CHARACTERIZATION AND POTENTIAL APPLICATIONS OF MILLED WOOD LIGNIN OBTAINED FROM SUGAR DEPOT BIOREFINERY PROCESS

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LIST OF ACRONYMS

ALK	alkaline
DACSL	dilute acid corn stover lignin
DES	deep eutectic solvent
DESL	deep eutectic solvent lignin
DCA	dicarboxylic acid
FTIR	Fourier transform infrared
GPC	gel-permeation chromatography
MWL	milled wood lignin
NMR	nuclear magnetic resonance
NREL	National Renewable Energy Laboratory
SESPL	steam exploded spruce lignin
SPORL	sulfite pretreatment to overcome recalcitrance of lignocellulose

EXECUTIVE SUMMARY

This one-year task aims at characterizing the structural properties of milled wood lignin (subtask 1) and identifying its potential application (subtask 2). There are three applications initially proposed: *depolymerization to chemicals (subtask 2.1), co-polymerization with carbon dioxide to produce polyurethanes (subtask 2.2), and apply as lignin slurry fuel (subtask 2.3).* The prolonged WSU BSLE labs closure (over 10 months starting November 9th 2015) has created significant difficulties to complete all these activities. We have been able to cope with this challenge and have made significant progress. We are able to complete the subtask 1 and subtask 2.1. We were not able to conduct the subtask 2.2 due to the lack of adequate facility. Due to departure of a key collaborator, Dr. Jinwu Wang, we did not complete subtask 2.3. Instead, we have developed a new method for extracting high quantity and high purity lignin from milled wood.

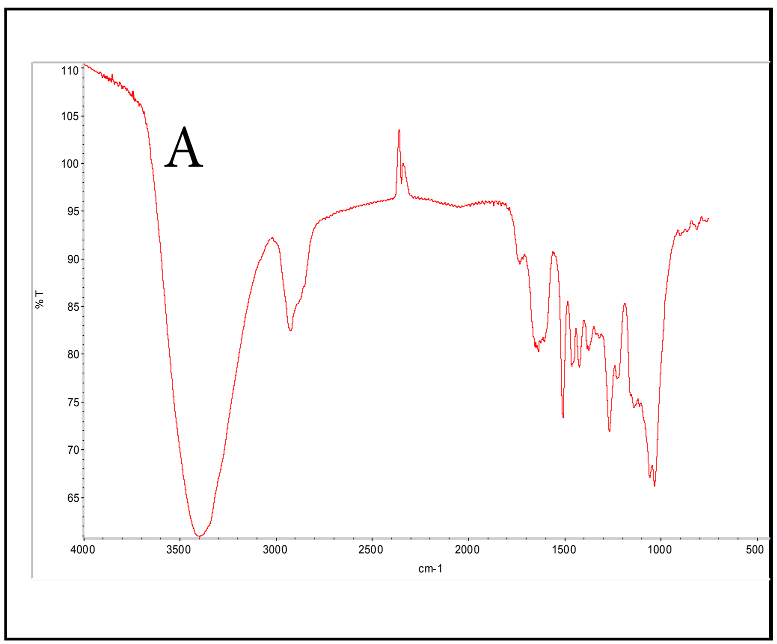
INTRODUCTION

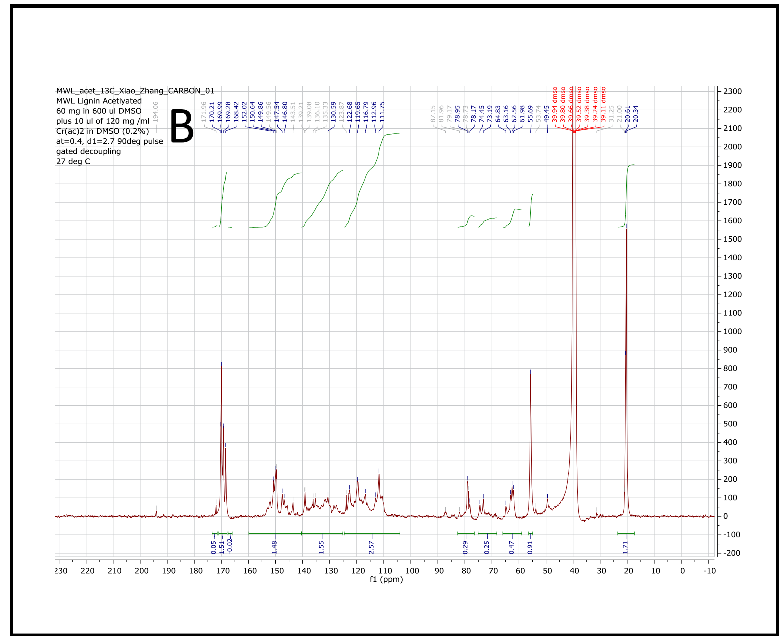
Wood milling presents a promising alternative wood deconstruction method to produce fermentable sugar for biofuel applications. One distinctive advantage of this physical biomass deconstruction over chemical pretreatments is the potential to preserve the physiochemical properties of native lignin. Native or "proto" lignin has long been held as a promising lignin feedstock for high value applications. However, neither the structural characteristics of native lignin nor its potential application has been well understood due the lack of a method to produce them in a large and consistent quantity. The large scale milling pretreatment of wood developed by NARA has produced a large quantify of milled wood lignin, which allows us to carry out detail analysis of milled wood lignin and determine its potential applications.

