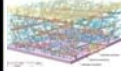




Bioenergy Program

Department of Forest Biomaterials



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Faculty in Bioenergy Science and Technology



Dimitris Argyropoulos
Professor
Wood Chem. & Biopolymer



Med Byrd
Associate Professor
Process Development



Hou-min Chang
Professor Emeritus
Wood Chemistry



Vincent Chiang
Professor
Forestry Biotechnology



Hasan Jameel
Professor
Process Engineering



Stephen Kelley
Dept Head & Professor
Polymer Chemistry



Adrianna Kirkman
Professor & Ass. Dean
Process Simulation



Lucian Lucia
Associate Professor
Wood Chem. & Biopolymer



Sunkyu Park
Assistant Professor
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Executive in Residence
Bioenergy Economics



Orlando Rojas
Associate Professor
Biomass Surface Chemistry



Daniel Saloni
Assistant Professor
Process Development



David Tilotta
Associate Professor
Process Chemistry



Richard Venditti
Associate Professor
Life Cycle Analysis

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Bioenergy Projects

- Bioethanol Pilot Plant
- Wood-to-Ethanol Research Consortium
- Value Prior to Pulping (VPP)
- Ethanol from Transgenic Hardwoods
- Ethanol from Coastal Bermuda Grass
- Enhancing Wood Penetration for More Efficient Hydrolysis and Optimized Saccharification
- Opportunities with Dissolved Wood for the Forest Biorefinery
- Validation of Thermochemical Syngas Cleanup
- Advanced Technology for Low Cost Ethanol from Engineered Cellulosic Biomass
- Economics and Feasibility of North Carolina Biomass Conversion
- Producing Ethanol from Biomass by Extracting Value Prior to Extraction
- Low Cost Conversion of Industrial Sludges to Ethanol
- Integrated Torrefaction-Gasification for the Production of Biofuels
- Economic Analysis of Pine Biomass Varieties for Ethanol Production
- Life Cycle Analysis for the Production of Transportation Fuels

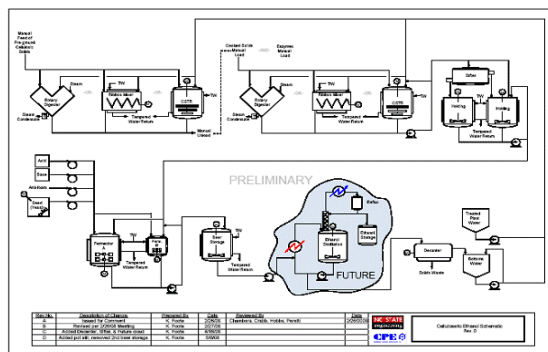
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Bioethanol Pilot Plant



- Golden Leaf Foundation and Company Consortium Funds, **\$2.94MM**
- College of Natural Resources, College of Agriculture and Life Sciences and North Carolina Solar Center
- Conversion of three different feedstocks
 - Industrial sweet potatoes
 - Switchgrass
 - Loblolly pine trees
- Unit Operations
 - Pretreatment
 - Separations
 - Enzymatic Hydrolysis
 - Fermentation
- Capacity - 10 kg/hr

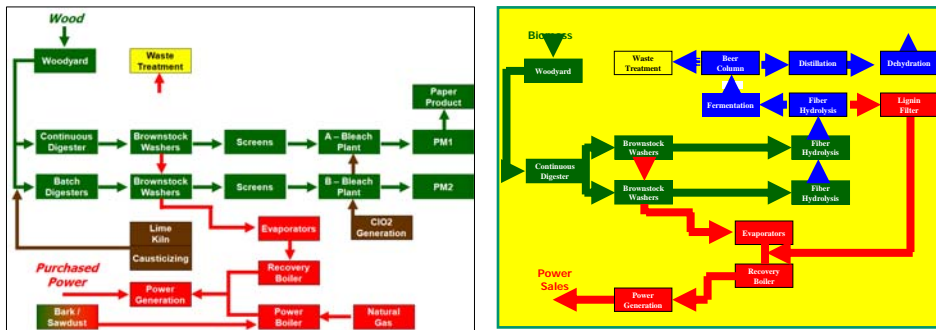


Wood to Ethanol Research Consortium (1)

- Industry consortium of six companies
- Repurposing a kraft pulp mill into an ethanol mill
- Develop cost effective process by reusing existing assets

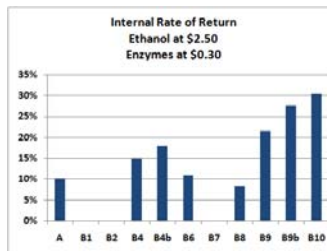


Wood to Ethanol Research Consortium (2)



Kraft Mill

Repurposed Kraft Mill To Produce Ethanol



Ethanol from Transgenic Hardwoods

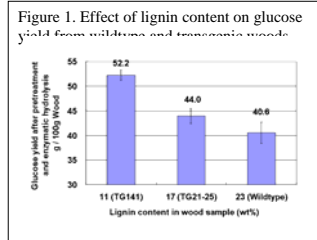


- Sungrant (DOT)
- Evaluate potential for simplifying pretreatments for low/modified lignin hardwoods
 - Autohydrolysis
 - Ozone
 - Mild alkaline

Samples	Lignin	S/G	Glucan
Wildtype	23	2.2	44
TG96	24	6.4	45
TG141	11	2.6	54



Populus

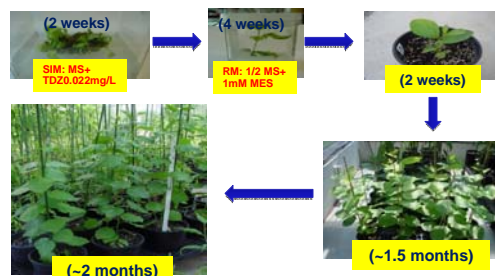
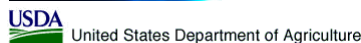


Advanced Technology for Low Cost Ethanol from Engineered Cellulosic Biomass

- USDA - DOE
- Demonstrate transgenic tree plantations with fast growing low lignin/high cellulose transgenic trees
- Demonstrate on a pilot scale the improved processability and economics, including simplified pretreatment strategies
- Economic evaluation of the different biomass and process options, using standard investment analysis techniques, including all applicable subsidies

Targets

Delivered wood cost <\$50/ODT
 Wood composition >80% carbohydrates
 (Typical SW:HW: 69:75%)
 Capital cost <\$3.00/annual gallon
 Manufacturing cost <\$1.70/gal



Economics and Feasibility of North Carolina Biomass Conversion

- Identify the most suitable and profitable scheme to produce ethanol in North Carolina with a complete analysis of the Supply Chain

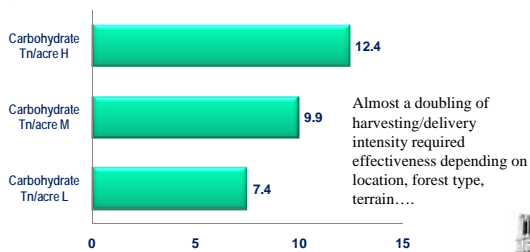


Forest biomass

1. Hardwoods: Eucalyptus, poplar, mixed hardwood
2. Pine
3. Forest residues

Agriculture biomass

1. Switch grass
2. Miscanthus
3. Coastal bermuda grass
4. Corn stover
5. Sugar beet
6. Arundo donax
7. Sweet sorghum

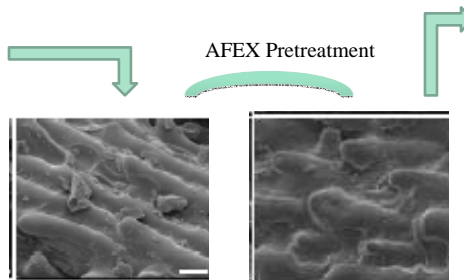


Ethanol from Coastal Bermuda Grass

- Develop simplified pretreatments for the conversion of coastal Bermuda grass to ethanol
 - Autohydrolysis (hot water, 60 m, 70% sugar yield)
 - Sodium Carbonate
 - Ozone
 - Ammonia Explosion (high capital cost, 95% sugar yield)
 - Microwave/NaOH
 - Lime



Coastal Bermuda Grass Bales

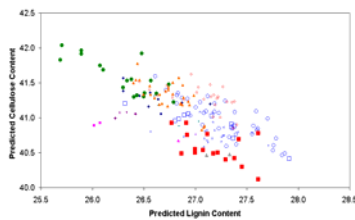


Bio-ethanol



Economic Analysis of Pine Biomass Varieties as Feedstock for the Production of Ethanol

- Characterize 178 pine varieties to identify those with varying lignin and cellulose content
- Select 20 varieties with different wood properties, and perform chemical and physical characterization of the wood properties
- Measure fermentable sugar yield using three pretreatments (dilute-acid, weak alkaline, organosolv)
- Compare feedstock value of different pine and poplar and recommend ideal loblolly pine feedstock

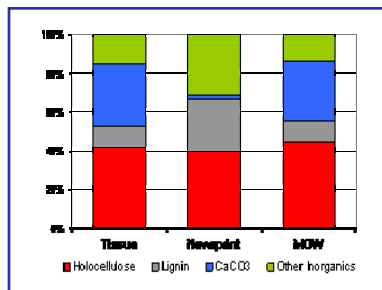


Low Cost Conversion of Industrial Sludges to Ethanol

- Biofuels Center of North Carolina
- Demonstrate an effective technology to convert industrial papermaking sludge as a cost effective feedstock for the efficient biochemical biomass conversion to ethanol



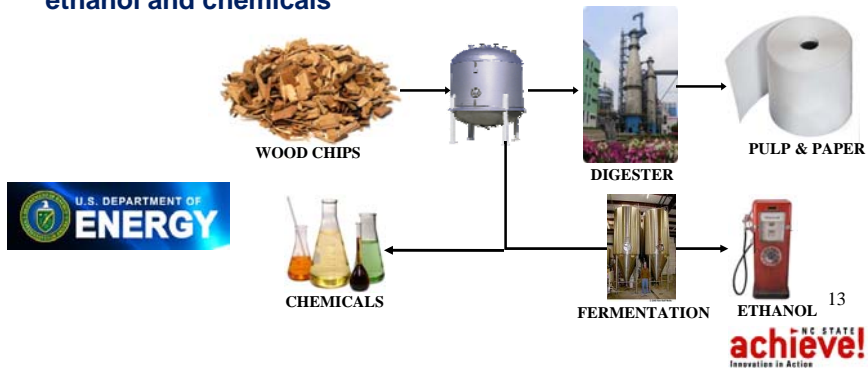
Papermaking Sludges



Negative feedstock cost
Contains CaCO₃ and inorganics

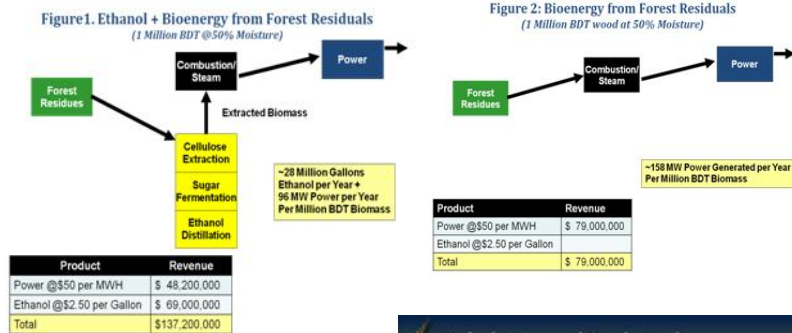
Value Prior to Pulping

- DOE and Consortium of Companies and various research organizations and universities
- Extract hemicelluloses prior to pulping and convert to ethanol and chemicals

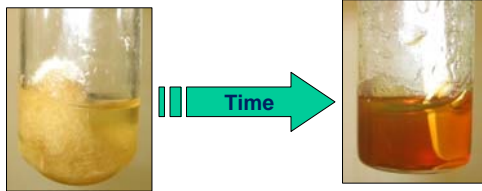


Producing Ethanol from Biomass by Extracting Value Prior to Combustion

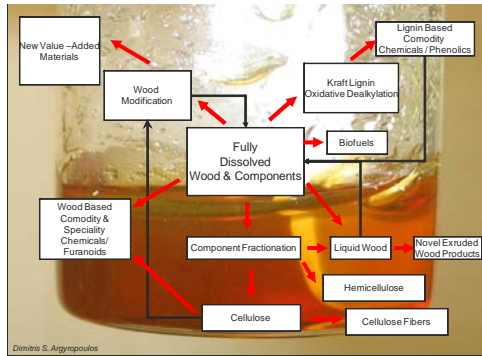
- Develop a process for hot water treatment of wood to extract the hemicelluloses.
- Following extraction, the wood residue is sent to a boiler and burned as conventionally practiced



Opportunities with Dissolved Wood for the Forest Biorefinery

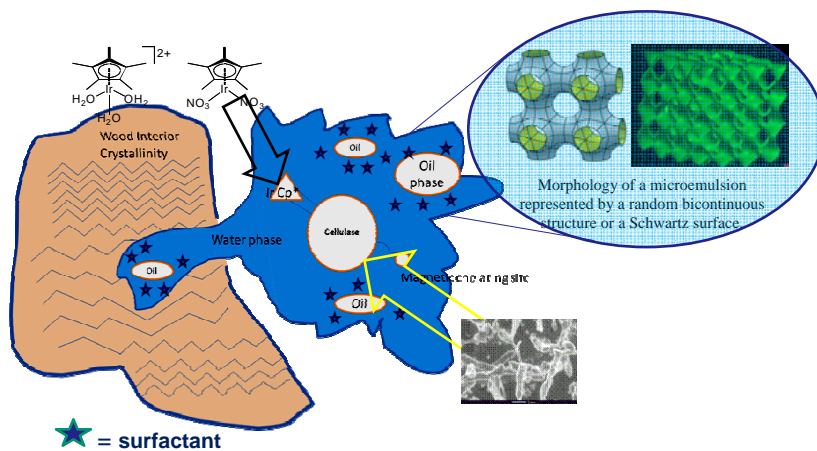


Certain Ionic Liquids Can Completely Dissolve Wood



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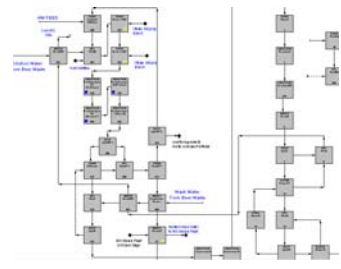
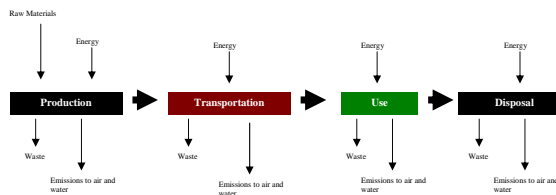
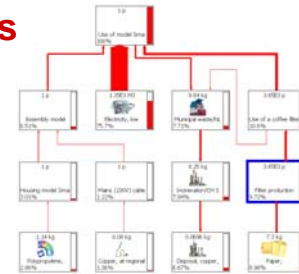
Enhancing Wood Penetration for More Efficient Hydrolysis and Optimized Saccharification



The metal (IrCp*)-cellulose complex is later recovered and the SOW (Surfactant Oil-Water) micro-emulsion may also be recycled

Life Cycle Analysis for the Production of Transportation Fuels

- Perform detailed material and energy balances on a set of biofuel manufacturing processes and feedstocks
- Develop equipment and facility engineering plans for the processes/feedstocks
- Perform a life cycle analysis on the processes/feedstocks and report the relative impacts of the different processes/feedstocks



CORRIM Consortium for Research on Renewable Industrial Material

Validation of Therminator Syngas Cleanup

- US Department of Energy
- Validate syngas cleanup technology (“Therminator”, RTI International) and syngas conversion unit operation
- Integrate into the gasification process at the University of Utah
- A fixed bed or slurry bubble column reactor will be integrated downstream of the “Therminator” to produce FT waxes from RTI’s proprietary iron-based catalyst



Integrated Torrefaction-Gasification for the Production of Biofuels

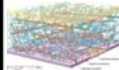
- Turn woodchips into a substitute for coal by using a process called torrefaction that is greener, cleaner and more efficient than traditional coal burning.
- Quantify relationship between time and temperature to produce torrefied wood
- Use of torrefied wood for gasification
- Scale up process to pilot plant evaluation
- Economic and life cycle analysis of combine process



Biomaterials Research 09092009.pptx



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Biomaterials Projects

- Use of Transgenics for Enhanced Saccharification
- Wood Pulp Chemical Composition Effects on the Development of Microfibrillated Cellulose
- Starch Microcellular Foams
- Opportunities with Dissolved Wood for the Forest Biorefinery
- Use of QCM to Determine Apparent Activation Energy and Hydrolysis Rates of Biomass
- GL pretreatment pulping



Use of Transgenics for Enhanced Saccharification

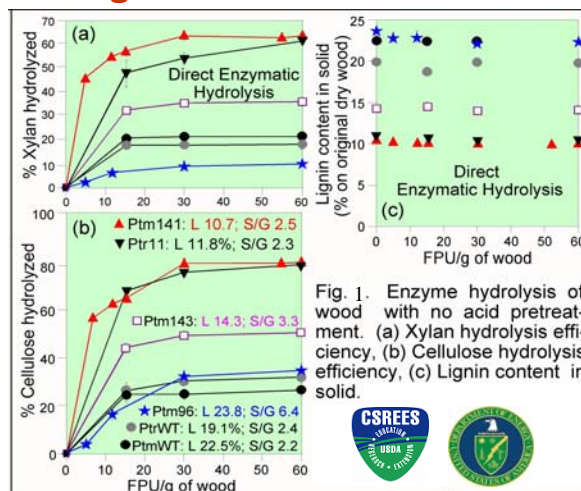


Fig. 1. Enzyme hydrolysis of wood with no acid pretreatment. (a) Xylan hydrolysis efficiency, (b) Cellulose hydrolysis efficiency, (c) Lignin content in solid.



Vincent Chiang

Wood with genetically reduced lignin does not require chemical pretreatment for releasing fermentable sugars by enzymes. In lignin reduced *Populus* wood, up to 80% of the cellulose could be converted to glucose with no chemical pretreatment, while for normal wood only 20% of cellulose was converted. The work is supported from a USDA AFRI and a DOE Feedstock Genome grants to Vincent Chiang of the Forest Biotech Group, NCSU.



Wood pulp chemical composition effects on the development of microfibrillated cellulose

PIs: R. Venditti, J. Pawlak, O. Rojas
Graduate Student: Kelley Spence

- Microfibrillated cellulose
 - Produced from mechanical treatments
 - Homogenization
 - Microfluidizers
 - Cryo-crushing
 - Grinding
 - Chemical pretreatments for energy reduction
 - Gel-like properties at 2%K
 - Have diameters ranging from 25-100 nm
 - Expanded surface area for better chemical access
 - Most studies focused on pure cellulose
 - Used in food, cosmetics, paints, composites, packaging...



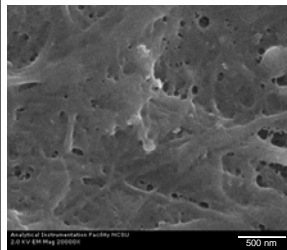
“Turning Science into Reality” Presentation by STFI-PACKFORSK

Microfibrillated Cellulose: A New Cellulose Product: Properties, uses and commercial potential
Turbak, A., Snyder, F., Sandberg, K.
Journal of Applied Polymer Science: Applied Polymer Symposium 37, 815-827 (1983)

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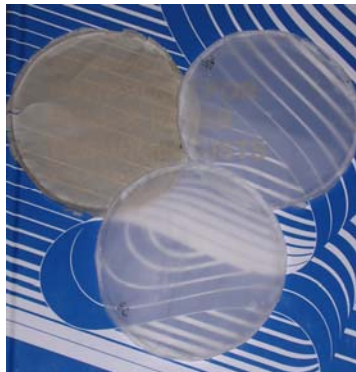
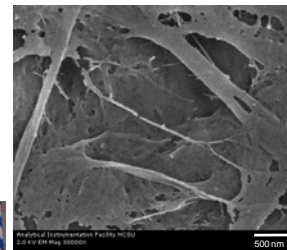


Film Appearance: Hardwoods



UBHW

BHW

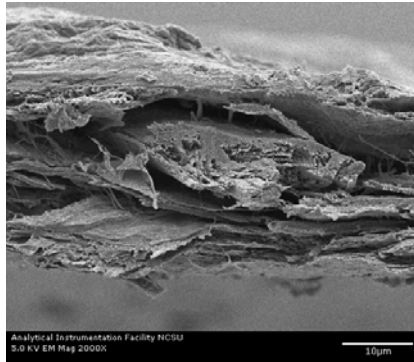


Hornified BHW

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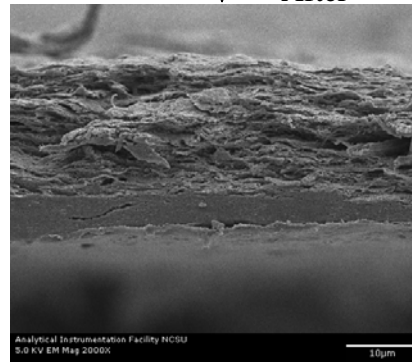


Film Density



Before

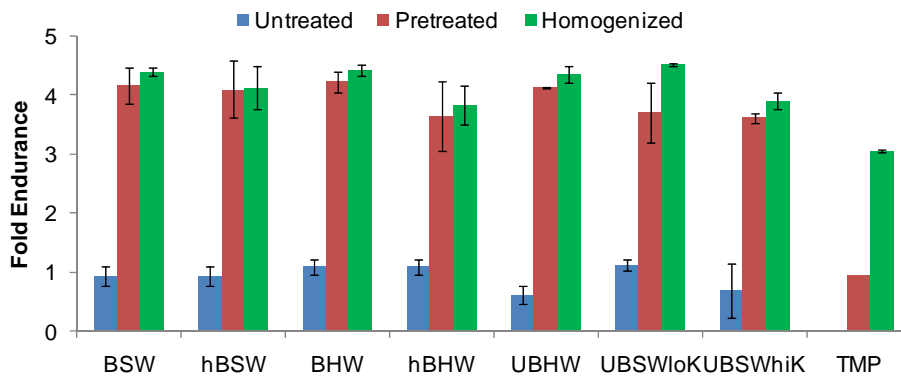
Homogenization



After

UBSWloK

Mechanical Properties: Fold Endurance

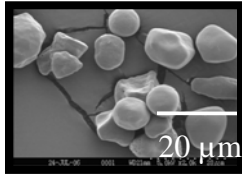


The microfibrillated cellulose (green) has dramatically improved folding endurance relative to fibers (blue) and refined fibers (Red). Note fold endurance on log scale.

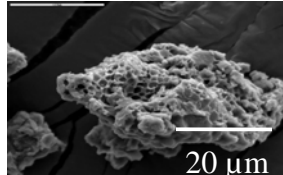
Starch Microcellular Foam (SMCF)

R. Venditti & J. Pawlak

- Starch based porous matrix with cell diameters 0.1 to 10 micron and high specific surface areas $>50 \text{ m}^2/\text{g}$.



Starch granules



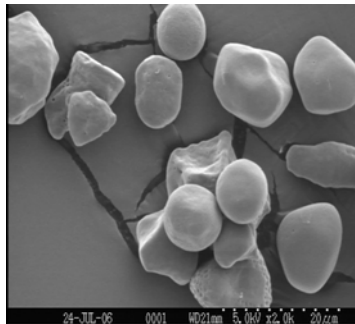
SMCF

El-Tahawy, Venditti, Pawlak
Carbohydrate Polymers, 2007.

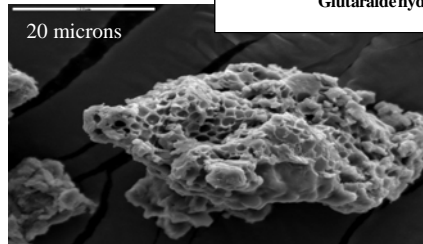
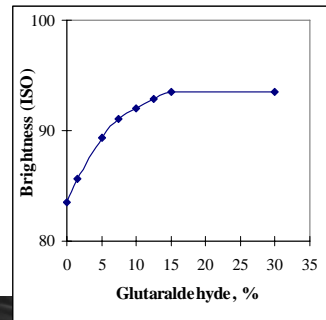
- Density of foams reduced by 5-95% of the matrix starch material
- Pore volume ranging from $0.17\text{-}0.63 \text{ cm}^3/\text{g}$.
- Cell density $>10^9$ cells per cm^3 .



SMCF Pigments for Paints, Paper, Coatings



Uncooked Starch



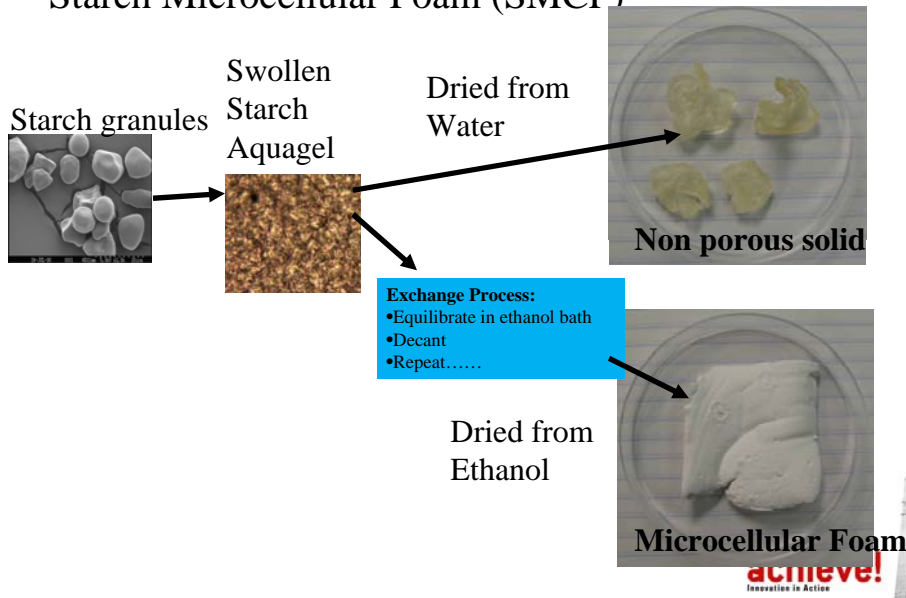
Ethanol ppt SMCF

7.5g glutaraldehyde / 100g starch

El-Tahawy, Venditti, Pawlak
Carbohydrate Polymers, 2007.

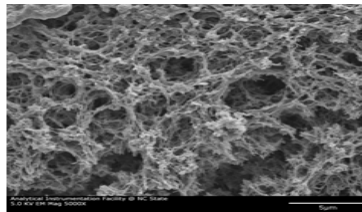


Pore Preserving Drying: Starch Microcellular Foam (SMCF)



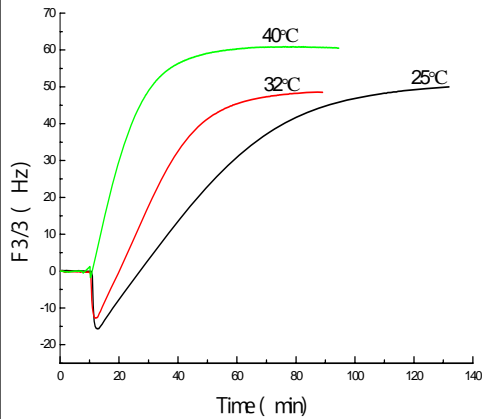
SMCF Applications

- Pigments for paints, coatings....
- Slow release agents; soil amendments
- Drug Delivery Systems
- Used as a "synthetic pollen" to carry medication to bee colonies (Glenn, coworkers)
- Adsorbants, absorbants, ion exchangers
- Carbon structures
- Future?
 - Thermal, acoustic insulation
 - Fuel cells
 - Platforms for green chemistry
 - Structural components in aerospace, automotive, electronic applications



Use of QCM to Determine Apparent Activation Energy and Hydrolysis Rates of Biomass

John Heltmann



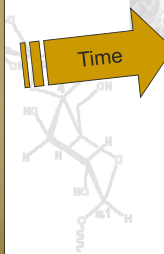
Parameter	25°C	32°C	40°C
A_1 (Hz)	-27.1	-33.2	-81.86
A_2 (Hz)	49.8	48.7	60.76
$\log t_0$ (min)	38.8	24.5	8.3
P (min^{-1})	0.0232	0.0397	0.0478
Adj. R^2	0.99337	0.99996	0.99987

P values can be used to indicate the maximum hydrolysis rate since it corresponds to the maximum slope in the frequency response curve.

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Opportunities with Dissolved Wood for the Forest Biorefinery

Dimitris S. Argyropoulos



Certain Ionic Liquids Can Completely Dissolve Wood

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Laboratory of Soft Materials & Green Chemistry

- Lucia Group
 - Renewable composites
 - Antibacterial surfaces based on anchored glucose oxidase
 - Tissue Scaffolds from PLA and cellulose
 - Hydrogel devices based on hemicelluloses
 - Nanocrystals
- International collaborations (China, Brazil)
- <http://www4.ncsu.edu/~lalucia>
- *BioResources*



GL Pulping Project

- Success story of collaboration
- Worked with DOE to implement pretreatment technology at a kraft pulping mill
- MeadWestvaco is our millpartner
- Collaborating extensively with Sujit Banerjee at IPST
- Look to have a trial within the next 6 mos.
- True participation from all sides (consultants, mill, DOE, IPST, NCSU)

