Optimization of Lignin Precipitation with Functional Group Control for Use in Bio-Based Polyurethane Foams

Lauren Spahn, Raisa Carmen Andeme Ela, Rebecca G. Ong

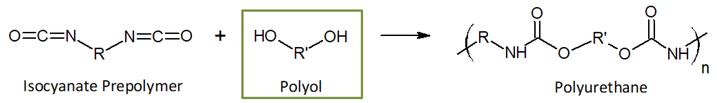
Department of Chemical Engineering, Michigan Technological University

Pavlis Honors College

Michigan Technological University

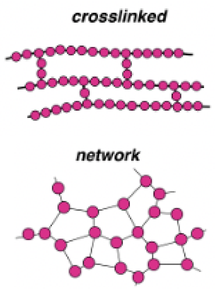
Lignin-Based Polyurethane Foams

- Increased demand for cost competitive and environmentally friendly methods of manufacturing polyurethane foams
- Lignin has potential to replace synthetic, petroleum-based polyols in polyurethane foams
- Increasing the hydroxyl group content in the lignin polyol will result in dense polymer crosslink networks for rigid foam applications



Addition of Hydroxyl Groups

- Reacting with a short chain mercapto-alcohol results in increased sites for cross linking, resulting in dense crosslink networks for rigid foams
- Demethylation using dodecanethiol was explored as possible method to increase hydroxyl content
- Reacting at alkaline conditions saves time and resources during precipitation process



3-mercapto-1,2-propanediol was chosen as reactant

Lignin Precipitation Procedure

Reaction

- 100 mL black liquor + 50 mL DI water at 75°C
  + 4.4 wt% mercapto-propanediol, 15 min residence time
  Or
  + 5 wt% dodecanethiol, 15 or 30 min residence time

Acidification

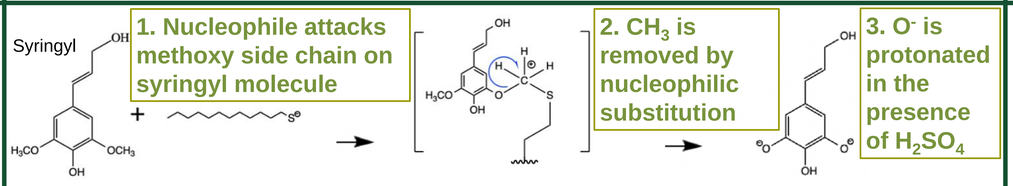
- CO_2 sparge 1 hour at 80 kPa, 75°C
- 50 mL DI water + 50 mL H_2SO_4 + 1.5 hours residence time at 85°C, pH=1.7

Product

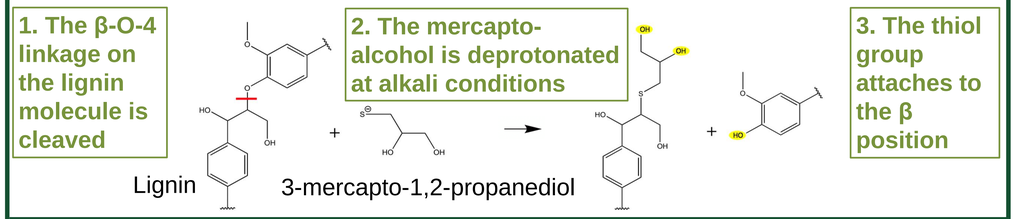
- Solid Mass Yield

- Previously optimized reaction conditions of a modified LignoBoost procedure were implemented