TASK 1: CHARACTERIZATION AND POTENTIAL APPLICATIONS OF MILLED WOOD LIGNIN OBTAINED FROM SUGAR DEPOT BIOREFINERY PROCESS

Characterization of milled wood lignin

The milled wood samples were received from Jinwu Wang/Mike Wolcott's group in July. The milled wood lignin was extracted from the sample by acidic dioxane/water mixture. The Klason lignin content of the milled wood lignin was determined using acidolysis protocol standarized by NREL, which showed a klason lignin content at around 58%. The GSH ratio was determined and compared by wet chemistry procedures including alkaline nitrobenzene oxidation and thioacidolysis. Compatible results were obtained from both methods, indicating guaiacyl unit (>95%) is the predominant subunit in milled wood lignin with the presence of small amount p-hydroxyphenyl unit (~5%). Fourier transform infrared spectroscopy (Figure MWL-1.1a) and 13C nuclear magnetic resonance (Figure MWL-1.1b) were applied to understand the side-chain functionalities and inter-unit linkages of milled wood lignin. Table MWL-1.1 summarizes the quantitative structural information of milled wood lignin obtained by 13C NMR analysis. The molecular weight distribution of milled wood lignin was determined by gel-permeation chromatography (GPC) with the peak molecular weight around 2950 (Figure MWL-1.1c).





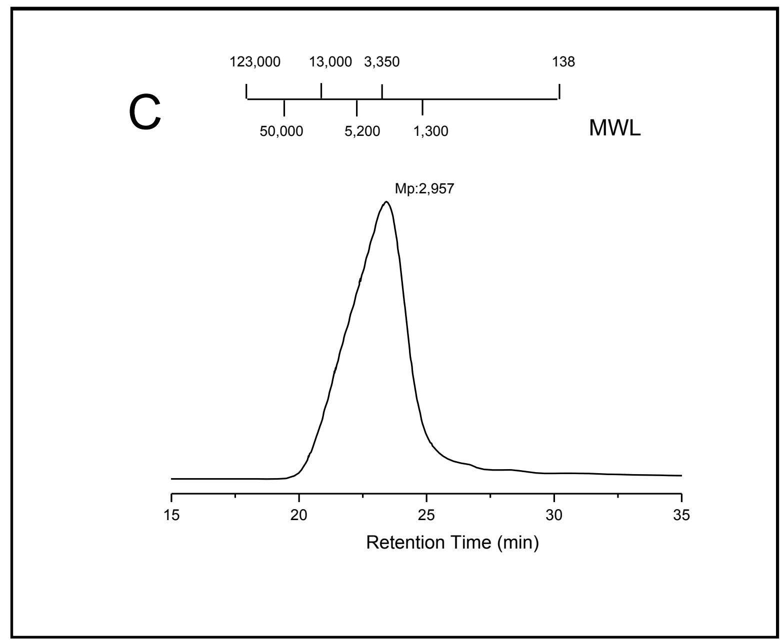


Figure MWL-1.1. Characterization of milled wood lignin a) FTIR spectrum, b) 13C NMR spectrum, c) molecular weight distribution

Table MWL-1.1. Quantitative structural analysis based on 13C NMR.

