The effects of dilute acid pretreatment on poplar lignin and recalcitrance

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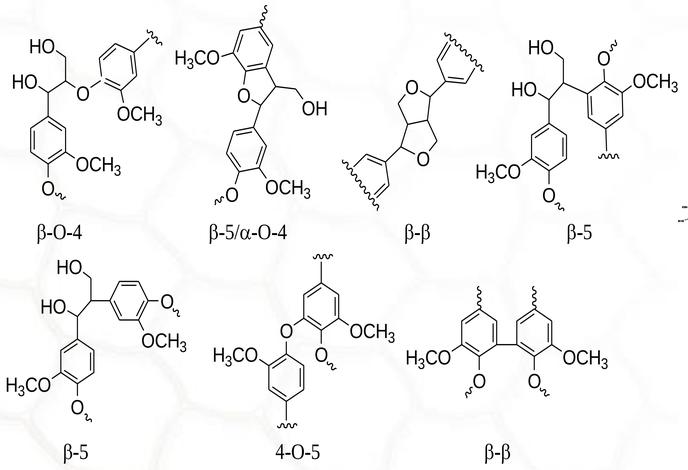
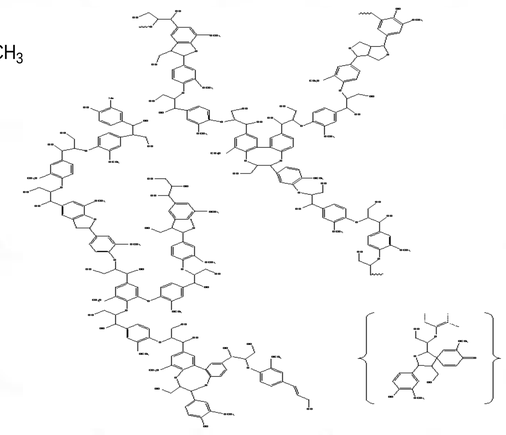
Introduction

The efficient, cost-effective depolymerization of polysaccharides in biomass to fermentable monosaccharides remains a pivotal operation in the utilization of the biomass for the fermentation to ethanol. Pretreatment is required to reduce the natural recalcitrance of biomass prior to enzymatic deconstruction for the effective utilization of these bioresources. Of the three major plant biopolymers, lignin is considered the most recalcitrant component of a plant cell wall. The objective of this study is to investigate the effects of dilute acid pretreatment on the structural changes of poplar lignin and examine their relationship to the reduced recalcitrance.



Primary inter-linkages in lignin.



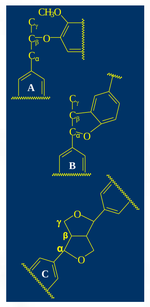
Representative schematic model of softwood lignin.

Experimental

Pretreatment

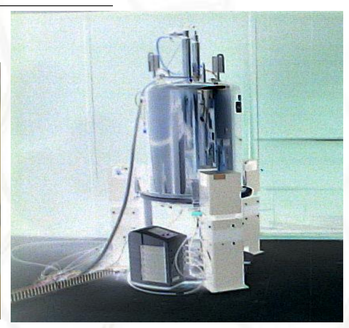
Poplar was pretreated with dilute acid (5% w/w)

Temp / ºC	Time / min	H_2SO_4 / % w/w	Severity
170	0.3	0.5	0.5
170	1.1	0.5	1.1
170	5.4	0.5	1.8
170	8.5	0.5	2.0
170	26.8	0.5	2.5



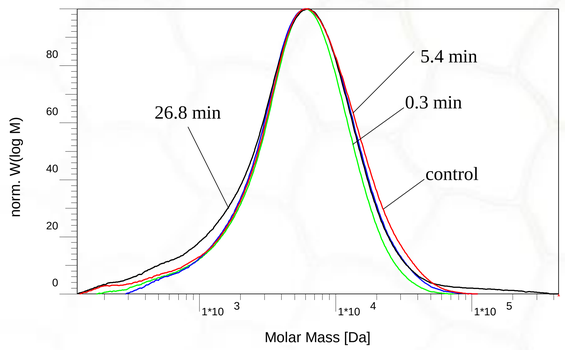
Lignin isolation and characterization

- **Ball-milled lignin**
- **Molecular weight distribution**
- **Quantitative ^{13}C NMR**
- **2D HSQC (^{13}C-^{1}H) heteronuclear correlation spectra**



