FBRI Theme II

Extraction and Residual Solids Utilization

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Theme II Objectives

- To generate new knowledge needed for selective and controlled extraction of hemicellulose from forest biomass

- To understand the effect of extraction on wood properties and resultant wood products, in addition to downstream pulp, fuels, chemicals and biomaterials

Selective Extraction Processes

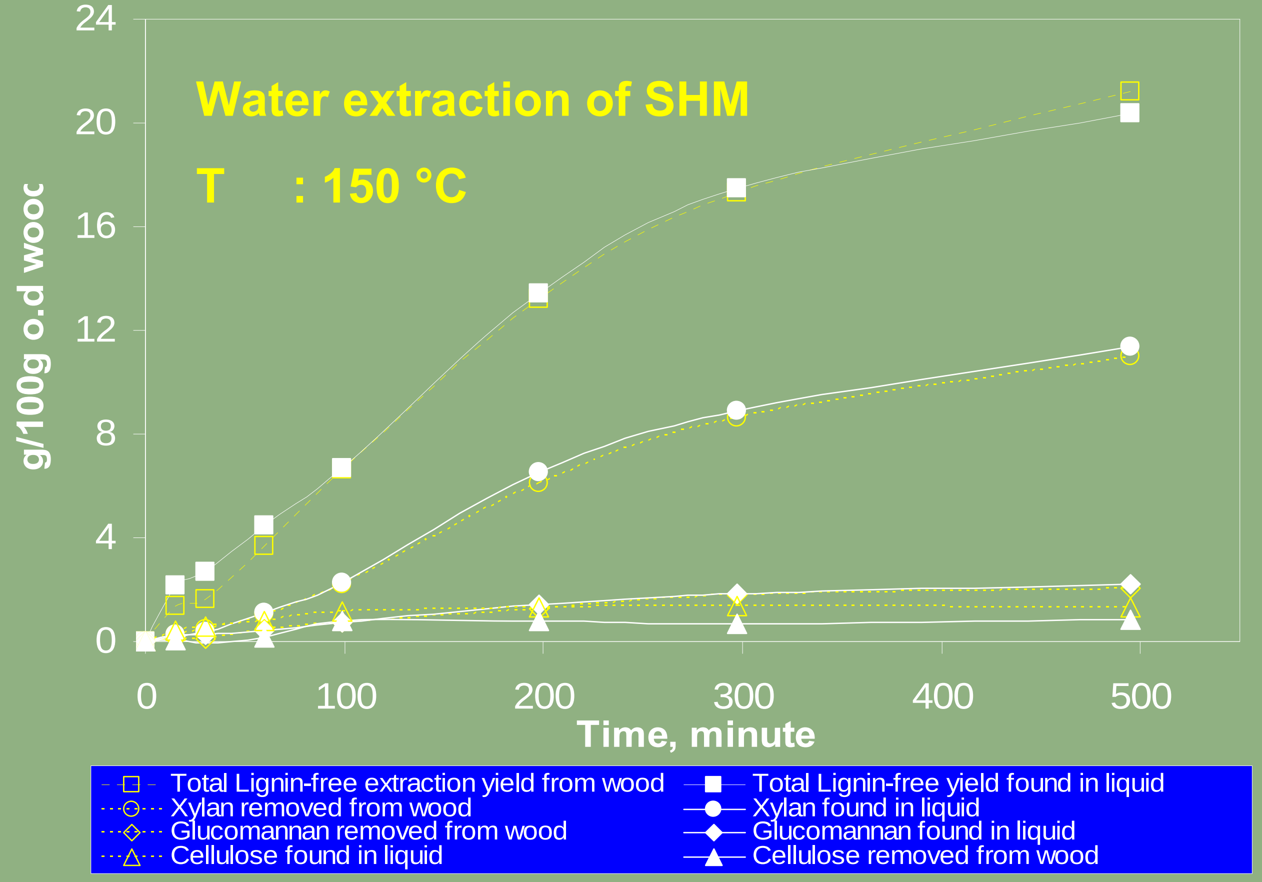
- Extraction of hemicelluloses from hardwood
- Prehydrolysis of phenyl glycosidic bonds in wood chips
- Adsorption of extracted and modified hemicelluloses on pulps

Hemicellulose Extraction of Mixed Southern Hardwood with Pure Water

Sefik Tunc, PhD candidate

Wood	**: Southern hardwood mixture (SHM)**
	(Extractives-free, 2mm)
Extractor	**: Modified Dionex ASE-100**
Time	**: 0 - 500 minutes**
Temp.	**: 150 °C**
Pressure	**: ~150 atm.**
Solvent	**: water**
L/W	**: ~4L/od kg**

Extraction Yields



- Lignin-free extraction yield increases with increasing time
- Cellulose stayed intact

Conclusions

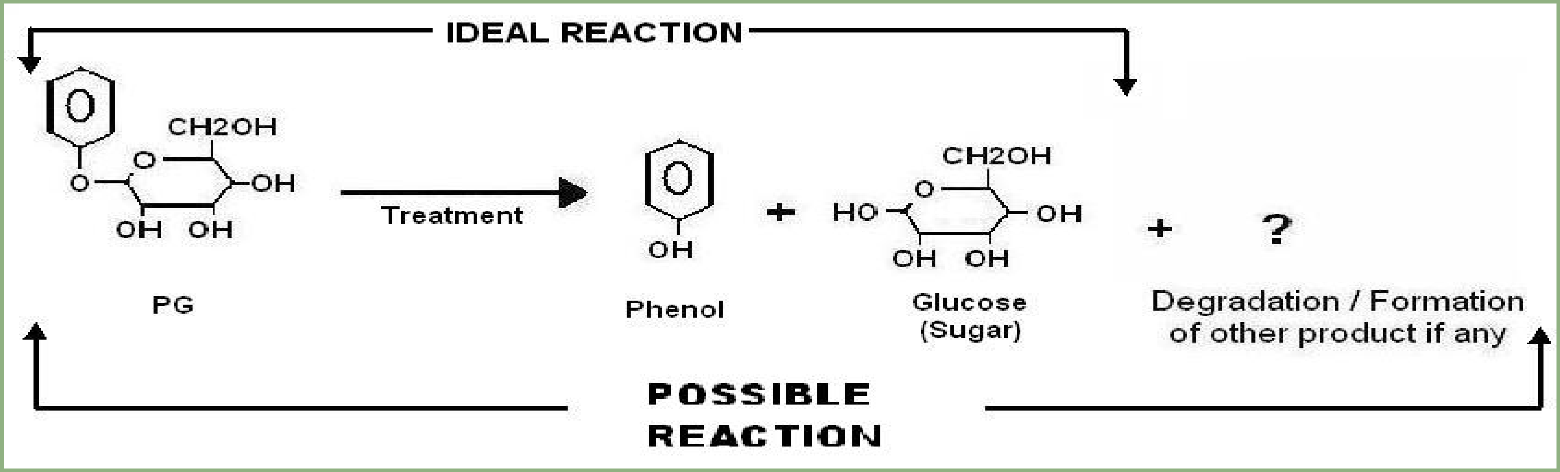
- Substantial hemicellulose dissolution, deacetylation and uronic anhydride removal with increasing time
- Cellulose stays intact during dissolution
- Xylan remaining in wood is highly acetylated and uronic acid content decreases with increasing time
- No significant amount of furfural is generated
- Xylan dissolves as oligosaccharides and then slowly depolymerizes to xylose at longer extraction times
- Dissolved oligosaccharides are initially highly acetylated; deacetylation takes place subsequently
- The acidity of the extract increases with time

Kinetics of Degradation of Lignin-Carbohydrate Model Compounds

Sagar Deshpande, MSc candidate

Aim : To study the effect of wood processing conditions on the cleavage of Lignin-Carbohydrate Bonds. (Special case Phenyl-glycoside)

Reaction :



