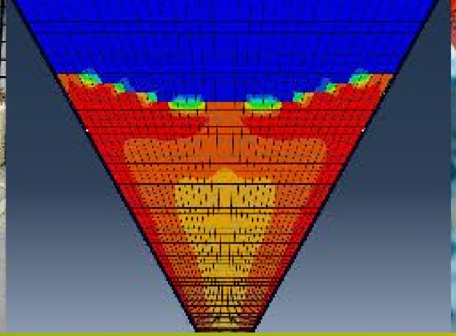
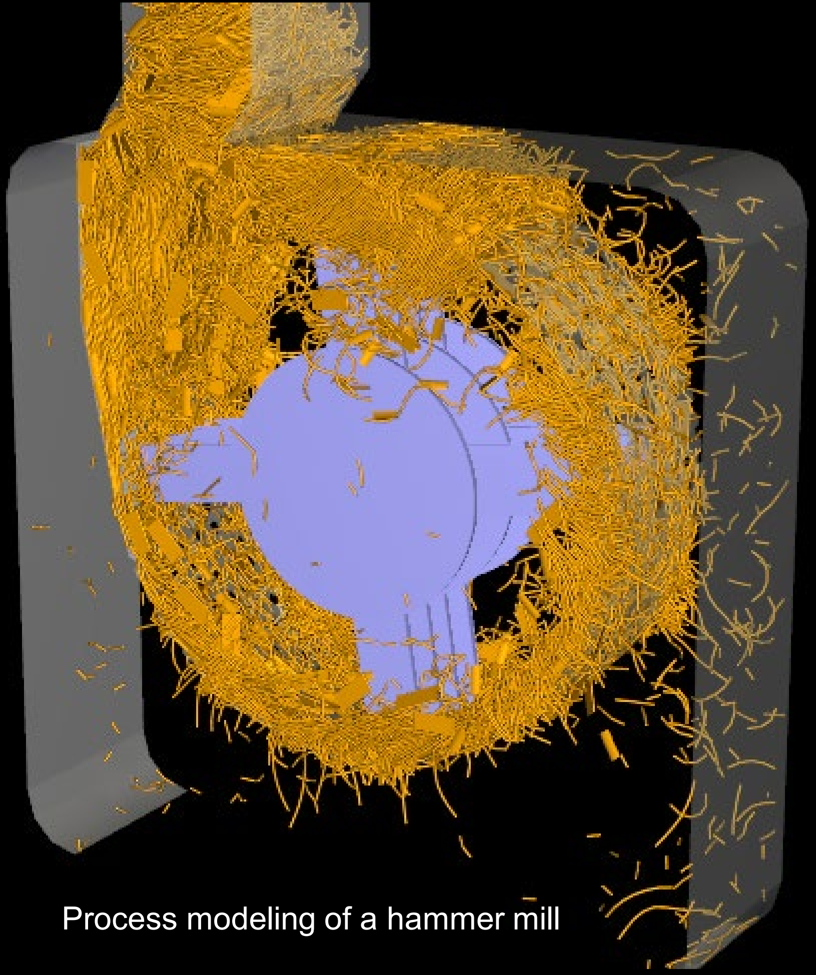





Developing Modeling Tools for the Emerging Biorefinery Industry

Part 1: Multiphysics Models for Biomass Preprocessing and Material Handling



Process modeling of a hammer mill

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FCIC Material Handling Task Lead

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Project coordination:

Allison Ray, Ph.D., INL Principal Investigator for FCIC

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FEEDSTOCK-CONVERSION INTERFACE CONSORTIUM

FCIC Task Organization

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FEEDSTOCK-CONVERSION INTERFACE CONSORTIUM

Feedstock → **Preprocessing** → **Conversion**

- **Task 2: Feedstock Variability**
- **Task 5: Preprocessing**
- **Task 6: Conversion High-Temp**
- **Task 7: Conversion Low-Temp**
- **Task 1: Materials of Construction**
- **Task 3: Materials Handling**

Enabling Tasks

- **Task X: Project Management**
- **Task 4: Data Integration**
- **Task 8: TEA/LCA**

Task X: Project Management: Provide scientific leadership and organizational project management

Task 1: Materials of Construction: Specify materials that do not corrode, wear, or break at unacceptable rates

Task 2: Feedstock Variability: Quantify & understand the sources of biomass resource and feedstock variability

Task 3: Materials Handling: Develop tools that enable continuous, steady, trouble free feed into reactors

Task 4: Data Integration: Ensure the data generated in the FCIC are curated and stored – FAIR guidelines