Results and Analysis

GPC analysis of lignin

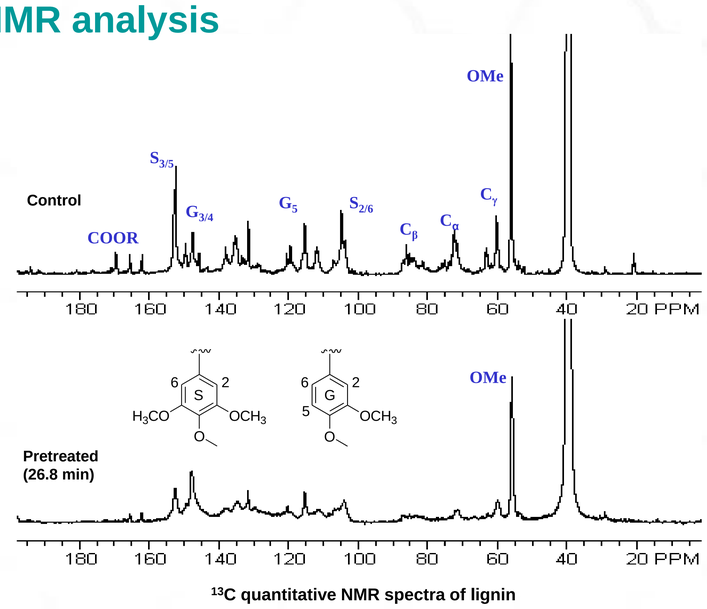


Molecular weight distribution of lignin.

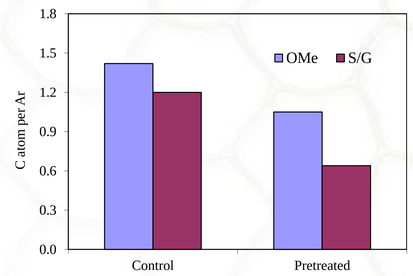
Time min	Mn g/mol	Mw g/mol	Mw/Mn
0	3.21 x 10^3	8.55 x 10^3	2.7
0.3	3.45 x 10^3	7.46 x 10^3	2.1
5.4	3.84 x 10^3	8.14 x 10^3	2.1
26.8	2.74 x 10^3	8.28 x 10^3	3.4

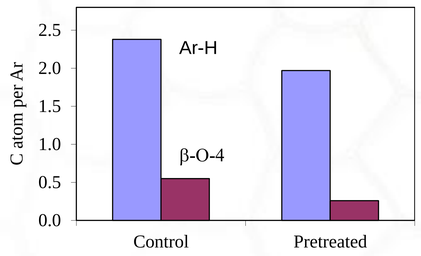
Mn: number-average molecular weight; Mw: weight-average molecular weight

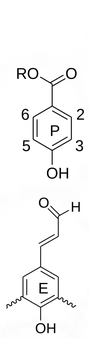
NMR analysis

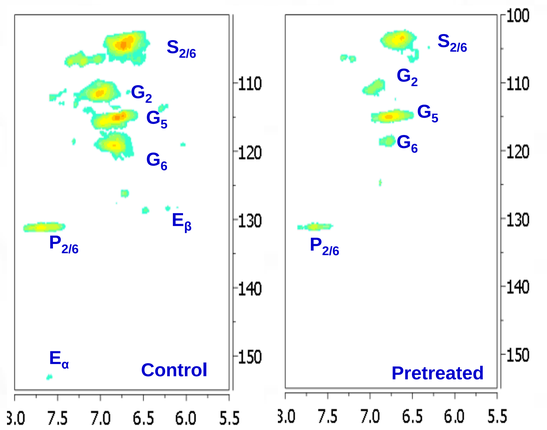


^{13}C quantitative NMR spectra of lignin

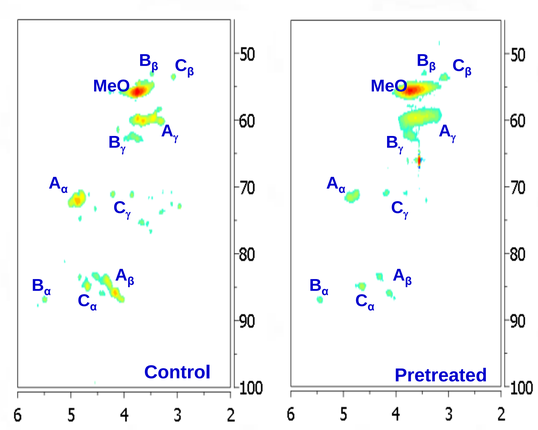








^{13}C-^{1}H HSQC correlation NMR spectra of lignin (aromatic region)



^{13}C-^{1}H HSQC correlation NMR spectra of lignin (aliphatic region)

Conclusion

- **Lignin structure significantly changed after dilute acid pretreatment;**
- **Lignin acetyl group removed; methoxyl group decrease; β-O-4 linkage decreased; S/G ratio decreased; Relative abundance of resinol linkage increase; lignin condensation observed;**
- **No significant change for lignin molecular weight;**

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