Catalytic Depolymerization and Upgrading of Lignin for Vanillin Production

Cooperative Research and Development Final Report

CRADA Number: CRD-14-545

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In accordance with Requirements set forth in Article XI. Reports and Abstracts A.(3), of the CRADA agreement, 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: R.J. Reynolds Tobacco Company

CRADA Number: CRD-14-545

CRADA Title: Catalytic Depolymerization and Upgrading of Lignin for Vanillin Production

Joint Work Statement Funding Table Showing DOE Commitment:

Estimated Costs	NREL Shared Resources
	$ .00

Abstract of CRADA Work:

Examine catalytic conversion of lignin using multifunctional catalysts that are able to depolymerize and oxidize lignin to a vanillin-rich stream. Examine separation processes for isolation of vanillin from product mixtures. Conduct preliminary experiments to determine if deconstructed lignin streams can be metabolized by *Pseudomonas putida*.

Summary of Research Results:

We have screened a series of Pd/C, Ni/C, and Ni/hydrotalcite (HTC) catalysts at the best reported literature conditions on the three lignin streams provided by RJRT: Lignol lignin, AST lignin, and black liquor, as well as ground tobacco stalk biomass. The lignol and AST lignins can be converted into substantially methanol-soluble material over Pd/C catalysts, but with minimal monomer production. In contrast, these lignins generate detectable yields of monomers over Ni/C catalysts (1-2% for lignol lignin and 0.5-1% for AST lignin), but at a lower conversion to methanol-soluble material. The Ni/C catalyst does not produce significant monomers from black liquor. Significant monomeric species could also be produced from tobacco stalk over Pd/C and Ni/C catalysts, with monomer yields approaching 6% based on lignin content compared to 2-3% for the control reaction. A physical mixture of Pd/C and Ni/C did not improve monomer yields. Ni/HTC increased monomer yields slightly for Lignol and AST lignins and raw tobacco stalk, but not for black liquor. Monomer yields over Ni/HTC were also less than 10%. Black liquor contains a significant fraction of monomeric species both before and after reaction, mainly as guaiacol (G) and syringol (S); total monomeric species could be recovered in yields up to 13% from black liquor after reacting without additional catalyst at 210 °C for 6 h.

Nitrobenzene oxidation could produce more than 10% yield to aromatic aldehydes from the Lignol and AST lignins, and more than 30% yield to aromatic aldehydes from raw tobacco stalk, though the scale-up potential of this approach is low. In contrast, monomer yields of 7% and

15% could be obtained over perovskite and CuO/Fe_2O_3 catalysts, respectively, at elevated temperatures under O_2 pressure. These yields are unoptimized, and could likely be improved. Interestingly, the corresponding control reactions gave monomer yields of 12% and 17%, respectively, suggesting that a catalyst may not be needed at all under conditions of sufficient temperature and O_2 pressure. Future work should include further exploration of these oxidative routes, both with and without catalyst.

Subject Inventions Listing:

None

Report Date:

22 February 2017

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