

**USE OF CYCLIC VOLTAMMETRY AS AN EFFECTIVE TOOL FOR
MONITORING THE LACCASE CATALYSED POLYMERIZATION OF
DIFFERENT LIGNINS IN ACETONE-WATER MIXTURE**

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Abstract

The applicability of oxidative laccase for both the degradation and the modification of lignin in aqueous media have been intensively studied but limitations still exists due to the low solubility of lignin in media that are compatible with laccase [1]. Organic water-miscible solvents are often required in laccase-catalyzed oxidations because many of the lignin substrates are insoluble in water. Due to the low electrochemical reduction potential, laccase can only oxidize the phenolic lignin moiety (<20% of total lignin) and not the non-phenolic aromatic structure (80% of total lignin) [2]. Moreover, lignin's microporous network is not readily accessible for laccase molecules due to their large size (~5-6 nm) [3] and further decreases the overall oxidation efficiency. The enzymatic oxidative polymerization of four technical lignins with different molecular properties, Soda Grass/Wheat straw Lignin (SGWL), Organosolv Hardwood Lignin (OHL), Soda Wheat straw Lignin (SWL) and Kraft Softwood (KSL) was studied. All lignins were previously fractionated by acetone/water 50:50 (v/v) and the polymerisation of the low molecular weight fractions ($M_w < 4000$ g/mol) was carried out in the same solvent system. The comparative electrochemical behavior of laccase-catalysed reactions of different substrate concentrations showed to be effective electron donor in the reduction of dioxygen to water and may help us elucidate the suitable experimental conditions for an effective catalysis of laccase in lignin reactions. The immersion of a laccase-coated glassy carbon electrode (GCE) in the solutions generated large catalytic currents easily recorded by cyclic voltammetry at low potential scan rates. Likewise, it was shown that the current record varied with the substrate concentration and the type of lignin. A polymerization process of lignins on the electrode surface was also observed by the decrease in the oxidation current recorded in the same solution, during a second scan. In order to easily assess the differences in the analytical signals to establish relationships between samples (objects) and points in a signal (variables) the principal component analysis (PCA) was applied to the voltammetric data. The multivariate method PCA was used to simplify the discrimination between the polymerization reactions of lignin samples from different sources to build a method for selection of favourable parameters in the catalytic reactions. Electrochemical studies indicated that the laccase immobilized on glassy carbon electrode surface was able to catalyse the oxidation of lignin in aqueous-acetone (50/50 vol. %) solution.

References

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