

# **Biomimetic Fenton catalyzed lignin depolymerization to Aromatics and Low Molecular Chemicals**

*Zhaohui Tong<sup>a</sup>, Jijiao Zeng<sup>a</sup>, Chang Geun Yoo<sup>b</sup>, Fei Wang<sup>a</sup>, Xuejun Pan<sup>b</sup> and Wilfred Vermerris<sup>c</sup>*

<sup>a</sup> Department of Agriculture & Biological Engineering, University of Florida, Gainesville, FL 32611, USA

<sup>b</sup> Department of Biological Systems Engineering, University of Wisconsin-Madison, Madison, WI 53706, USA

<sup>c</sup> Department of Microbiology and Cell Science, University of Florida, Gainesville, FL 32611, USA

Contact Email: ztong@ufl.edu

## **Abstract:**

Lignin, as the second abundant natural polymer in plant cell wall, has great potential to produce aromatic chemical platforms or fuel precursors due to its unique structure as cross-linked aromatic structures comprised of *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units. Depolymerization of lignin into aromatics or small molecular chemicals provides additional value to current sugar platform biorefinery processes. In the present study, we report that by mimicking natural lignin degradation systems, Fenton catalyst (Fe<sup>2+</sup>, H<sub>2</sub>O<sub>2</sub>) can effectively facilitate lignin's depolymerization in supercritical ethanol (7 MPa, 250 °C) to organic oils including monomer aromatics, phenols, dicarboxylic acids and their derivatives in a yield up to 78%. The thermal properties, functional groups, surface chemistry of lignin before and after Fenton treatment were examined by thermogravimetric analysis (TGA), pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS), <sup>13</sup>P-nuclear magnetic resonance (NMR), and X-ray photoelectron spectroscopy (XPS). The results indicated that Fenton modification facilitated lignin depolymerization through effectively cleavage of β-ether bonds. The results also supported the formation of a lignin-Fe chelating complex that could stabilize the lignin quinone intermediates and effectively depress of lignin re-condensation to minimize char coke production and enhance the lignin conversion yield. In addition, dicarboxylic acids and their derivatives as the major products of Fenton catalyzed lignin depolymerization in supercritical ethanol was derived from ring opening reaction of lignin quinone monomers.