



## **ABSTRACTS**

**Wednesday, October 20, 2010**

**Plenary Session: Biorefinery Concepts for  
Chemicals and Products**

## ALTERING PLANT CELL WALL BIOSYNTHESIS TO IMPROVE BIOMASS PROCESSING

*John Ralph, Co-workers and Collaborators*

DOE Great Lakes Bioenergy Research Center, Madison, WI, and Department of Biochemistry, U. Wisconsin, Madison, and Department of Biological Systems Engineering, U. Wisconsin, Madison, and The Wisconsin Bioenergy Initiative, U. Wisconsin, Madison

[jralph@wisc.edu](mailto:jralph@wisc.edu)

Lignin remains one of the most significant barriers to the efficient utilization of cellulosic substrates, in processes ranging from ruminant digestibility to industrial pulping, and in the current focus on biofuels production. Up- and down-regulating genes for enzymes in the monolignol biosynthetic pathway can produce at times striking alterations in lignin composition and structure that may positively or negatively impact a given processes. A few approaches hold considerable promise for reducing the severity and energy demands of various processes. At the same time, we are gaining some insight into what features are required by ideal lignin monomers and are beginning explorations into possible lignin monomer replacements. And now that monomer substitution in the lignification process is well authenticated in various transgenic plants, it is opportune to begin explorations into actually *designing* lignins to improve the ease with which they can be removed from the cell wall. Here we highlight the logic behind one approach, our idea of utilizing monolignol conjugates to introduce readily (industrially) cleavable bonds into the backbone of the polymer. Already, model-cell wall studies have shown dramatic improvements in processing efficiency, reducing the temperature required for pulping, for example. Successfully engineering plants to incorporate such monomer conjugates, or other monomer replacement strategies, therefore has the potential to vastly reduce the energy demands of processing.

An underlying theme will be the use of NMR methods to structurally profile unfractionated plant materials, before and after (pre)treatments, to aid in the selection of ideal plant materials and in the characterization of cell wall alterations occurring during conversion processes.

## RECENT EFFORTS FOR DEPOLYMERIZATION OF CELLULOSE IN IONIC LIQUIDS

*Roberto Rinaldi*

Max-Planck-Institut für Kohlenforschung  
Kaiser-Wilhelm-Platz 1  
Mülheim an der Ruhr, Germany

[rinaldi@mpi-muelheim.mpg.de](mailto:rinaldi@mpi-muelheim.mpg.de)

Cellulose is a renewable and widely available feedstock. It is a biopolymer that is typically found in wood, straw, grass, municipal solid waste, and crop residues. Its use as raw material for biofuel production opens up the possibility of sustainable biorefinery schemes that do not compete with food supply. Tapping into this feedstock for the production of biofuels and chemicals requires - as the first step - its depolymerization or its hydrolysis into intermediates that are more susceptible to chemical and/or biological transformations. In this contribution, the recent efforts for depolymerization of cellulose, especially in ionic liquids, will be discussed in details.

## TAILORING BIOMASS TO FIT THE BIOFUELS PIPELINE

Maureen C. McCann

Purdue University  
Bindley Bioscience Center  
1203 W. State Street  
West Lafayette, IN 47906

[mmccann@purdue.edu](mailto:mmccann@purdue.edu)

Second-generation biofuels will be derived from lignocellulosic biomass using biological catalysts to convert the carbon in plant cell wall polysaccharides to ethanol or other biofuels. The Center for Direct Catalytic Conversion of Biomass to Biofuels (C3Bio) is a DOE-funded Energy Frontier Research Center, which aims to develop transformational technologies to maximize the energy and carbon efficiencies of biofuels production. Heterogeneous chemical catalysis using inorganic and robust catalysts provides an alternative strategy to biological fermentation routes for the production of advanced biofuels, including alkanes and the aromatic components characteristic of gasoline. Designing new catalysts for converting lignocellulosic biomass to biofuels requires understanding the interactions of catalysts with the chemical and physical structures of the biomass at scales ranging from atoms to macromolecules. We are also exploring thermal treatments, including fast-hydropyrolysis, that may generate a bio-crude oil suitable for catalytic upgrading. Our preliminary data show that the composition of maize stover impacts the spectrum of fragments derived from pyrolysis molecular-beam mass spectrometry (PyMBMS). This method relies on thermal degradation of the cell wall constituents under anoxic conditions to provide information about hexose and pentose content, and the content and composition of phenolic compounds derived from lignin and hydroxycinnamic acids. The fact that we can detect changes in spectral profiles from PyMBMS of different genetic lines of maize indicates that specific alterations in the carbohydrate-lignin architecture of the cell wall may improve the selectivity of reaction products and the efficiency of fast-hydropyrolytic and catalytic conversion. We are generating variants of cell wall structures by manipulation of endogenous plant genes, in both Arabidopsis and maize, and transgenic lines that incorporate catalysts directly or functionalized sites for future catalysis as the plants grow, that is, biomass tailored for its end-use in new conversion processes.

