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KRAFT LIGNIN POLYMERIZATION BY LACCASE

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ABSTRACT

During the production of dissolving pulp by the prehydrolysis kraft process, hemicellulose and lignin are removed from the wood in different stages of the process. Prehydrolysis aims at the removal of hemicellulose by applying water or dilute acid solutions at high temperatures. The lower thermal stable compounds (hemicellulose) are dissolved and removed in the hydrolysate. Following prehydrolysis, the second stage of the process (kraft cooking) aims to remove lignin from the wood chips. An alkaline solution (white liquor) and high temperature are used to degrade and dissolve lignin from the solid residue recovered in the previous stage. This lignin can have several applications, in addition to burning.

Wood lignin is produced by the oxidative polymerization of three monolignols: p-coumaric alcohol, coniferyl alcohol and sinapyl alcohol. The three compounds work as building blocks for the lignin macromolecule. The proportion of the building blocks is wood species dependent. In the pulp production process, the lignin macromolecules are depolymerized resulting in lignin fragments that can be used as starting materials for other polymer production and as chemical blocks (1).

This work studied the enzymatic oxidation/polymerization of lignin extracted from the prehydrolysis kraft cooking of *Eucalyptus globulus* by exposure to laccase. This enzyme is well known for oxidizing lignin. The effect of different conditions such as pH, temperature, inhibitors, and lignin characteristics can result in the formation of new chemical bonds or the breaking of existing ones.

In the present work, lignin from the prehydrolysis kraft process was fractioned and submitted to the laccase treatment under different conditions. The preliminary results strongly suggest that the balance between polymerization and depolymerization is strongly dependent on the functional groups and the composition of the lignin fragments used as raw material, in accordance with the literature results (1). In fact, the pH medium and the laccase source play a key role in this balance. Fungal-derived laccase under a neutral pH medium led to inconclusive results; despite a decrease in the phenolic content of 16%, there was no significant changes in the lignin molecular weight. On the contrary, bacterial-derived alkaliphilic laccase, modified to work at high temperatures and alkaline pH, provoked a more significant decrease in the phenolic groups (41%) and the polymerization was noticeable. The process was monitored by size exclusion chromatography, using a set of Ultrahydrogel Columns (120Aº and 250Aº) operating under alkaline pH. After 4-hour of reaction, the retention time of the main pick decreased from 25.36 to 25.01 minutes and about 20% of the initial lignin was retained in a 0.2 µm filter, indicating severe polymerization. The polymerization probably occurred in the lignin chain instead of small fragments, resulting in the formation of a complex, three-dimensional structure.

Both polymerization and depolymerization can have interesting applications. Depolymerization results in smaller fragments with important applications like biofuel, water coagulants, or even polymers, while higher size molecules can be applied as bioplastics, binders for the pulp and paper industry or even as adhesives to increase the structural properties of composites.

Keywords: Biopolymers, biorefinery, enzymatic treatment, laccase, lignin valorisation.

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