Spectral Region	Chemical Shift range (ppm)	Numbers of moieties per aromatic rings
Methoxyl content	57-54	0.97
Car-H	125-103	2.75
Car-C	141-125	1.66
Car-O	160-141	1.59
Phenolic hydroxyl	171-174	0.05
Aliphatic hydroxyl	171-168.5	1.62
Saturated CH2 or CH3 on aliphatic side chain	40-20	1.83
C-γ in β-5 and β-O-4 with C=O	64-62	0.65
Cα in β-O-4	71-78	0.57
Cβ in β-O-4	83-78	0.42

Conversion of milled wood lignin to chemicals: monomeric phenolic compounds and dicarboxylic acids.

The conversion of milled wood lignin to monomeric phenolic compounds and dicarboxylic acids was investigated and compared with several other bio refinery lignin samples (Figure MWL-2.2). It appears that MWL is not an ideal lignin for chemical productions, showing a low conversion yield to either phenolic compounds or dicarboxylic acids. In addition, it is very difficult to extract a large quantity of pure lignin from the hydrolysis residues after enzyme saccharification of milled wood sample.

We therefore attempted to develop a new lignin separation method from the milled wood. A novel method of applying Deep Eutectic Solvents (DES) to extract high purity lignin (up to 95%) from Douglas-fir milled wood with 58% recovery was established. The resulting from Douglas-fir lignin product, DESL, has several distinctive characteristics: lower and narrowly distributed molecular weight compared to MWL, and the lack of ether linkages, representing a new source of lignin. The mechanism involved in DES depolymerization of lignin from wood was investigated suggesting that both DES-catalyzed ether bond cleavage and solvent effects are important to facilitate lignin extraction from wood (Figure MWL-1.3). The findings from this study may provide a breakthrough toward truly realizing the high value potential of lignin. The results were published and featured as a cover picture of volume 18 issue 19 Green Chemistry Journal (Alverez-Vasco et al., 2016).

We have further demonstrated that the DESL lignin can replace The DES lignin has shown high reactivity to replace the resorcinol for organic aerogel synthesis (Figure MWL-1.4).

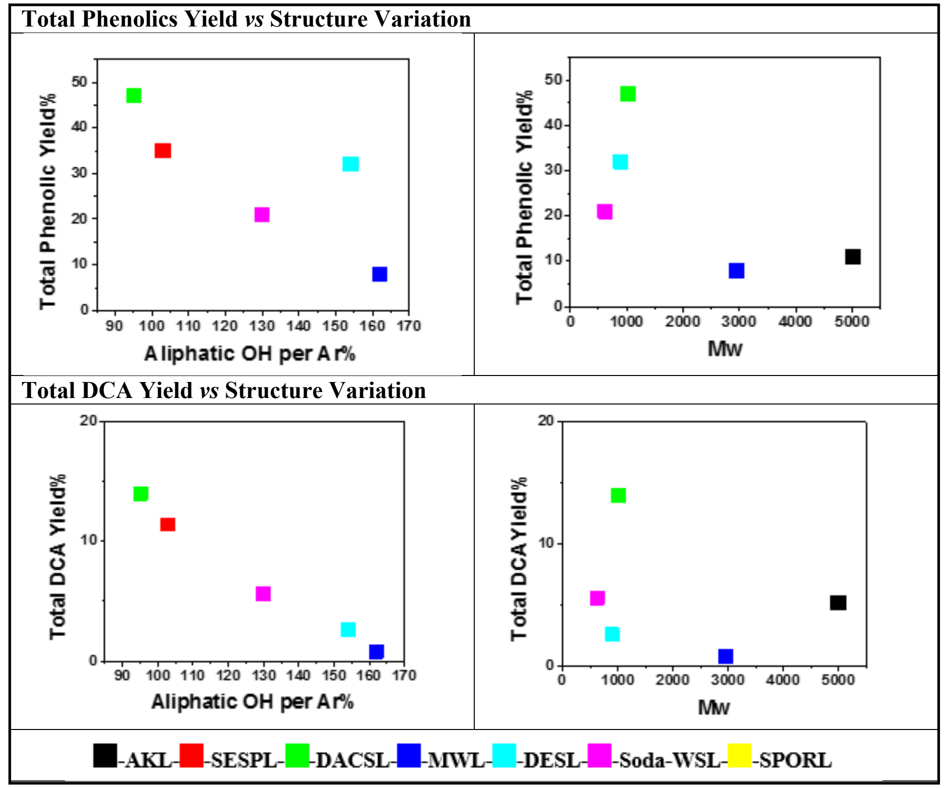


Figure MWL-1.2. Conversion of milled wood lignin and several other bio refinery lignin samples to monomeric phenolic compounds and dicarboxylic acids (unpublished results)

