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Understanding Fundamental Mechanisms of Lignin Depolymerization

Lignin is a heterogeneous, energy dense, alkyl-aromatic polymer found in plants that confers mechanical strength and aids in water transport. Lignin content varies by feedstock, and in some woody biomass, it can comprise up to 40% of the cell wall. In selective conversion routes of biomass such as pretreatment, enzymatic saccharification, and fermentation or catalytic conversion of sugars to fuels, lignin is typically burned for heat and power. Selective strategies for lignin deconstruction have received less attention to date, but efficient lignin valorization could potentially open significant value streams from biomass and enable the utilization of a substantial fraction of carbon in plant cell walls for fuels or chemicals production.

In nature, oxidative enzymes are responsible for mineralizing lignin to CO₂, such that microbes can access structural polysaccharides for food. Unlike cellulases, however, lignin-degrading enzymes require co-factors for activity, thus their application is limited in industrial lignin deconstruction. Additionally, as lignin is insoluble in water at mild conditions, homogeneous catalysts are required to efficiently deconstruct lignin *in situ* at mild conditions, such as mineral acids or aqueous-phase bases, or alternatively requiring application of organic solvents for separation of lignin and carbohydrates as (mostly) intact polymers followed by catalytic or thermal depolymerization to monomers.

In the NABC Biomass Deconstruction Task, we employ a mechanistic approach to understand lignin depolymerization in a variety of chemical environments with the aim of designing improved processes for lignin deconstruction to upgradable, monomeric species. This approach relies on the use of an integrated experimental and theoretical approach to understand the chemistry of depolymerization at a fundamental level (Figure 1).

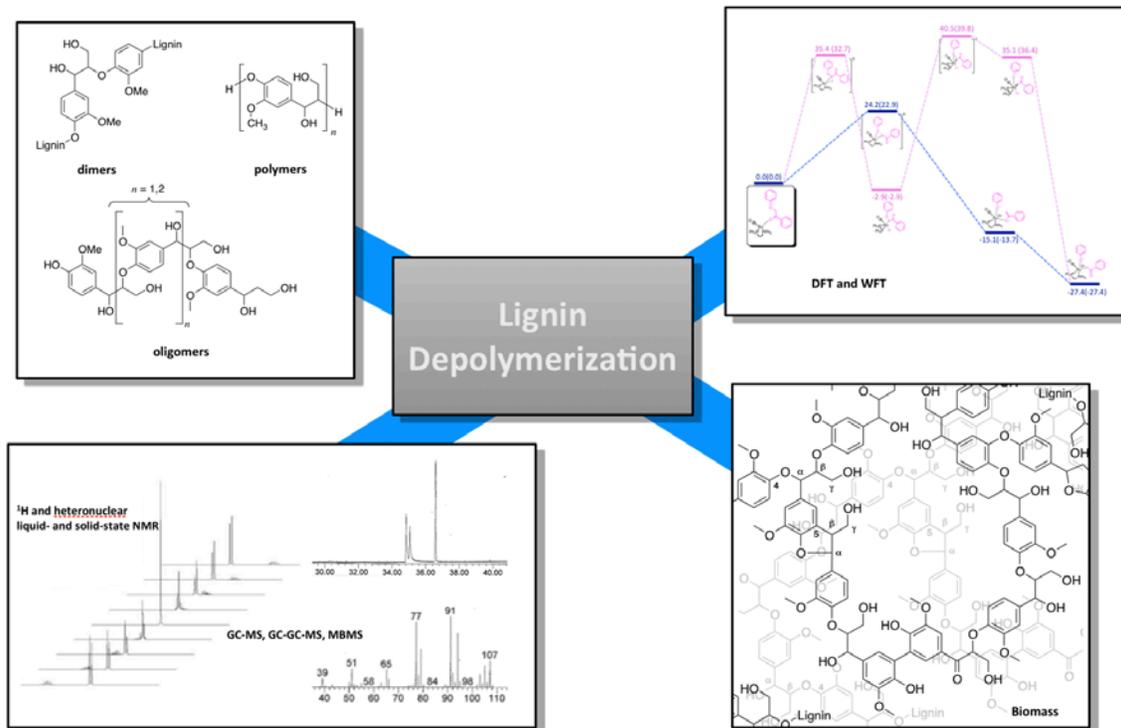


Figure 1. The NABC Biomass Deconstruction Task utilizes model dimers and oligomers, quantum mechanical calculations, spectroscopy, and biomass-derived lignin feedstocks to understand and design enhanced processes for lignin utilization.

