Studies on lignin degradation by free radicals

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Continued usage of fossil fuels caused serious problems such as global warming and depletion of fossil fuels. Development of conversion systems from lignocellulosics into biofuels and chemicals has received much attention due to immense potentials for the utilization of renewable bioresources. Biological systems decomposing lignin by white rot fungi are attractive to develop the lignicellulosic biorefinery system. The lignin biodegradation by white rot fungi is an extracellular free radical event that proceeds in concert with the activation of molecular oxygen and redox cycling of transition metals. In contrast to brown rot and non-selective white rot fungi, selective lignin-degrading fungi like *Ceriporiopsis subvermispora* are able to decompose lignin in wood cell walls at a site far from enzymes without the intensive damage of cellulose. As for the lignin degradation system at a site far from enzymes, lipid peroxidation has been proposed. We analyzed reactivity of free radical species from hydroperoxides or peroxidizable compounds, and developed lignin-degrading free radical reactions. In this thesis, the author synthesized lignin model compounds and analyzed reactions with free radicals, with special emphasis on enantioselectivity of the reactions.

Threo and *erythro* forms of non-phenolic β-*O*-4 lignin dimmer model compounds and a dehydrogenation polymer (DHP) from coniferyl alcohol were chemically synthesized. Radical species were generated by one-electron redox reactions using metal-ligand complexes, enzymes, or thermolysis of azo compounds, and allowed to react with the lignin model compounds in various solvents. Degradation products from the lignin model compounds were analyzed by GC-MS, NMR, and MALDI-TOF-MS. The author found radical reaction systems with different enantioselectivity to the recalcitrant non-phenolic lignin dimmer models. The synthetic lignin, DHP was intensively depolymerized by the radical reactions.