

## **Kinetic and mechanistic insights into hydrogenolytic production of lignin monomers in a continuous flow-through system**

Yanding Li,<sup>1,2,†\*</sup> (yli594@wisc.edu) Benginur Demir,<sup>2,3,†</sup> Leida M. Vázquez Ramos,<sup>2,3</sup> Mingjie Chen,<sup>2</sup> **James A. Dumesic,<sup>2,3</sup> John Ralph<sup>1,2,4</sup>**

<sup>1</sup>Department of Biological Systems Engineering, University of Wisconsin–Madison, Madison, WI. <sup>2</sup>DOE Great Lakes Bioenergy Research Center, University of Wisconsin–Madison, Madison, WI. <sup>3</sup>Department of Chemical and Biological Engineering, University of Wisconsin–Madison, Madison, WI. <sup>4</sup>Department of Biochemistry, University of Wisconsin–Madison, Madison, WI.

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**Project Goals: The mission of the Great Lakes Bioenergy Research Center (GLBRC) is grand, but simply stated: to perform the basic research that generates technology to convert cellulosic biomass to advanced biofuels. The project combines aims for the “design” of superior plant lignins with methods that allow their depolymerization to the highest yields of phenolic monomers. Lignin depolymerization by catalytic hydrogenolysis is one of the most promising depolymerization methods to produce platform lignin monomers with both high yield and selectivity. This study focuses on the kinetic and mechanistic insights into the lignin hydrogenolysis reaction in a continuous flow-through system. Understanding the function of each reaction parameter is the first and essential step to upscaling this method.**

Environmental issues caused by the unrestrained use of fossil energy require a renewable carbon-neutral substitute. Lignocellulosic biomass is one of the most promising alternatives as a widely available sustainable resource. It typically consists of 40-50% cellulose, 25-30% hemicelluloses, and 15-25% lignin. It can be fractionated into these three component streams, and each stream can be upgraded to fuels and chemicals. However, the recalcitrance of the plant cell wall, lignin in particular, makes biomass fractionation and upgrading inefficient. Most of the current biorefinery processes focus on the conversion of the polysaccharides, in which the biomass fractionation using harsh acids, bases, or additional chemicals, destroys the native lignin structure.<sup>1</sup> The lignin undergoes irreversible condensation reactions, such that essentially the only option left for the condensed lignin is to burn it to generate low-value heat.

Native lignin is biosynthesized from its three monolignols: *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, via combinatorial radical coupling reactions. The most common type of native lignin unit is characterized by its  $\beta$ -O-4 ether units (50-60%), and the rest are minor C-C and diaryl ether units. Full cleavage of the  $\beta$ -ethers leads to effective lignin depolymerization. For this purpose, reductive catalytic fractionation (RCF) of lignin simultaneously fractionates the biomass

and cleaves the  $\beta$ -ether linkages.<sup>2</sup> Lignin hydrogenolysis has been studied since 1938 and, with the evolution of the technique, high monomer yields with high selectivity can be achieved. However, the reaction kinetics and mechanism of lignin hydrogenolysis are still not well understood. Elucidation of the fundamentals of lignin hydrogenolysis was sought to guide us not only to create active and robust catalysts, but also to model selective reaction environments for the complex upgrading process.

Lignins are often obtained from bulk biomass fractionation processes. Kraft and organosolv lignins are the major technical lignins currently produced on a large scale by the pulp and paper industry. However, the high sulfur content in the former and the often extremely condensed structure of especially the latter make them unsuitable for further upgrading. A high-quality lignin stream is essential to add value to the biorefinery process. Researchers have emphasized the limiting factors towards the lignin depolymerization process, and rationalized a few basic principles of a high-quality lignin ideotype for depolymerization.<sup>3</sup> Briefly, when wild-type biomass is used, pretreated lignin with a high  $\beta$ -ether content, such as Cu-AHP lignin, aldehyde-protected lignin, and GVL-lignin, is more valuable for downstream lignin upgrading.

We propose herein a fully continuous biomass refinery as a combination of a traditional biomass pretreatment process with a continuous lignin hydrogenolysis pathway in a flow-through system using a Pd/C catalyst. We describe a method to obtain value-added platform monomers from the downstream processing of the isolated lignin stream to enhance the biorefinery. With the help of lignin model compounds, the reaction pathways of lignin hydrogenolysis were investigated and a kinetic model developed. Understanding the reactivity of lignin model compounds helps us design the reaction conditions for actual lignin hydrogenolysis.

## References

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