Base-Catalyzed Depolymerization of Lignin with Heterogeneous Catalysts

Cooperative Research and Development Final Report

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In accordance with Requirements set forth in Article XI, A(3) of the CRADA document, this document is the final CRADA report, including a list of Subject Inventions, to be forwarded to the Office of Science and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

Parties to the Agreement: Shell Global Solutions

CRADA Number: CRD-13-513

CRADA Title: Base-catalyzed Depolymerization of Lignin with Heterogeneous Catalysts

Joint Work Statement Funding Table Showing DOE Commitment:

Estimated Costs	NREL Shared Resources
Year 1	$ 125,000.00
TOTALS	$ 125,000.00

Abstract of CRADA Work:

We will synthesize and screen solid catalysts for the depolymerization of lignin to monomeric and oligomeric oxygenated species, which could be fractionated and integrated into refinery intermediate streams for selective upgrading, or catalytically upgraded to fuels and chemicals. This work will primarily focus on the synthesis and application of layered double hydroxides (LDHs) as recyclable, heterogeneous catalysts for depolymerization of lignin model compounds and softwood lignin. LDHs have been shown in our group to offer good supports and catalysts to promote base-catalyzed depolymerization of lignin model compounds and in preliminary experiments for the depolymerization of lignin from an Organosolv process. We will also include additional catalyst supports such as silica, alumina, and carbon as identified in ongoing and past efforts at NREL. This work will consist of two tasks. Overall, this work will be synergistic with ongoing efforts at NREL, funded by the DOE Biomass Program, on the development of catalysts for lignin depolymerization in the context of biochemical and thermochemical conversion of corn stover and other biomass feedstocks to advanced fuels and chemicals.

Summary of Research Results:

We have synthesized a library of more than 20 hydrotalcite-based catalysts and evaluated them for activity in the conversion of the lignin model dimer 2-phenoxy-1-phenylethanol (PE) to phenol and acetophenone. PE is a lignin model dimer containing a *b*-O-4 bond, a common linkage between monomers in real lignin streams. Some of the catalysts screened are active for cleavage of the *b*-O-4 bond, showing generally more than 80% conversion of PE and more than 70% yield to *b*-O-4 bond scission products from PE in the best performing solvents.

These catalysts also show activity for monomer generation from other compounds representing more complex *b*-O-4 linkages than PE, and from compounds representing non-*b*-O-4 linkages. We have screened our hydrotalcite catalysts with multiple lignin model dimers encompassing *b*-O-4, *a*-O-4, 4-O-5', *b*-5 (or *b*-1), and 5-5' linkages. The catalysts are selective for cleavage of uncondensed bonds (*b*-O-4, *a*-O-4, and *b*-5/*b*-1 linkages) in phenolic and non-phenolic model dimers. The main products are unalkylated monomers, such as guaiacol and syringol, from real lignin streams in aqueous solvent. Separation of these monomers is facilitated by their high solubility in aqueous media relative to other monomeric and oligomeric species, and residual lignin and catalyst solids.

Subject Inventions Listing:

NREL Record of Invention 14-53 "Hydroxide Catalysts for Lignin Depolymerization" as filed as U.S. provisional patent applications 62/032,817 and 62/100,435.

Report Date:

May 24, 2015

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