Characterization of Biorefinery Lignins and Comparison of Reactivity for Value-added Chemical Production

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INTRODUCTION

Utilizing biomass solely for biofuel production poses an economic challenge mainly due to the low value of fuel. Generating valuable co-products in addition to biofuel from the biomass-to-biofuel conversion process is the key to overcome this economic barrier. It is expected that enormous amounts of bio-refinery lignin will be generated as a waste stream during the bio-refining process. Thus, there are increasing interests in converting lignin to value added co-products. Promising pathways have been discovered whereby lignin can be oxidatively converted to valuable chemicals such as dicarboxylic acids and monomeric phenolic compounds. New lignin sources have been identified by National Advanced Renewables Alliance (NARA). However, the structural characteristics of these lignin samples and their potential for value added chemical conversion is not well understood. This project aims to characterize and compare the structures of five representative bio-refinery lignins and determine their reactivity toward oxidative conversion to dicarboxylic acids and monomeric phenolic compounds.

MATERIALS AND METHOD

Nitrobenzene oxidation, thioacidolysis and Klason lignin content(National Renewable Energy Laboratory (NREL) laboratory analytical procedure (2011)) , were carried out on Milled Wood Lignin (MWL), Diluted Acid Corn Stover Lignin (DACSL), Alkali-extracted Wheat Straw Lignin (Soda- WSL), Sulfite Pretreatment to Overcome Recalcitrance of Lignocellulose (SPORL) Douglas Fir lignin and Deep Eutectic Solvent (DES) Douglas Fir lignin. Lignin reactivity was tested and compared based on previously reported oxidative depolymerization methods for monophenol and dicarboxylic acid production.

Image 1. Teflon tube and reactors used in nitrobenzene oxidation.

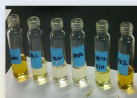Image 2. Reactors for nitrobenzene oxidation right before being submerged in oil bath.

Image 3. Thioacidolysis extracts.

Nitrobenzene Oxidation

This method was used for the determination of p-hydroxyphenyl (H), syringly (S) and guaiacyl (G) lignin substructures ratio. Lignin samples were heated with aqueous sodium hydroxide and nitrobenzene after which extractions were done under alkaline conditions then acidic. Gas Chromatography- Mass Spectrometry (GC-MS) was used for product analysis.

Thioacidolysis

This method was used for the determination of H/S/G ratio by cleavage of β-O-4 linkages in lignin. Lignin samples were heated with dioxane/ ethanthiol solution, containing boron trifluoride etherate, and docosane. Extractions were then done under acidic conditions. GC-MS was used for product analysis.

Klason Lignin Content

This method was used to approximate the Klason lignin content of samples. Samples were subjected to a two- step acid hydrolysis procedure then analyzed on an oven weight basis.
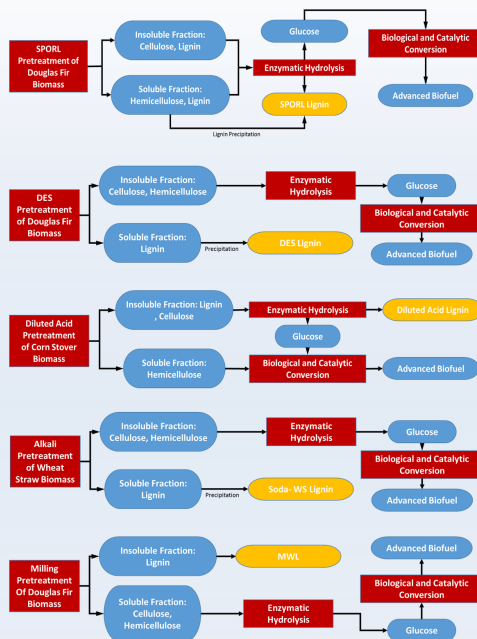
Bio-refinery Lignin Streams

Figure 1. Demonstration of lignin derivation from different pretreatment methods.

RESULTS

Lignin Characterization

Lignin	Klason Lignin	Nitrobenzene			Thioacidolysis		
	%	H	S	G	H	S	G
DACSL	72	25	30	45	19	35	46
SPORL	23	5	-	95	8	-	92
DES Lignin	90	14	-	85	5	-	95
Soda- WSL	58	7	43	50	8	45	47
MWL	54	3	-	97	4	-	96

Table 1. Klason lignin content and H/G/S ratios of lignin samples as determined by NREL lignin fractionation, nitrobenzene oxidation and thioacidolysis .

Lignin Reactivity towards Oxidative Conversion to Low Molecular Weight Phenolic Compounds (LMWPC) and Dicarboxylic acids (DCA)
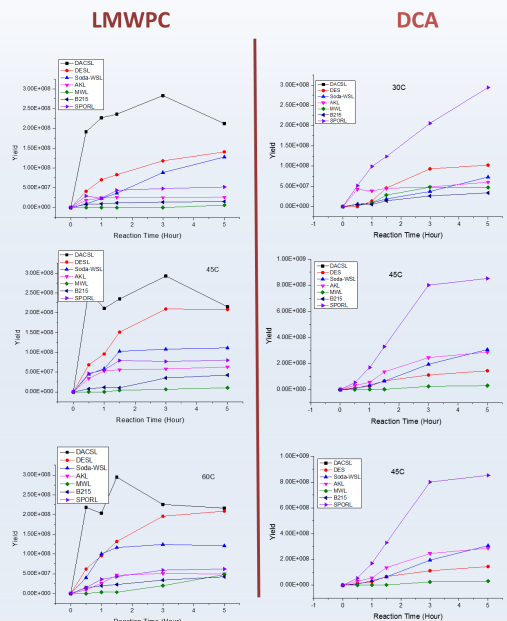
LMWPC   DCA

Figure 2. LMWPC and DCA yields determined by GC-MS from catalysts assisted oxidative conversion of biorefinery lignin at 30-60 °C during a period of 0-5 hours.

CONCLUSION

In this work, we have prepared five representative biorefinery lignins. The HSG ratio of lignin was determined by both nitrobenzene oxidation and thioacidolysis. These lignins also showed different reactivity towards niobium assisted paa conversion to LMWPC and chalcopyrite catalyzed direct conversion to DCAs.

ACKNOWLEDGEMENT