Catalytic Oxidation of Biorefinery Lignin to Value-added Chemicals to Support Sustainable Biofuel Production

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Introduction

Transforming plant biomass to biofuel is one of the few solutions that can truly sustain mankind ' s long-term needs for liquid transportation fuel with minimized environmental impact. However, despite decades of effort, commercial development of biomass-to-biofuel conversion processes is still not an economically viable proposition. Identifying value-added co-products along with the production of biofuel provides a key solution to overcoming this economic barrier. Lignin is the second most abundant carbon sources and the largest renewable material with an aromatic skeleton[1]. More than 60 million metric ton of lignin is currently generated during the papermaking industry annually. Depolymerizing lignin to low molecular weight aromatic and phenolic compounds offers attractive opportunities to produce a range of high value products/chemicals [2-4]. Significant advancement in the recent decade toward development of commercial viable biomass refinery process has reinvigorated the interest in "lignin valorization" to an unprecedented level. An area of key importance to the success of lignin valorization research is the selective production of target compounds. We will present recent results from the study on niobium penoxides catalyzed peroxygen chemicals oxidative conversion of biorefinery lignin to selective production of low molecular weight phenolic compounds.

Materials and Methods

Two representative biorefinery lignin samples were prepared according to our previous work. [5] The structural information of lignin samples were characterized by ^{13}C NMR, CHNO elemental analysis and nitrobenzene oxidation. The lignin oxidation reactions were conducted with presence of peroxygen chemicals (e.g. hydrogen peroxide, peroxy acids) under various reaction conditions. The reaction products were identified by gas chromatography-mass spectrometry (GC-MS). The quantitative yields of products were obtained by high performance liquid chromatography (HPLC).

Results and Discussion

High monomeric phenolic compound selectivity was achieved. According to the GC-MS results, a few predominant phenolic products were observed. Both biorefinery lignin samples are almost entirely solubilized into aqueous phase after the reaction. High conversions of biorefinery lignin samples were obtained by tracking the solid residue. Detailed reaction mechanisms were investigated by using carbon-carbon linkage dimer model compounds HMR and monomeric model compound isoeugenol. The intermediates and final stable products identified from model compound study suggested a side-chain structural related reaction mechanism, which lead to selective production of low molecular weight phenolic compounds from lignin. Applying niobium oxides catalyst could significantly improve the products yield while maintaining the high products selectivity.

Significance

This work demonstrates a new reactive species that could selective oxidation biorefinery lignin to low molecular weight phenolic compounds. High conversions of all tested lignin samples were achieved. Investigation of C-C bond linkage model compounds completed a comprehensive mechanism study which pointed out generation of selective species was the key of lignin effective conversion. Moreover, identifying new catalyst significant enhanced the reaction yields and gave a direction for future study.

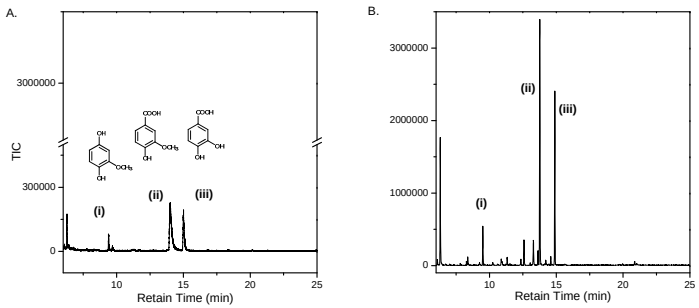

Figure 1. GC-MS spectrum of products identification for Steam Explosion Spruce lignin under tested conditions A) without catalyst B) with Nb_2O_5 catalyst.

References

1. *Holladay, J.E., J.J. Bozell, J.F. White, and D. Johnson, Top Value-Added Chemicals from Biomass: Volume II—Results of Screening for Potential Candidates from Biorefinery Lignin, 2007, U.S. Department of Energy.*
2. *Whiting, D.A., Natural phenolic compounds 1900-2000: a bird's eye view of a century's chemistry. Nat Prod Rep, 2001.* ***18****(6): p. 583-606.*
3. *Zhang, X., M.B. Tu, and M.G. Paice, Routes to Potential Bioproducts from Lignocellulosic Biomass Lignin and Hemicelluloses. Bioenergy Research, 2011.* ***4****(4): p. 246-257.*
4. *Ma, R., Y. Xu, and X. Zhang, Catalytic Oxidation of Biorefinery Lignin to Value-added Chemicals to Support Sustainable Biofuel Production. Chemsuschem, 2014.*
5. *Ma, R., M. Guo, and X. Zhang, Selective Conversion of Biorefinery Lignin into Dicarboxylic Acids. ChemSusChem, 2014.* ***7****(2): p. 412-415.*