Task 5: Preprocessing: Enable well-defined and homogeneous feedstock from variable biomass resources

Task 6 & 7: Conversion (High- & Low-Temp Pathways): Produce homogeneous intermediates to convert into market-ready products

Task 8:Crosscutting Analyses TEA/LCA: Valuation of intermediate streams & quantify variability impact

Contributors and Collaborators

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FCIC Material Handling & Preprocessing Tasks are partners in BETO Consortium for Computational Physics and Chemistry (CCPC)

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William Rogers et al. — U.S. Department of Energy, National Energy Technology Laboratory

Preprocessing and Material Handling

Preprocessing and Material Handling (continued)

A Process Demonstration Unit (PDU) @ Idaho National Laboratory (dated 2019)

Process Upsets & Downtime

Relevance to TEA (Techno-Economic Analysis) and LCA (Life Cycle Assessment) :

- Commercial-scale conversion of biomass in biorefineries has remained limited.

- A primary challenge in the design of a biorefinery is the storage, transport, and reactor feeding of the biomass feedstocks.

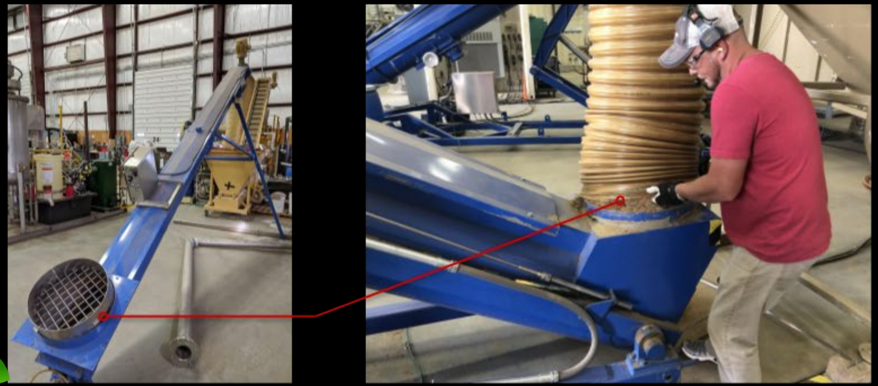
- Milling and handling have been prone to process upsets such as jamming and clogging, resulting in increased downtime and ultimately higher costs.