## REDESIGNING FEEDSTOCKS FOR IMPROVED BIOPROCESSING

*Richard A. Dixon, Huanzhong Wang, Qiao Zhao, Lina Gallego-Giraldo, Fang Chen, Chunxiang Fu, Zeng-Yu Wang, Jonathan Mielenz*

Samuel Roberts Noble Foundation, Plant Biology and Forage Improvement Divisions  
2510 Sam Noble Parkway  
Ardmore, Oklahoma, USA (RAD, HW, QZ, LG-G, FC, CF, Z-YW)  
Biosciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA (JM).  
BioEnergy Science Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA (RAD, FC, Z-YW, JM)

[radixon@noble.org](mailto:radixon@noble.org)

Economic and environmental factors favor the adoption of lignocellulosic bioenergy crops for liquid biofuel production. However, lignocellulosic biomass is recalcitrant to saccharification, and this is, at least in part, due to the presence of the phenylpropanoid-derived cell wall polymer lignin. Analysis of alfalfa plants in which lignin content and composition had been modified through independently down-regulating each of eight enzymes in the lignin pathway revealed that reduction in lignin content increased sugar release from dried biomass by both acid pre-treatment (hot sulfuric acid) and digestion by a cellulase mixture (1). Acid pre-treatment could effectively be omitted in the processing of biomass with the lowest lignin levels. Transfer of this technology to switchgrass both improves ethanol yields and reduces enzyme loading for simultaneous saccharification and fermentation.

Genetic modification of the lignin biosynthetic pathway can sometimes result in decreased biomass yields. Mechanisms underlying these effects are currently under investigation. An alternative approach is to target transcriptional regulators of lignification, such that the whole pathway is turned on or off in specific cell types. We will describe the identification of two such regulators, one of which controls secondary cell wall formation in interfascicular fibers, the other of which acts as a negative regulator of secondary wall formation in pith cells. Experiments in model systems suggest that these genes may provide excellent targets for modifying plant architecture and cell wall composition in ways that will increase saccharifiable sugar content of dedicated lignocellulosic feedstocks.

- (1) Chen, F., and Dixon, R.A. (2007) Lignin modification improves fermentable sugar yields for biofuel production. *Nature Biotechnology* **25**, 759-761.

## The Efficient Conversion of Sugars, Cellulose, and Cellulosic Biomass into Furan- and Levulinate-Based Chemicals

*Mark Mascal, Edward B. Nikitin*

Department of Chemistry, University of California Davis  
1 Shields Avenue  
Davis, California

[mascal@chem.ucdavis.edu](mailto:mascal@chem.ucdavis.edu)

We describe a novel method to efficiently convert waste biomass (agricultural, municipal, forestry) into biofuels and value-added products. The process is completely chemical in nature, operates under mild conditions, involves no expensive catalysts, and produces no waste stream. The technology involves the acidic digestion of the carbohydrate content of biomass (cellulose, starch, sugars) in a biphasic reactor at 80 °C for 2-3 hours to give 5-(chloromethyl)furfural (CMF) as the main product in isolated yields of 80–90%. To our knowledge, no other method of biomass deconstruction gives such complete conversion of cellulose into a simple organic molecule. We present CMF here as an emerging renewable platform chemical, providing access to a versatile portfolio of derivatives, including non-toxic, energy-dense fuels, monomers for renewable plastics, and specialty chemicals (agricultural and pharmaceutical).

