Exploring Catalytic Conditions for C-C Bond Cleavage of Lignin-Based Compounds

Nina Gu*[1,2] (mailto:mnina.gu@nrel.gov), Sean Woodworth[1,2] Rui Katahira[1,2] Gregg Beckham[1,2] and **Gerald A. Tuskan**[1,2]

[1]National Renewable Energy Laboratory, Golden, CO; [2]Center for Bioenergy Innovation, Oak Ridge National Laboratory, TN

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Project Goals: The Center for Bioenergy Innovation (CBI) vision is *to accelerate domestication of bioenergy-relevant, non-model plants and microbes to enable high-impact innovations at multiple points in the bioenergy supply chain.* CBI addresses strategic barriers to the current bioeconomy in the areas of 1) high-yielding, robust feedstocks, 2) lower capital and processing costs via consolidated bioprocessing (CBP) to specialty biofuels, and 3) methods to create valuable byproducts from the lignin. CBI will identify and utilize key plant genes for growth, composition and sustainability phenotypes as a means of achieving lower feedstock costs, focusing on poplar and switchgrass. We will convert these feedstocks to specialty biofuels (C4 alcohols, C6 esters and hydrocarbons) using CBP at high rates, titers and yield in combination with cotreatment, pretreatment or catalytic upgrading. CBI will maximize product value by *in planta* modifications and biological funneling of lignin to value-added chemicals.

Lignin depolymerization is a highly desirable approach to generate feedstocks of aromatic monomers, but a significant challenge to efficient depolymerization is the presence of recalcitrant carbon-carbon linkages. The goal of this task is to develop catalytic conditions suitable for carbon-carbon bond cleavage of lignin-derived oligomers to increase the yield of aromatic monomers for downstream processes. High-yielding lignin depolymerization methods would facilitate the conversion of lignin into value-added products.

Efforts to carry out oxidative strategies for carbon-carbon bond cleavage are complicated by the prevalence of phenolic motifs in lignin streams such as RCF oil. One major barrier arising from the presence of phenols is that its antioxidant properties (due to facile hydrogen atom donation) can inhibit radical chain oxidation mechanisms. Additionally, the formation of reactive phenoxyl radicals under oxidative conditions can readily lead to the generation of undesired polymeric tars. The approach utilized in this work to carry out phenol-tolerant oxidation is to employ transition metal catalysts that do not operate via radical chain mechanisms. Based on literature reports of benzylic oxidation of 4-Me-phenols (and related substituted derivatives) to the corresponding aldehyde, the use of such conditions are explored for the aerobic oxidation of RCF oil model compounds. In particular, substrate models featuring a bibenzyl backbone akin to β-1 and β-5 linkages are utilized, in addition to propylphenol compounds as models of β-β linkages. Efforts to couple this oxidation chemistry with various carbon-carbon cleavage methods are discussed herein.

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