Analysis Approach :

a) Disappearance of Phenyl glucoside (PG)
b) Formation of Phenol and Glucose

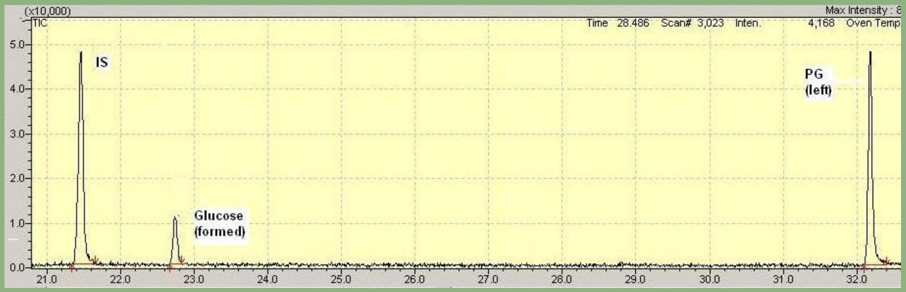
Methodology

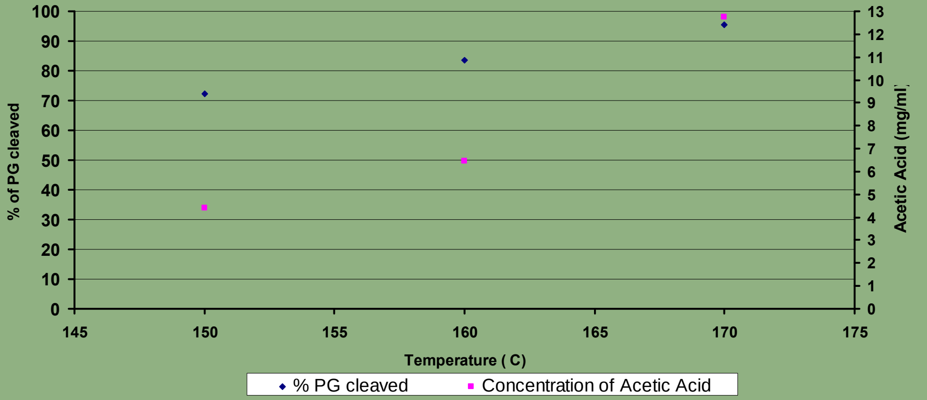
Case 1 : Analysis of PG left and Glucose formed by GC-MS.

Sample preparation:

Reduction → Acetylation → Analysis of Alditol Acetates.

Inositol used as Internal Standard (IS)



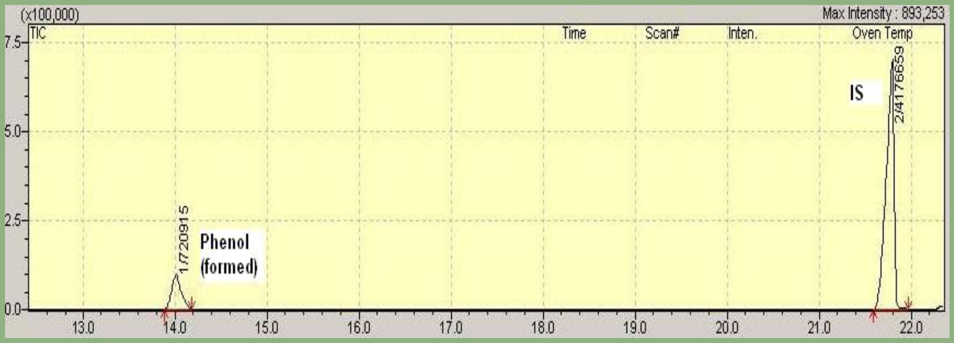


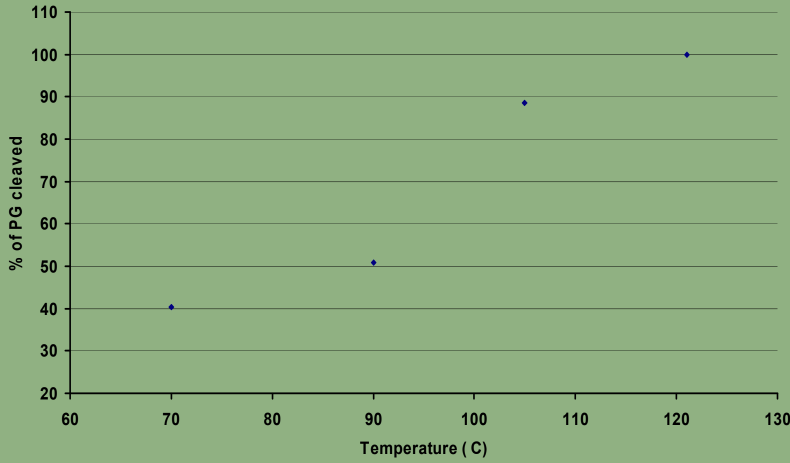
Chromatogram from GC-MS: Reaction conditions: 90C – 5 hours , Acidic nature (0.05M HCl)

Case 2 : Analysis of Phenol produced by GC-MS

Approach: Direct two phase extraction from water phase with Dichloromethane and analysis of the latter phase by GC-MS.

Guaiacol used as Internal Standard (IS)





Chromatogram from GC-MS: Reaction conditions: 90C – 5 hours , Acidic nature (0.05M HCl)

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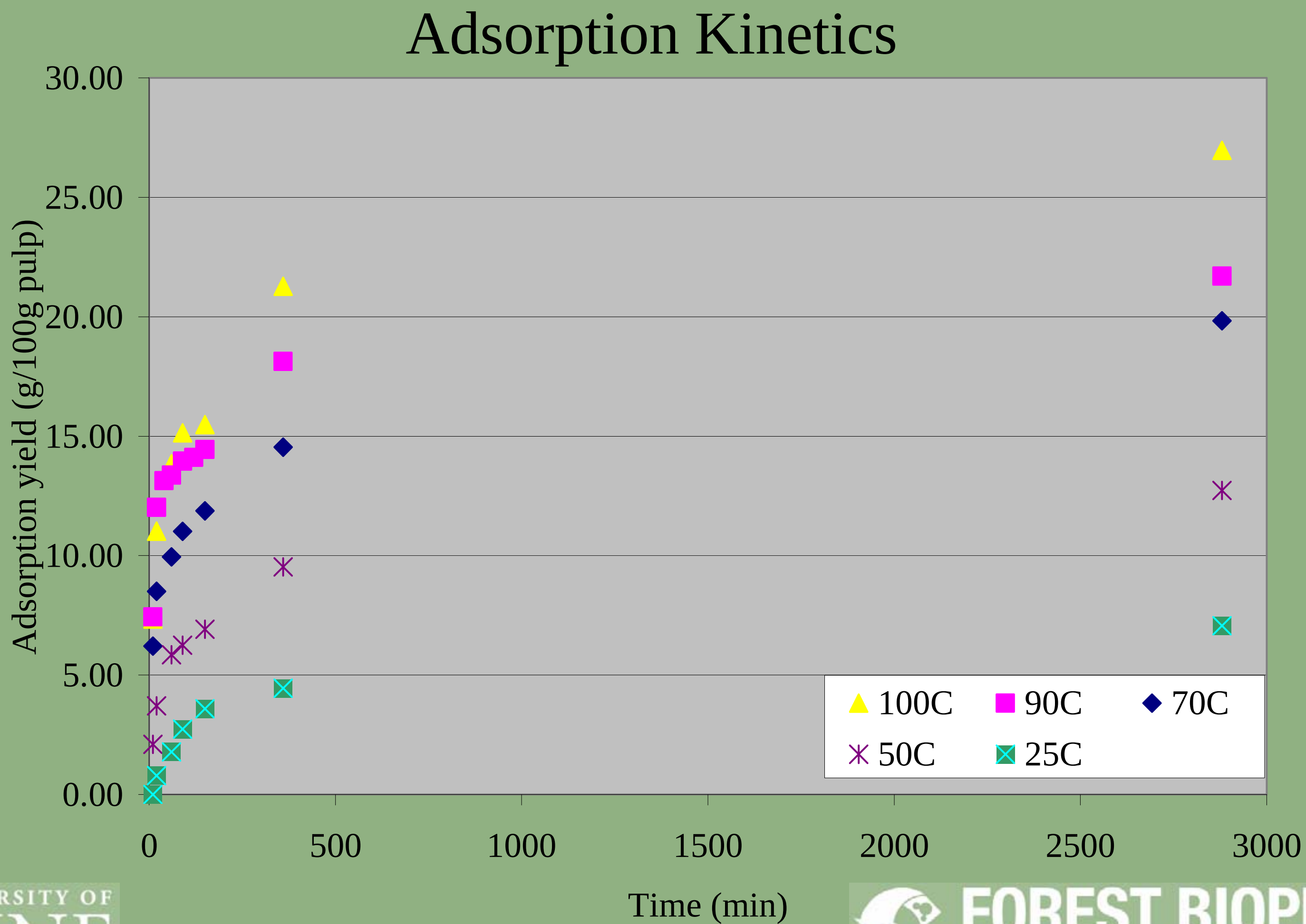
Adsorption of Extracted and Modified Hemicelluloses on Pulps

