

Chemoselective Aerobic Oxidation of Aliphatic Alcohols in Lignin in Micellar Systems

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Abstract

A micellar catalytic system for chemoselective aerobic oxidation of primary alcohol in the diol fragment guaiacylglycerol- β -guaiacyl ether as one of the most common structure in lignin has been proposed. The catalyst system consists of TEMPO/Cu (II), mediated by oxygen gas. Our studies highlight the prospect of combining this method with a PEO-PPO-PEO micellar system in basic aqueous effluent of delignification processes of lignocellulosic materials to achieve the oxidation of primary alcohol to aldehyde.

Central hypothesis

Delignification processes allow converting lignocellulosic biomass into delignified cellulosic fibers and process effluent. The process effluent is laden with lignin-based phenolic compounds which are derived from lignocellulosic cell walls. The structural heterogeneity of lignin isolated from effluent makes it difficult to break down and isolate into a value-added product. In order to harness lignin, the identification of new chemical transformations that go forward with high efficiency and selectivity on a complex starting material will be required.

The hypothesis of the present work is derived from the recognition that selective oxidation of either alcohol (secondary and primary) in the diol fragment guaiacylglycerol- β -guaiacyl ether as one of the most common structure in lignin could provide a starting structure for the production of low molecular weight aromatics from lignin, presumably by increasing cleavage of the β -O-4 linkage.

Hence, in the present work, we decided that it was of paramount importance to first study the structure of lignin obtained from effluent produced by the sequential ozone and soaking ammonia pretreatment of wheat straw and then investigate the formation of block copolymer PEO-PPO-PEO micelles in aqueous environment of process effluent, as well as their ability to solubilize guest molecules, including lignin fragments from process streams, and to elucidate the interactions that occur between host micelles and guest compounds representing a preferred molecular orientation in self-assembled nanostructures, in which aerobic oxidation of vicinal alcohols can be performed, selectively.

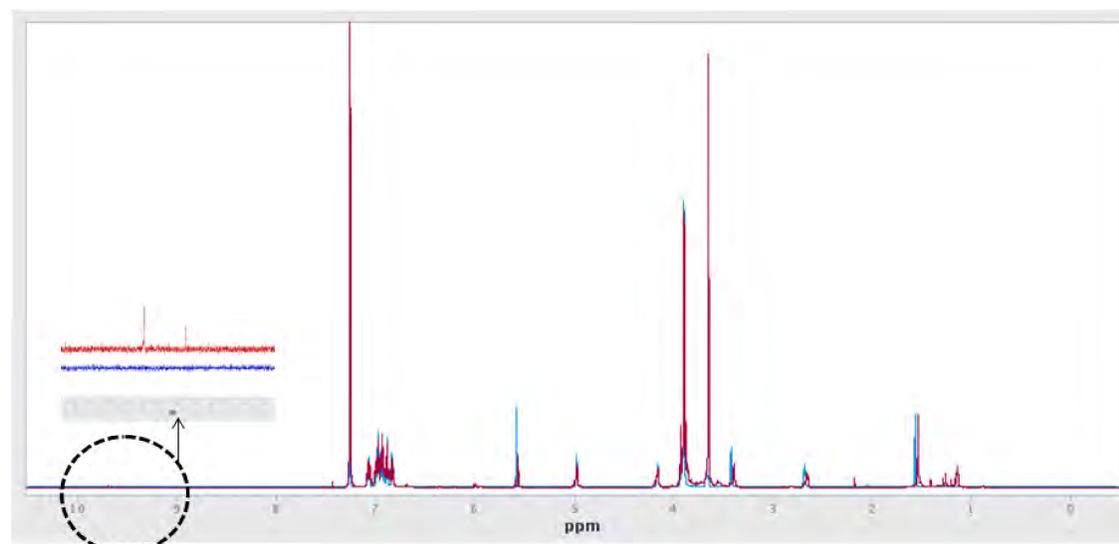
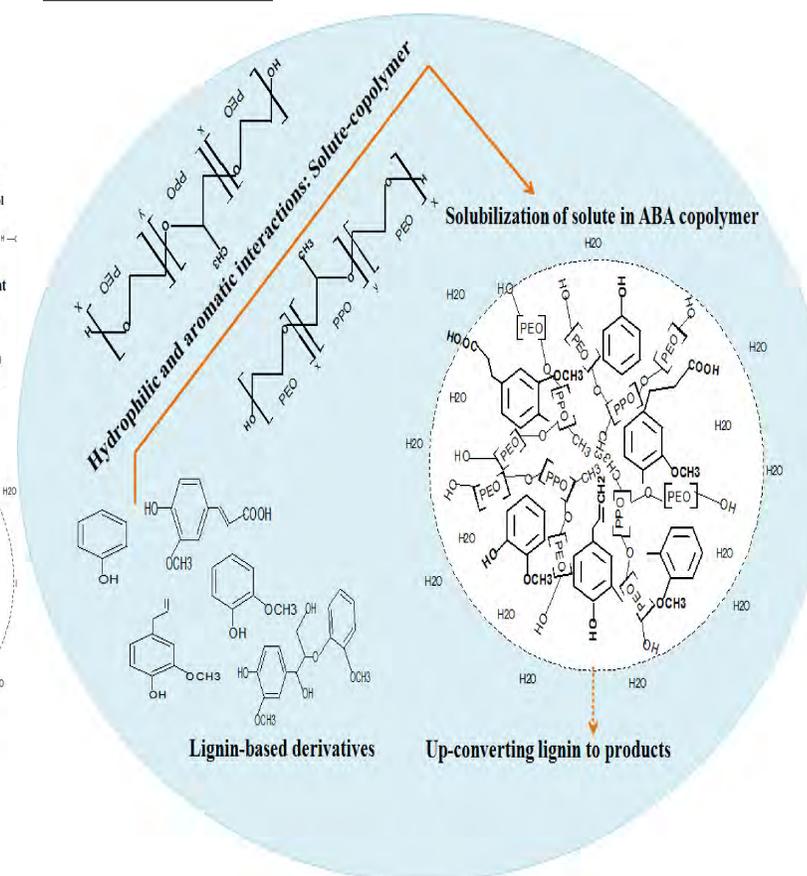
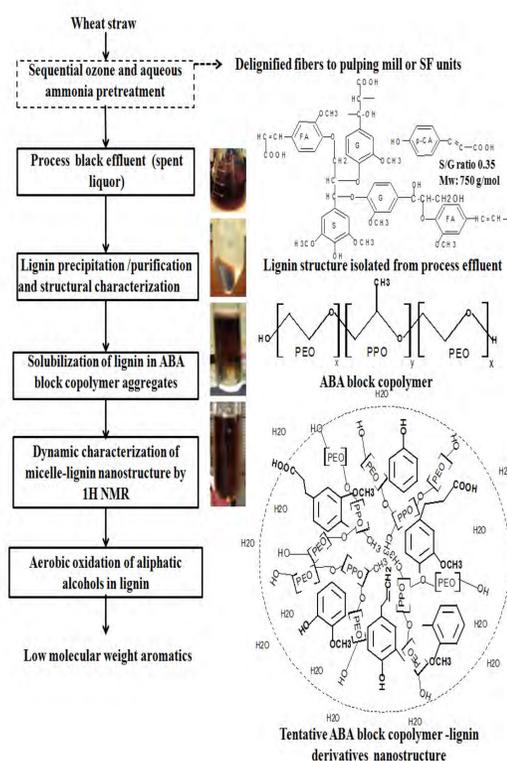
Overall objectives

- Determine the structure of lignin isolated from pretreatment effluent using acidifying method for precipitation of lignin and employing chemical-analytical techniques such as FT-IR, UV-Vis, Py-GC/MS, Py/TMAH-GC/MS, GPC, and DPPH assay.
- Investigate the solubilization, hydrophilic and aromatic interactions, of lignin in block copolymer PEO-PPO-PEO micelles in basic aqueous solution using ^1H NMR and DOSY NMR techniques.
- Investigate the mechanisms of aerobic oxidation of primary and secondary alcohols in an advanced lignin model compounds guaiacylglycerol- β -guaiacyl ether in combination of micellar systems by ^1H NMR techniques.

Key references:

- (1) Mohammadali Azadfar, Allan Haiming Gao, Mahesh V. Bule and Shulin Chen: "Structural characterization of lignin: A potential source of antioxidants guaiacol and 4-vinylguaiacol." *International journal of biological macromolecules* 75 (2015): 58-66.
- (2) Mohammadali Azadfar, William C. Hiscox, Shulin Chen: "Solubilization of lignin in copolymer micelles in aqueous solution" *Colloids and Surfaces (In print)*.
- (3) Mohammadali Azadfar, William C. Hiscox, Shulin Chen: "Selective aerobic oxidation of aliphatic alcohols in lignin in micellar system" (In preparation; to be submitted to *ACS Nano*).

Process flowchart

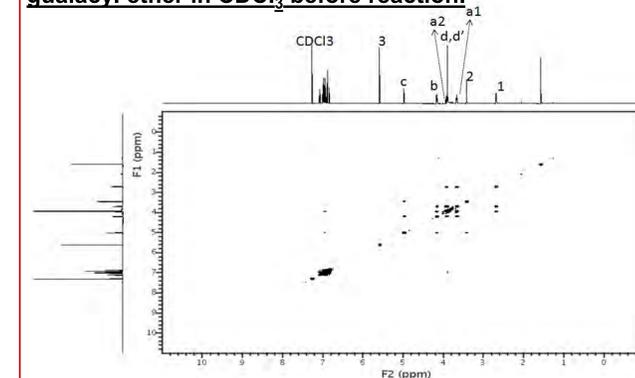


^1H NMR spectrum of the diol fragment guaiacylglycerol- β -guaiacyl ether in CDCl_3 (blue line) and isolated guaiacylglycerol- β -guaiacyl ether from the reaction media (red line-after reaction) in CDCl_3 .

^1H NMR data of structure of diol fragments, guaiacylglycerol- β -guaiacyl ether as one of the most structure in lignin

Label	^1H -NMR: δ_{H} [ppm], J [Hz]
3	5.57 (J= 1.11 Hz, 1H)
c	4.97 (J= 1.09 Hz, 1H)
b	4.15 (J= 1.01 Hz, 1H)
a ₂ , d, d'	3.91-3.89 (J= 3.91, 3.89 Hz, 7H)
a ₁	3.65 (J= 1.02 Hz, 1H)
2	3.41 (J= 1.00 Hz, 1H)
1	2.67 (J= 1 Hz, 1H)

^1H - ^1H gCOSY correlation spectrum of guaiacylglycerol- β -guaiacyl ether in CDCl_3 before reaction.



Overall conclusions

- A new micellar catalytic system for selective aerobic oxidation of vicinal alcohols in the diol fragment guaiacylglycerol- β -guaiacyl ether as one of the most common structure in lignin has been proposed employing TEMPO/Cu (II), mediated by oxygen gas in combination of PEO-PPO-PEO micelles in basic aqueous effluent of delignification processes.
- The ^1H NMR spectrum of the diol fragment isolated from oxidation reaction media revealed that the resonance position of proton bonded to aldehyde carbon is positioned between 9-10 ppm.
- With the recognition that the steric rearrangement of the diol fragment after solubilization in micelle interior presumably have caused a steric hindrance around the N-oxoammonium functionality in the N-oxoammonium salts resulting in a much easier attack by the relatively less hindered primary alcohols, it has concluded that self-assembled micelle-lignin nanostructures in aqueous solution have the potential to be considered as nanoreactors for selective oxidation of primary alcohol in lignin structure and provide starting structure for chemical transformation of lignin into low molecular weight aromatics from lignin.

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