flow through Reactor

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Considerable research has been conducted into understanding the distribution of lignin in pretreated biomass and the effects of this distribution on enzymatic hydrolysis for bioethanol production. Enzyme accessibility is postulated to be one of the key factors affecting enzymatic conversion of pretreated biomass into fermentable sugars, with the lignin-hemicellulosic sheath seen as a barrier to enzymatic hydrolysis. It has been shown that thermal chemical dilute acid pretreatments of biomass disrupt this lignin-hemicellulosic matrix in such a way as to allow hydrolysis of hemicellulose into soluble sugars, and to coalesce lignin away from the cellulose microfibril thereby increasing localized enzymatic accessibility. Published results suggest that lignin redeposition could be a problem for enzymatic hydrolysis in batch reactor designs (Selig et al 2007). In this study, lignin distribution and morphology during dilute-acid pretreatment of corn stover are investigated using a flow through reactor at different reaction temperatures (150°, 170°C and 190°C) and different acid concentrations (0, 0.5 and 0.8 wt% H_2SO_4). Pretreatments using the flow-through reactor system result in continuous removal of the solublized hemicellulose and lignin with the flowing liquid. The lignin is collected with the effluent fractions and precipitates upon cooling. Representative samples of the residual solids were digested with spezyme and xylanase enzymes to determine the effects of pretreatments. In addition, the residual solids were washed with a various dissociation agents to remove the surface associated lignin in an attempt to understand the lignin/biomass interaction and to account for the mass of the lignin that is involved with the re-deposition phenomena. The washed solids were then exhaustively digested enzymatically and the residual lignin analyzed. Three lignin fractions (acid soluble lignin from liquid, acid insoluble lignin from liquid and residual lignin in the pretreated solid) were collected and characterized using different analytical methods including solid state NMR, FTIR, and HPLC-MS for detailed compositional analysis.

The results show that thermal /chemical pretreatment (dilute acid) hydrolyzed most part of xylan in the biomass. At the same time, lignin is also somewhat depolymerized and becomes less entrained with the cell wall matrix. It is clear that most of the lignin remains coalesced and trapped in the residual solids (85-95%). However, as the native lignin is hydrolyzed, smaller molecular weight fractions seem to migrate from their original location to the point where a small population (5-15%) makes its way into the aqueous phase of the flowing pretreatment liquor. A small portion of the lignin is redeposited on the cooled cell wall surface. The results give an understanding of the effects of lignin mobility due to pretreatment on enzymatic digestibility with application to further process development of commercial bioethanol plants.

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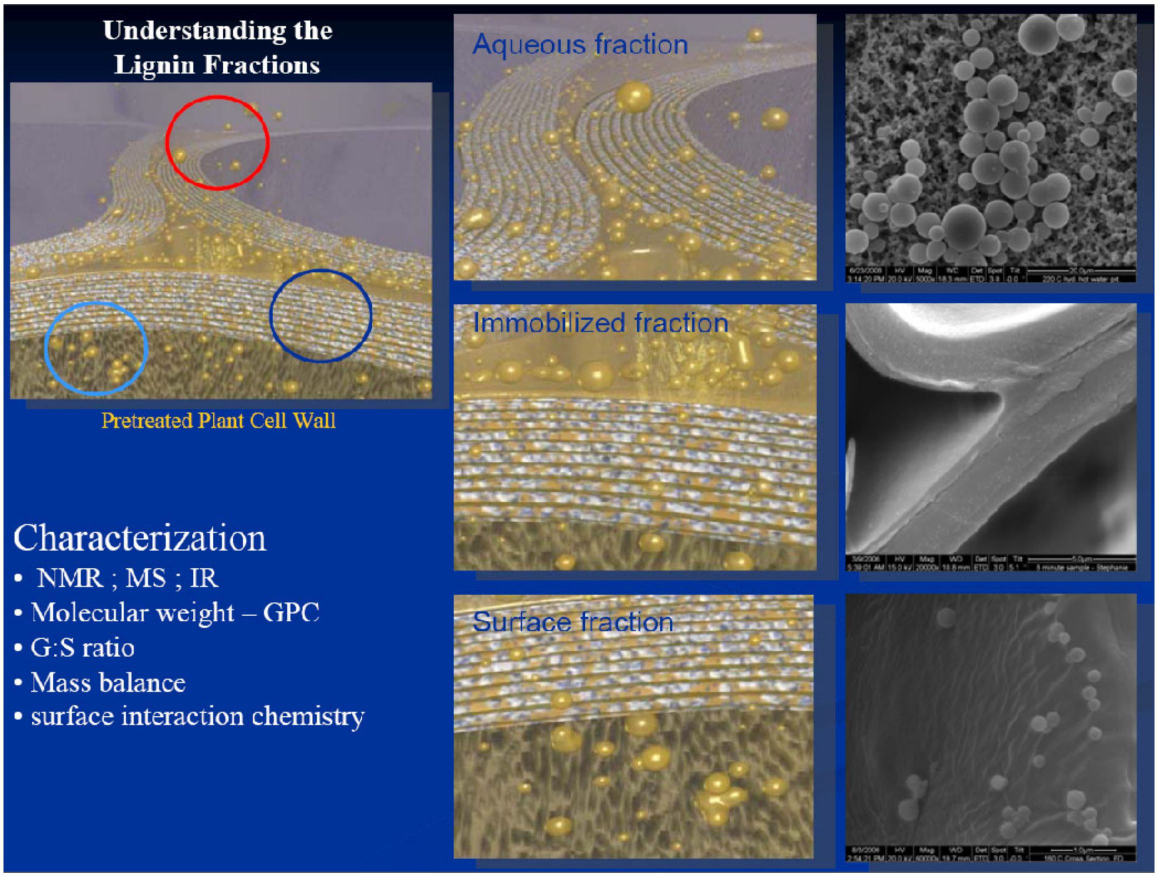
Understanding the
Lignin Fractions
Pretreated Plant Cell Wall
Characterization
• NMR ; MS ; IR
• Molecular weight – GPC
• G:S ratio
• Mass balance
• surface interaction chemistry
Aqueous fraction
Immobilized fraction
Surface fraction