Xiaowen Chen, PhD candidate



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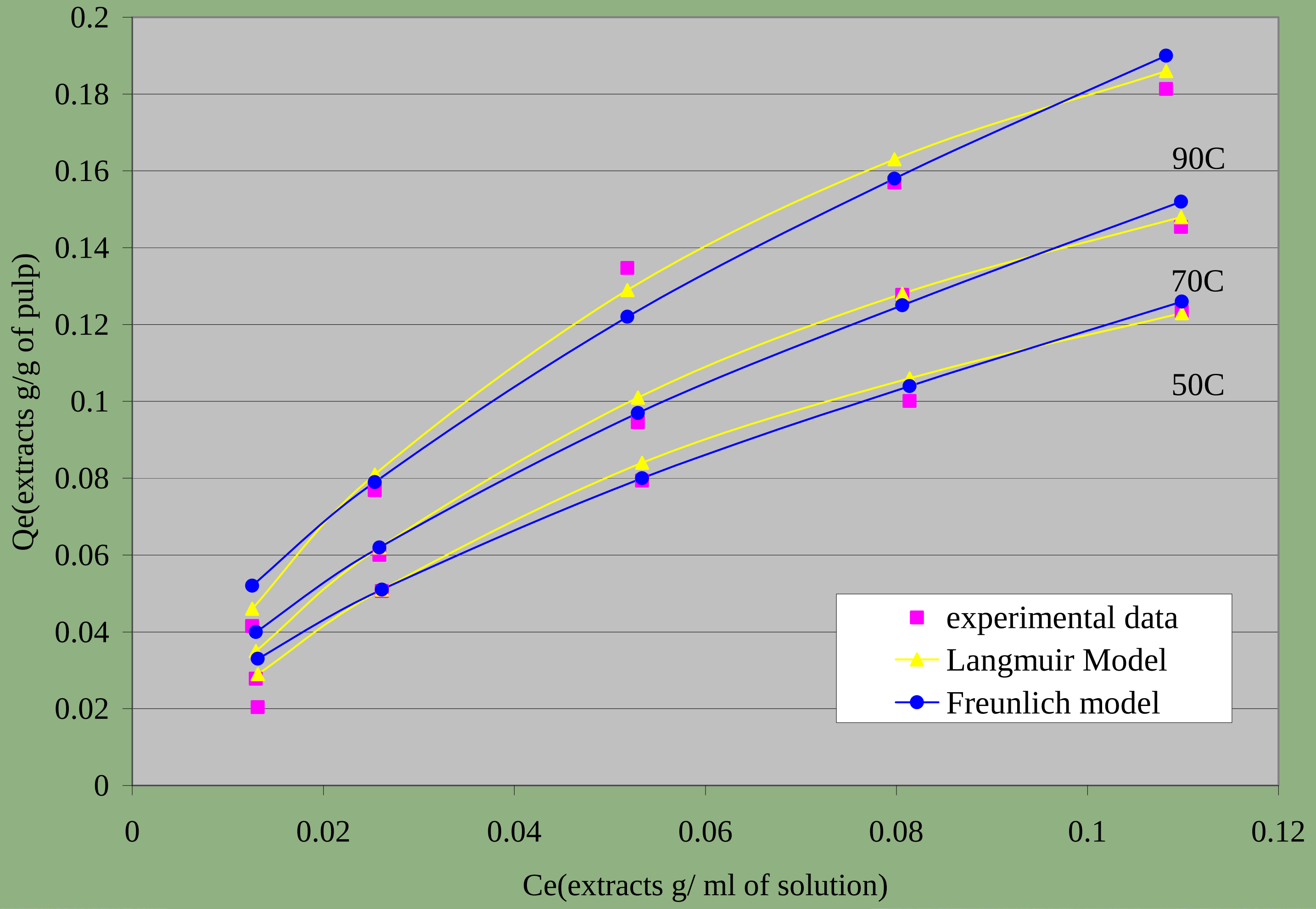
Adsorption Isotherm



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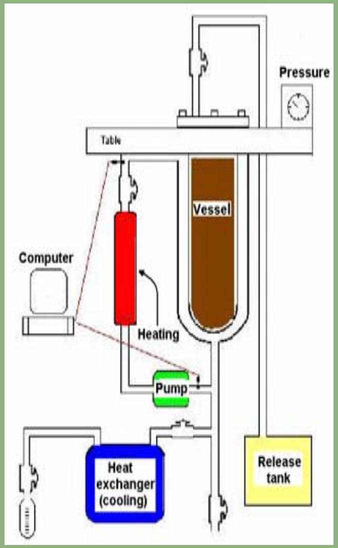
Influence of Hot Water Extraction on OSB Behavior

Juan Parades, PhD candidate



- Objective: Determine the influence of hot water extraction on physical, mechanical, and microstructure properties of wood strands and the subsequent behavior of OSB panels made from the modified wood
- Wood Species: Red Maple
- Extraction Conditions: 160 C (50 minute temperature ramp following by 45 or 90 minutes at temperature).

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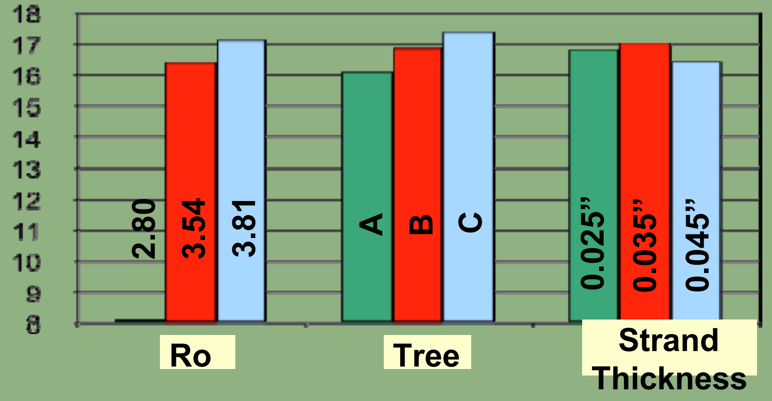
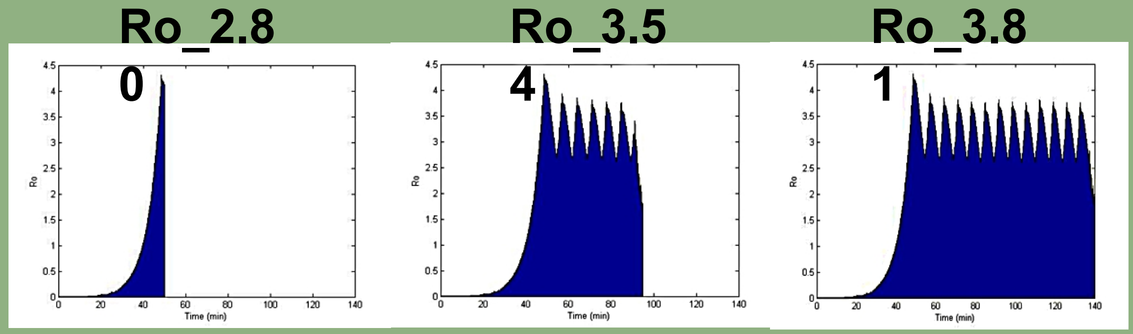
Results - Extraction Process

