Integrating Advanced Microscopy, Structural Modeling, and Multiphysics Simulation to Understand Transport Phenomena and Conversion Processes in Lignocellulosic Biomass

Dr. Peter Ciesielski
Senior Research Scientist
Biosciences Center

National Renewable Energy Lab
National Renewable Energy Lab (NREL), Golden, CO
Biomass exhibits a complex hierarchical structure that spans many orders of magnitude in length scales.

Presentation Outline

**Nanoscale:** Mechanics and Defects of Cellulose Nanofibrils

**Mesoscale:** Structure of Lignocellulose and Cell Walls

**Tissue Scale and Bulk Scale:** Biomass Particles
In lignocellulosic biomass, cell walls that contain the most cellulose are also typically the most recalcitrant.

**Transmission Electron Microscopy: Wild type Arabidopsis**

Parenchyma cell walls

Sclerenchyma cell walls

2 \( \mu \text{m} \)
Disrupting the structure of cell walls facilitates their enzymatic conversion to fuels and chemicals

Untreated corn stover cell walls

Steam exploded corn stover cell walls

21.5 % cellulose converted after 96 h of enzymatic digestion

88.0 % cellulose converted after 96 h of enzymatic digestion

Transmission Electron Tomography

- Electron beam
- Sample
- CCD camera

Scale Bar 500 nm
Transmission Electron Tomography

Scale Bar 500 nm
Transmission Electron Tomography

Image Tilt Series

Volume Reconstruction

software-assisted volume reconstruction

Scale Bars 500 nm
What is the structure of cellulose in process-relevant biomass?

Dilute Acid w/ Fe, Steam Explosion

Ammonia Fiber Expansion (AFEX)

Scale bars 200 nm

TEM tomography provides 3D reconstructions of the nanostructure of a sample and facilitates advanced quantitative analysis.

Curvature:
\[ \kappa(t) = \left| \frac{dT}{ds} \right| \]

Radius of curvature:
\[ r_{\kappa}(t) = \frac{1}{\kappa(t)} \]

Nearest-neighbor distance:
\[ \langle D_{i,j} \rangle = \frac{1}{n} \sum_{i=0}^{t_f} \sqrt{\left( h_i(t) - h_j(t) \right)^2} \]

TEM tomography provides 3D reconstructions of the nanostructure of a sample and facilitates advanced quantitative analysis.
Previously, we predicted kink-defects to form in cellulose fibrils by energy minimization of bent 36-chain models of cellulose I-β.

Kink-defects are clearly observable in cellulose nanofibrils by electron and scanning probe microscopy

Tunicate Cellulose (TEM)

![Image of Tunicate Cellulose](image)

Elazzouzi-Hafraoui et al., 2008

Cladophora Cellulose (AFM)

![Image of Cladophora Cellulose](image)

P. Ciesielski, NREL BSCL

Softwood Cellulose (TEM)

![Image of Softwood Cellulose](image)

Wang, Q., et al., 2012

Usov et al., 2015
TEM: Softwood Cellulose Nanofibrils
Disrupting the structure of cell walls facilitates their enzymatic conversion to fuels and chemicals

Untreated corn stover cell walls

Steam exploded corn stover cell walls

21.5 % cellulose converted after 96 h of enzymatic digestion

88.0 % cellulose converted after 96 h of enzymatic digestion

Can we develop mesoscale models of plant cell wall to help elucidate structure-property-function relationships?

Modeling the structure of lignocellulose with constructive solid geometry (CSG)

Lignocellulose composite

Cellulose component

Lignin component

Hemicellulose is added to cellulose fibril scaffolding based on fibril coordinates
Parametric sweep over kernel size in lignin generation function
Multiscale Modeling: Parameterizing bulk lignocellulose diffusion with molecular dynamics simulation

Interpolate local composition onto finite element grid

finite element model
Multiscale Modeling: Parameterizing bulk lignocellulose diffusion with molecular dynamics simulation

MD Simulations: Josh Vermaas
Multiscale Modeling: Parameterizing bulk lignocellulose diffusion with molecular dynamics simulation

MD Simulations: Josh Vermaas
Multiscale Modeling: Parameterizing bulk lignocellulose diffusion with molecular dynamics simulation

MD Simulations: Josh Vermaas
Finite element simulation of intra-cell wall diffusion

Mass Balance with Fick’s 2nd Law:

\[
\frac{\partial c_i}{\partial t} + \nabla \cdot ( -D \nabla c_i ) + \mathbf{u} \cdot \nabla c_i = R_i
\]
Intra-cell wall diffusion is anisotropic due to the arrangement of cell wall biopolymers.

