Fundamental Investigation into Oxoreductase Enzymatioc Bleaching Systems (1996)

A Dissertation by James Sealey

Abstract: Biobleaching has been studied for many years with little success. Enzymatic bleaching systems that incorporate a mediator or a small molecular weight compound have shown promise. Of these, laccase and manganese peroxidase-based biobleaching systems have been the two most promising. The mediator's role in delignification has been proposed to be radical based with the mediator being activated by the enzyme. The purpose of this study is to examine the mechanism of laccase mediator biobleaching. Residual lignins isolated from kraft pulps bleached with laccase hydroxybenzotriazole (HBT) were shown to be structurally altered. Oxidation appeared to be the main delignification mechanism, as indicated by measured increases in carboxylic acid groups and decreases in free phenolic groups. Demethylation of the residual lignins was also detected.

Reactions between laccase and HBT revealed a new species which was determined to be benzotriazole (BT). Since laccase BT biobleaching trials revealed no delignification, the generation of BT was concluded to be a negative by-product of the reaction. Further investigations revealed that HBT was converted to BT rapidly during laccase biobleaching, and delignification appeared to be greatly limited by the conversion of HBT to BT. Derivatives ofHBT and closely related compounds were tested as possible mediators, and the RR'N-OH functional group was needed to facilitate delignification for the class of compounds tested. Bond dissociation energies and the polar character of the mediators appear to influence reactivity of the laccase mediator biobleaching system.

Full-sequence bleaching with laccase HBT was performed, and an ISO brightness of 85 was obtained with an OL(E+O+P)LED sequence. Recently introduced mediators, violuric acid (VIO) and N-acetyl-N-phenylhydroxylamine (NHAA), were also tested and shown to delignify kraft pulps with a much lower dose of enzyme than HBT. The selectivity of all the biobleaching systems remained high. The radical mechanism proposed for laccase mediator delignification was tested with a selective radical quenching catalyst in the presence of pulp. Results were positive, as delignification was almost completely inhibited. Almost no laccase activity remained after a 4-hour biobleaching trial regardless of the mediator used. Further investigation of laccase mediator delignification revealed that lignin was modified differently, depending on the mediator used.