- The severity factor (extraction time, Ro) and Tree source significantly influenced weight loss
- Strand thickness had no significant impact on weight loss.

$$Ro = \int_0^t \exp\left[\frac{T_r - T_b}{14.75}\right] dt$$



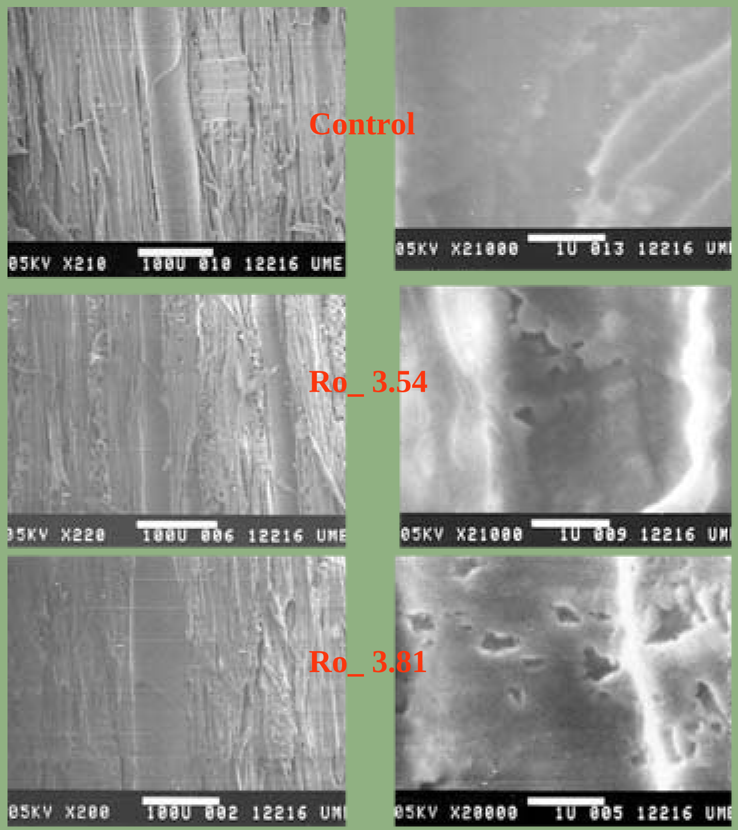


Results - Wood Modification

- Cellulose crystallinity and size exhibited a significant increase.
- The intra cell wall porosity was shown to be approx. 12% higher.
- Cell wall damage was shown to occur as evidenced by pitting.
- A significant increase in liquid penetration rate was exhibited.

Surface evaluation

Low magnification | **High magnification**



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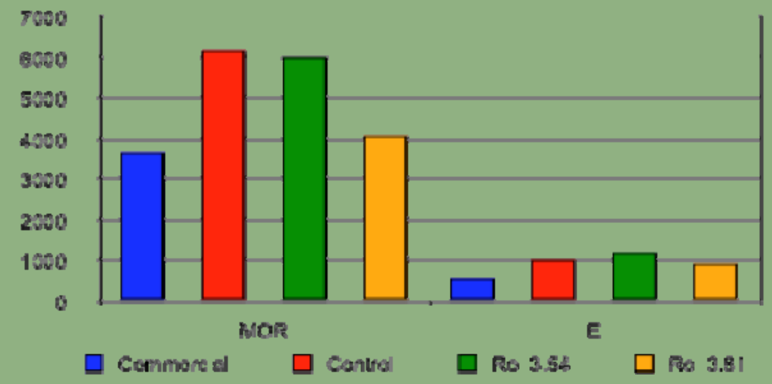
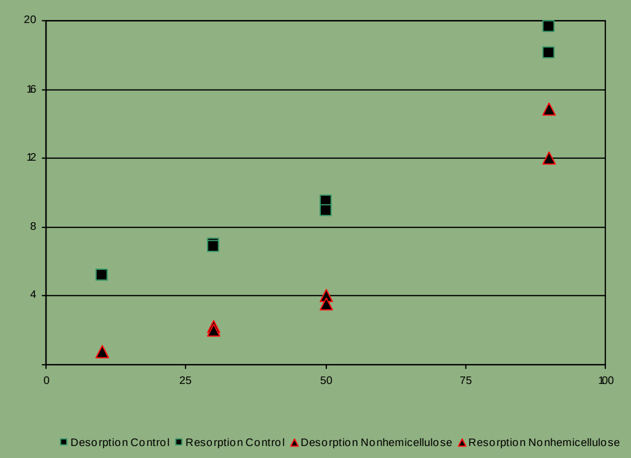
Results - OSB Panels

- The sorption curves of extracted wood strands were strongly lowered compared to control material.



- Dimensional stability in air of OSB panels were enhanced after hemicellulose removal.

- The flexural strength (MOR) was similar for control and Ro_3.54 but exhibited a significant decrease at Ro_3.81 (cell wall damage).



- The internal bond in dry and wet conditions from both extractions were significantly lower (overpenetration).

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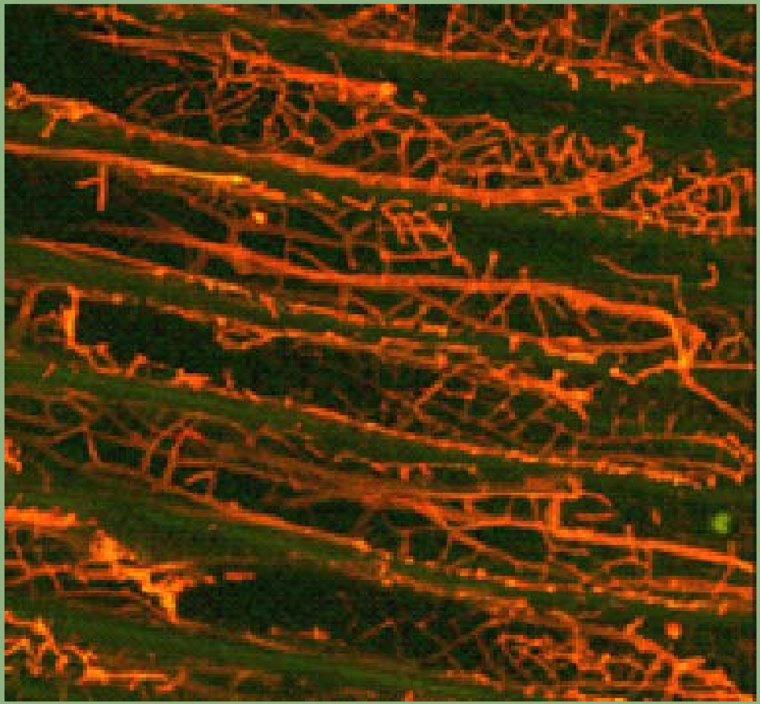
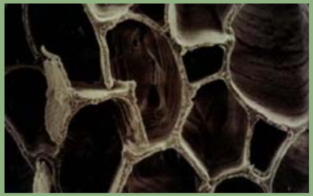
Biomodification of Wood

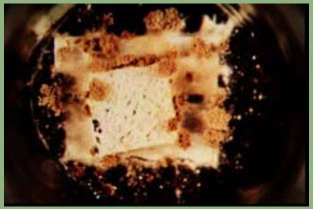
- Breakdown of wood cell wall
- Fungi involved are filamentous, capable of penetrating and colonizing wood cells
- Utilize cell wall constituents as a nutrient source