Typical biomass materials

Loblolly pine particles

Corn stover particles

Typical feedstock feeding and preprocessing issues

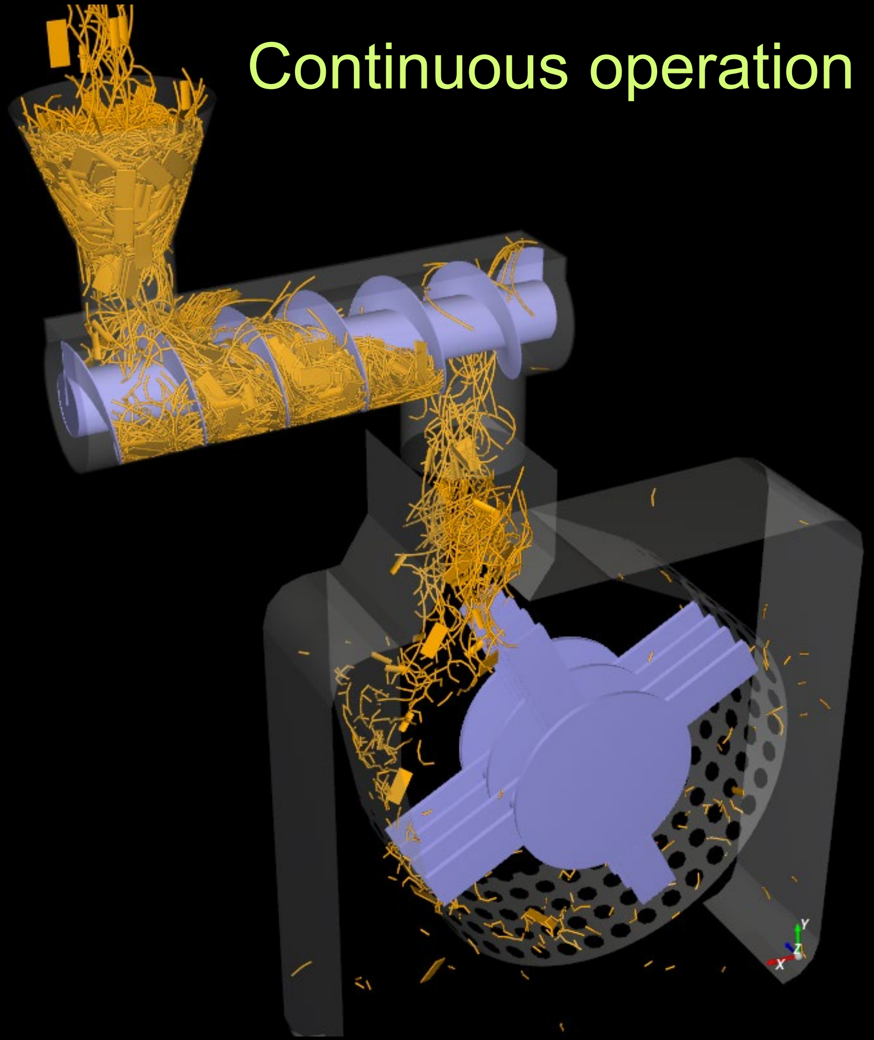


Material clogging in screw conveyor

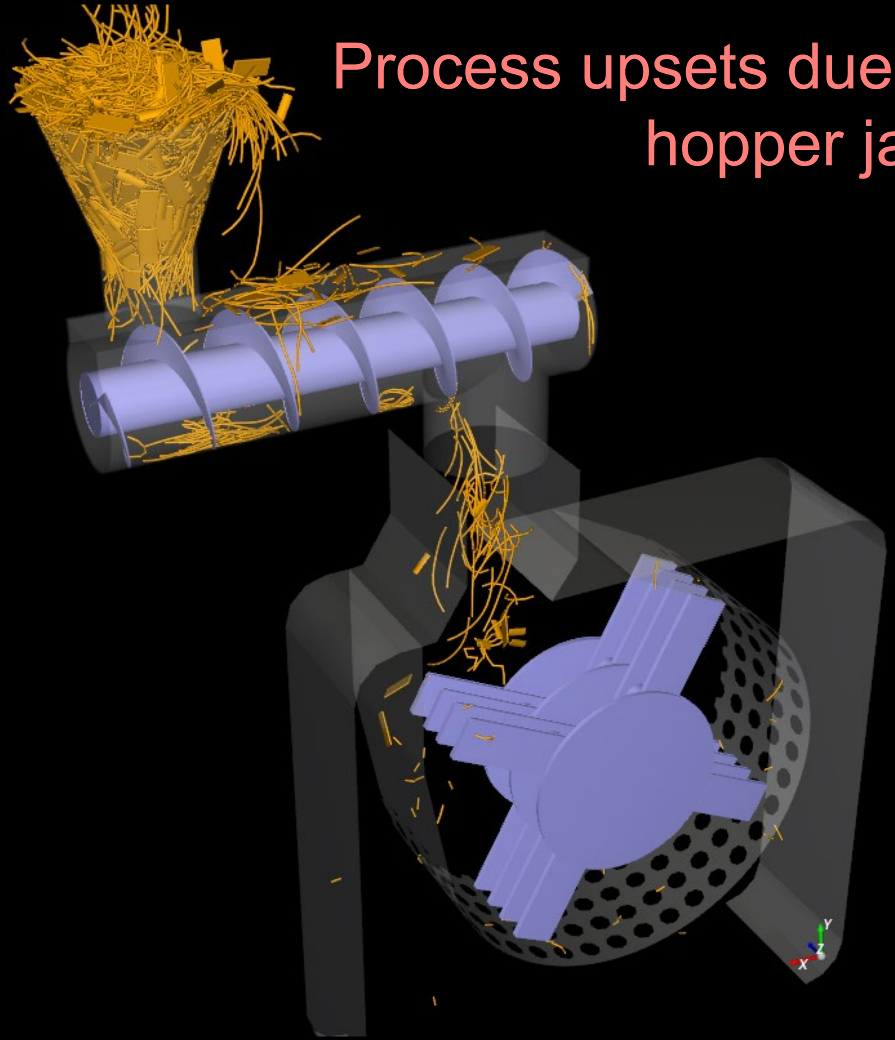
Material jamming in hammer mill grinder

A Numerical Demo of Process Upsets

Continuous operation



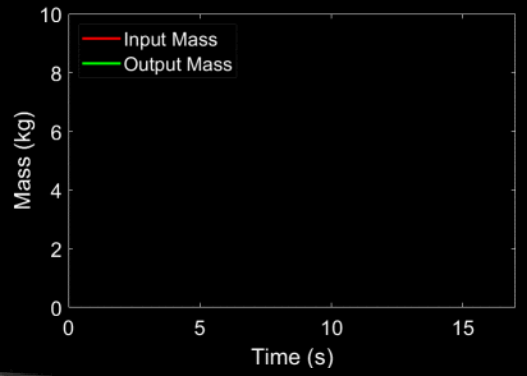
Process upsets due to hopper jam

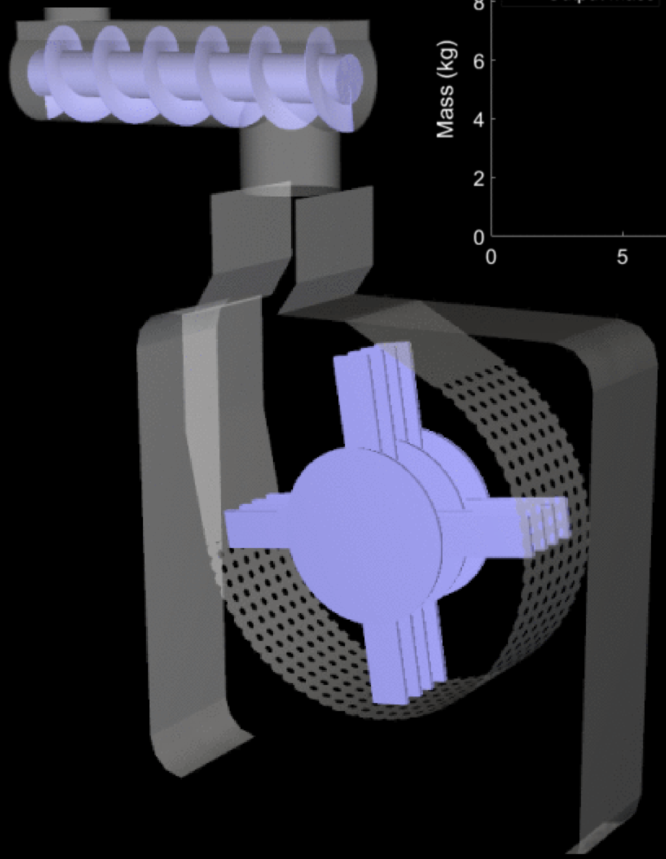


How Can Modeling Assist Quality-by-Design (QbD)?

An experiment-informed hammer milling model

Example





Modeling facilitates massive testing for QbD

- **CMA:** input PSD, particle shapes, etc.
- **CPP:** rotor speed, blade size, input mass rate, screen sieve size.
- **CQA:** output PSD, output mass rate etc.

Feedstock materials	Corn stovers
	Pine residuals
Morphology	shape & size
Water/moisture content	internal
	surface
Density	Intrinsic
	Envelope
Stiffness	Intrinsic
	Effective
Friction	Sliding
	Rolling
Adhesion	Other types

Description

- Developed a hammer milling model (particle flow & deconstruction) for assisting QbD

Value of new tool

- First-of-its-kind virtual laboratory
- Enabled fast massive testing and real-time performance diagnosis

Potential Customers & Outreach

- Feedstock preprocessing industry partner, biorefinery designers

How difficult is it to model biomass?

Granular flow models have been successfully applied for granular materials such as pharmaceutical and agricultural products, where the particles manifest relatively uniform **material attributes (MAs)** such as particle shapes, size distributions and material, and mechanical properties.

Milled pine particles

Milled corn stover particles

Challenges

- For the flow of irregular-shaped granular biomass, major challenges including:
  - How to formulate constitutive models to capture the complex behavior
  - How to account for the large variability of those MAs in the models
  - How to link the MAs to the model parameters.

Flow Models: Limitations & Best Practices

Knowledge

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Identified particle- & bulk-scale models suitable for the flow of milled biomass and recommended best practices (part 1)

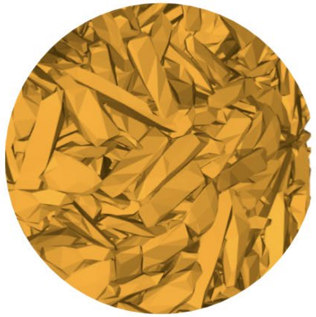
Current Knowledge Gap

- Lack of computational models suitable for biomass flow
- Lack of experimental data for new model development
- Lack of open-source model platforms for user coverage

