In-situ NMR of the Catalytic Depolymerization of Lignin Model Polymers

Lignin (an aromatic macromolecule in biomass), the only renewable source of aromatics, is currently treated as waste and underutilized. A more appealing and value-added use of lignin is as a precursor for the production of aromatic chemicals. The depolymerization of lignin selectively into its monomers can be achieved by the appropriate combinations of solvent, catalyst, and reaction conditions. However, due to the considerable complexity and natural variation in the molecular structure of lignin, mechanistic studies of catalytic lignin depolymerization are challenging. Beyond that, lignin depolymerization usually (1) requires relatively high temperature (above 200 °C) and pressure (above 80 bar); (2) involves co-existence of solid, liquid and gas phases; and (3) differs from typical catalytic reactions due to the macromolecular nature of the substrate. In this study, we have synthesized 13C labeled lignin model polymers with only β-O-4 linkages and hydroxyphenyl monomers of different molecular weights to perform in-situ magic angle spinning (MAS) solid-state nuclear magnetic resonance (NMR). This project leverages the unique high-temperature and –pressure MAS NMR technology at the Pacific Northwest National Laboratory (PNNL). Using the 13C labeled lignin model polymers at different reaction conditions, we were able to monitor the real-time mechanistic reaction network of lignin depolymerization while also accounting for the potential effects of the macromolecular size of lignin.