- Normal to cellulose fibrils; Parallel to lamella
- Parallel to cellulose fibrils
- Normal to cellulose fibrils; Normal to lamella

Concentration (mol/m³)
Modeling heat transfer in lignocellulose

\[ k_{\text{cellulose}} = 5.7 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1} \text{ direction of glucan chains}; 0.72 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1} \text{ in transverse direction} \ (a) \]

\[ k_{\text{hemicellulose}} = 0.34 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1} \ (b) \]

\[ k_{\text{lignin}} = 0.38 \text{ W} \cdot \text{m}^{-1} \text{K}^{-1} \ (c) \]

\[ a \text{ Diaz et al., Biomacromolecules, 2014} \]
\[ b \text{ Green et al., J Chem. Phys., 1941} \]
\[ c \text{ Eitelberger et al., Comp. Sci. Technol., 2010} \]
Modeling heat transfer in lignocellulose

Evolution of heat flux profile

Heat Flux Magnitude (W/m²)

Time=0 s
Modeling heat transfer in lignocellulose

Hypothesis: The temporal volatization profile of lignocellulose is largely affected by the mesoscale architecture of lignocellulose.
Fast pyrolysis: rapid heat transfer is the key to high yields

Biomass particles retain internal tissue structure that varies substantially between feedstocks
In simulations of most biomass conversion processes, biomass particles are typically modeled using very simple geometries.

Particle size and morphology may be quantified for large ensembles simultaneously using analytical microscopy\(^1,2\)
Biomass microstructure visualized by Confocal Scanning Laser Microscopy (CSLM)
Measuring microstructural parameters from CSLM micrographs

Cell wall thickness is calculated from distance maps

Cell lumen dimensions are calculated by image binary analysis
CAD particle models are built with a Constructive Solid Geometry function that accepts morphological parameters as input.

CAD particle models are built with a Constructive Solid Geometry function that accepts morphological parameters as input.
CAD particle models are build with a Constructive Solid Geometry function that accepts morphological parameters as input.

CAD particle models are built with a Constructive Solid Geometry function that accepts morphological parameters as input.
CAD particle models are build with a Constructive Solid Geometry function that accepts morphological parameters as input.
CAD particle models are build with a Constructive Solid Geometry function that accepts morphological parameters as input.

Particle models constructed by these methods can represent large variation in particle sizes present in real feedstocks.
Comparison of microstructured particle models to SEM micrographs of real biomass particles of comparable size

Finite element simulation of Conjugate Heat Transfer

Conservation equations:

Mass
\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0
\]

Momentum
\[
\rho \frac{\partial \mathbf{u}}{\partial t} + \rho \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p + \nabla \left[ \mu \left( \nabla \mathbf{u} + (\nabla \mathbf{u})^T \right) - \frac{2}{3} \mu (\nabla \cdot \mathbf{u}) \mathbf{I} \right]
\]

Heat
\[
\rho C_p \left( \frac{\partial T}{\partial t} + (\mathbf{u} \cdot \nabla) T \right) = \nabla \cdot (k \nabla T)
\]
Finite element simulations of conjugate heat transfer

Simulations of heat transfer comparing particle size and biomass feedstock species

Mass balance with simple 5 homogenous reactions using kinetics reported by Chan and Di Blasi.¹

\[ \frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{u}) = \sum_j R_j \]

\[ R_j = \frac{\partial \rho_i}{\partial t} = k_j \rho_i = A_j \exp \left( \frac{-E_j}{RT} \right) \rho_i \]

Heat transfer

\[ \rho C_p \left( \frac{\partial T}{\partial t} + (\mathbf{u} \cdot \nabla) T \right) = \nabla \cdot (k \nabla T) \]

All materials properties and transport coefficients are calculated as a weighted average the local composition:

\[ \theta = \sum_i m_i \theta_i \]

\( m_i \) is the mass fraction of \( i^{th} \) species and \( \theta_i \) is its property (density, thermal conductivity, diffusivity)

¹Chan, W.-C. R et al. Modelling and experimental verification of physical and chemical processes during pyrolysis of a large biomass particle. Fuel 1985, 64
Finite element simulation of Fast Pyrolysis
Yield predictions for a ~ 3mm pine particle at 2 different moisture contents

- **Peak tar yield**; **Optimal Residence Time**
- Increase moisture content from 1.5 – 5%

- Incomplete conversion
- Tar cracking to light gases and condensing to char

**Product Yield**

- Wood
- Tar
- Light gas
- Char

**Heat-transfer delay time**

- **Time (s)**
  - 0
  - 2
  - 4
  - 6
  - 8
  - 10

**1.5% moisture**

**5% moisture**
Optimal residence time is highly dependent on particle size

Real feedstocks will always contain a distribution of particle sizes. Therefore, the optimal residence time for the feedstock ensemble will differ from that of any of the individual particles.

Particle Ensemble Calculations

- Particles are placed into “bins” based on their size.
- Individual simulations are performed using particle models representing each bin.
- Using the particle size distribution, the yield of the feedstock ensemble is estimated by summing the mass-weighted contribution of the particles in each bin.
These methods can be used to predict the optimal residence time for a given feedstock.

Using residence time estimations from reactor mixing models, we extended these models to predict reactor yields within 2% of experimental measurements (in collaboration with Gavin Wiggins and Stuart Daw from ORNL).
Acknowledgments

**Financial Support**

The constructive solid geometry algorithm, model visualization methods, and finite element simulation portions of this work were supported by the Computational Pyrolysis Consortium funded by the U.S. Department of Energy, BioEnergy Technologies Office (BETO). Computational resources were provided by the National Renewable Energy Sciences Center supported by the DOE Office of Energy Efficiency and Renewable Energy under contract DE-AC36-08G028308. The imaging, image analysis, and atomic modeling portions of this work was supported by the Center for Direct Catalytic Conversion of Biomass to Biofuels (C3Bio), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under award number DE-SC0000997. The views and opinions of the authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.