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Exploring the effect of different plant lignin content and composition on ionic liquid pretreatment efficiency and enzymatic saccharification of *Eucalyptus globulus* L. mutants

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HIGHLIGHTS

- ▶ We aimed to describe the effect of lignin S/G ratio of eucalyptus on wood saccharification.
- ▶ S/G ratio modify 3D cell wall structure and so cellulose availability to enzymatic attack.
- ▶ Cellulose, hemicelluloses and lignin formed a sheath protecting cellulose from the enzymatic attack.
- ▶ Ionic liquid were used to destroy 3D structure to improve cellulose availability.

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ABSTRACT

There are several approaches being investigated to improve the efficiency of biomass conversion into fermentable sugars, including those that engineer the feedstocks to enhance digestibility. In this study it was evaluated the impact of genotype modifications of three mutants of *Eucalyptus globulus* L., and of the corresponding wild type on cellulose hydrolyzability before and after ionic liquid (IL) pretreatment. Both untreated and IL-treated samples were chemically characterized and tested for cellulose hydrolizability. Results obtained indicate that genetic modifications altered wood lignin-S/G ratio. This alteration resulted in a different hydrolyzability of cellulose for untreated samples, i.e. high lignin-S/G ratio produced low glucose yield ($r = -0.97$; $P < 0.03$; $n = 4$), but did not affect glucose yield after IL pretreatment. IL pretreated samples had increased glucose yields compared to that of untreated samples due to the modification of microcrystalline cellulose I to mixtures of more hydrolysable cellulose II and amorphous cellulose, and to the partial removal of the steric impediment, or removal of the lignin "sheath" protecting cellulose, to enzymes. The efficiency of the IL pretreatment used in this study does not appear to be affected by the S/G content of the *E. globulus*.

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1. Introduction

Lignin, one of the most studied subcomponents of the cell wall, has been always deemed as having a negative impact during saccharification and in all other bioprocess industries (i.e. digestibility for pulping, and paper) (Chen and Dixon, 2007; Simmons et al., 2010). Even though the association between plant lignin levels and cellulose hydrolyzability has been extensively recognized, this mechanism has not yet been fully understood. In order to achieve more efficient deconstruction of the plant cell wall, extensive research efforts are currently being directed towards regulating lignin pathway genes and 'redesigning' lignin composition by altering the relative ratio of its sub-units (Simmons et al., 2010). Specifically, the influence of syringyl (S)/guaiacyl (G) ratio moieties in lignin on chemical and physical properties of cell wall is being actively studied (Chen and Dixon, 2007). The fact that these subunits are not distinct in the cell wall and that the compositional ratios of these moieties varies significantly in the biomass makes it extremely difficult to delineate a common model to correlate the changes in lignin structure to the sugar released after enzymatic hydrolysis. Moreover, the limited number of studies performed to date that mechanistically identify the association between S/G ratio and resultant efficiencies in sugar release after enzymatic

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