Synchrotron-radiation Infrared Microscopy Analysis of Structure of Lignin Irradiated with Infrared Free Electron Laser

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Lignin is a wood-base biomass that is polymerized via β-O-4 ether bonds by p-hydroxy cinnamic alcohols such as coniferyl alcohol and p-coumaryl alcohol. The degradation products are useful for synthesis of polyphenols that are antioxidant agents. However, the lignin molecule is unsolved in water and it is difficult to degrade the lignin backbone unless using specific microorganism enzymes.

In the last study using BL15 synchrotron-radiation infrared microscopy beamline, we found that the cellulose fiber was efficiently broken by using infrared free electron laser (IR-FEL): glucose and cellobiose were produced by the IR-FEL tuned to 9.1 μm that corresponds to C-O stretching mode (1). The study indicates that the glucoside-bond selective irradiation by the IR-FEL can release glucose monomer unit from the cellulose polymer.

In this study, we applied the same strategy to degradation of lignin polymer. At first, we measured the FT-IR spectrum of lignin by KBr tablet method and determined the irradiation wavelengths as follows: 6.3 μm (C=C stretching mode in benzene ring) and 7.1 μm (C-O-H bending mode in ether bonds). Next, the lignin powder was put into the glass tube, and the IR-FEL beam was focused onto the sample surface by using parabolic mirror under atmosphere at Kyoto University. After the irradiation for 10 min, the sample was dried and analyzed by using BL15 infrared microscopy with reflection mode, 64 scans, and 20 μm apertures.

Synchrotron-radiation based infrared microscopy analysis revealed that absorption intensity around 1500-1800 cm^{-1} was largely changed by the irradiation (yellow circle). Interestingly, the two-step irradiation at 6.3 μm following 7.1 μm(red) gave decrease of peak intensity at about 1600 cm^{-1} more than the single irradiation at 6.3 μm(blue). In addition, there can be seen somewhat changes around 1200 cm^{-1} after those irradiations.

The above observations indicate that the phenol structures containing C-O bonds in lignin molecule was altered by the IR-FEL irradiation. We are planning to analyze the lignin structure by using multi-nuclear NMR in future.

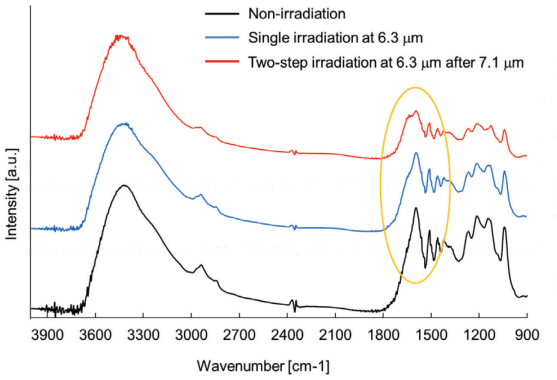

Fig. 1 FT-IR spectra of lignin. Black: lignin before FEL irradiation. Blue: lignin irradiated at 6.3 μm. Red: lignin irradiated at 6.3 μm following 7.1 μm.

References

(1) T. Kawasaki, T. Sakai, H. Zen, Y. Sumitomo, K. Nogami, K. Hayakawa, T. Yaji, T. Ohta, K. Tsukiyama, and Y. Hayakawa, *Energy & Fuels*, May 8, **2020**.