Fragmentation of organosolv lignin by Fenton reaction facilitates production of lignin derived mucolic acid and aromatic compounds.

Jijiao Zeng[a], Changgeun Yoo, Xuejun Pan, Wilfred Vermerris

Fei Wang, Zhaohui Tong[a*]

[a] Department of Agriculture & Biological Engineering, IFAS, University of Florida, Gainesville, FL 32611, USA

* Corresponding author: Tel.:+01-3523921864; fax: +01-3523924902. E-mail address: ztong@ufl.edu (Z. Tong).

Abstract: Valorization of lignin has recently drawn a great of attentions in biorefinery process. One of alternative pathways is disruption of complicate lignin into monomolecular by either reductive or oxidative reaction. However, lignin depolymerization process is challenging because functionality and complex structure of lignin hinders external attack and usually requires harsh reaction conditions. It is know that, the transition metals (like Fe^{2+}, Mn^{2+} and Cu^{2+} ions) can reduce H_2O_2 to generate free •OH which can oxidize almost all organic chemicals in mild condition. We propose that Fenton reaction could modify and fragment of lignin which results in increasing the conversion rate of lignin in subsequent liquefaction reaction. Therefore, in this study, organosolv lignin was pretreated with Fe^{3+}/ H_2O_2 (Fenton catalyst) in different levels by adding gradient enhanced H_2O_2 concentration. The oxidation of α-OH and γ-OH to corresponding aldehydes on lignin side chain were observed by FTIR, XPS and HSQC NMR analysis. Interestingly, Fenton reaction pretreatment also caused fragmentation of lignin together with side chain oxidation. Up to 60% w/w lignin transferred into water soluble phase in highest reaction condition. The molecular weight of soluble and insoluble lignin was determined by GPC. The overall conversion rate of Fenton treated lignin was tested by subsequent supercritical liquefaction. The results showed that lignin was liquefied into high yield of mucolic acid like compounds (relatively 22% of total oil yield) and various aromatic monomers. The total liquid yield was increased from 50% to 60% w/w, while the char yield was decreased from 30% to 20% w/w. The mechanism has been ascribed to Fenton reaction hydroxylates organosolv lignin to form a Fe^{2+} or Fe^{3+}–lignin complex which greatly prohibits intramolecular interaction and reduces the chance of arrangement of $–OCH_3$.