Laccase catalyzed grafting of-N-OH type mediators to lignin via radical-radical coupling

Lignin is an underexploited resource in biomass refining. Laccases (EC 1.10.3.2) catalyze oxidation of phenolic hydroxyls using O2 as electron acceptor and may facilitate lignin modification in the presence of mediators. This study assessed the reactivity of four different synthetic mediators by laccases from Trametes versicolor and Pleurotus ostreatus by quantitative analysis of the reaction outcome by pyrolysis gas chromatography mass spectroscopy. The two laccases were equally efficient in catalyzing grafting, but only-N-OH type mediators grafted. HPI (N-hydroxyacetanilide) grafted 7-10 times better than HBT (1-hydroxybenzotriazole). Three different mechanisms are suggested to explain the grafting of HPI and HBT, all involving radical-radical coupling to produce covalent bonding to lignin. Lignin from exhaustive cellulase treatment of wheat straw was more susceptible to grafting than beech organosolv lignin with the relative abundance of grafting being 35% vs. 11% for HPI and 5% vs. 1% for HBT on these lignin substrates. The data imply that lignin can be functionalized via laccase catalysis with-N-OH type mediators.

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