Characterizing Lignocellulosics from Pine to Bioethanol

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INTRODUCTION

The efficient processing of lignocellulosics into bioethanol is contingent on the characterization of the chemical constituents of plant carbohydrates and lignin and their changes in structure throughout the process. This program will evaluate the impact of process chemistry for three different biomass resources. The first year of this research program focused on a softwood biomass resource Loblolly Pine, while the second year is focused on the hardwood feedstock Sweetgum. Highlights of results from FY 2006-2007 are presented here along with comparison of the two different biomass feedstocks.

BIOMASS FEEDSTOCK

- Widely prevalent softwood species in Eastern US
- Used for lumber, furniture, pulpwood and plywood
- Mature tree from Baldwin Co., GA sectioned, debarked and chipped
- Chips stored at < -5 °C
- Composite sample used for all analyses

Distribution map of Loblolly Pine

PRETREATMENT STRATEGIES

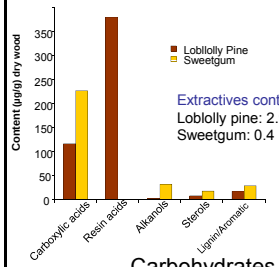
- Dilute sulfuric acid
  - Step 1: 0.5% H_2SO_4; 180 °C; 10 min
  - Step 2: 1% H_2SO_4; 200 °C; 2 min
- Aqueous Ammonia
  - 5.6 M NH_4OH; 50 °C; 48 h.
- Organosolv
  - 65% Ethanol, 1.1% H_2SO_4, 170 °C, 60 min

ENZYME HYDROLYSIS AND FERMENTATION

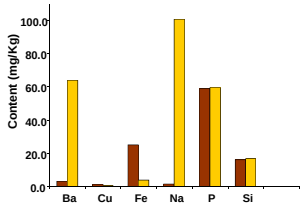
- Cellulase and Cellobiase enzymes
  - Celluclast 1.5L--20 FPU/g cellulose
  - Novozym 188--40 IU/g cellulose
  - 50 mM acetate buffer, pH 4.8; 45 °C; 96 h.
- Fermentation with *Saccharomyces cerevisiae*
  - pH 5.5; 30 °C; 48 h; 10 g/l yeast

LOBLOLLY PINE vs. SWEETGUM

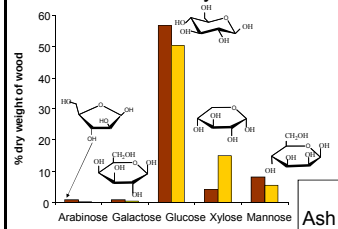
Extractives

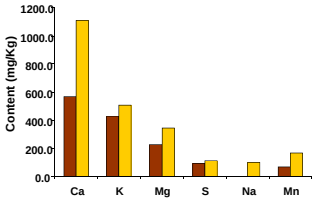


Inorganic elements



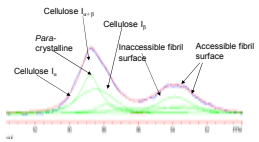
Carbohydrates





	Loblolly pine	Sweetgum
Ash	0.2%	0.8%
Klason lignin	29.3%	26.0%
Acid-soluble lignin	0.4%	2.4%

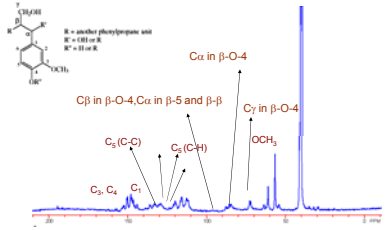
Cellulose: Solid-state CP/MAS ^{13}C NMR

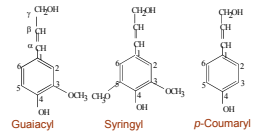


Spectral fitting results of the C4 region of cellulose NMR spectra

Comparison to Sweetgum
- Higher degree of crystallinity in Pine
  - 62.5 % vs. 53.3 %
- Smaller proportion of cellulose Iα
- More *para*-crystalline cellulose
- Greater proportion of cellulose Iα+β

Milled wood lignin: Quantitative ^{13}C NMR



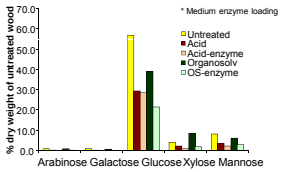


	Guaiacyl	Syringyl	p-Coumaryl
SW	x		x
HW	x	x	x

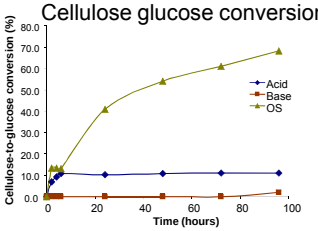
Comparison to Sweetgum
- Fewer β-O-4 and β-β structures
- More phenolic structures
- More β-5
- Greater no. of syringyl residues in sweetgum

RESULTS: Enzyme hydrolysis and fermentation of Pine

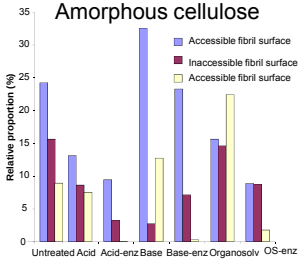
Carbohydrate Profile



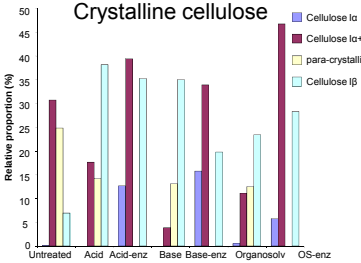
Cellulose glucose conversion



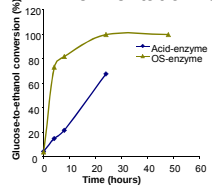
Amorphous cellulose



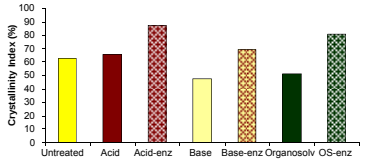
Crystalline cellulose



Fermentation results



Cellulose Crystallinity Index



CONCLUSIONS: Loblolly Pine

- Organo-solv pretreatment is most effective
  - Supported by SEM and chemical analysis
- Effects of pretreatments
  - Decrease in ash
    - Pretreatments effectively remove metals
  - Increased condensation of lignin
  - Lignin molecular weight decreases
  - Generate new 'extractives'
  - Change in cellulose ultrastructure
- Effects of enzyme hydrolysis
  - Increased cellulose crystallinity index
    - Preferential removal of amorphous cellulose
  - Data suggests need to develop enzyme capable of degrading more stable cellulose forms (eg. I_β)