SAND2022-10136C

JBEI

Joint BioEnergy Institute

Chemical Upgradation of Ionic Liquid-Based Biorefinery Lignin

Hemant Choudhary[1,2] (hchoudhary@lbl.gov), John M. Gladden,[1,3] Blake A. Simmons,[1,4] and Seema Singh[1,2]

[1]Deconstruction Division, Joint BioEnergy Institute; [2]Department of Bioresource and Environmental Security, Sandia National Laboratories; [3]Department of Biomaterials and Biomanufacturing, Sandia National Laboratories; [4]Biosciences and Engineering Division, Lawrence Berkeley National Laboratory

Abstract

Lignin, an aromatic-based natural polymer accounting for one-third of the organic carbon in the biosphere, is underutilized when compared to holocellulosic fraction of lignocellulosic biomass – mostly due to the randomness and heterogeneity in the chemical structure. Additionally, conventional delignification processes (Kraft, sulfite, etc.) employed in pulp and paper industries cause condensation of lignin units through the formation of stable C-C bonds rendering depolymerization highly challenging. In contrast, ionic liquid (IL)-based processes, among various delignification processes, have attracted much attention because of high sugar yields, bio-compatible processes, and sulfur-free lignin with minimal structural changes. The structure, composition, and purity of IL-based biorefinery lignin is discussed for grassy (sorghum) and woody (poplar and pine) biomass in the first section, followed by the hydrogenolytic and oxidative conversion of the cholinium lysinate ([Ch][Lys]) process-based lignin from sorghum and poplar.

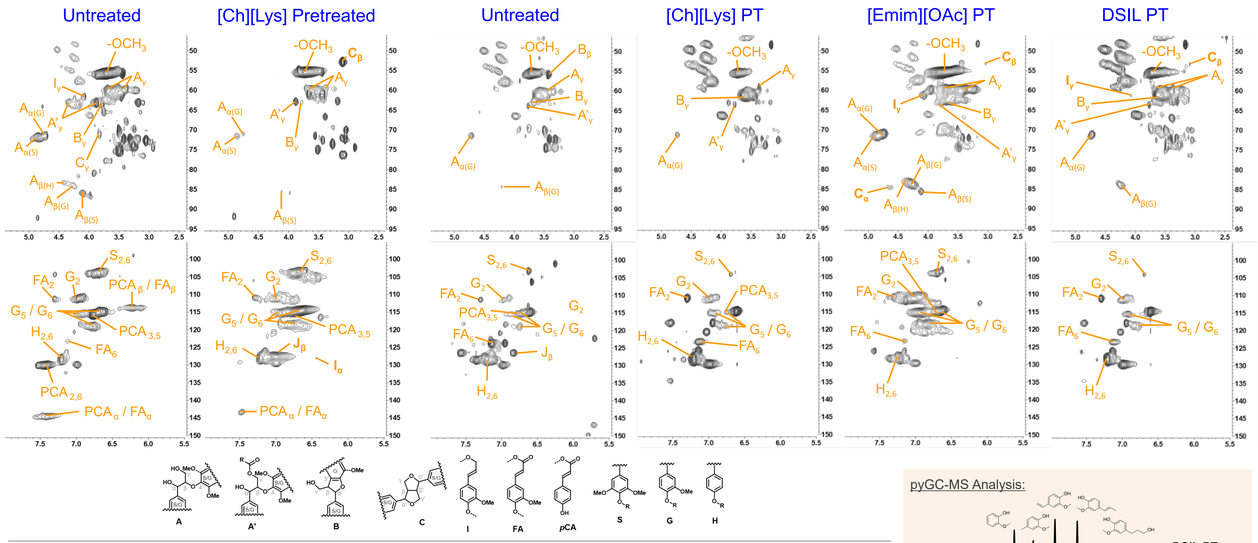
Objective

To develop and demonstrate integrated, feedstock agnostic, and efficient chemical deconstruction technologies using biocompatible ionic liquids for

- non-technical grade lignin stream for facile depolymerization into monomers
- high yields of intermediates compatible with downstream processing
- processing of various biomass sources including softwood such as pine
- replacing significant fraction of petroleum-derived fuels and chemicals with cost-competitive and renewable biofuels and bioproducts
- overall lower economic and environmental impact