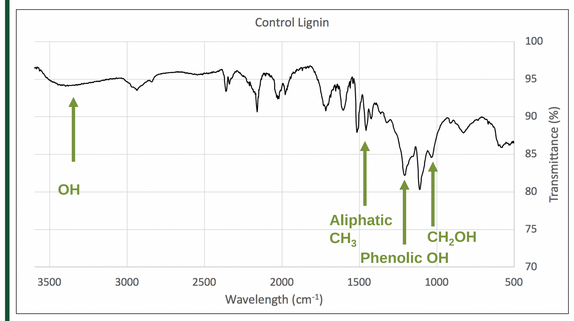
Proposed Demethylation Reaction

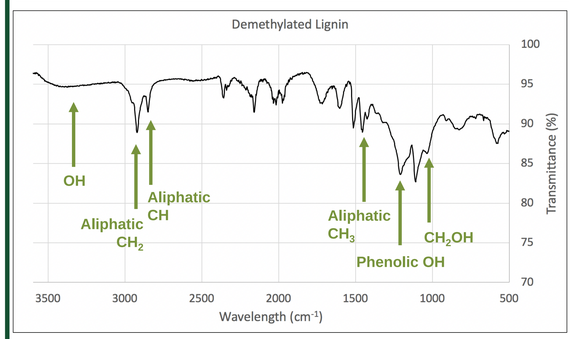


Proposed Mercapto-Alcohol Reaction



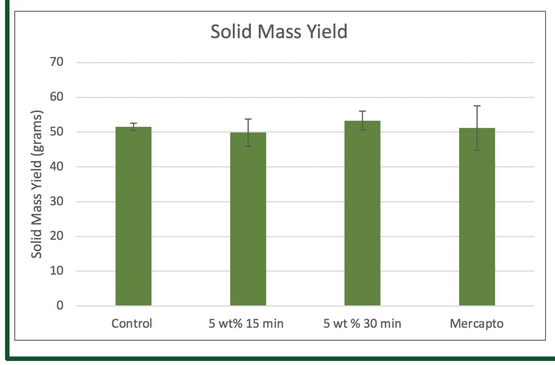
Demethylation FTIR Functional Group Analysis





- Samples dried at 105 °C prior to testing
- Control lignin shows phenolic OH and CH_2OH characteristic of syringyl
- C-O ring of syringyl at 1330 cm^{-1}
- C-O ring of guaiacyl at 1265 cm^{-1}
- Demethylated lignin has significant aliphatic carbon peaks, evidence that the thiol is still bonded to the lignin molecule, suggesting the use of a mercapto-alcohol

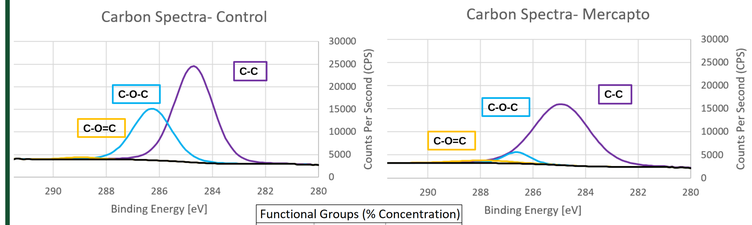
Lignin Precipitation Results



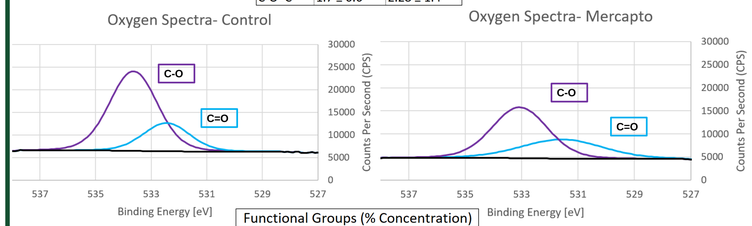
- Solid mass yield is relatively similar compared to control experiments
- Neither the addition of the thiol, thiol residence time, or mercapto-alcohol addition have a significant effect on solid mass yield

This method of lignin precipitation is repeatable and reliable

XPS Functional Group Quantification



Functional Groups (% Concentration)	Control	Mercapto
C-C	62.2 ± 5.0	76.8 ± 13.2
C-O-C	36.1 ± 5.2	20.9 ± 14.4
C-O=C	1.7 ± 0.6	2.28 ± 1.4



Functional Groups (% Concentration)	Control	Mercapto
C-O	74.0 ± 2.0	70.3 ± 12.6
C=O	26.0 ± 2.0	29.7 ± 12.6

Elemental Composition

Sample	O%	C%	S%
Control	22.1 ± 1.3	76.3 ± 1.4	1.63 ± 0.1
Mercapto	23 ± 1.1	74.2 ± 1.9	2.8 ± .9

- Decrease in C-O-C in mercapto-alcohol samples signifies cleaving of β-O-4 linkage
- Increase in C-C in mercapto-alcohol samples suggest thiol group is attached

Conclusions

- Demethylation attempts using dodecanethiol were unsuccessful
- XPS analysis indicates successful cleavage of the β-O-4 ether by the mercapto-alcohol and incorporation of the thiol
- Current precipitation procedure is reliable and can be used for future experimentation

Generating Lignin-Polyurethane Foams

- Lignin product will act as a polyol and react with an isocyanate in the formation of bio foams
- Polymethylene polyphenyl isocyanate chosen as isocyanate and glycerol propoxylate chosen as a synthetic polyol for rigid foam formation
- Lignin-polyurethane foams will be prepared in a range of ratios of synthetic to bio polyol
- Lignin-based foams will be compared to a 100% synthetic control foam in order to compare mechanical properties

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