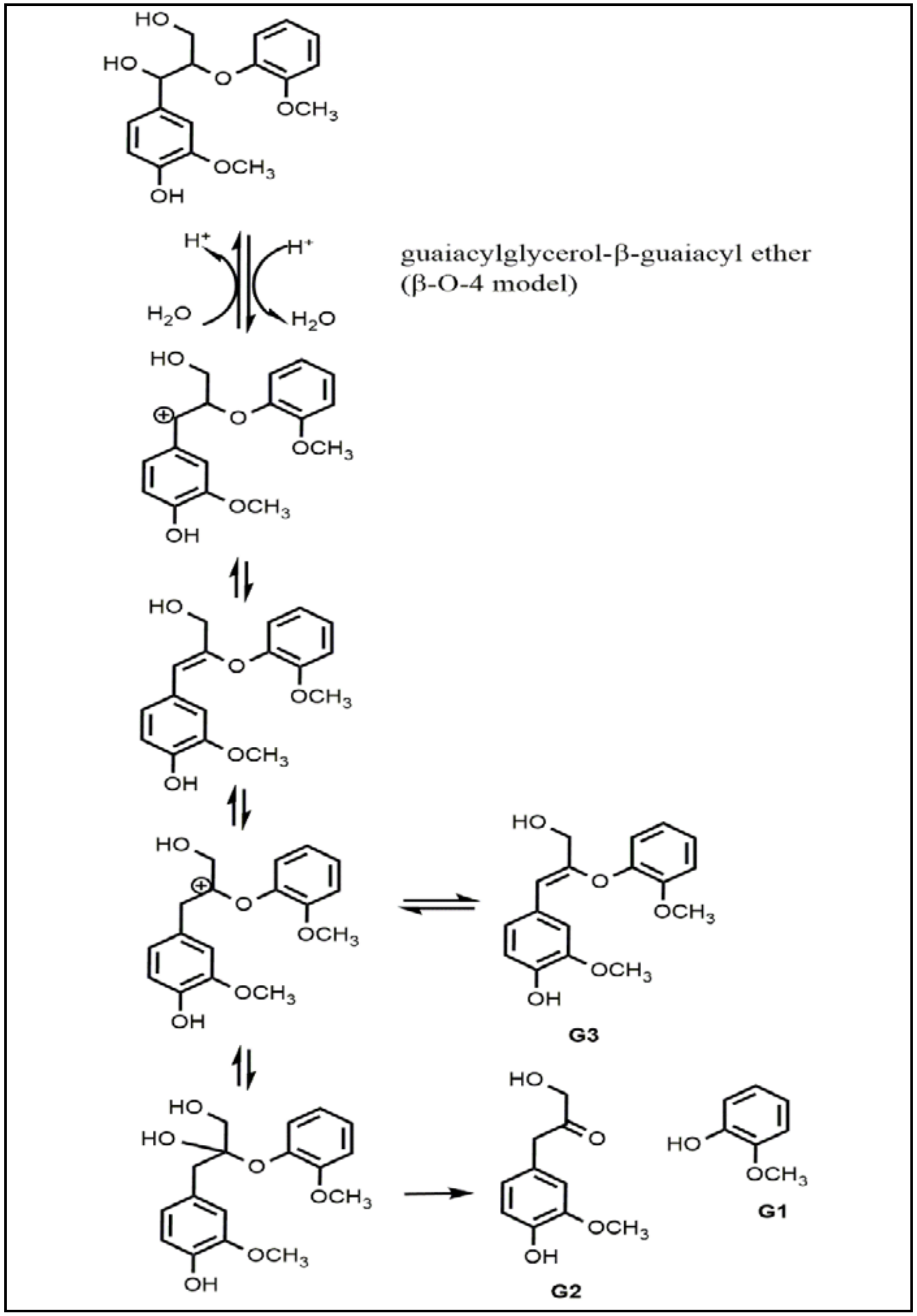


Figure MWL-1.3. Main mechanisms of β-O-4 linkage cleavage reaction during DES treatment of lignin based on study of model compound guaiacylglycerol-β-guaiacyl ether.

