

Reductive Conversion of Lignin with Earth Abundant Catalysts to Aromatic Chemicals

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Technical Summary

This thesis focused on developing scalable extraction and depolymerization methods for lignin, and the conversion of monomers produced from lignin into direct replacements of petroleum-based chemicals. Lignin, cellulose and hemicellulose are principal components of biomass. Biomass is an abundant and renewable source of carbon. It is an excellent feedstock to economically and sustainably produce carbon-neutral fuels and chemicals. Such production is critical as the environmental effects of mankind's energy use grow increasingly acute. Although carbohydrates have long been studied and shown to be versatile feedstocks, lignin, the largest source of natural aromatics, is typically destroyed in carbohydrate processing. We constructed a reductive pathway to extract and depolymerize lignin into phenols. Furthermore, we developed a mechanistic understanding of the process and designed a novel reactor for the conversion of biomass. Finally, we converted lignin derived phenols into alkylated aromatics for integration into existing chemical and energy infrastructure.

Lignin is an aromatic polymer synthesized in the cell walls of plants through a free radical polymerization. The primary building blocks of lignin are p-hydroxycoumaryl alcohol, coniferyl alcohol and sinapyl alcohol. The polymerization of these phenolic monomers can lead to a variety of different chemical linkages, chain lengths and branching within the lignin polymer. The most abundant and labile bond in the lignin structure is the β -O-4 ether linkage with the remaining linkages consisting of a myriad of strong carbon-carbon bonds. Therefore, lignin conversion strategies rely on the selective cleavage of β -O-4 ether bonds to depolymerize lignin. Industrially, lignin is typically removed from biomass through extraction processes, which utilize strong acid or base to cleave lignin-carbohydrate linkages. Lignin undergoes many side reactions in these extraction processes that lead to the degradation of β -O-4 bonds. This causes the condensation of lignin into a recalcitrant solid, which is burned as a low grade fuel.

We have established a lignin extraction procedure to produce phenols from lignin by stabilizing intermediates produced during the extraction of lignin from biomass. Our strategy to fractionate lignin from biomass into phenolic monomers is called reductive catalytic fractionation. The process operates by adding a heterogeneous reduction catalyst with whole biomass (milled corn stover, poplar wood or pine wood), solvent and a reducing agent. Lignin extraction, when coupled with a reduction catalyst, produces stable phenols. My research focuses on understanding and improving this process. We discovered two key steps in the reductive conversion of lignin. First, lignin oligomers are solubilized in a solvolytic step, as confirmed by gel permeation chromatography and 2-D NMR. Therefore, lignin extraction is independent of the catalyst. This is followed by the reduction of lignin at the catalyst. Identifying these two steps allowed us to design and construct a dual bed flow-through reactor. In this design, the biomass and catalyst are separated into two reactors where lignin solvolysis occurs in the first bed and then lignin reduction occurs in the second bed. Flow-through chemistry allows for time resolved sampling, independent control of each step, and semi-continuous conversion of biomass.

The physical separation of solvolysis and lignin reduction in flow-through reactors allows for the direct measurement of the intrinsic kinetics and activation barriers for the solvolytic extraction of lignin from biomass. Independent control of the temperature of each process as well as the catalyst loading allowed lignin solvolysis to be isolated as the rate-limiting step in the process. The near instantaneous yields obtained from the flow-through reactor allowed initial extraction rates to be measured with real biomass. Extrapolation of the initial rates of monomer formations at different extraction temperatures revealed the apparent activation barrier for lignin extraction. Apparent activation barriers were also measured in batch systems, which were found to have severe mass transport limitations as evidenced by a low barrier. A

reaction-diffusion model was derived from first principles to confirm the scaling of the activation barrier between the two reactor configurations. The method developed to measure the kinetics of lignin extraction from biomass is essential for systematically studying solvent effect, co-catalysts and innate differences between plant species.

Solvolysis limited conditions allowed us to study the impact of the relative ratio of syringyl units to guaiacyl units (S/G) in poplar lignin. The S/G ratio of the lignin has been considered one of the deciding factors towards how many β -O-4 bonds form in lignin. Therefore, S/G ratio has been predicted to impact the monomer yields that can be obtained from biomass. High S lignin has less potential to make C-C bonds due to the presence of a methoxy group in the 5 position on the aromatic ring. To study the impact of S/G ratio, five natural genetic variants of poplar were studied, which have S/G ratios ranging from 1.4 to 3.6 (58% S to 78% S). Surprisingly, all five wood samples showed identical monomer yields, despite the distribution of monomers trending with syringol and guaiacol content in the biomass. HSQC-NMR and GC-MS were used to identify oligomer and dimer linkage types to understand if G type units form more carbon-carbon bonds, as is hypothesized by the lignin research community. Mole balances generated from NMR showed that S units were involved in more carbon-carbon bonds than G units, which was further confirmed from the distribution of linkages from dimers measured by GC-MS. S/G is not a critical parameter in the formation of β -O-4 linkages based on studies with poplar natural variants.

Semi-continuous operation of the flow-through reactor allowed us to study the stability of the catalyst under reaction conditions. A single catalyst bed was loaded into the reactor. Fresh biomass beds were sequentially extracted and were fragmented over the single catalyst bed. The monomer yield decreased as the reaction progressed suggesting catalyst deactivation. To assess what caused the catalyst to deactivate, the catalyst was characterized by TEM, ICP-AES and TGA. TEM of the catalyst before and after reaction indicated that Ni nanoparticles sintered on the carbon support. ICP-AES showed that Ni also leached from the carbon support when treated with biomass. TGA indicated that material was strongly adsorbed to the surface of the catalyst or support potentially leading to catalyst poisoning. Flow-through conversion of biomass is a powerful tool to gain fundamental insights into the activity and stability of catalysts.

We have additionally developed an effective route to reductively convert lignin derived phenols into multi-alkylated aromatics or propyl benzene by tuning the active sites on molybdenum catalysts. Phenols from lignin contain 20–30 wt% oxygen as hydroxyl and methoxy substituents on the aromatic ring. Therefore, hydrodeoxygenation can selectively remove oxygen to improve volatility and reduce product complexity. We studied the upgrading of lignin products in both liquid and gas phase flow-through reactors. In the gas phase, we demonstrated that hydrodeoxygenation with molybdenum polyoxometalates could selectively cleave aromatic C-O bonds without hydrogenating the aromatic ring. Furthermore, the product distributions produced could be modified by altering the surface properties of the catalyst. When the catalyst had both Lewis acidic deoxygenation sites and Brønsted acidic alkylation sites, alkylated aromatics were produced. Alternatively, alkylation was suppressed by removing Brønsted acidity through ion exchange with Na^+ . We were able to then convert lignin into a single product – propyl benzene. Propyl benzene can then be dehydrogenated to methyl styrene which when polymerized has identical thermal and mechanical properties as polystyrene.

In the liquid phase, a process was developed to extract, depolymerize and upgrade lignin from whole biomass into aromatics. Kinetic studies with different solvents identified solvent pairs suitable for solvolysis and compatible with deoxygenation catalysts. Moderate yields of propyl benzene and ethyl benzene were achieved with whole corn stover, over a molybdenum carbide catalyst, in a single unit operation. Direct production of aromatics from biomass removes many separations from lignin conversion. Therefore, lignin conversion and deoxygenation provide a route to renewable production of valuable aromatic chemicals and fuels.