63x Microscopy - confocal
Trametes versicolor, in Pine wood



Brown Rot Wood Decay Fungi



- Cause an extensive, rapid reduction in cellulose DP 10000 to 250
- Capable of converting cellulose into simple sugars
- Primary group responsible for degradation of wood products and recycling of carbon and nutrients in northern ecosystems
- Bioremediation of pollutants: dichlorophenol, pentachlorophenol, heavy metals
- Potential utilization in bioprocessing of lignocellulose and production of ethanol and value added bio-based materials

Biological Degradation Overview

Caitlin Howel, MS candidate

- 1 faculty member, 2 research associates, 3 graduate students, 3 undergraduates
- Basic biodegradation and biomodification mechanisms
- Enzymatic and non-enzymatic processes involved in lignocellulose modification
- Use of X-ray diffraction, NIR, and MBMS to follow lignin and cellulose modifications

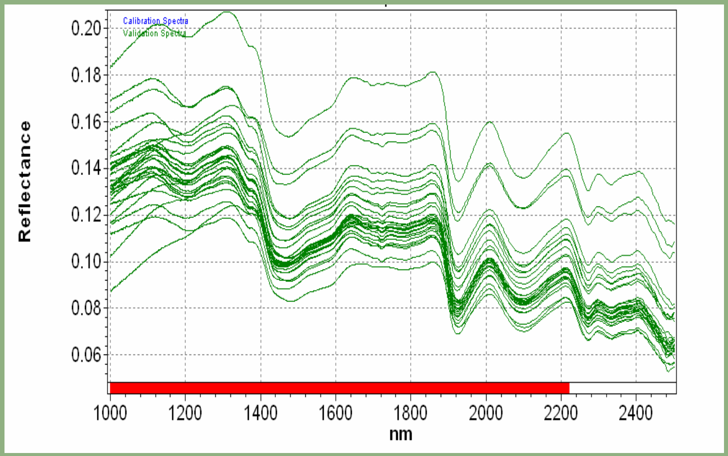
Identification of Forest Bio-Products through Near-Infrared Spectroscopy

- Use near-infrared spectroscopy (NIRS) to identify woody biomass components

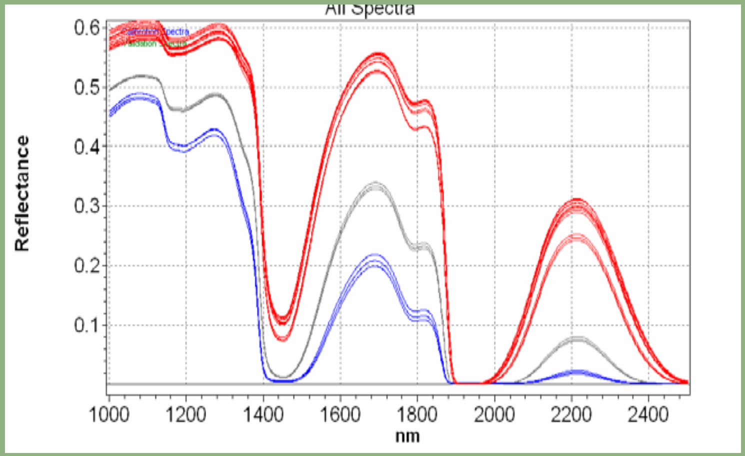
- Advantage to using NIRS:
  - No need for sample preparation
  - NIR does not interfere with sample composition

- Ultimately can be used in-process-line in the forest bio-products process

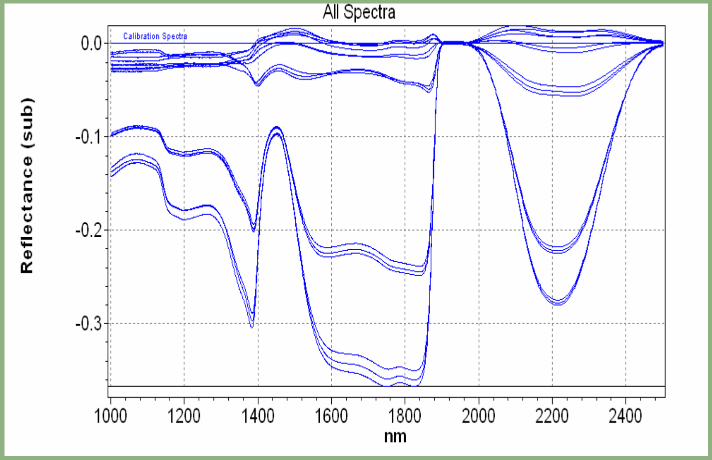
Original Wood Chip Spectra

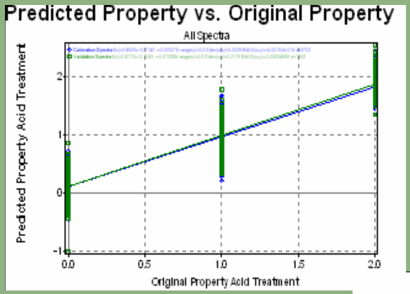


Original Spectra of Glucomannan Aqueous Solutions

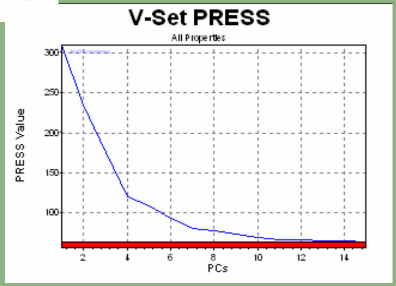


Glucomannan Spectra after Subtracting the Water





Results after a Calibration



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(near) Future Work

- Create a vast near-IR spectral database of woody biomass processing streams
  - Create liquid solutions for both hardwood and softwood extract components in the laboratory and acquire their spectra
  - Note any deviation of the NIR spectra due to change in viscosity, surface texture, etc in the database
- Perform a multivariate calibration of spectra with the partial least squares method (PLS)
- Test calibration (validate) by scanning liquid extracts that come directly from the forest bio-products extraction process (van Heiningen's lab)

Surface Modification of WPCs for Enhanced Adhesion

Gloria Oporto, PhD candidate

- For structural applications wood-polymer composites require lamination

- Given the inert nature of the polyolefin comprising ~50% of the WPC, gluing WPCs typically leads to low shear strength

- Surface modification of WPCs prior to adhesion may lead to improved shear strength

- To date have investigated chromic acid, sanded (P60, P220), flame, heat, water, water-flame and flame-water treatments.

