Scientific Achievement

- All three major components of biomass (lignin, cellulose and xylan) are converted in two steps into high value chemicals with an overall 55% yield.

Significance and Impact

- Lignin as a natural aromatic polymer has great potential to be a source for liquid fuels and chemicals. Its selective conversion is key to the viability of future biorefineries.
- Our study demonstrates a method for transforming 69% of the lignin in Miscanthus into four aromatic compounds while separating the carbohydrate components as a solid primed for upgrading.

Research Details

- Reaction of Miscanthus biomass in alcohol solvent at 200 °C and 30 bar pressure results in fragmentation of lignin into soluble oligomers.
- Nickel catalyst supported on activated carbon depolymerizes lignin (CDL) fragments and deoxygenates (HDO) them to yield four phenolic products.
- The leftover carbohydrate byproduct (solid residue) is reacted in a second step in biphasic medium with iron chloride catalyst to make furfural and levulinic acid.

Work was performed at Purdue
Biomass accessibility analysis using electron tomography

Scientific Achievement
Developed new method for quantifying catalyst accessibility to biomass using 3D electron tomography.

Significance and Impact
- Our characterization over range of <5nm to >100nm catalyst sizes not possible with existing accessibility measures
- Image-based method suggests mechanisms for increased accessibility as opposed to bulk measures
- Quantify threshold where bottlenecks erase accessibility improvements

Research Details
- Pore network is summarized by computing distance contour tree using segmented 3D tomograms
- Efficient algorithm allows computing large range of catalyst sizes on large volumes
- Analyzed native, dilute acid + zipperclave, and dilute acid + steam explosion treated samples.

Targeting iron catalysts to cellulose microfibrils

Scientific Achievement
- Proof-of-concept that we can tailor biomass to incorporate chemical catalysts in living plants.

Significance and Impact
- Iron ions are inexpensive, earth-abundant catalysts that defibrillate and delaminate cell wall structure when used in pretreatments.
- By engineering plants to accumulate iron in their cell walls, the catalyst can be used at less than thousand-fold lower concentrations than for exogeneous treatments.
- Biomass yield is not compromised in transgenic plants.

Citation: Yang et al. (2016) Plant Biotechnology Journal, pp1-12, doi: 10.1111/pbi.12557
Work was performed at Purdue University and NREL

Research Details
- We engineered CBM-IBP fusion polypeptides composed of a carbohydrate-binding module family 11 (CBM11) and an iron binding peptide (IBP) for secretion into Arabidopsis and rice cell walls.
- Shoot iron concentrations in cell walls, release of glucose by hydrolases, and amounts of dry biomass are increased compared to control genotypes.
Lignin deposition impacts cellulose organization in the plant cell wall

Scientific Achievement
- Direct demonstration that altering lignin content alters the molecular organization of cellulose in plant cell walls

Significance and Impact
- Assembly of plant cell walls is a complex process. Perturbation of one component may alter final structure in unexpected ways
- Lignin deficiency led to decrease in the order and orientation of cellulose fibrils in cell walls
- Distinctions between tissues were maintained in all variants even those with dramatic changes in cellulosic order
- The resilience of cellulose to degradative processes was much lower in plants rich in aldehyde- or H-lignin
- Engineering of lignin composition may provide route to plants with lowered recalcitrance to deconstruction

Research Details
- 16,000 diffraction patterns to study 7 Arabidopsis variants
- Combination of plant biochem and x-ray biophysics
- Correlation of structural change and digestibility
- Importance of serendipity in research

A thin section of Arabidopsis stem was scanned past a 5 μ x-ray beam to collect full diffraction patterns at each raster point. This generated a rich data set used to extract detailed information about cellulose order, orientation and content within the tissues that make up the stem.


Work was performed at Northeastern University, Purdue University and Argonne National Laboratory
Scientific Achievement
- An efficient stereospecific synthesis of lignin model dimers and trimers has been achieved

Significance and Impact
- Although lignin is optically inactive, biosynthesis leads to localized stereochemical differences
- Multiple biochemical processes show different rates of reaction with different lignin stereoisomers
- Localized stereochemical differences could be used for targeted deconstruction of lignin
- Access to stereochemically defined models to probe these differences is difficult
- Our approach offers access to both dimeric and trimeric lignin models
- Computational modeling reveals different conformational preferences for different isomers

Research Details
- Two approaches to synthesis; most recent version uses an Evans chiral auxiliary as the key step
- First approach (J. Org. Chem. 2015, 80, 1771-1780) required 9 steps; new approach sets stereochemistry in only 5
- Combination of two approaches leads to lignin trimer


Performed at the University of Tennessee Center for Renewable Carbon
Maleic Acid and Aluminum Chloride Catalyzed Conversion of Glucose to 5-(Hydroxymethyl) furfural and Levulinic Acid in Aqueous Media

Scientific Achievement

We synthesized a dual-function catalyst that can convert glucose to HMF, a fuel and chemical intermediate, in one pot with higher selectivity.

Significance and Impact

Maleic acid (MA) and AlCl₃ self-assemble into catalytic complexes that lower the activation for the rate limiting step (isomerization glucose to fructose) and enhances the selectivity of converting fructose to HMF and levulinic acid conversion.

Research Details

- ¹³C NMR spectra indicate that maleic acid stabilizes the open-chain form of glucose to facilitate isomerization of glucose to fructose.
- The catalyst complex converts fructose to HMF 1.7 × faster and with 3.3 × higher selectivity than a mixture of HCl and AlCl₃ at 180°C.
- Improved selectivity of glucose to HMF and levulinic acid lowers cost.


Work was performed at Purdue University
Cellulose crystal allomorph and crystallinity in fast pyrolysis

Scientific Achievement

Demonstrated that crystal allomorph and relative crystallinity of cellulose can impact the products produced by fast pyrolysis.

Significance and Impact

- relationship between cellulose crystal forms and their high temperature properties suggests a control point to tune the slate of pyrolysis products.
- treatments known to alter the crystal structure of cellulose may be able to direct the slate of pyrolysis products to more desirable set of intermediates.
- gaining control over the cellulose synthase complex to change cellulose properties could help overcome remaining barriers for deployment of biomass fast pyrolysis.

Research Details

- Cellulose allomorphs (I, II, III) of varying crystallinity generated from cotton linters.
- Cellulose fast pyrolysis with extensive MBMS, GCMS, TGA, XRD, and microscopic analysis of products and remaining char.

Thermo gravimetric analysis CI-H, CII-H, and CIII at all crystallinity levels exhibited the highest mass loss and the highest onset of mass loss temperature.


Work was performed at NREL
Identification of the phenol functionality in lignin degradation products via tandem mass spectrometry based on ion-molecule reactions

Scientific Achievement
Tandem mass spectrometry (MS²) based on reactions of deprotonated analytes with diethylmethoxyborane (DEMB) allows the identification of the phenol functionality in lignin degradation products while they are eluting from HPLC.

Significance and Impact
- Traditionally used collision-activated dissociation (CAD) cannot be used to distinguish many isomeric lignin degradation products
- Certain deprotonated isomeric compounds with both phenol and carboxylic acid, aldehyde, carboxylic acid ester or nitro functionalities can be differentiated via these reactions.

Research Details
- Either a stable DEMB adduct or an adduct that has lost a methanol molecule (DEMB adduct-MeOH) is formed for deprotonated phenols
- Deprotonated phenols with an adjacent phenol or hydroxymethyl functionality or a conjugated carboxylic acid functionality can be identified based on the formation of DEMB adduct-MeOH.

Work performed at Purdue University