Characterizing Sweetgum from Biomass to Bioethanol

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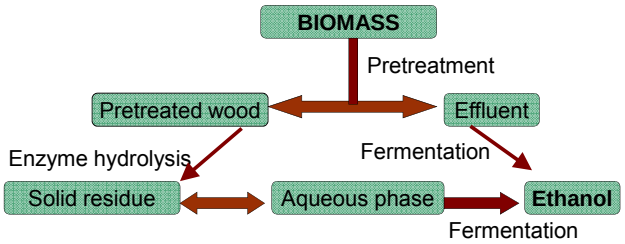
INTRODUCTION

The conversion of lignocellulosics into bioethanol remains a technically demanding process due to the complicated cell wall structure of lignocellulosics and their recalcitrant properties. The efficient processing of lignocellulosics into biofuels is contingent on the characterization of the chemical constituents of plant carbohydrates and lignin and their changes in structure throughout the process. This research program is directed at developing the fundamental knowledge needed to (1) describe the changes in biomass constituents during the overall conversion of plant polysaccharides into bioethanol and (2) optimize the overall process. New pretreatment strategies are also being developed.

RESEARCH OBJECTIVES

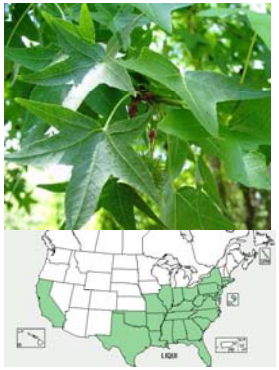
- Chemical characterization of the incoming feedstock
- Impact of pretreatment technologies on chemical structure and reactivity of biomass resources towards enzymatic hydrolysis
- Determination of reactive and unreactive components of pretreated biomass towards enzymatic hydrolysis
- Analysis of chemical constituents impacting fermentation of enzyme hydrolyzed biomass to bioethanol

PROCESS OVERVIEW



Research Quarter	FY 2007-08 Milestone Overview
1 **12/2007 to 02/2008**	Secure and characterize sample of hardwood feedstock for lignin, cellulose, hemicellulose, extractives and ash -- Determine cellulose crystallinity, hemicellulose sugars, lignin, extractives and trace elemental content in starting biomass resource -- Perform pretreatments on hardwood feedstock
2 **03/2008 to 05/2008**	Characterize chemical changes in hardwood feedstock after pretreatments -- Determine cellulose, hemicellulose, lignin, extractives and trace elemental content --Preliminary enzyme hydrolysis experiments on pretreated feedstock --Characterize dissolved biomass components in pretreatment effluent

BIOMASS FEEDSTOCK



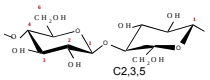
- Widely prevalent hardwood species in South-Eastern US
- Used for lumber, veneer, plywood and pulpwood
- Bark-free Sweetgum chips obtained from chipping mill in Dewey Rose, GA.
- Chips stored at < -5 ° C
- Composite sample being used for all analyses

Distribution map of Sweetgum

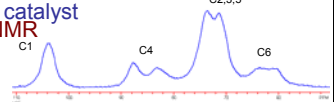
PRETREATMENT STRATEGIES

- Dilute acid (Sulfuric and Formic)
  - ➢204 ° C; 10 min; pH:2
- Ammonia Fiber Explosion
  - ➢Wood: Ammonia=1:1.3; 90 ° C, 10 min.
- Organosolv
  - ➢60% Ethanol, 1.2% H_2SO_4, 180 ° C, 60 min
- New** Oxidative + high temperature treatment
  - ➢Step 1:Oxidative treatment (75 ° C; 3 hours--oxidizes lignin, generates in-situ acidity)
  - ➢Oxone ($KHSO_5$); Chlorine dioxide
  - ➢Step 2:High temperature (204 ° C; 10 min)
  - ➢Potentially patentable pretreatment
- New **Organosolv with ClO_2 as catalyst

