Towards Whole Biomass Utilization: Development of Ionic Liquid Technologies for Lignin

Seema Singh[1,2*] (ssingh@lbl.gov), Mood Mohan[1,2], Lalitendu Das[1,2], Hemant Choudhary[1,2], Alexander Landera[2], Anthe George[1,2], Blake A. Simmons[1,3], John Gladden[1,2], **Jay Keasling[1,3,4]**

[1]Joint BioEnergy Institute, 5885 Hollis Street, Emeryville, California 94608, United States

[2]Biological and Engineering Science Center, Sandia National Laboratories, 7011 East Avenue, Livermore, California 94551, United States

[3]Biological Systems and Engineering Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, United States

[4]Department of Chemical & Biomolecular Engineering, Department of Bioengineering, University of California, Berkeley, Berkeley, California 94720

Project Goals: Establish the scientific knowledge and new technologies to transform the maximum amount of carbon available in bioenergy crops into biofuels and bioproducts.

Abstract: Lignin is a multifunctional polymer and integral part of the plant cell wall. Lignin's full potential as a renewable source of aromatic compounds can be, in part, unlocked only if an efficient and economic method for lignin depolymerization and valorization is developed. Alternative solvents such as ionic liquids (ILs) and deep eutectic solvents (DESs) have received increasing interest because of their high efficacy in fractionating and pretreating lignocellulosic biomass. However, the lignin-carbohydrate complex degradation mechanism in DES, especially metal containing DESs (mDESs), computational predictability of eutectic points, and mDESs' characteristics are not well understood. This study aims to i) develop and understand the atomistic behavior of known/newly designed ILs on lignin via multiscale simulation approaches, ii) predict the eutectic points for the mDES and their impact on lignin depolymerization, iii) experimental validation of predicted results for biomass fractionation and process parameter optimization, and iv) characterize and upgrade the lignin streams from ILs/mDESs treated biomass to value-added compounds. In this study, a quantum chemical-based molecular simulation namely COSMO-RS (*CO*nductor like *S*creening *MO*del for *R*eal *S*olvents) model was used to screen rational combinations of ILs (60 anions and 90 cations) for the solubility of lignin. The activity coefficient and excess enthalpy of IL and lignin mixtures were evaluated as reference property to describe the affinity of lignin for different ILs. Furthermore, based on the COSMO-RS results, the selected ILs were visualized by observing their structural properties and dynamics with lignin by performing the molecular dynamics (MD) simulations. Subsequently, we demonstrate *simultaneous fractionation of biomass and lignin depolymerization* using mDES. We studied the product profile of depolymerized biopolymers (qualitatively and quantitatively) along with the molecular weight distribution profile as a function of reaction coordinates. Notably, the employed DES system not only achieved ~95% glucose and ~25% lignin monomer yields, but also had limited enzyme inhibition and microbial toxicity (>5wt%), opening the possibility for a subsequent downstream

biological conversion of the depolymerized stream(s). This study provides a mechanistic understanding of biomass fractionation and lignin depolymerization in mDES and explores the potential of catalytic upgrading of lignin to value-added products.

Funding Acknowledgement:

"This work was part of the DOE Joint BioEnergy Institute (http://www.jbei.org) supported by the U. S. Department of Energy, Office of Science, Office of Biological and Environmental Research, through contract DE-AC02-05CH11231 between Lawrence Berkeley National Laboratory and the U. S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes."