



FINAL REPORT FOR AWARD # 0531371

GA Tech Res Corp - GIT

Defining the Opportunities, Challenges, and Research Needs for NanoBiomaterials Derived from Lignocellulosics

Participant Individuals:

CoPrincipal Investigator(s) : William R Ashurst; Timothy G Rials

Participants' Detail

Partner Organizations:

Other collaborators:

Workshop speakers:

Lori A. Perine Executive Director Agenda 2020 Technology Alliance, American Forest and Paper Association - Forest Products Industry Needs, Challenges, and Opportunities

Professor Alaine Dufresne, EFPG-INPG, Cedex, France - Research Challenges in NanoLignocellulosic Chemistry and Engineering

Professor Robert Pelton, Depart. of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada - Challenges of Integrating Nanotechnology with Biotechnology

Professor Kristiina Oksman, Dept. of Engineering Design and Materials Norwegian University of Science and Technology, Trondheim, Norway - Cellulose Nanocomposites, Challenges to Overcome

Professor Paul Gatenholm, Department of Materials and Surface Chemistry, Chalmers University of Technology, Göteborg, Sweden - Engineering of cellulosic fibers with xylan nanoparticles

Activities and findings:

Training and Development:

The workshop involved several graduate and postdoctoral students that were educated in new concepts in nanolignocellulosic materials. The two-day workshop facilitated an exchange of ideas and concepts in differing fields of science and engineering centering about the development of innovative nanolignocellulosic materials. Several new inter-disciplinary research opportunities were identified and new multi-disciplinary research teams have begun to examine these issues.

Outreach Activities:

This grant was for a workshop that was open to the public.

Presentations Resulting From the Workshop

1. Ragauskas, A.J.; Rials, T.G.; Ashurst, R.W.; Cullinan, H.T.; Wegner, T.H.; Holbery, J.D. Path Forward for NanoBiomaterials Derived From Lignocellulosics, TAPPI International Conference on Nanotechnology for the Forest Products Industry (2006)
2. Ragauskas, Arthur J.; Rials, Timothy G.; Ashurt, Robert W.; Cullinan, Harry T.; Wegner, Theodore H.; Holbery, James D. Arboreal nanotechnology. 231st ACS National Meeting, Atlanta, GA, March 26-30 (2006)
3. Seeing Fibers in a Pulp Forest, Royal Institute of Technology, Stockholm, Sweden (March, 2007)
4. Ragauskas, Arthur J. (i) University of Aveiro, Department of Chemistry; Aveiro, Portugal (June, 2007) (ii) Cacia Soporcel Kraft Pulp Mill, Research Department; Averio, Portugal (June, 2007) (iii) RAIZ - Instituto de Investigacao da Floresta e Papel; Averio, Portugal (June, 2007) Cellulose Microfibrills and Nanotechnology

Journal Publications:

Book(s) of other one-time publications(s):

- A. J. Ragauskas, T. G. Rials, R. W. Ashurst, H. T. Cullinan, T. H. Wegner, J. D. Holbery, "Path forward for nanobiomaterials derived from lignocellulosics" , bibl. Tappi International Conference on Nanotechnology for the Forest Products Industry, (2006). *Conference paper* Accepted
- A. J. Ragauskas, Timothy G. Rials, Robert W. Ashurst, Harry T. Cullinan, Theodore H. Wegner, James D. Holbery, "Arboreal nanotechnology" , bibl. 231st ACS National Meeting, Atlanta GA, March 26-30, 2006, (2006). *Conference paper* Accepted

Other Specific Products:

Internet Dissemination:

http://www.ipst.gatech.edu/expertise_new/faculty_bios/nsf_sponsored_workshops.html

The results of this workshop have been summarized on an open web-site.

Contributions:

Contributions within Discipline:

This two day NSF sponsored workshop assisted the nanoscience/engineering and lignocellulosic research communities to identify key research opportunities in the sustainable utilization of wood-derived cellulose, hemicellulose and lignin ultra-structures for novel material applications.

Contributions to Other Disciplines:

The two-day workshop was a true multidisciplinary effort involving researchers from nanoscience/engineering, analytical chemistry, material science, sustainable biomaterials, chemical engineering, chemistry and polymer science. As such, representatives from each of these disciplines worked together to develop a common research vision and roadmap that has impacted

all of these research divisions equally.

Contributions to Education and Human Resources:

The two-day workshop facilitated an exchange of ideas and concepts in differing fields of science and engineering centering about the development of innovative nanolignocellulosic materials. Several new inter-disciplinary research opportunities were identified and new multi-disciplinary research teams have begun to examine these issues.

Contributions to Resources for Science and Technology:

The workshop involved several graduate and postdoctoral students that were educated in new concepts in nanolignocellulosic materials. The results of this workshop have been discussed at national meetings including ACS and TAPPI and the results have been mounted on a public web-site for an on-going educational influence and technical resource.

Contributions Beyond Science and Engineering:

The workshop involved several representatives from the forest products industry and the information exchanged at the workshop has been pivotal for Drs. Ragauskas and Deng to develop an industry supported nanotechnology program in wood based composites utilizing modern concepts in nanotechnology.

Categories for which nothing is reported:

Participants: Partner organizations

Research and Education Activities

Findings

Products: Journal Publications

Products: Other Specific Product

Submit

Return

View Activities PDF File

View Findings PDF File



We welcome [comments](#) on this system

**Report for NSF Sponsored Workshop Titled
Defining the Opportunities, Challenges, and Research Needs for NanoBiomaterials
Derived from Lignocellulosics**

by

Dr. Arthur J. Ragauskas, Professor of Chemistry
School of Chemistry and Biochemistry, Institute of Paper Science and Technology
Georgia Institute of Technology, 500 10th St., NW Atlanta, GA 30043

The two-day workshop was held at the Institute of Paper Science and Technology on September 22, 2005. Including participants, presenters, and students in excess of 65 people attended this two-day workshop (see Appendix 1 for a complete list of attendees). The workshop was directed at developing a roadmap for new structural and non-structural opportunities for using nanoscale lignocellulosic-derived biomaterials. The workshop participants and speakers examined:

1. How recent advances in nanoscience and engineering can be employed or adapted to lignocellulosics
2. New and important opportunities for nanoscale lignocellulosics as structural and nonstructural materials
3. Fundamental research and development challenges, knowledge gaps, and research needs related to:
 - a. Capturing identified opportunities for nanoscale lignocellulosics as structural and nonstructural materials
 - b. Designing efficient lignocellulosic extraction and utilization technologies for nanostructured materials
 - c. Developing controlled assembly methodologies for nano lignocellulosics structures and their interactions with other nanosystems.

Lignocellulose in woody plants is one of nature's most abundant materials, and wood-based lignocellulose at the macroscale level is one of our most used and ubiquitous materials. However, to-date, the intrinsic self-assembling nanoscale structure of wood lignocellulose as well as the versatility of its three key biopolymers: cellulose, hemicellulose, and lignin have been largely overlooked in nanoscience and engineering. This workshop addressed this oversight and provided a research pathway by which these lignocellulosic biopolymers will become the cornerstone of innovative structural and nonstructural nanoscale biomaterials that will contribute to the next generation of nanobiocomposite materials based on nature's preeminent renewable and sustainable resource.

The workshop itinerary is summarized below:

Thursday, September 22, 2005 at IPST@GT

- | | |
|----------------|--|
| 7:30 – 8:30 am | Program coordination meeting for
Working Group Chairs and Co-Chairs (<i>IPST@GT</i>) |
| 8:00 – 8:45 am | Morning Registration/Continental Breakfast/
Set-up Posters <i>IPST@GT Members Lounge</i>
Welcome -- Dr. Jorn Larsen-Basse, NSF |
| 8:45 - 9:00 am | Professor/Vice Provost C. Liotta Welcoming Comments

Dr. Art J. Ragauskas Opening Remarks |

Key Note Speaker: Richard W. Siegel, Ph.D.

Robert W. Hunt Professor, Materials Science and Engineering
Director, Rensselaer Nanotechnology Center, Rensselaer Polytechnic
Institute

Cross Roads of Nanotechnology and Biotechnology Sustainability and
Research Needs for 2050 With a World Population of 9 Billion.

Abstract: Great strides are being made worldwide in our ability to assemble nanoscale building blocks to create advanced hierarchical materials and devices with novel properties and functionalities. This rapidly growing effort has been enriched and accelerated over the past several years by the confluence of interest in matter at the nanoscale in physics, chemistry, and biology and by research funding from the U.S. National Nanotechnology Initiative and similar national and international efforts around the world. A perspective on the intersection of nanotechnology and biotechnology and its implications for research and society in the coming years will be presented based upon specific examples from our work in our NSF-NSEC at Rensselaer. Several examples from recent research results will be presented including investigations of functional nanoscale materials that could find commercial use in a variety of structural, electrical, environmental, and biomedical applications. The opportunities and challenges facing the worldwide nanotechnology and biotechnology research communities in moving forward in a sustainable world with a growing population will be considered.

Program Speakers and Round Table Discussion

- Lori A. Perine Executive Director Agenda 2020 Technology Alliance, American Forest and Paper Association
 - Forest Products Industry Needs, Challenges, and Opportunities
- Professor Alaine Dufresne, EFPG-INPG, Cedex, France
 - Research Challenges in NanoLignocellosic Chemistry and Engineering
- Professor Robert Pelton, Depart. of Chemical Engineering, McMaster University, Hamilton, Ontario, Canada
 - Challenges of Integrating Nanotechnology with Biotechnology
- Professor Kristiina Oksman, Dept. of Engineering Design and Materials Norwegian University of Science and Technology, Trondheim, Norway
 - Cellulose Nanocomposites, Challenges to Overcome
- Professor Paul Gatenholm, Department of Materials and Surface Chemistry, Chalmers University of Technology, Göteborg, Sweden
 - Engineering of cellulosic fibers with xylan nanoparticles

12:00 – 2:00 Lunch (*IPST@GT Members Lounge*)

Professor/Director IPST@GT J. Frederick
Dr. Jorn Larsen-Basse:

Welcome Comments
Overview of NSF's
role in Supporting
Nanotechnology in the
Nation

Poster Session & Working Groups Assignments

Workshop Working Groups

- Group 1: Novel Isolation/Directed Production of Nano-lignocellulosic Structures
- Group 2: Engineering Functionalized Nano-lignocellulosics
- Group 3: Structure and Design of Nano-lignocellulosic materials
- Group 4: Education - Environmental Challenges and Opportunities
- Group 5: Metrology for Lignocellulosics

Group	Working Group Chair	Working Group Co-Chair	Working Group Scribe
1	A.J. Ragauskas	K. Oksman	K. Nelson
2	J. Holbery	Z.L. Wang	J. Zhang
3	P. Gatenholm	T. Elder	Y. Pu
4	T. Rials	M. Wolcott	A Saxena
5	R.W. Ashurst	A. Rudie	C. Thomson

- 2:00 – 5:30 Breakout Sessions
 - Working Groups retreat to address program assignments
- 5:30 – 6:30 Report of Working Groups (*IPST@GT Auditorium*)
- 6:30 Reception (*IPST@GT Members Lounge: First Floor*)
- 7:00 Dinner
- 7:30 Dinner Speaker: Richard Murphy, Department of Biological Sciences
 Imperial College London, London, England
 Sustainability & its Role in Nanotechnology: Forest Products Industry
 (*IPST@GT Members Lounge*)

Friday, September 23, 2005 at IPST@GT

- 8:00 – 8:45 am Continental Breakfast (*IPST@GT Members Lounge*)
- 8:45 – 9:00 Workshop Status: Drs. Rials; Ashurst, Cullinan; Wegner (*IPST@GT*)
- 9:00 – 12:00 Work Group retreat to breakout sessions (*IPST@GT Rms 272, 316, 472, 572*)
- 12:00 – 1:00 Lunch (*IPST@GT Members Lounge: First Floor*)
- 1:00 – 1:40 Speaker: Mark E. Meaney, Director and Associate Professor
 Department of Health Care Ethics, Executive Director, Center of
 Health Care Ethics and Emerging Technologies, Rueckert-Hartman
 School for Health Professions, Regis University
 Presentation: Nanotechnology: International Opportunities in
 Education, Safety and Environment (*IPST@GT*)
- 1:45 – 3:00 Work Group Sessions (*IPST@GT Rms 272, 316, 472, 572*)
- 3:00 – 4:00 Report from Working Groups (*IPST@GT Auditorium*)
- Workshop Summary and Program Conclusions (*IPST@GT*)
- 4:00 - Program Review by Working Group Chairs
 and Co-Chairs (*IPST@GT President's Conference Rm*)

Lignocellulosic in plants are one of nature's most abundant biomaterials and wood-based lignocellulose at the macroscale level is one of our most used and ubiquitous biomaterials. However until recently the intrinsic self-assembling nanoscale structure of lignocellulosics in plants as well as the versatility of its three key biopolymers: cellulose, hemicellulose, and lignin have been largely overlooked in nanoscience and engineering. The needs of the forest products industry to develop new materials from wood has been frequently discussed.^{1,2} Indeed, a workshop held in Washington 2004 titled "Nanotechnology for the Forest Products Industry" resulted in the formation of a roadmap document that highlighted these needs.³ In brief, five R&D focus areas were highlighted that need to be developed to advance the forest products industry, including:

- Polymer composites and nanoreinforced materials based on wood-derived components
- Self-assembly and biomimetics by templating and/or replicating woody structures
- Enhancing plant cell wall nanostructures to improve the manufacturing and/or the performance of conventional materials
- Nanotechnology in sensors, processing and process control
- New analytical methods for characterization of nanostructure of lignocellulosics.

The NSF sponsored workshop and this report examined the fundamental challenges that need to be addressed in lignocellulosic nanotechnology including: 1) identifying new and important opportunities for nanoscale lignocellulosics as structural and nonstructural materials; 2) examine how recent advances in nanoscience and engineering can be employed or adapted to lignocellulosics from wood; and 3) identify fundamental research and development challenges, knowledge gaps, and research needs.

Technical Report - Background

Cellulose:

As a natural fiber, cellulose is the most abundant and potentially useful biopolymeric material available. Although the basic chemical structure of cellulose is well known, its ultrastructure remains a source of active investigation. Cellulose has a chain length of nearly 10,000 cellobiose monomer units in native wood but can decrease to less than 2000 after kraft pulping.⁴ Suckling *et al.* have observed that the average chain length of cellulose in *Pinus radiata* is approximately 9,000 but decreases to 4,000 – 5,000 after kraft pulping.⁵

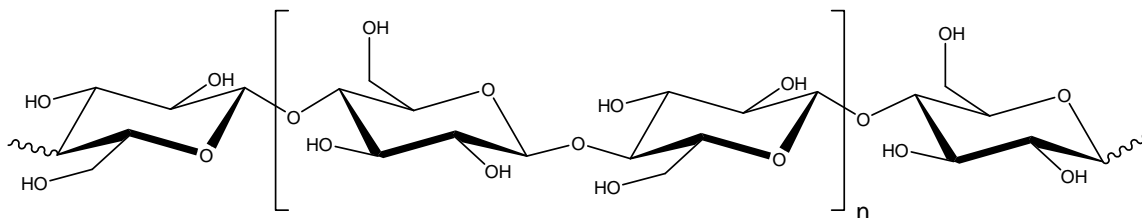


Figure 1. Chemical structure of cellulose
1,4- β -D-glucopyranose monomers and cellobiose repeating units

Cellulose macromolecules can be organized into crystalline structures due to the presence of numerous hydroxyl groups on the chain backbone which lead to both intermolecular and intramolecular hydrogen bonds. In the cell wall, cellulose is organized into thin crystalline structures known as microfibrils that are helical about the fiber axis. In most wood species, elementary fibrils with a width of 3.5 nm are first constructed by the crystallization of 36 parallel cellulose chains.⁶ Microfibrils are then formed by aggregation of these elementary fibrils into bundles that can reach 50 nm in width. Hult *et al.* calculated the width of cellulose microfibril aggregates in kraft pulps to be on the order of 14-20 μm using CPMAS ^{13}C NMR data.⁷

Table 1. Cellulose degree of polymerization
Change in DP due to kraft pulping and ECF bleaching for softwoods.⁸

Cellulose Source	Cellulose Degree of Polymerization
Native wood	9000 - 10000
Unbleached kraft pulp	4000 - 6000
Fully bleached kraft pulp	1500 - 2000

Cellulose has six crystalline polymorphs of which cellulose I and II are the most commonly found. Cellulose I is composed of parallel cellulose chains and is the native form produced in plants and other organisms.⁶ In nature it exists as two sub-allomorphs, I_{α} and I_{β} , which can both be described as dense, highly hydrogen bonded sheets of parallel chains which are arranged in stacks.^{9,10} The main difference between the two allomorphs has been reported to be due the stacking of these sheets that are displaced in the chain direction. The two allomorphs are often found together although bacterial cellulose tends to be rich in I_{α} while cotton tends to be higher in cellulose I_{β} .¹¹ The ratio of cellulose I_{α} and I_{β} in woody plants depends greatly on the species. In general, softwoods are higher in I_{α} , while hardwoods contain more I_{β} . Cellulose II is the most common alternative polymorph found in synthetic cellulosic materials and is obtained from cellulose I by mercerization or various cellulose regeneration processes. Cellulose II consists of antiparallel cellulose chains that are arranged into less dense sheets.

Table 2. Distribution of cellulose crystalline allomorphs

Cellulose source	% Cellulose crystalline allomorphs		
	I_{α}	I_{β}	II
Native spruce wood	74	26	-
Cotton	41	59	-
Bacterial cellulose	62	30	trace
Bleached spruce kraft pulp	30	61	9
Viscose	-	-	100

Microfibrils are made up of long threadlike bundles of cellulose molecules that are bonded to each other through hydrogen bonding. The microfibrils themselves then further

aggregate to form cellulose fibers. Microfibrils normally have a diameter between 2 and 20 nm, and can be as long as 10-20 microns. The modulus of native cellulose is considered to be approximately 150 GPa, with a strength around 10 GPa. It is because of these impressive mechanical properties and its intrinsic sustainability that the use of cellulose in composite materials has garnered world-wide interest.

The high strength of cellulose fibers makes them an attractive alternative for use as fillers in composite materials. Specifically, nano-sized cellulose dispersed in a polymer matrix. Cellulose microfibrils contain amorphous regions which are susceptible to hydrolysis. Thus microfibrils in the presence of strong acids can be cleaved into shorter monocrytals referred to as cellulose whiskers because of the stiffness and rodlike shape of these particles. The ability to remove the amorphous regions while still retaining the crystalline segments of microfibrils is due to the faster hydrolysis of the amorphous regions compared to the crystalline ones. It was reported that for cotton whiskers, the length and lateral dimensions were approximately 200 nm and 50 Å respectively. For tunicin cellulose whiskers, these values were 1 µm and 150 Å. Terech et al. also showed the tunicin whiskers were rod shaped with a cross-sectional rectangular shape estimated to be 88 x 182 Å.¹² Preparation conditions of the cellulose whiskers also affect the stability of whisker suspensions, when they are suspended in water for example. If the acid catalyzed hydrolysis employs sulfuric acid, a stable aqueous suspension is formed compared to hydrolysis in hydrochloric acid. This is due to the negatively charged sulfonated whisker surface that is created with sulfuric acid, as opposed to the charge free whiskers prepared in hydrochloric acid.¹³ The exact dimensional size of cellulose whiskers is dependent upon the reaction conditions employed and the source of cellulose employed.^{14,15,16,17,18}

Commercially available forms of microcrystalline cellulose were first reported in 1961 by Battista and Smith in a patent¹⁹ and it was well known for the past three decades that cellulose fibers consisted of whisker-like microfibrils.²⁰ Nonetheless the use of cellulose whiskers as a filler material in nanocomposites was not reported until Favier et al in 1995.²¹ This field has evolved rapidly since then with publications chronicling the incorporation of cellulose whiskers into a variety of polymeric matrices to form novel nanocomposite materials. Amash et al. used cellulose II and polypropylene to produce nanocomposite films with varying fiber content. They found that the material became stiffer as the filler content increased and also the storage modulus increased from about 1560 MPa for the polypropylene alone, to 2865 MPa for the composite material containing 50 wt% filler.²² They also observed that these composite materials have higher storage modulus at higher temperatures which can extend the temperature range over which they could be used. These general improvements in strength properties have been reported for several natural polymers including polylactic acid,²³ starch,²⁴ poly(β-hydroxyoctanoate)²⁵ and synthetic polymers such as acrylic,²⁶ PVC,^{27,28} poly(oxyethylene),²⁹ waterborne epoxy,³⁰ and poly(vinyl acetate).³¹ In many of these cases the improvements of mechanical properties have been attributed to the formation of a cellulose whisker network within the polymeric matrix governed by a percolation effect.³²

In terms of preparing cellulose whisker nanocomposites a common approach is solvent casting and evaporation although electrospinning,³³ and heat pressing have also been reported. Samir et al. studied the synthesis of composites made with polyethers and tunicin whiskers in which a stable suspension of nanocellulose was made in an organic medium (DMF), and used to produce the composite.³⁴ The resulting thermal and mechanical properties of the nanocomposite material were comparable to that of the properties obtained when an aqueous suspension is used. This opens up new possibilities in terms of the flexibility of polymer types and solvent systems that can be employed in the nanocomposite synthesis. Oksman et al. used a novel method for producing nanocomposites based on cellulose whiskers dispersed in a polylactic acid matrix.^{35,36} They developed a process that fed the nanowhiskers suspension directly into the polymer melt during extrusion. This decreases the tendency of the whiskers to re-aggregate during drying and allowed for better dispersal in the polymer matrix. They showed an increase in the Young's modulus for the nanocomposite material, but the reported value of 3.9GPa, was lower than the values seen in the other studies previously mentioned. This may be due to the different processing conditions. These studies demonstrate an increased interest in the synthesis of cellulose nanocomposites using different solvent systems, nanocellulose forms and even processing conditions.

Recently, the application of cellulose whiskers to nanocomposites has been broadened beyond improvement of physical strength properties. For example, cellulose whiskers have been utilized in the synthesis of nanocomposite polymer electrolytes^{37,38,39} employing poly(oxyethylene) and lithium trifluoromethyl sulfonyl imide. The storage modulus results obtained using cellulose whiskers as the filler were even better than those obtained when an inorganic filler such as TiO₂ was used by a factor of 50. Berg et al. has reported that nanocomposites from cellulose whiskers with (semi)conducting conjugated polymers yield films that synergistically combine the electronic and mechanical properties of individual components.⁴⁰

The use of chemically modified whiskers has begun to be studied to provide access to novel functionality. For example, charge neutral tunicin whiskers generated by HCl hydrolysis can be oxidized to yield a homogenous coverage of surface carboxylic acid when treated with TEMPO and NaBr/NaOCl. Solutions of the carboxylated whiskers exhibited liquid crystal behavior.⁴¹ The development of hydrophobic whiskers has also been recently demonstrated by Yuan et al. which employed a modified acetylation procedure to surface acetylated whiskers.⁴² These esterified whiskers were shown to be soluble in low-polarity solvents and could be well dispersed in polystyrene to yield a novel nanocomposite.

An alternative nanocellulose structure that has been reported is the synthesis of spherical cellulose particles from 500 – 80 nm in diameter, prepared by initially swelling cellulose fibers followed by a controlled acid hydrolysis.⁴³ These spherical structures are currently being examined as novel drug delivery structures. Lignocellulosic fibers have also been used to prepare hierarchically ordered ceramic materials by infiltrating wood fibers with mineralization agents followed by calcination. The final nanostructured ceramic has no

‘woody’ material but has replicated the ultra-structure of the lignocellulosic starting material.⁴⁴

Hemicellulose

Wood hemicelluloses are entrained within the cell wall matrix along with the lignin and cellulose.⁴⁵ Hemicelluloses are branched heteropolysaccharides that consist of a number of different sugar building units that are linked together in a variety of bonding arrangements. Prevalent hexose units include glucose, mannose and galactose, while the pentoses are primarily xylose and arabinose. Hemicellulose has an average degree of polymerization of only 100 to 200 units and has varying degrees of branching sugars off of the main chain.⁴⁶ Hemicellulose is an amorphous polymer and this is attributed to the low degree of polymerization and the branched structure.

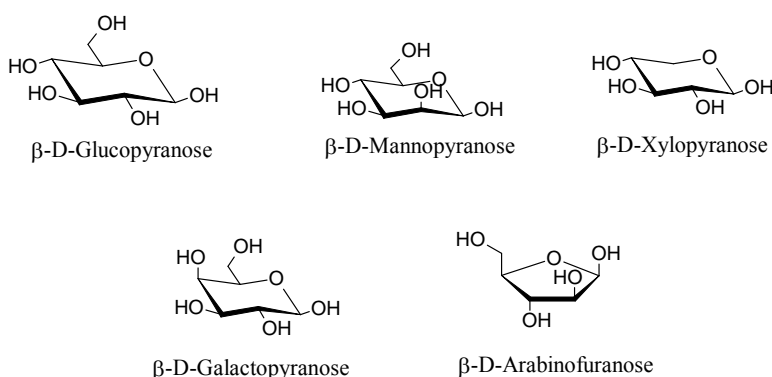


Figure 2: Common sugar monomers in hemicellulose

Both the proportions and the composition of hemicellulose vary from species to species as can be seen in Table 3. Hemicellulose content is typically 20 to 30% of oven dry wood in softwoods and 25 to 35% in hardwoods. The hemicellulose of hardwoods is primarily comprised of xylan with lesser amounts of unbranched glucomannan. Softwood hemicellulose is principally composed of branched galactoglucomannan with lesser amounts of arabinoxylan and trace amounts of arabinogalactan.

Table 3. Chemical composition of representative hardwoods and softwoods

	Cellulose (%)	Lignin (%)	Glucuronoxylan (%)	Glucomannan (%)	Other (%)
Softwoods					
<i>Pinus taeda</i>	42	30	9	17	3
<i>Picea glauca</i>	41	27	13	18	1
<i>Abies balsamea</i>	42	29	9	18	2
<i>Pinus strobus</i>	41	29	9	18	3
<i>Tsuga Canadensis</i>	41	33	7	16	3
<i>Thuja occidentalis</i>	41	31	14	12	2

Hardwoods

<i>Acer rubrum</i>	45	24	25	4	2
<i>Populus tremuloides</i>	48	21	24	3	4
<i>Betula papyrifera</i>	42	19	35	3	1
<i>Eucalyptus goniocalyx</i>	44	30	18	4	4
<i>Fagus grandifolia</i>	45	22	26	3	4
<i>Ulmus americana</i>	51	24	19	4	2

Xylans are a major class of hemicelluloses present in virtually all forms of lignocellulosic materials. Hardwoods, softwoods, cereal straws, grasses, sugarcane, bagasse, and corn stovers all contain xylan to some extent. There are two predominant types of xylan – acetylglucuronoxylan and arabinoglucuronoxylan.⁴⁷ Both polymers have homosaccharide backbones of 1,4- β -linked xylopyranose units, but the branching of the polymers is different. Figure 3 shows acetylglucuronoxylan with 30-70% of the 2 positions are substituted with acetyl groups and about 10% with 4-O-methylglucuronic acid groups. This type of xylan is prevalent in the hardwoods.

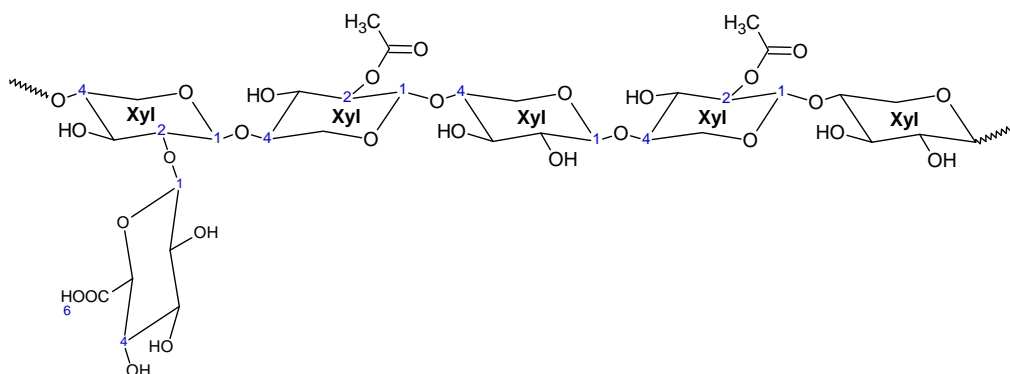


Figure 3: Xylan structure found in hardwoods

1,4- β -linked xylopyranose units and acetyl groups at C2 positions and 4-O-methyluronic acid branches at C2 position.⁴⁷

In softwoods, the xylan has the same basic structure, but usually with no attached acetate groups. Softwood xylan shown in Figure 4 has 4-methylglucuronic acid side chains at approximately 20% of the C2 positions but it also has arabinose sugars attached to either C2 or C3. In general, the softwood xylans are more branched with uronic acids but are less substituted overall because there are no acetate groups. The typical arabinose/uronic acid/xylose ratio is 1:2:8.⁴⁸ This tends to make softwood xylans less soluble than hardwood xylans in most aqueous solvents.

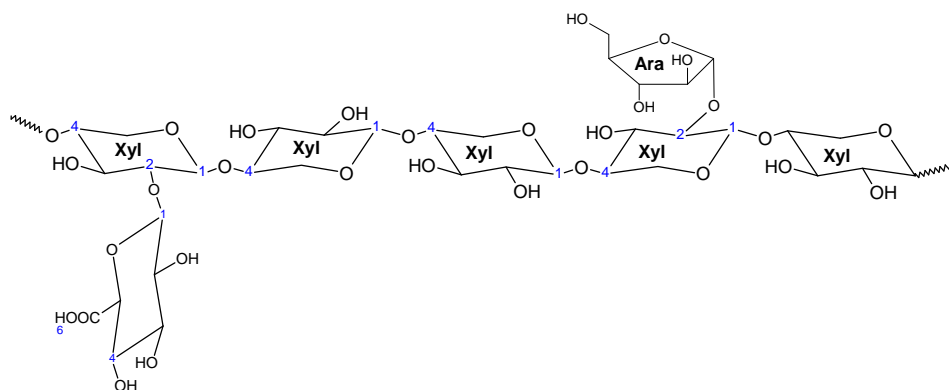


Figure 4. Xylan structure found in softwoods
1,3 linked arabinose units and 4-O-methylglucuronic acid.

Glucomannan is far more important than arabinoglucuronoxylan to the hemicellulose of softwood. Galactoglucomannan contributes 15-20% of the dry wood mass of softwoods and thus is the principal component of the hemicellulose in the conifer species.⁴⁹ It is comprised of 1,4- β -linked glucose and mannose units that are partially acetylated at C2 and C3 and partly substituted by single galactose units attached to the 6 position.⁵⁰ It has an approximate DP of 100-150 and is found primarily in the lignified secondary wall. Softwoods generally have two different types of galactoglucomannan – one highly branched form with a 1:1:3 galactose/glucose/mannose ratio and another that is less branched with a 0.1:1:3 galactose/glucose/mannose ratio. In hardwoods, glucomannan has little or no branching and a lower glucose/mannose ratio of 1:1 or 1:2.

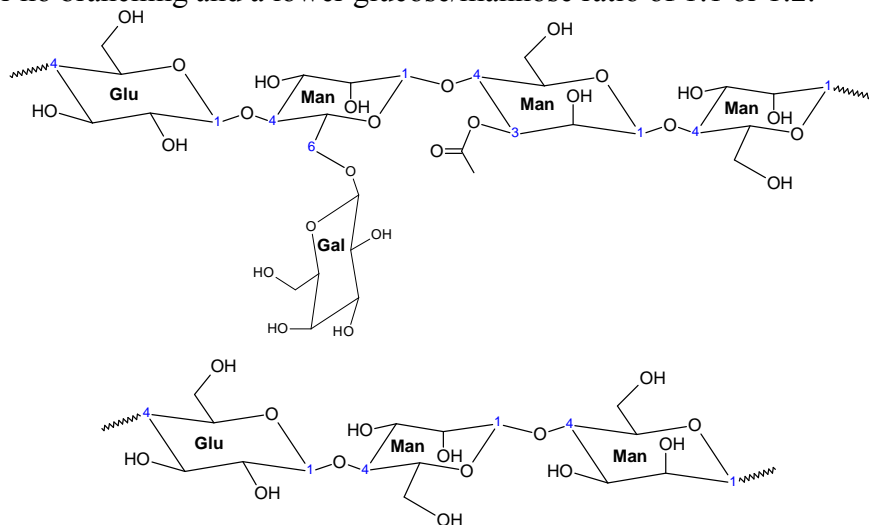


Figure 5: Structures of Glucomannan
Softwood galactoglucomannan (top) and hardwood glucomannan (bottom).

The last major type of hemicellulose is arabinogalactan, a highly water soluble hemicellulose that is present in many woods to a minor extent (0.5-2%) but is the major component of larch hemicellulose (10-30%).⁵¹ The backbone of arabinogalactan is 1,3- β -linked galactopyranose units and it is highly branched with two unit sidechains of 1,6- β -linked galactose units or 1,3- β -linked arabinose units. The high degree of branching as shown in Figure 6 makes arabinogalactan highly soluble in aqueous solutions. Unlike the

hemicelluloses in other species, larch arabinogalactan is actually deposited outside of the cell wall and can be fully extracted with hot water.

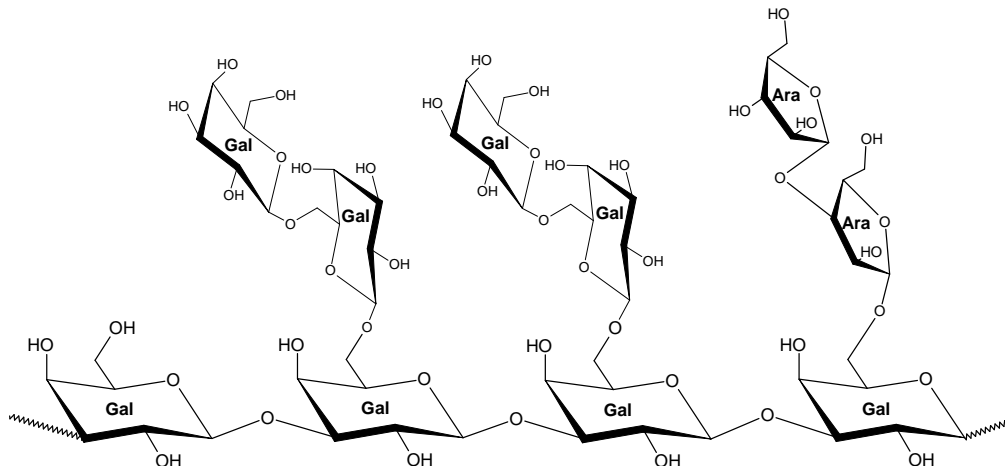


Figure 6: Structure of Arabinogalactan in Larch species

The utilization of hemicelluloses to prepare nanostructure materials remains in its infancy. Recent studies by Gatenholm et al. have documented the ability to control the aggregation properties of dissolved xylan on a nano-scale yielding novel xylan films which could be plasticized with xylitol or sorbitol.⁵² These films were shown to exhibit low oxygen permeability and have novel applications for food packaging.⁵³ The formation of xylan nanoparticles in solution has been shown to be influenced by the presence of lignin and hydrophobic interactions.^{52, 54}

In a related study, Garcia et al. reported that acid precipitation of an alkaline solution of corn cob xylan could generate nanoparticles of 100 - 900 nm in diameter dependent upon the conditions employed.⁵⁵ These materials were reported to be viable candidates for drug delivery systems

Lignin

Lignin is a complex three-dimensional network polymer made up of phenylpropane units.⁵⁶ The profusion of lignin in nature is due to its importance to the cell walls of both woody and non-woody plants. Trees are the most significant contributor to the production of lignin in the biosphere due to their relatively high lignin content and their ubiquitous presence on the planet. Although lignin is critical to the structural properties of wood, its removal is essential to the production of high quality and high strength paper. The pulp and paper industry devotes a vast amount of effort and capital to intensive pulping and bleaching primarily designed to remove lignin from wood fibers. In spite of the efforts of many researchers over the past fifty years, the structure of native lignin is unknown, largely due to the difficulty in isolating lignin without modification.

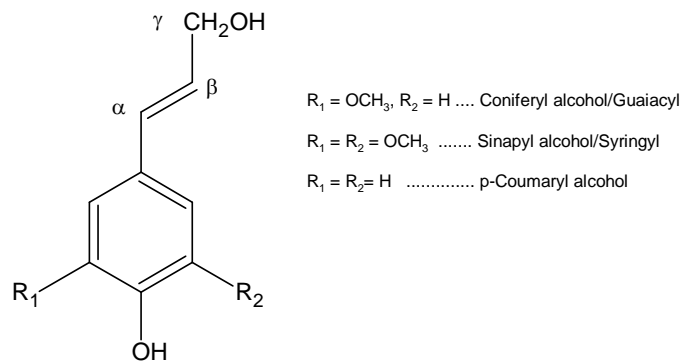


Figure 7: The building blocks of lignin

Although the structure of native lignin is not yet known, a great deal of information has been inferred from lignin degradation products and model compound studies. Lignin formation originates from the polymerization of three different phenylpropane units known as monolignols: sinapyl, coniferyl and p-coumaryl alcohol (Figure 9).^{57,58,59}

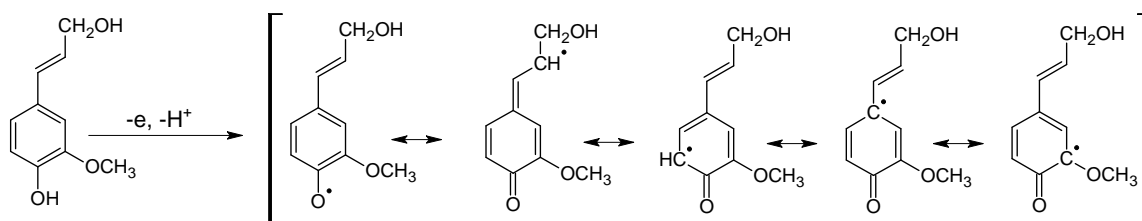


Figure 8: Resonance structures of lignin building blocks
Phenoxy radical precursors for lignin formation

The polymerization of lignin is believed to occur via the formation and subsequent coupling of phenoxy radicals. There are five main resonance structures (Figure 10) of the phenoxy radical and thus a wide variety of linkages are formed during the coupling. The multi-functionality of the phenoxy radical monomer ultimately results in the formation of a complex network polymer. The phenylpropane units are connected by carbon – carbon or ether bonds. There are eight common interunit linkages in lignin as shown in Figure 11. The most abundant linkage in lignin is by far the β -O-4 ether linkage, which typically makes up approximately 50% of the total linkages in softwood lignin.

Table 4. Frequency of different lignin linkages
For hardwood and softwood lignin

Type	Name	Softwood (%)	Hardwood (%)
β -O-4	β -aryl ether	45 - 50	60
α -O-4	α -aryl ether	6 - 8	7
β - 5	Phenylcoumaran	9 - 12	6
5 - 5'	Biphenyl and Dibenzodioxocins	18 - 25	7
4-O-5	Diphenyl ether	4 - 8	5
β - 1	1,2 - diphenylpropane	7 - 10	7
β - β	β - β linked structures	3	3

The distribution of covalent linkages in lignin is believed to play a significant role in its reactivity. Table 5 shows the frequency of linkages found in softwood lignin. Certain linkages are easily broken during pulping and bleaching, while other structures are less susceptible to certain modes of chemical attack. The frequencies of key functional groups that also contribute to lignin reactivity are summarized in Table 6. The difference in reactivity amongst the various lignin units and linkages is particularly evident when comparing post-pulping or post-bleaching residual lignin to native lignin.

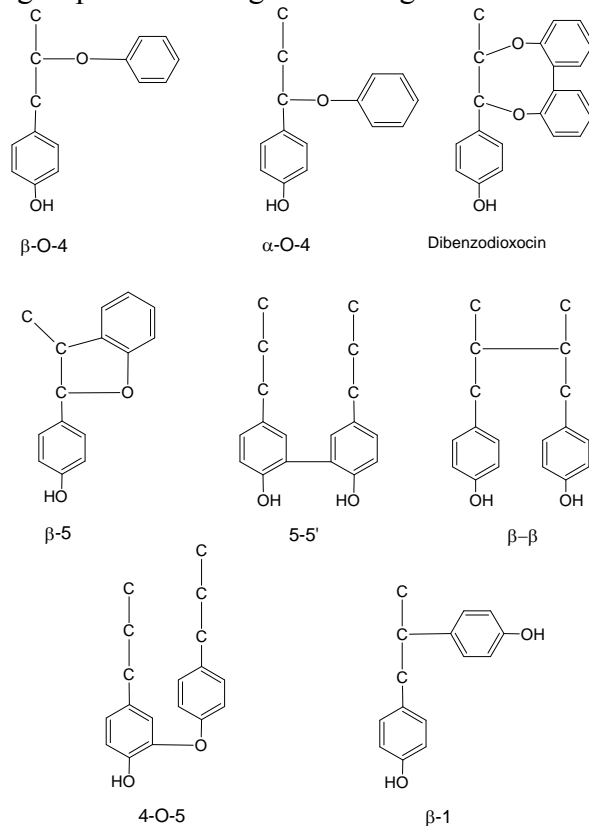


Figure 9: Structures of common lignin linkages

Table 5. Functional groups in softwood lignin per 100 phenylpropane units

Functional Group	Softwood Lignin (per 100 C-9)
Carbonyl	10 - 15
α -hydroxyl	15 - 20
Phenolic hydroxyl	15 - 30
Methoxyl	92 - 96

The use of lignin to prepare nanostructures has only recently begun to be examined with several recent exciting developments being reported. For example, Umetsu et al. has shown that the addition of thermally stable lignosulfates in the hydrothermal synthesis of CeO₂ resulted in the downsizing of CeO₂ particles to 5 nm. The lignosulfonate functions as an accelerator for the synthesis of CeO₂ nanoparticles.⁶⁰ Lignosulfonates have also grafted to polyaniline to prepare a conducting ferromagnetic ligno-pani nanocomposite.⁶¹ The use of lignin for nanostructured composite films⁶² and for electro-hydro-dynamic spinning to yield nanofibers after thermal treatment has also been reported.⁶³ These recent advances highlight the potential of engineering novel nanostructure materials and composites for nature's premiere renewable biomaterial.

Working Group Assignments

Each working group for the workshop was guided by a chair and co-chair that were chartered to address the following program topics:

I. IDENTIFY KEY OPPORTUNITIES/APPLICATIONS OF NANOTECHNOLOGY IN ASSIGNED TOPIC AREA

Session Purpose: Identify unique synergies of nano and wood science. What are the primary opportunities and benefits to society? How could nanotechnology fundamentally change the “new” forest products industry (FPI) to manufacture nanostructured products, including novel biomaterials, functional smart nanobiostructures?

How can nanotechnology change the wood-based products that are produced? How can it change manufacturing processes in the FPI? What are the fundamental concepts for manufacturing forest products on the nanoscale? How can it enhance productivity, save energy, improve environmental performance, improve sustainability, and benefit national competitiveness and rural economies?

What are the engineering/manufacturing challenges?

What are the public benefits of government support for R&D in this area?

II. GOAL STATEMENT & SUPPORTING OBJECTIVES FOR TECHNOLOGY AREA

Session Purpose: Goal Statement:

Objective: Imagine that the goal has been successfully completed:
What will you need to have done to achieve this goal?

III. IDENTIFY BARRIERS

Session Purpose: Identify problems – that is, to identify the barriers/challenges to achieving the goals.

IV. R&D AND RELATED NEEDS

Session Purpose: Identify solutions and technical roadmap needed.

The results of these break-out team efforts are summarized below.

Team 1: Novel Isolation/Directed Production of Nano-lignocellulosic Structures

Key research nano-structures exist with:

Cellulose

- Fibrils
- Whiskers
- Spheres
- Regenerated nano-particles
- Electrospun fibers

Lignin

- Spheres
- Rods
- Cylinders
- Carbon nanostructures
- Electrospun fibers
- Self-associated structures

Hemicelluloses

- Spheres
- Films
- Electrospun fibers
- Self-associated structures

Each of these nanostructured materials need to be characterized and modeled according to their unique size dependent properties including morphological, mechanical, chemical, optical, magnetic, electronic and transport properties. The research goal in this field is to develop fundamental knowledge for the separation, processing, and reassembly technologies needed to address both high value and high volume applications for nano-lignocellulosic polymers and structures. Programs addressing this goal must systematically identify fundamental properties of association of biopolymers and how to disaggregate this association. Researchers must recognize that separation technologies are oftentimes coupled to the intended application and it would be best to elucidate the

unique properties of nano-lignocellulosics for innovative applications and develop modeling capabilities to explain and predict properties of nanolignocellulosic structures. Some of the most attractive separation technologies include acid hydrolysis, dissolving solvent extraction methodologies, enzymatic/biological treatments, mechanical/ milling/ grinding, ionic liquids, near supercritical extraction, steam explosion, high pressure homogenization, surface acetylation of fiber- can release nanocrystals by surface derivatization and high shear mechanical treatments. These separation technologies need to utilize 50% or more of the intrinsic strength and self-assembly of nanostructured components of cellulose, lignin and hemicellulose.

Application of these nanostructures components include high volume materials, such as: water purification systems, papermaking components for strength enhancement and dimensional stability; novel imaging technology built into paper, tunable hydrophilic/hydrophobic surfaces and wood based composites for strength enhancement, creep, moisture and dimensional stability. Barriers to the development of these breakthrough technologies include: Current laboratory separation technologies which are often inadequate for nanolignocellulosic systems.

- Separation science is not fully developed for nanoscale systems.
- Separation technologies currently used in laboratory are often not viable processes on the industrial scale, such as
 - Separate nanoparticles from product stream- nanofiltration and/or centrifugation
 - Drying
 - Size fractionation
- Metrology and characterization tools are inadequate.
- Principles of disassembly and reassembly are not sufficiently advanced.
- Difficult to advance the underlying science if one or more applications are not readily apparent.
- Particular value of nanolignocellulosics and their contributions for sustainable development is not widely understood in the materials science community
- Elements of a successful research program to address these barriers need to address: Identify structure of available lignocellulosic nanomaterials from wood
- Characterize, measure, and model properties making full use of available biological research and techniques
- Engage separations research community and prepare inventory of potential separation processes and effective models for application and scale-up
- Develop library of properties of nanolignocellulosics
- Establish uniqueness and benefits of nanolignocellulosics compared to other nanomaterials
- Identify relationships between separation and purification technologies, nanomaterial properties, and end use applications
- Investigate economic viability of nanomaterials as application opportunities arise

The anticipated benefits from research in this field include the large scale availability, low cost production of nanostructures of cellulose, lignin, hemicelluloses,

environmentally benign nanostructures and superior properties of sustainability of lignocellulosic over synthetic polymers.

Team 2: Engineering Functionalized Nano-lignocellulosics

The agreed upon concise team goal statement was that research should “define the science that identifies, characterizes, and aims to utilize functionalized nano-structures from lignocellulosics.” Supporting research objectives in this field were (1) Define scaleable and non-scaleable properties of nano-lignocellulosics; (2) To understand the thermodynamics and driving forces for nano-lignocellulosic structures; (3) Fundamentals of nano-lignocellulosic surface chemistry; (4) Understanding the behavior of nano-scale fluidics with lignocellulosic structures; (5) Nano-scale processes within lignocellulosics; (6) To understand physical-chemical-biological properties of nano-scale lignocellulosic materials; (7) Develop organic and enzymatic transformations to take advantage of chirality and other unique characteristics of nano-lignocellulosic structure. The benefits of research activities associated with this field were multifaceted and included:

Lignocellulose is a bridge to life science

- Controlled nano-properties via genetic manipulation
- Dynamic driving forces that dictate properties at the nano-scale
- Nano-scale manufacturing template
- Nano-scale porosity
- Flexibility of functionalization
- Mechanical & other properties (Specific modulus and strength)
- Ease of processibility, chirality of structure
- Diverse & controllable morphology
- Potentially low cost nano material
- New products for the forest product industry

The impacts of these studies on the wood and wood-based materials industry would lead to increased diversification of the forest products industry; new markets with potentially higher value added products; an increase in current product performance coupled with a decrease in total energy consumption and enhanced water management capabilities. The public would benefit from these programs given the intrinsic sustainability of nanolignocellulosics that would replace petrochemicals and open the door for new products and processes for industry while stimulating rural economies by increasing demand for high-value products from agricultural crops. The research needs required to pursue this vision need address (1) The scaleable and non-scaleable properties of nano-lignocellulosics; (2) The thermodynamics and driving forces for nano-lignocellulosic structures; (3) Fundamentals of nano-lignocellulosic surface chemistry; (4) Understanding the behavior of nano-scale fluidics with lignocellulosic structures (5) Nano-scale processes within lignocellulosics; (6) Understand physical-chemical-biological properties of nano-scale lignocellulosic materials; (7) Develop organic and enzymatic transformations to take advantages of chirality and other unique characteristics of nano-lignocellulosic structure.

Team 3: Structure and Design of Nanolignocellulosic Materials

Research Goal: Production of sustainable materials with unique properties from nanoscale lignocellulosic building blocks hierarchically assembled using low energy processes

The break out team initially examined the well accepted limitations of modern paper and wood related materials which includes orthotropic, microbial degradation, moisture sensitivity, combustible, processability, defect, biological variability and incompatibility with other materials especially synthetic plastics.

Yet, lignocellulosic materials are the most abundant, renewable and carbon neutral resource on the planet and nanotechnology could provide a means of addressing many of the limitations described above. In addition to these advantages, there is an existing industrial infrastructure by which these biomaterials can be and are processed. These advantages notwithstanding, lignocellulosics are not without limitations. These include orthotropicity, susceptibility to degradation by biological, chemical and physical agents, dimensional instability, biological variability and incompatibility with other materials. These limitations may be overcome if the chemical constituents of lignocellulosics can be disassembled and then reassembled into new nanobiomaterials that can be used in new applications which were not feasible in the past.

Identify fundamental advantages of lignocellulosic materials with both individual nanoblocks and assemblies

- Identify specific needs addressed by these materials and expand performance envelope
- Develop low energy manufacturing processes: (phase separation, agglomeration, adsorption, spontaneous assembly etc)
- Work towards a renewable biomaterials industry as opposed to traditional forest products industry
 - Replacement /substitution of non renewable materials
 - Production of nanoscale building blocks from biorefineries

The breakout team chartered with Structure and Design of Nanolignocellulosic Materials identified the following key elements of viable research:

New isolation methods will provide Cellulose in the form of

- Fibrils
- Whiskers
- Spheres
- Regenerated nano-particles
- Electrospun fibers

Cellulose microfibrils

- Dimension, size distribution
- Surface chemistry
- Order – morphology

Cellulose crystals

- Size
- Form
- Surface (chemistry, charge)
- Degree of crystallinity

Hemicelluloses

- Spheres
- Films
- Electrospun fibers
- Self-associated structures

Lignin

- Spheres, Rods, Cylinders
- Carbon nanostructures
- Electrospun fibers
- Self-associated structures

Assembly (putting blocks together)

- Scale, composition and distribution of blocks
- Dimensions (1D, 2D, 3D)
- Orientation
- Morphology
- Assembly 1D – example nanofibers
- Assembly 2D – example tubes, whiskers, layers, coatings
- Assembly 3D – particles, structures
- Scale integration into hierarchical structures - products

- Assembly of 1D cellulose crystals
 - Example: utilization of nanoprocessing tools for preparation of cellulose nanonecklace
 - Electrospinning, Nanoinjection
 - Nanospinning through molecular spinneret of cyclodextran

- Assembly (putting blocks together)
 - Control of Interactions between blocks
 - Van der Waals forces
 - Ionic interactions
 - Hydrophobic interactions
 - Hydrogen bonding
- Assembly Conditions
 - Dielectric field
 - Magnetic field
 - Flow and shear
 - Electrostatic interactions
 - Centrifugal forces.....
- Assembly

- Control by labeling building blocks
- Integrating biosynthesis with assembly
- Nanoglue
- Nanonails

Research Recommendations

Lignocellulose is quite complex chemically, and there is limited knowledge of how (or if) the components are interconnected and how the cell wall is assembled in nature. The former point also limits the ability to separate the constituents without degradation or contamination. From an analytical standpoint, tools for in situ imaging of the cell wall need to be developed. Assuming that the cellulose, hemicellulose and lignin nanoblocks can be separated, they need to be both kept apart and combined in specific ways, giving materials with predictable and novel properties. Success at this level will require improved and increased interdisciplinary work incorporating expertise in chemistry, biology and engineering.

Barriers to be overcome:

- Lack of understanding of sequences of chemical and physical linkages between cellulose, hemicellulose and lignin
- Lack of understanding of cell wall assembly process and driving forces
- Lack of tools for in situ imaging
- Lack of methods to separate, disperse, and keep nanoblocks apart
- Lack of efficient phase separation techniques preserving nanoblocks
- Inability to closely control size, shape and composition of nanoscale blocks
- Incomplete understanding and lack of control of water interaction with lignocellulosics
- Lack of communication between chemistry, engineering with biology
- Inability to control the synthesis of cellulose
- Inability to control composition of hemicelluloses and lignin
- Lack of ability to control the bonding between lignocellulosic components
- Lack of knowledge of mechanical properties of blocks

R&D Needs

- Fundamental study of water/lignocellulosic interactions
- Develop methods to measure the individual bonds and forces between lignocellulosic components
- Modeling and preparation of tailor-made hemicelluloses and LCC (lignin carbohydrate complexes)
- Processes for separation technology and handling of nanoblocks
- Study of assembly process in nature and develop biomimetic commercial technologies
- Evaluation of properties of assembled blocks with various compositions and architectures
- Synthesis of lignocellulosics
- Perception of forest product industry: low tech perception / image, like biomaterial science and engineering

- Get commitment from companies, industry need to become more market-driven
- Develop new products

Identify possible approaches to addressing the research need

- Large teams, focus on (management board, technical team)
- Industry/academia/government funding center
- Multi-disciplinary teams

Resources & Equipment

- Metrology/Image (visualization) for measurement
- Mechanical properties-measurement on nanoscale
- Modeling at molecular level/nano level
- Separation / fractionation plant
- Cohesion process

Team 4: Education and Environment

This break-out team examined the issues surrounding nanolignocellulosics, but from a differing charter directed at identifying key educational and environmental issues that need be addressed to facilitate R&D plans. The objectives for this endeavor need to include:

- The development of introductory nanotechnology course material for universities, colleges, etc.
- Develop continuing education modules for existing workforce (producers and suppliers)
- Enhanced graduate education for sustainable nanotechnology- Centers of Excellence
- Designate a web-based information clearinghouse for update and developing information
- Contribute specific information for efforts educating general public through K-12 students and teachers.

Coupled to an educational initiative, environmental issues of nanolignocellulosics need to be studied for example:

- Undertake LCA studies on the environmental impact of nanotechnology in the forest products industry
- Engage current health and environment centers on specifics for the forest industry
- Develop understanding of disposal and recycling issues of nano materials
- Develop opportunities for ongoing dialogue with willing stakeholders (*e.g. interactive forums, listening sessions, etc.*)
- To address these issues research program need to be structured to address the following issues: Discern the stakeholder groups' perception of the potential for nanotechnology
- Assess the current teaching capacity of nanotechnology issues
- Identify successful models for educational material built for rapidly changing science and technology

- Establishment of proposal to establish an interdisciplinary graduate education program in the area of sustainable nanotechnology
- Develop support and interest in post graduate research for nanotechnologies for forest
- Obtain funding to develop support for expanding NANOFORREST.ORG, Potential sources:UFSF and AF&PA

Team 5: Metrology Aspects of Nanolignocellulosics

The top priority research needs in this field need to be directed at:

- Experimental studies with new and existing techniques to characterize the relevant chemical and mechanical properties of bonding at interfaces in lignocellulosic materials at the nanoscale.
- Development of *in vivo* methods to study the development of the cell wall from its differing chemical constituents on the nanoscale.
- Development of robust, rapid, and inexpensive characterization methods for lignocellulosic nanostructures.
- Development of a “whole body imaging” technique (tomography, confocal microscopy, fluorescence microscopy, etc.) for lignocellulosic nanostructures with sub-nanometer resolution. Characterize and image directed self assembled nanoporous materials in three dimensions.
- Experimental studies with new and existing techniques to characterize the relevant chemical and mechanical properties of bonding at interfaces in lignocellulosic materials at the nanoscale. Relevant interfaces that need characterization include cellulose-cellulose; cellulose-inorganic; cellulose-synthetic polymers; cellulose-lignocellulose matrix polymers

The most attractive means of accomplishing this goal is to establish a dedicated user centre for characterization of lignocellulosics at the nanoscale that would be fully equipped with state-of-the-instrumentation. This would include existing techniques such as AFM, neutron scattering, x-ray synchrotron facilities, HR-EM, NMR, and EELS dedicated to lignocellulosics. The techniques developed in this center need to be broadly available and accepted in the research community to ensure that these technologies are broadly applied to the study of lignocellulosic nanostructures. Barriers to developing this vision are a hesitancy from industry to fund these efforts and a disconnect between the wood chemistry community and other fields of metrology. The development of such a user facility will need a partnership between academicians, national labs and federal funding agencies.

References:

¹ Wegner, T.H.; Jones, P.E. Advancing cellulose-based nanotechnology. *Cellulose* (2006), 13(2), 115-118.

-
- ² Wegner, T.H.; Winandy, J.E.; Ritter, M.A. Nanotechnology opportunities in residential and non-residential construction. RILEM Proceedings (2005), PRO 45(2nd International Symposium on Nanotechnology in Construction (NICOM2), 2005), 339-347.
- ³ http://www.agenda2020.org/PDF/fp_nanotechnology.pdf
- ⁴ Heiningen, A.V.; Tunc, M.S.; Gao, Y.; Silva Perez, D.D. Relationship between Alkaline Pulp Yield and the Mass Fraction and Degree of Polymerization of Cellulose in the Pulp. *Journal of Pulp and Paper Science* (2004) 30(8), 211-217.
- ⁵ Suckling, I. D.; Allison, R. W.; Campion, S. H.; McGrouther, K. G.; McDonald, A. G. Monitoring cellulose degradation during conventional and modified kraft pulping. *Journal of Pulp and Paper Science* (2001), 27(10), 336-341.
- ⁶ Saxena, I.M., Brown, Jr. R.M. Cellulose biosynthesis: Current views and evolving concepts. *Annals of Botany (Oxford, United Kingdom)*, 2005, 96(1), 9-21.
- ⁷ (a) Hult, E.-L.; Larsson, P.T.; Iversen, T., A comparative CP/MAS ¹³C-NMR study of cellulose structure in spruce wood and kraft pulp. *Cellulose* (2000) 7(1), 35-55. (b) Hult, E.-L., Larsson, P.Y.; Iversen, T. Cellulose fibril aggregation - an inherent property of kraft pulps. *Polymer* (2001) 42(8), 3309-3314.
- ⁸ Bouchard, J.; Methot, M.; Lapierre, L.; Berry, R. Combined effects of polysulphide pulping and ECF bleaching on softwood polysaccharides. *Journal of Pulp and Paper Science* (2004), 30(6), 172-176.
- ⁹ Atalla, R.H.; VanderHart, D.L. Native cellulose: a composite of two distinct crystalline forms. *Science*, 1984. 223(4633): p. 283-5.
- ¹⁰ Langan, P.; Sukumar, N.; Nishiyama, Y.; Chanzy, H. Synchrotron X-ray structures of cellulose I β and regenerated cellulose II at ambient temperature and 100 K. *Cellulose* (2005), 12(6), 551-562.
- ¹¹ Maunu, S.; Liitia, T.; Kauliomaki, S.; Hortling, B.; Sundquist, J. Carbon-13 CP/MAS NMR investigations of cellulose polymorphs in different pulps. *Cellulose* (2000), 7(2), 147-159.
- ¹² Terech, P.; Chazeau, L.; Cavaille, J.Y.; A small-angle scattering study of cellulose whiskers in aqueous suspensions. *Macromolecules* (1999), 32, 1872-1875.
- ¹³ Eichhorn, S.J.; Baillie, C.A.; Zafeiropoulos, N.; Mwaikambo, L.Y.; Ansell, M.P.; Dufresne, A.; Entwistle, K.M.; Herrera-Franco, P.J.; Escamilla, G.C.; Groom, L.; Hughes, M.; Hill, C.; Rials, T.G.; Wild, P.M. Current international research into cellulosic fibres and composites. *Journal of Materials Science*, (2001), 36, 2107-2131.

-
- ¹⁴ Dufresne, A. Comparing the mechanical properties of high performances polymer nanocomposites from biological sources. *Journal of Nanoscience and Nanotechnology* (2006), 6(2), 322-330.
- ¹⁵ Bondeson, D.; Kvien, I.; Oksman, K. Strategies for preparation of cellulose whiskers from microcrystalline cellulose as reinforcement in nanocomposites. *ACS Symposium Series* (2006), 938(Cellulose Nanocomposites), 10-25.
- ¹⁶ Bondeson, D.; Mathew, A.; Oksman, K. Optimization of the isolation of nanocrystals from microcrystalline cellulose by acid hydrolysis. *Cellulose* (2006), 13(2), 171-180.
- ¹⁷ Beck-Candanedo, S.; Roman, M.; Gray, D.G. Effect of Reaction Conditions on the Properties and Behavior of Wood Cellulose Nanocrystal Suspensions. *Biomacromolecules* (2005), 6(2), 1048-1054.
- ¹⁸ Samir, M.A.S.A.; Alloin, F.; Dufresne, Alain. Review of Recent Research into Cellulosic Whiskers, Their Properties and Their Application in Nanocomposite Field. *Biomacromolecules* (2005), 6(2), 612-626.
- ¹⁹ Battista, O.A.; Smith, P.A. Level-off degree of polymerization cellulose products. (1961), US 2978446
- ²⁰ Benziman, M.; Haigler, C.H.; Brown, R.M., Jr.; White, A.R.; Cooper, K.M. Cellulose biogenesis: Polymerization and crystallization are coupled processes in *Acetobacter xylinum*. *Proceedings of the National Academy of Sciences of the United States of America* (1980), 77(11), 6678-82.
- ²¹ Favier, V.; Canova, G. R.; Cavaille, J. Y.; Chanzy, H.; Dufreshne, A.; Gauthier, C. Nanocomposite materials from latex and cellulose whiskers. *Polymers for Advanced Technologies* (1995), 6(5), 351-5.
- ²² Amash, A.; Hildebrandt, F.; Zugenmaier, P. Dynamic Mechanical and thermal studies of cellulose and cellulose composites. *Designed Monomers and Polymers* (2002), 5(4), 385-399.
- ²³ Petersson, L.; Kvien, I.; Oksman, K. Structure and thermal properties of poly(lactic acid)/ cellulose whiskers nanocomposite materials. *Composites Science and Technology* (2007), 67(11-12), 2535-2544.
- ²⁴ Kvien, I; Sugiyama, J.; Votrubic, M.; Oksman, K. Characterization of starch based nanocomposites. *Journal of Materials Science* (2007), 42(19), 8163-8171.
- ²⁵ Dufresne, A. Dynamic mechanical analysis of the interphase in bacterial polyester/ cellulose whiskers natural composites. *Composite Interfaces* (2000), 7(1), 53-67.

-
- ²⁶ Pu, Y.; Zhang, J.; Elder, T.; Deng, Y.; Gatenholm, P.; Ragauskas, A.J. Investigation into nanocellulosics versus acacia reinforced acrylic films. *Composites, Part B: Engineering* (2007), 38B(3), 360-366.
- ²⁷ Chazeau, L.; Cavaille, J. Y.; Canova, G.; Dendievel, R.; Boutherein, B. Viscoelastic properties of plasticized PVC reinforced with cellulose whiskers. *Journal of Applied Polymer Science* (1999), 71(11), 1797-1808.
- ²⁸ Chazeau, L.; Cavaille, J. Y.; Terech, P. Mechanical behaviour above Tg of a plasticized PVC reinforced with cellulose whiskers ; a SANS structural study. *Polymer* (1999), 40(19), 5333-5344.
- ²⁹ Azizi Samir, M.A.S.; Alloin, F.; Sanchez, J.Y.; Dufresne, A. Cellulose nanocrystals reinforced poly(oxyethylene). *Polymer* (2004), 45(12), 4149-4157.
- ³⁰ Ruiz, M.M.; Cavaille, Jean Y.; Dufresne, A.; Graillat, C.; Gerard, J.F. New waterborne epoxy coatings based on cellulose nanofillers. *Macromolecular Symposia* (2001), 169, 211-222.
- ³¹ Garcia de Rodriguez, N.L.; Thielemans, W.; Dufresne, A. Sisal cellulose whiskers reinforced polyvinyl acetate nanocomposites. *Cellulose* (2006), 13(3), 261-270.
- ³² Favier, V.; Canova, G. R.; Shrivastava, S. C.; Cavaille, J. Y. Mechanical percolation in cellulose whisker nanocomposites. *Polymer Engineering and Science* (1997), 37(10), 1732-1739.
- ³³ Park, W.I.; Kang, M.; Kim, H.S.; Jin, H.J. Electrospinning of poly(ethylene oxide) with bacterial cellulose whiskers. *Macromolecular Symposia* (2007), 249/250(Advanced Polymers for Emerging Technologies), 289-294.
- ³⁴ Samir, M.A.S.A.; Alloin, F.; Sanchez, J.Y.; Dufresne, A. Cross-Linked Nanocomposite Polymer Electrolytes Reinforced with Cellulose Whiskers. *Macromolecules* (2004), 37(13), 4839-4844
- ³⁵ Oksman, K.; Mathew, A. P.; Bondeson, D.; Kvien, I. Manufacturing process of cellulose whiskers /polylactic acid nanocomposites. *Composites Science and Technology* (2006), 66(15), 2776-2784.
- ³⁶ Mathew, A.P.; Chakraborty, A.; Oksman, K.; Sain, M. The structure and mechanical properties of cellulose nanocomposites prepared by twin screw extrusion. *ACS Symposium Series* (2006), 938(Cellulose Nanocomposites), 114-131.
- ³⁷ Samir, M.A.S.A.; Chazeau, L.; Alloin, F.; Cavaille, J.-Y.; Dufresne, A.; Sanchez, J.-Y. POE-based nanocomposite polymer electrolytes reinforced with cellulose whiskers. *Electrochimica Acta* (2005), 50(19), 3897-3903.

-
- ³⁸ Samir, M.A.S.A.; Alloin, F.; Dufresne, A. High performance nanocomposite polymer electrolytes. *Composite Interfaces* (2006), 13(4-6), 545-559.
- ³⁹ Samir, M.A.S.A.; Alloin, F.; Gorecki, W.; Sanchez, J.Y.; Dufresne, A. Nanocomposite Polymer Electrolytes Based on Poly(oxyethylene) and Cellulose Nanocrystals. *Journal of Physical Chemistry B* (2004), 108(30), 10845-10852.
- ⁴⁰ van den Berg, O.; Schroeter, M.; Capadona, J.R.; Weder, C. Nanocomposites based on cellulose whiskers and (semi)conducting conjugated polymers. *Journal of Materials Chemistry* (2007), 17(26), 2746-2753.
- ⁴¹ Habibi, Y.; Chanzy, H.; Vignon, M.R. TEMPO -mediated surface oxidation of cellulose whiskers. *Cellulose* (2006), 13(6), 679-687.
- ⁴² Yuan, H.; Nishiyama, Y.; Wada, M.; Kuga, S. Surface Acylation of Cellulose Whiskers by Drying Aqueous Emulsion. *Biomacromolecules* (2006), 7(3), 696-700.
- ⁴³ Zhang, J.; Elder, T.J.; Pu, Y.; Ragauskas, A.J. Facile synthesis of spherical cellulose nanoparticles. *Carbohydrate Polymers* (2007), 69(3), 607-611.
- ⁴⁴ Shin, Y.; Exarhos, G.J. Conversion of cellulose materials into nanostructured ceramics by biomineralization. *Cellulose* (2007), 14(3), 269-279.
- ⁴⁵ Sun, R.; Sun, X.F.; Tomkinson, J. Hemicelluloses and their derivatives, in *Hemicelluloses: Science and Technology*, P. Gatenholm and M. Tenkanen, Editors (2004) ACS: Washington, D.C.
- ⁴⁶ Ragauskas, A.J.; Nagy, M.; Kim, D.H.; Eckert, C.A.; Hallett, J.P.; Liotta, C.L. From wood to fuels: Integrating biofuels and pulp production. *Industrial Biotechnology* (2006), 2(1), 55-65.
- ⁴⁷ Ebringerova, A., Heinze, T. Xylan and xylan derivatives - biopolymers with valuable properties, 1. Naturally occurring xylans structures, isolation procedures and properties. *Macromolecular Rapid Communications* (2000) 21(9), 542-556.
- ⁴⁸ Timell, T.E., Recent Progress in the Chemistry of Wood Hemicelluloses. *Wood Science and Technology*, (1967) 1(1), 45-70.
- ⁴⁹ Dahlman, O.; Jacobs, A.; Sjoeborg, J. Molecular properties of hemicelluloses located in the surface and inner layers of hardwood and softwood pulps. *Cellulose*, (2003) 10(4), 325-334.
- ⁵⁰ Stalbrand, H.; Lundqvist, J.; Andersson, A.; Haeggglund, P.; Anderson, L.; Tjerneld, F.; Jacobs, A.; Teleman, A.; Dahlman, O.; Palm, M.; Zacchi, G. Isolation, Characterization, and Enzymatic Hydrolysis of Acetyl-Galactoglucomanan from Spruce (*Picea abies*), in

Hemicelluloses: Science and Technology, P. Gatenholm and M. Tenkanen, Editors (2004) ACS: Washington, D.C., 66-78.

⁵¹ Chandrasekaran, R.; Janaswamy, S. Morphology of Western larch arabinogalactan. *Carbohydrate Research* (2002), 337(21-23), 2211-2222.

⁵² Linder, A.P.; Bergman, R.; Bodin, A.; Gatenholm, P. Mechanism of assembly of xylan onto cellulose surfaces. *Langmuir* (2003), 19(12), 5072-5077.

⁵³ Groendahl, M.; Gatenholm, P. Oxygen barrier films based on xylans isolated from biomass. *ACS Symposium Series* (2007), 954(Materials, Chemicals, and Energy from Forest Biomass), 137-152.

⁵⁴ Barakat, A.; Putaux, J.L.; Saulnier, L.; Chabbert, B.; Cathala, B. Characterization of Arabinoxylan-Dehydrogenation Polymer (Synthetic Lignin Polymer) Nanoparticles. *Biomacromolecules* (2007), 8(4), 1236-1245.

⁵⁵ Garcia, R.B.; Nagashima, T. Jr.; Praxedes, A.K.C.; Raffin, F. N.; Moura, T.F.A.L.; Do Egito, E.S.T. Preparation of micro and nanoparticles from corn cobs xylan. *Polymer Bulletin* (Berlin, Germany) (2001), 46(5), 371-379

⁵⁶ Ralph, J.; Bunzel, M.; Marita, J.M.; Hatfield, R.D.; Lu, F.; Kim, H.; Schatz, P.F.; Grabber, J.H.; Steinhart, H. Peroxidase-dependent cross-linking reactions of p-hydroxycinnamates in plant cell walls. *Phytochemistry Reviews* (2004), 3(1-2), 79-96.

⁵⁷ Chakar, F.S.; Ragauskas, A.J. Review of current and future softwood kraft lignin process chemistry. *Industrial Crops and Products* (2004), 20(2), 131-141.

⁵⁸ Chiang, Vincent L. Monolignol biosynthesis and genetic engineering of lignin in trees, a review. *Environmental Chemistry Letters* (2006), 4(3), 143-146.

⁵⁹ Halpin, C. Investigating and manipulating lignin biosynthesis in the postgenomic era. *Advances in Botanical Research* (2004), 41 63-106.

⁶⁰ Umetsu, M.; Man, X.; Okuda, K.; Tahereh, M.; Ohara, S.; Zhang, J.; Takami, S.; Adschiri, T. Biomass-assisted hydrothermal synthesis of ceria nanoparticle - A new application of lignin as a bio-nanopool. *Chemistry Letters* (2006), 35(7), 732-733.

⁶¹ Berry, B. C.; Lindquist, D.; Smith, J. P.; Viswanathan, T. A novel ferromagnetic conducting lignosulfonic acid-doped polyaniline nanocomposite. *Polymer Preprints* (American Chemical Society, Division of Polymer Chemistry) (2000), 41(2), 1110-1111.

⁶² da Silva, B. A.; Antunes, P. A.; Pasquini, D.; Curvelo, A. A. S.; Aroca, R. F.; Riul, A., Jr.; Constantino, C. J. L. Nanostructured films employed as sensing units in an "electronic tongue" system. *Journal of Nanoscience and Nanotechnology* (2007), 7(2), 510-514

⁶³ Diaz, Juan E.; Lallave, Manuel; Marquez, Manuel; Barrero, Antonio; Loscertales, Ignacio G. Electrospinning coaxial nanofibers for carbon nanofibers and nanotubes. *PMSE Preprints* (2006), 94, 69.