Results

One-Pot Sorghum Lignin

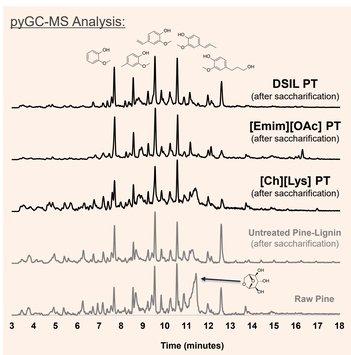


	%AIL[a]	M_w[b]	Units					Linkages		
			%S[c]	%G[c]	%H[c]	S/G	H/G	%C-C[c]	%C-O[c]	%OMe[c]
untreated	29.7	12817	6.0	64.0	30.0	0.09	0.47	7.3	16.5	76.3
[Ch][Lys] PT	42.3[d]	9626	1.3	66.3	32.4	0.02	0.49	14.4	17.4	68.3
[Emim][OAc] PT	75.9[d]	3873	7.4	82.4	10.2	0.09	0.12	11.9	18.2	69.9
DSIL PT	62.3[d]	6403	0.6	64.7	34.6	0.01	0.53	2.1	15.5	82.4

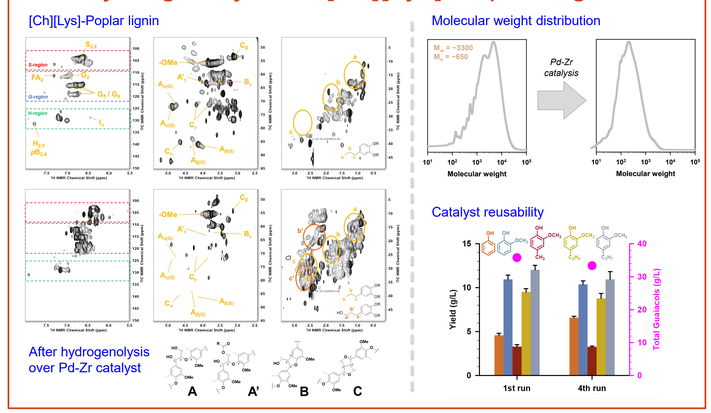
Pretreatment conditions: pine (20 wt%), IL (80 wt%), 140 °C, 3 h. [a]Acid-insoluble lignin. [b]Weighted average molecular weight based on GPC analysis. [c]Based on HSQC NMR. [d]Lignin content of the solid residue obtained after pretreatment and saccharification.

Pine Lignin Before and After Pretreatment

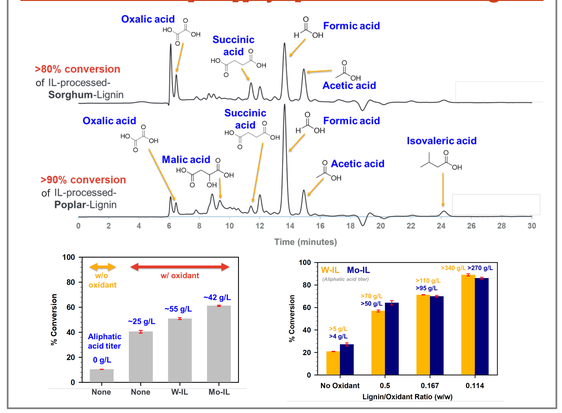
pyGC-MS Analysis:



Hydrogenolysis of [Ch][Lys]-Poplar Lignin



Oxidation of [Ch][Lys]-Processed Lignin



Conclusions

Commercial biorefineries must be able to convert the majority of components present in lignocellulosic biomass, including sugars and lignin-derived intermediates, into biofuels and bioproducts. IL-based processes, as a function of the ions involved, influenced the structure, composition, and purity of the generated lignin as established by the analysis using HSQC NMR and pyroGC-MS, among others. Furthermore, the hydrogenolytic conversion of [Ch][Lys] process-based lignin into guaiacols (upto 60 g/L) over reusable Pd-Zr catalyst was also demonstrated. The viability of oxidative depolymerization of [Ch][Lys] process-based lignin into aliphatic acids over air-stable heterogeneous W- or Mo-ILs was also exhibited, producing >300 g/L of aliphatic acids. This study demonstrates potential catalytic conversion (hydrogenolytic and oxidative) of IL-based biorefinery lignin; and rigorous models to understand the reaction pathways, catalytic sites, and environmental and economic impacts are required to enable overall sustainability and economic viability.

Acknowledgments

This work conducted by the Joint BioEnergy Institute was supported by the Office of Science, Office of Biological and Environmental Research, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

SAND No. XXXXXXX

U.S. DEPARTMENT OF ENERGY | Office of Science

Sandia National Laboratories