Reactor used for pretreatments



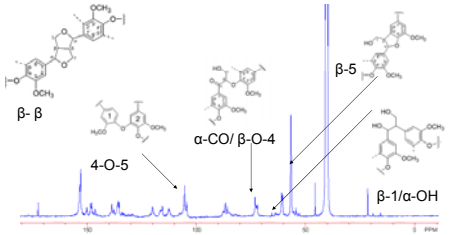
Cellulose: Solid-state CP/MAS ^{13}C NMR



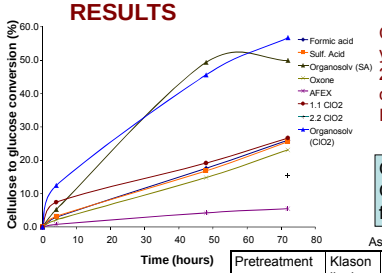
Degree of Crystallinity: 53.3%

Cellulose I_{alpha}	Cellulose $I_{alpha+beta}$	*Para*-crystalline	Cellulose I_{beta}	Accessible fibril surface	Inaccessible fibril surface
9.6 %	1.4%	33.7%	5.2%	22.3%	17.8%

Milled wood lignin: Quantitative ^{13}C NMR



RESULTS



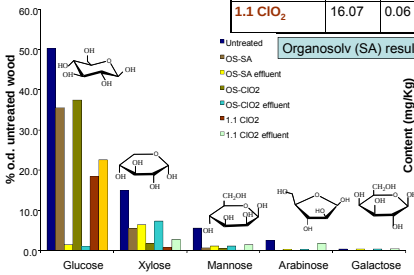
Cellulose to glucose conversion yields for low enzyme dose experiments. 20 U cellulase; 40 U beta-glucosidase /g cellulose in 50 mM, pH 4.8 acetate buffer. Incubated at 45 ° C and 150 rpm.

Organosolv (SA); 1.1ClO_2 and Organosolv (ClO_2) were selected for further investigation

As % o.d. weight of untreated sweetgum

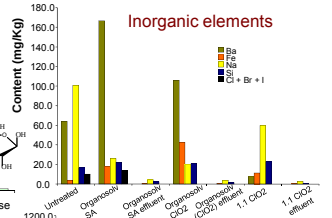
Pretreatment	Klason lignin	Acid soluble lignin	Organosolv lignin	Lignin in effluent	Total
Untreated	25.90	2.60	-	-	28.50
Organosolv (SA)	4.06	0.04	13.45	8.35	25.90
Organosolv (ClO_2)	6.27	0.19	12.53	5.85	24.84
1.1 ClO_2	16.07	0.06	-	9.28	25.41

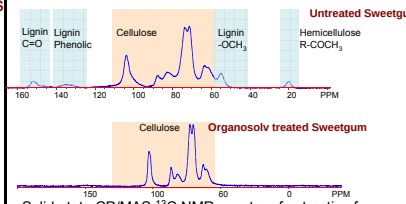
Carbohydrates

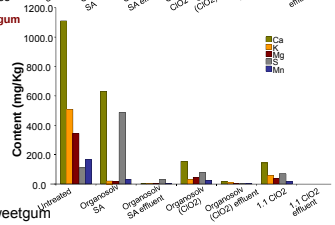


Organosolv (SA) results in highest lignin removal from wood – 84%

Inorganic elements







Solid-state CP/MAS ^{13}C NMR spectra of extractive free sweetgum

CONCLUSIONS

- On the basis of cellulose to glucose conversion, Organosolv (sulfuric acid), Organosolv (ClO_2) and 1.1 ClO_2 pretreatments were selected for detailed investigation
- Main effects of pretreatments
  - ➢Decrease in ash content
  - ➢Decrease in acid soluble and insoluble lignin
    - ➢ In the organosolv pretreatments, up to 50 % lignin recovered as Ethanol Organosolv Lignin which has potential commercial value
  - ➢Increase in proportion of glucose in carbohydrates
  - ➢Low furan (fermentation inhibitors) content in pretreatment liquids

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