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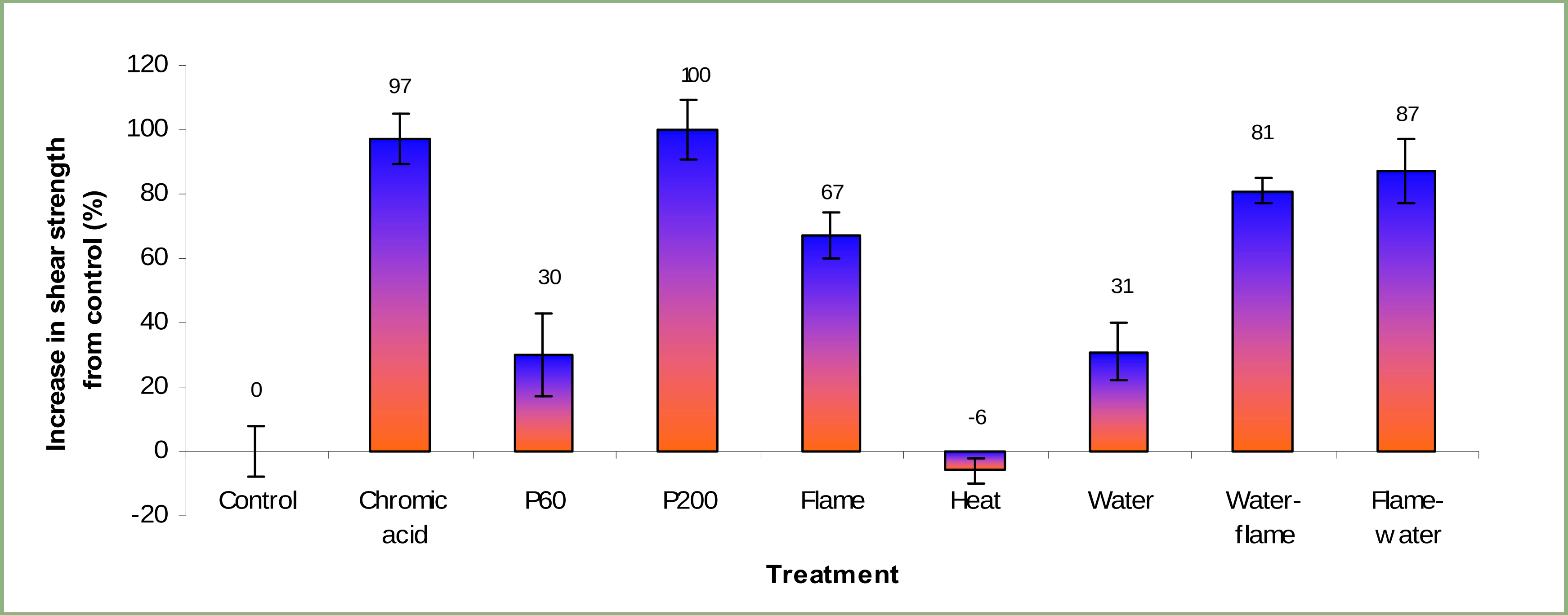
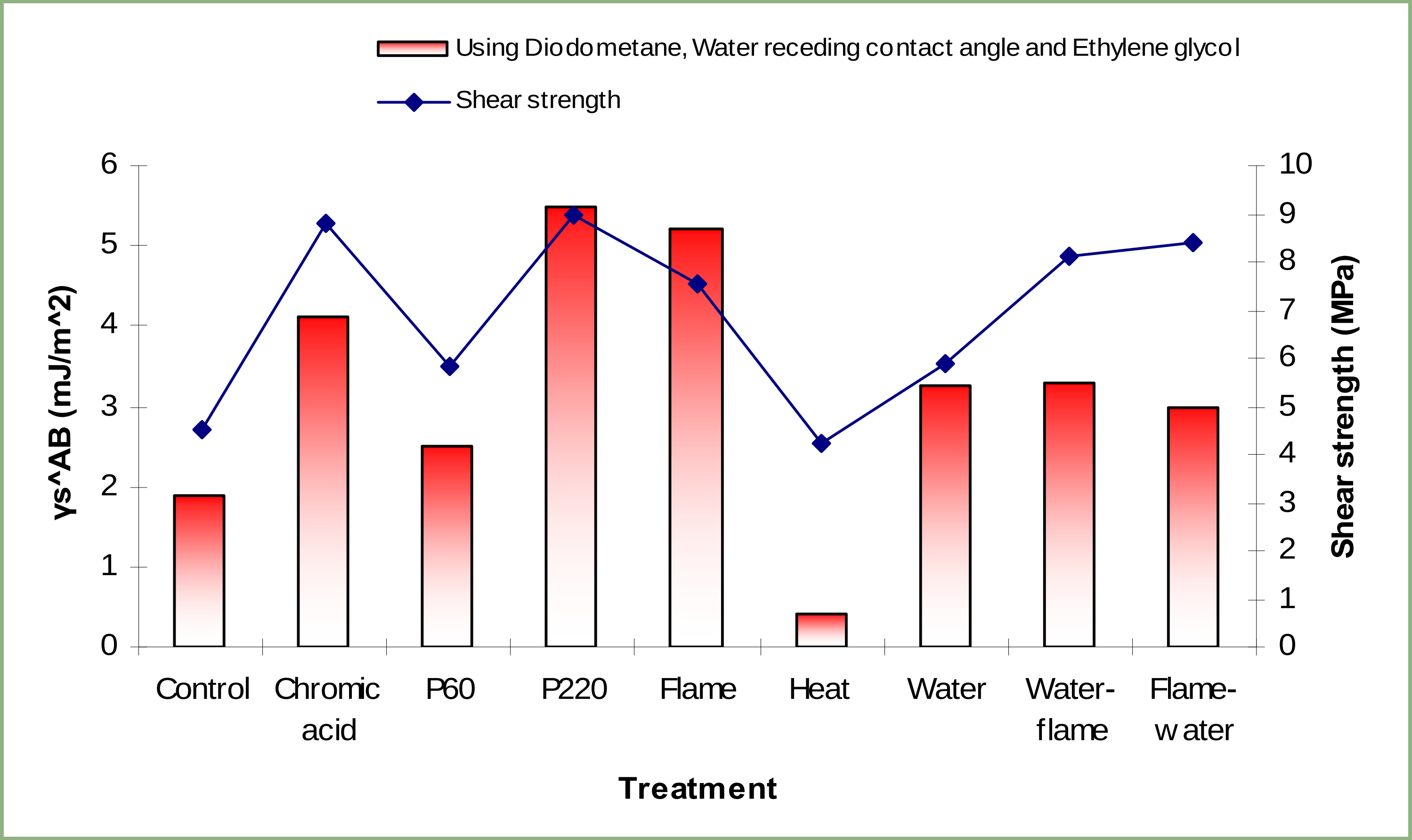
Treatment Effect on Shear Strength



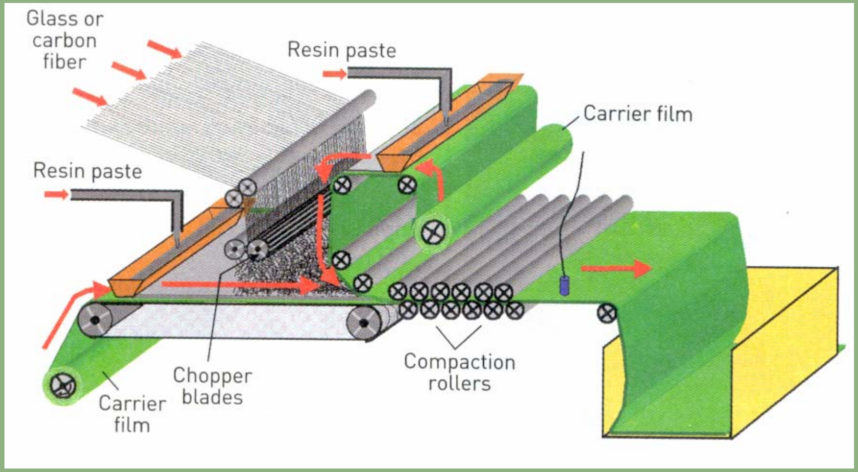
Correlation Between Surface Energy and Shear Stress



Fabrication and Testing of Biobased and Synthetic Sheet Molding Compound

Ryan Mills, PhD candidate

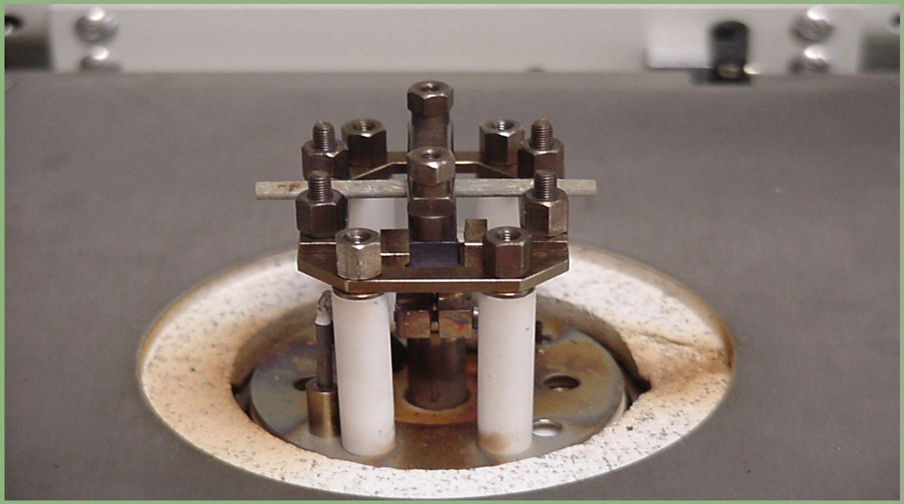
- Can biobased reinforcing fiber be employed in SMC with acceptable mechanical and durability properties?
- Need to understand the surface chemistry of the biobased fibers in order to compatibilize with the matix
- Inverse Gas Chromotography (IGC) is being employed to determine surface energy and polar nature
- Hygrothermal treatment of the resultant composite is used to simulate aging
- Dynamic mechanical thermal analysis of composite



