Ligninolytic free radicals in selective white rot

Yukiko Uno
Laboratory of Biomass Conversion, RISH, Kyoto University

There is a growing demand to produce fuels and chemicals from biomass to solve the problems of global warming and deficiency of fossil fuels because the biomass feedstock is produced by fixation of carbon dioxide by the photosynthesis of plants. In enzymatic conversion of lignocellulosics it is necessary to decompose the network of lignin prior to the enzymatic hydrolysis because lignin makes the access of cellulolytic enzymes to cellulose difficult. Thus, effective pretreatments are needed for enzymatic saccharification and fermenataion of lignocellulosics. Physical, physicochemical, thermochemical, chemical and biological pretreatments have been studied to decompose the network of lignin. Natural processes that occur during fungal biodegradation of wood have a great potential to decompose the lignin network. Treatments of lignified plant materials with selective lignin-degrading fungi (white rot fungi) assist to expose cell wall polysaccharides to increase accessibility of cellulolytic enzymes to the cell wall polysaccharide.

A selective white rot fungus, *Ceriporiopsis suibvermispora* is able to degrade lignin selectively without intensive damage of cellulose. In the selective delignification, extensive delignification was observed without penetration of extracellular enzyme into wood cell wall regions [1]. This phenomenon indicates that low molecular mass oxidant play an important role for the selective delignification. In incipient stage of wood decay, this fungus secretes manganese peroxidase (MnP) and lipids, and catalyzes the MnP-dependent lipid peroxidation [2,3]. In lipid peroxidation, carbon-centered ($R^{\bullet}$), alkoxyl ($RO^{\bullet}$) and peroxyl ($ROO^{\bullet}$) radicals are produced by chain reactions. However, little is known about reactivity of these free radicals to lignin. In the present study, $ROO^{\bullet}$, $RO^{\bullet}$ and both radicals were generated by decomposing organic peroxides with transition metal complexes. We analyzed reactivity of $RO^{\bullet}$ and $ROO^{\bullet}$ radicals with non-phenolic β-*O*-4 lignin model compounds by electron spin resonance (ESR) and gas chromatography/mass spectrometry (GC-MS).

REFERENCES

[1] Messener K., Srebotnik E. (1994) *FEMS Microbiol. Rev.*, **13**: 351-364.
[2] Enoki, M., Watanabe, T., Nakagame, S., Koller, K., Messner, K. Honda, Y., Kuwahara, M. (1999) *FEMS Microbiol. Lett.*, **180**: 205-211.
[3] Watanabe, T., Katayama, S., Enoki, M., Honda, Y., Kuwahara, M. (2000) *Eur. J. Biochem.*, **267**: 4222-4231.