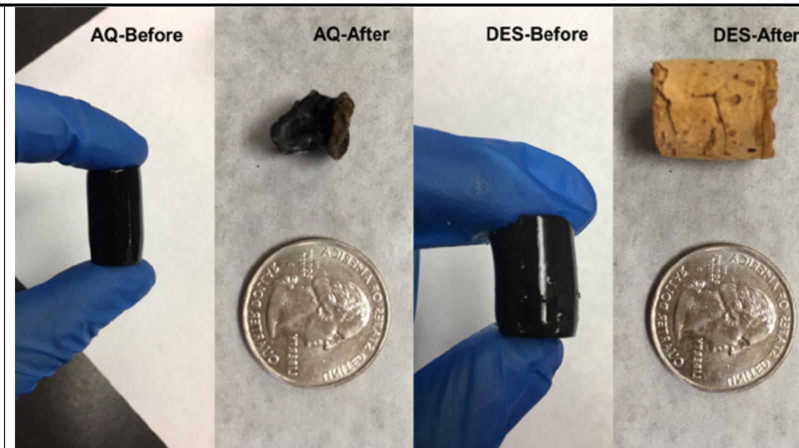
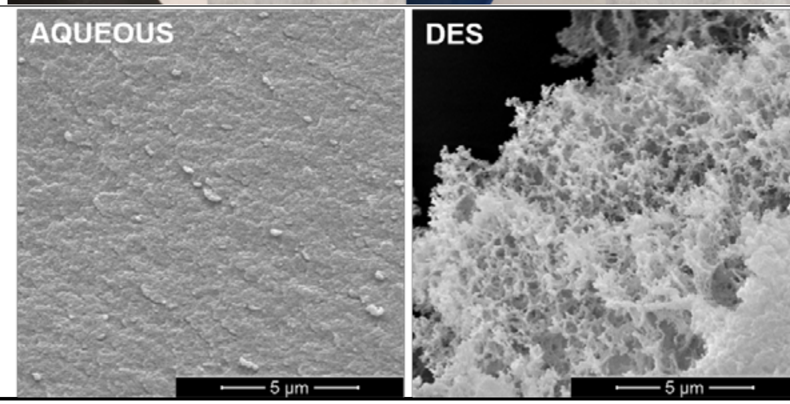
Photo Before and After Freeze Dry	
SEM Image	

Figure MWL-1.4. DES Assisted synthesis of lignin aerogel (unpublished results)

NARA OUTPUTS

PhD Thesis:

DICARBOXYLIC ACIDS PLATFORM CHEMICALS FOR VALORIZATION OF BIOREFINERY LIGNIN, by Ruoshui Ma

Publications:

Alvarez, C.V., Ma, R.S., Quintero, M., Guo, M., Geleynse, S., Ramasamy, K.K., Wolcott, M.P., Zhang, X.*, Unique Low-molecular-weight Lignin with High Purity Extracted from Wood by Deep Eutectic Solvents (DES): a New Source of Lignin for Valorization, Green Chemistry (2016) DOI: 10.1039/C6GC01007E

Ma, R.S., Guo, M., Lin, K.T., Hebert, V.R., Zhang, J.W., Wolcott, M.P., Quintero, M., Ramasamy, K.K., Chen, X.W., Zhang, X.*, Peracetic Acid Depolymerization of Biorefinery Lignin for Production of Selective Monomeric Phenolic Compounds, Chemistry - A European Journal (2016) DOI: 10.1002/chem.201600546

Invited presentations:

Xiao Zhang, 2nd Northwest Wood-Based Biofuels + Co-Products Conference, "Dicarboxylic acids platform for lignin valorization" May 3rd 2016, Seattle WA

Xiao Zhang, The International Symposium on Catalytic Conversions of Biomass, "New Routes to Transform Lignin Macromolecules for Sustainable Production of Aviation Fuel, Chemicals and Materials" Taipei June 29th 2016.

NARA OUTCOMES

This research is still preliminary. No outcomes produced to date.

FUTURE DEVELOPMENT

Future research will focus on evaluating the potential of DESL for biopolymer applications.

LIST OF REFERENCES

Alvarez-Vasco, C., Ma, R., Quintero, M., Guo, M., Geleynse, S., Ramasamy, K.K., Wolcott, M. & Zhang, X. (2016). Unique low-molecular-weight lignin with high purity extracted from wood by deep eutectic solvents (DES): a source of lignin for valorization. *Green Chemistry,* 18, 5133-5141. doi: 10.1039/C6GC01007E