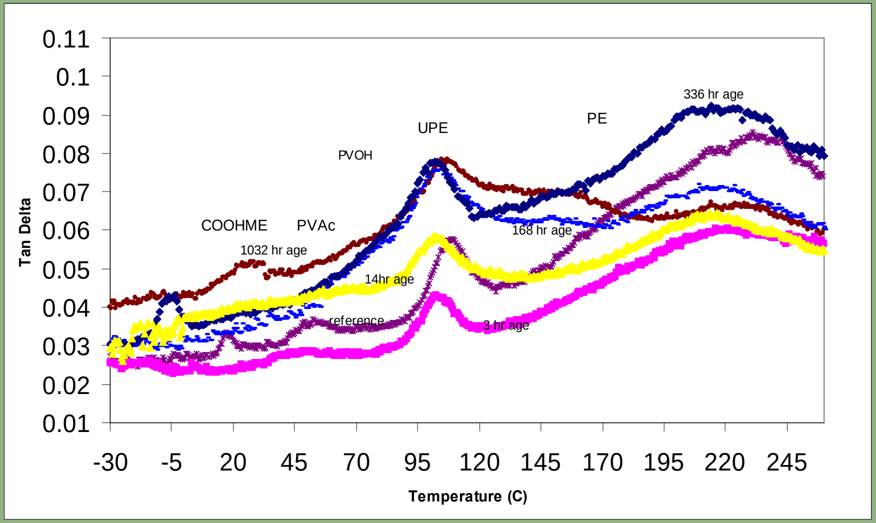
Compounding of SMC done at AOC resins

3 minute cure at 1000psi and 150 Celsius at the AEWC

3 Point bending testing from -50˚C to 250˚C



Glass transitions of various components in traditional SMC as a function of aging time



•Natural fibers are very hydrophilic; whereas, the polyester matrix is hydrophobic. Therefore need sizing agents

•Natural fibers typically have lower Young's modulus and other mechanical properties as compared to glass reinforcements; therefore, the interaction between the fibers and matrix must be maximized.

•The acid characteristics of the natural fibers are higher then that of the glass fibers indicating a better interaction between natural fibers and the matrix than with the glass fibers.

•In general, the cost of natural fibers is much less then glass.

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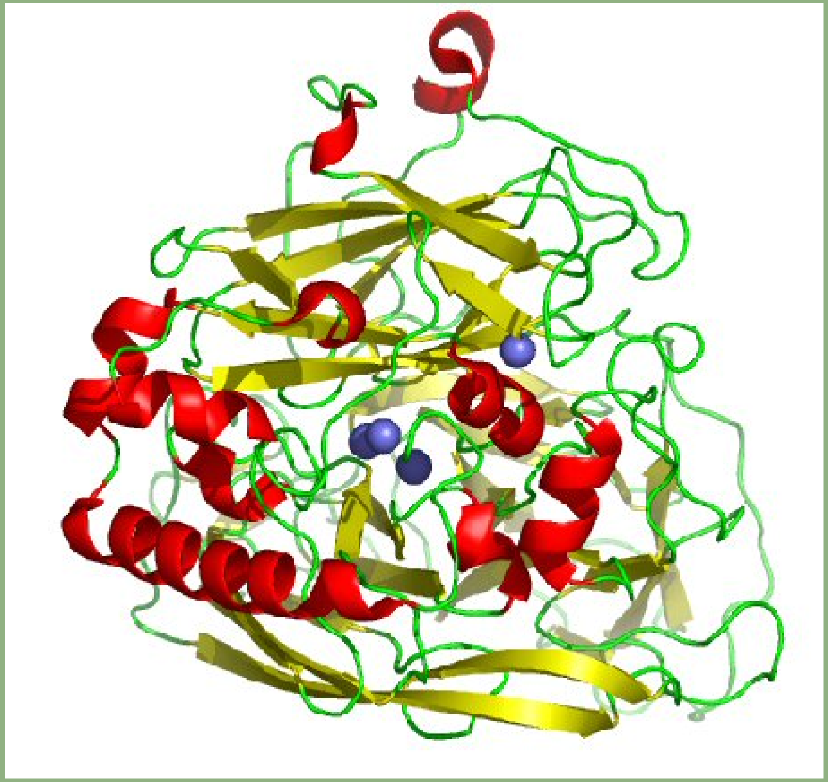
Chemistry of Hemicelluloses

LeRae Graham, PhD candidate
Dylan Montgomery, Undergradate

- Delignify hemicelluloses from both hardwood and softwood
- Hydrolyze delignified hemicelluloses to component sugars
- Develop chemistry for high-value chemicals from the sugars (*e.g.*, itaconic acid)
- Accomplish goals using green chemistry

Can Delignification Be Effected Enzymatically?



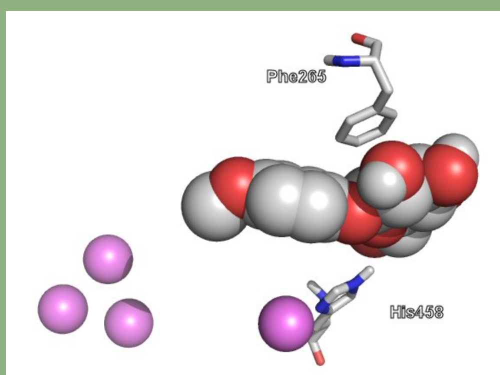
Laccase, from white rot fungi

- Three-Cu site reduces O_2 to H_2O
- One-Cu site oxidizes phenolics
- Capable of depolymerizing lignin

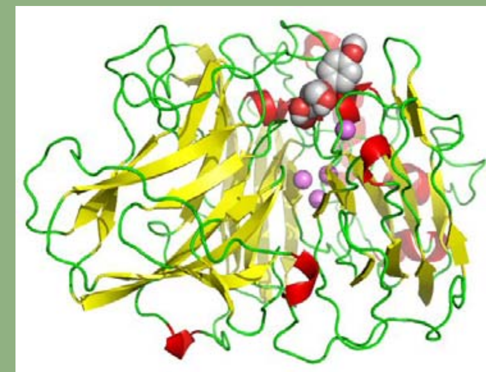
Computer Docking of Lignin-Carbohydrate Models

Docked Aromatic In

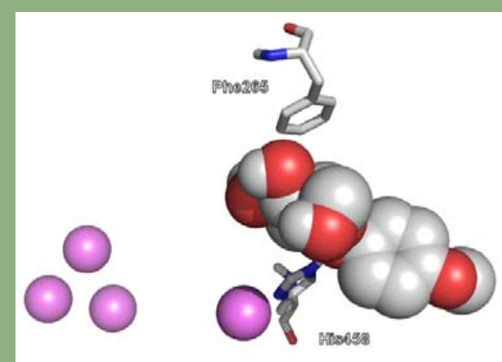
E_{bind} = -8.6 kcal/mol



Docked Sugar In



E_{bind} = -7.6 kcal/mol



Note: stacking of sugar with Phe265; H-bonding to His458

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- Commercially available birch xylan was used as our hemicellulose
- Xylan suspension sonicated 1 hr
- Xylanase from *Trichoderma viride*
- pH 4.5, 30º, 24 hr
- Analysis by HPLC-MS, chemical ionization
- Yield: 86% by weight

Given one unreactive branched residue in ten, this is close to theoretical yield

Preliminary attempts to delignify birch xylan:

• Lignin detected by UV absorption of aromatics at about 270 nm

• Reacted with H_2O_2, $h\nu$, pH 12, 1 hr

• 90% reduction in intensity of aromatic UV absorption

• No organic products from aromatics detectable by GC-MS; only product appears to be CO_2

• Some hydrolysis of hemicellulose occurs, liberating xylose

SFS of the Model Cellulose & Lignin Substrates

Lei Li, PhD candidate

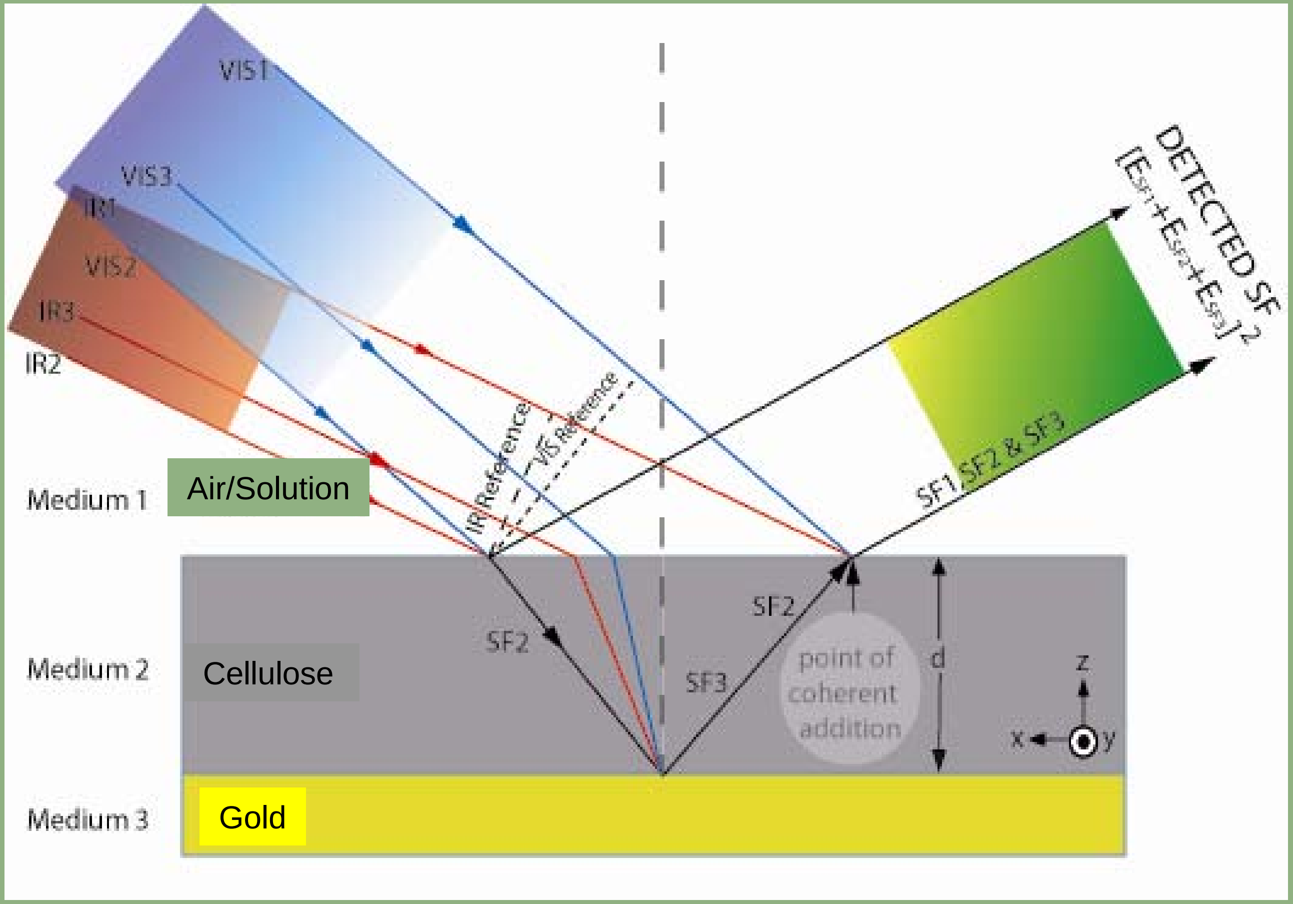
- Sum Frequency Spectroscopy, provides surface specific vibrational spectra

- Provides detailed orientation and conformational information of interfacial species

- In conjunction with traditional spectroscopies and microscopies, will enable detailed characterization of cellulose surface pre and post modification

- Must develop a cellulose substrate suitable for SFS and other techniques

Theory Developed of SF Generation from Model Cellulose Substrates



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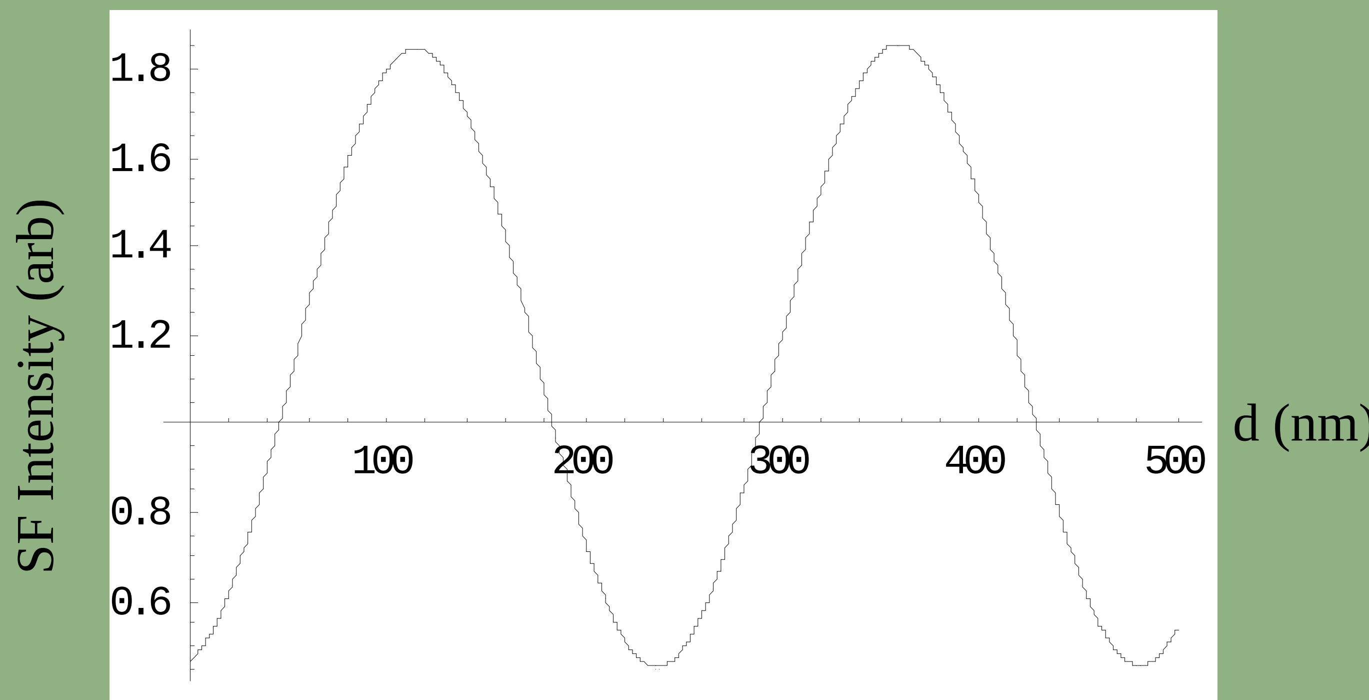
Model Complete, Currently Being Verified



Dominant Periodicity = 246 nm

Minor Periodicities = 276 nm, 2.252 μm

• Have created both cellulose and lignin films

• rms roughness on the order of nm’s

• film thickness in the correct region (~120 nm)

•Issue with stability of films in water currently being addressed