ABSTRACTS (MASTER THESIS)

Analysis of microwave effects in transesterification by lipase and oxidative degradation of lignin

(Graduate School of Agriculture, Laboratory of Biomass Conversion, RISH, Kyoto University)

Keigo Ito

Conversion of lignocellulosic biomass is emerging as one of the most important technologies for sustainable production of renewable fuels and chemicals due to its widespread availability, large quantity, non-competitiveness with food supply, potential as platform for green chemicals and high mitigation effects on GHG emissions. In conversion of lignocellulosic biomass, increase in conversion efficiency with low energy input is essential. Microwave heating is attractive for this purpose due to its rapid heating behavior toward the materials with high permittivity loss. In some chemical reactions, acceleration of reaction rate by microwave heating has been reported, and mechanisms for the phenomena have been discussed in terms of thermal and non-thermal effects. The effects observed in microwave-irradiated chemical transformations can in most cases be rationalized by purely bulk thermal phenomena associated with rapid heating to elevated temperatures[1], but other factors may affect the reaction efficiency. Thus, the mechanisms behind the acceleration, and in some cases changes in reaction selectivity, are not fully understood. In this research, effects of chain length of substrates on lipase-catalyzed transesterification between methyl methacrylate and aliphatic alcohols were analyzed to understand the factors affecting the reaction rate by microwave irradiation. Immobilized lipase was reacted in toluene with methyl methacrylate and aliphatic alcohols with different chain length (C6-C18) using conventional heating (CH) and microwave heating (MH) at 2.45 GHz using the same test tube by controlling the temperature profile to minimize the differences between CH and MH. A semiconductor amplifier was used to generate the microwave, and the temperatures in solutions were monitored using a fiber optic thermometer. Differential behavior in the reaction rate between CH and MH were observed, depending on the chain length of the alcohols used. This phenomenon was interpreted by applying an Arrhenius plot and transition state theory[2].

In addition to the enzymatic reaction, degradation of β-*O*-4 linin dimer model compound by copper complex and H_2O_2 were analyzed. When the reaction system was applied to wood particles, vanillin and vanillic acid were produced from softwood, and vanillin, vanillic acid, syringaldehyde and syringic acid were released from hardwood in a high yield comparable to that of nitrobenzene oxidation. MH gave these monomers by up to around two times higher yields than those of CH. Because the reaction toward wood involves multiple reactions including wood cell wall swelling, dissociation of the components, and oxidative lignin degradation, the accelerating effects of MH was not able to solely ascribe to the enhanced degradation of lignin substructures. This research aimed at elucidating if the MH affects directly on release of vanillin and vanillic acid by cleavage of Cα-Cβ bonds from a β-*O*-4 linin dimer model compound. The results showed that MH accelerated the degradation of lignin model compounds.

References

[1] Rosana, M. R., J. Hunt, A.Ferrari, T. A. Southworth, Y. Tao, A. E. Stiegman and G. B. Dudley, "Microwave-Specific Acceleration of a Friedel-Crafts Reaction: Evidence for Selective Heating in Homogeneous Solution", *J. Org. Chem.* 2014, 79, 7437-7450.

[2] Ito, K., H. Nishimura, T. Mitani and T. Watanabe, "Analysis of specific microwave effects in transesterification by lipase", *Abst. of the 66th Annual Meeting of the Japan Wood Res. Soc.*, 2016, Z27-08-1345.