Modifying Lignin and its Model Compounds to Enhance Oxidative Ring Cleavage to Dicarboxylic Acids

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Introduction

Lignin is an abundant component in nearly all plant biomass. Large quantities of industrial lignin are already produced annually as a waste product of the pulp and paper industry and the emerging biomass refinery industry will further introduce an enormous amount of lignin. However, selectively and effectively converting lignin into valuable products is a well-recognized challenge. With the methyl group present, the reaction yield falls significantly from 75wt% to 8.2wt%, which suggests the methyl group is the key barrier for direct conversion of biorefinery lignin to valuable Dicarboxylic acid (DCA) products. We will compare several approaches and developing novel catalytic pathways for selective demethylation of representative biorefinery lignin's to support the oxidative conversion of these lignin's to DCAs.

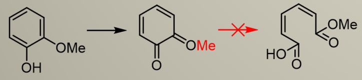


Figure 1: Demethylation step is key to DCA production.

Objective

Develop novel solvent and catalytic system for selective lignin demethylation and further conversion. Understanding the reaction mechanisms and kinetics to optimize the demethylation conditions.

Methods and Materials

Hydroiodic acid treatment

Hydroiodic acid aqueous solution was used as demethylation reagent in this test. Lignin model compounds were pre-solubilized in certain concentration of hydroiodic acid solutions and reflux for a period of 0-5 hours.

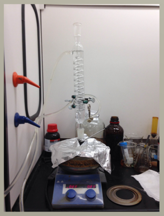


Figure 2: Reflux apparatus used to carry out demethylation.

Peracetic acid treatment

Peracetic acid acetic acid solution was used as demethylation reagent in this test. Lignin model compounds were pre-solubilized in certain concentration of peracetic acid solutions and reflux for a period of 0-5 hours. Several transition metal oxide catalysts were also tested.

GC-MS Analysis of Demethylated samples

The chemical compositions of the organic phase demethylated samples were determined using a Gas chromatography–mass spectrometry (GC-MS). Ethyl acetate extractions were conducted to obtain samples for GC-MS analysis. The combined ethyl acetate extracts were dried under a stream of nitrogen. The samples were further silylated and were analyzed by a GC-MS (Agilent 7890A/5975C) equipped with a DB-5 capillary column.

FTIR Analysis of Demethylated samples

The chemical composition of the solid phase demethylated samples were determined using a Fourier Transform Infrared Spectroscopy (FTIR). FTIR analysis was carried out using Nicolet™ iS™50 FTIR Spectrometer (Thermo Scientific) equipment with resolution of 4 cm^{-1}, 32 scan per minute and transmittance technique. The pellets of lignin were obtained by mixing and pressing lignin and KBr at 0.1% (w/w) of lignin. The range of wavenumber was set from 400 cm^{-1} to 4000 cm^{-1}.

Results

Value-Added Product Production Process

This schematic outlines the pathway of methylated and demethylated lignin to the more valuable DCA form. With demethylation, formation of the Quinone is easier and thus the DCA product yield increased.

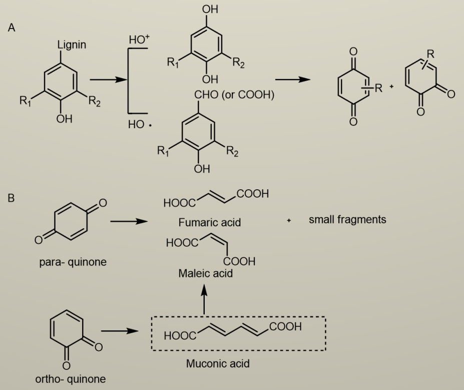


Figure 3: Mechanisms of DCA product generation process in previous study. (A) Quinone production, (B) DCA production.

Analytical Analysis

With analytical techniques such as GC-MS and FTIR the demethylation can be observed and easily compared with a visual change between the substrate and the product.

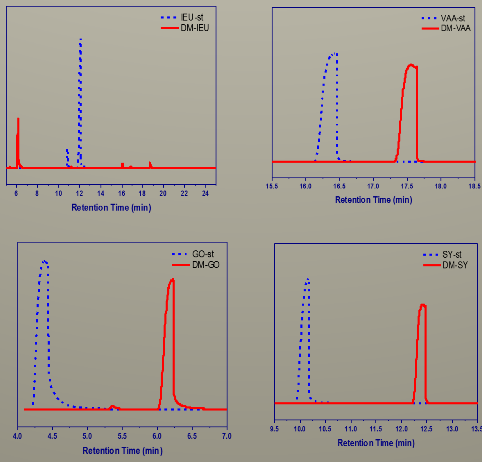


Figure 4: The GC-MS spectrums for both the original compounds and their demethylated counterparts. Model compounds shown: Isoeugenol, Vanillic Acid, Guaiacol, 2,4-dimethoxy-4-methyl-phenol.

Results Continued

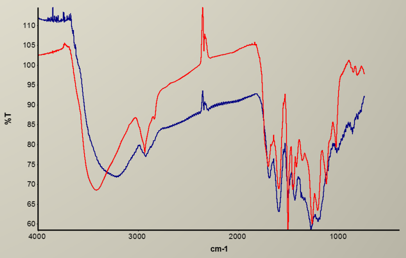
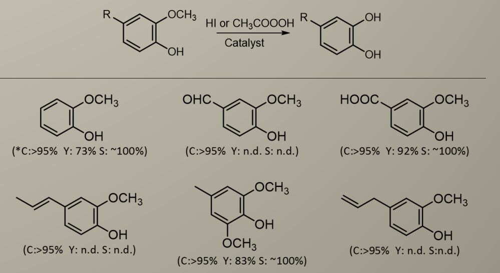


Figure 5: FTIR spectrum for both the original and demethylated Deep Eutectic Solvent (DES) treated Douglas Fir Lignin.

Yield, Selectivity and Conversion

Cleavage of ether bond under high concentration of hydroiodic acid has been employed as an effective characterization method determining the methoxy content by measuring the CH_3I during the process. However, the selectivity and yield of demethylation products will be significantly affected by side chain variation. Peracetic acid has been evaluated in this work as well together with niobium, aluminum oxide catalysts.



(*C:>95% Y: 73% S: ~100%)
(C:>95% Y: n.d. S: n.d.)
(C:>95% Y: 92% S: ~100%)
(C:>95% Y: n.d. S: n.d.)
(C:>95% Y: 83% S: ~100%)
(C:>95% Y: n.d. S:n.d.)

*: C: Conversion based on GC-MS peak change; Y: Molar yield recovered by liquid-liquid extraction and vacuum dry of the sample; S: Selectivity based on GC-MS; n.d.: not determined

Figure 6: Yield, selectivity and conversion for each of the demethylated lignin model compounds with the Hydroiodic acid procedure.

Conclusion

Methoxy group has been identified as one of the major barriers for further cleavage of aromatic ring for DCA production. Cleavage of ether bond to produce catechol derivatives can be achieved effectively and selectively under very acidic conditions. Thus, chemical modification of lignin and its model compound structures have been demonstrated as a promising method to enhance the lignin reactivity for DCA production and has improved the potential of lignin valorization to support economy of biofuel production.

Acknowledgements

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