For example, it is known that acid treatment of lignin cleaves aryl-ether and lignin-hemicellulose linkages, but mass-action kinetic models for this process are based on empirical approaches, which limits their predictive capability. To construct a first-principles model of lignin depolymerization in acidic environments, NREL researchers have synthesized a library of model dimers that exhibit the abundant β -O-4 and α -O-4 linkages in lignin with various functional groups present that mimic chemical linkages observed in plant cell wall lignin, as shown in Figure 1. Bench-scale experiments have been undertaken to hydrolyze these model dimers in sulfuric acid at conditions similar to flow-through hydrolysis of lignocellulosic biomass to produce mixed carbohydrate and lignin deconstruction products. Figure 2 shows a summary of the products obtained via hydrolysis of representative model dimers for both linkage types.

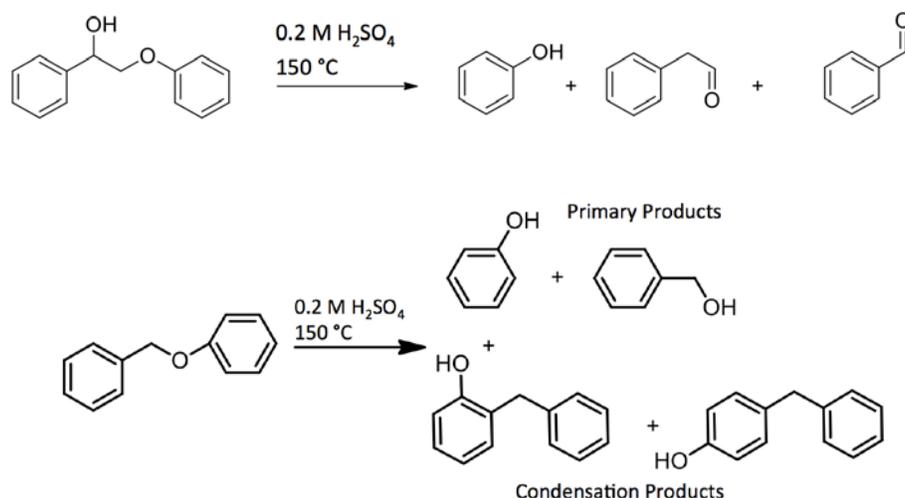


Figure 2. *Top*, acid treatment of a β -O-4 lignin model dimer yields a mixture of aldehydes and phenol as primary deconstruction products, and a myriad of condensation products (the latter are not shown here). *Bottom*, acid treatment of an α -O-4 model compound yields phenol and benzyl alcohol as well as a mixture of two condensation products.

From these experiments, proposed elementary steps for aryl-ether cleavage in acid have been constructed and tested with quantum mechanical calculations conducted at NREL and Northwestern University. After detailed examination of these mechanistic hypotheses with theory, several proposed intermediates were synthesized to test mechanistic hypotheses. These results generally highlight the slate of potential phenolics and other oxygenated aromatics that could potentially be derived from acidolysis of lignin present in biomass.

Overall, the combined efforts of Northwestern University and NREL will eventually lead to a database of chemical reactions and the subsequent construction of a kinetic model whereby lignin depolymerization in acidic environments to monomeric species can be more effectively understood. Moreover, this work is complementary to ongoing experimental and theoretical work on lignin depolymerization in higher temperature regimes at the Colorado School of Mines, Los Alamos National Laboratory, Iowa State University, and Northwestern University. This body of work will in turn enable the design of optimal deconstruction strategies for conversion of lignin-derived molecules to fuels and chemicals.