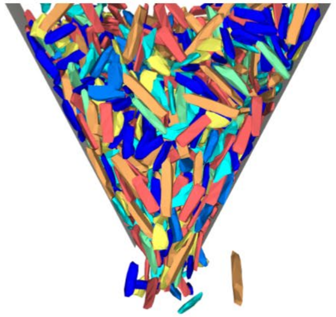
Achievement

- Identified limitations of existing models as knowledge base
- Recommended potential flow models & codes for biomass

Chipped loblolly pine particles (3-4 mm sieve size)

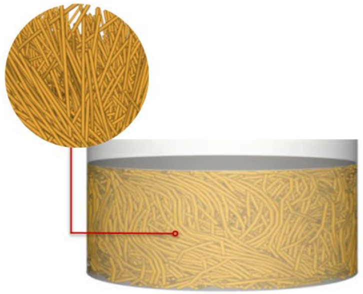


Custom polyhedral particles of arbitrary shapes

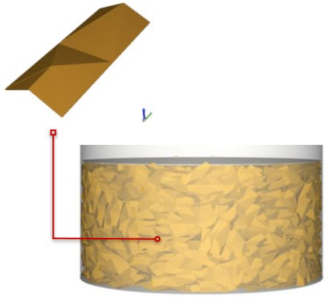


A v-shape hopper discharge of polyhedral particles

Milled corn stover particles (e.g. fiber & shell shapes)



Flexible fiber particles of arbitrary aspect ratio



Flexible thin shell of arbitrary aspect ratio

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Yidong Xia, Jonathan Stickel, Wencheng Jin, Jordan Klinger. A review of computational models for the flow of milled biomass I: Discrete-particle models, *ACS Sustainable Chemistry & Engineering*, 8, No. 16 (2020): 6142-6156. https://pubs.acs.org/doi/abs/10.1021/acssuschemeng.0c00402

Flow Models: Limitations & Best Practices

Knowledge

Identified particle- & bulk-scale models suitable for the flow of milled biomass and recommended best practices (part 2)

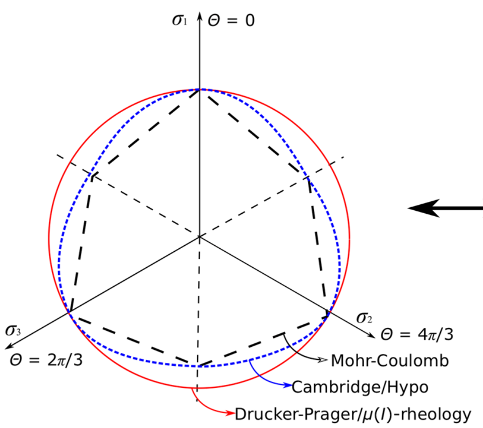
Current Knowledge Gap

- Lack of computational models suitable for the flow of milled biomass
- Lack of experimental data for supporting new model development
- Lack of open-source model platforms for user coverage

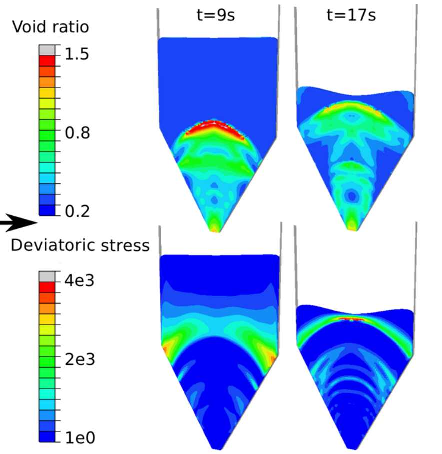
Achievement

- Identified limitations of existing models as knowledge base
- Recommended potential flow models & codes for biomass materials

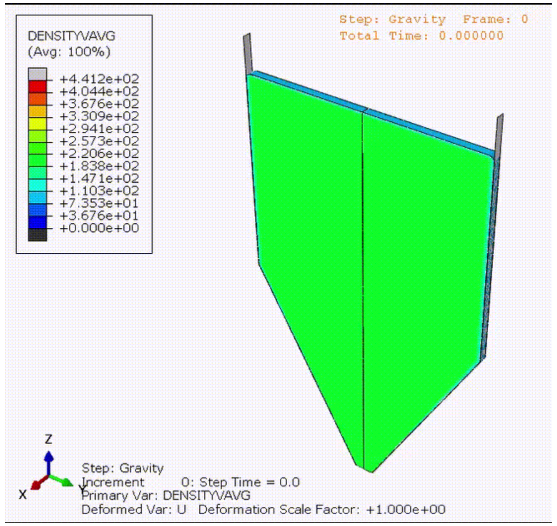
Wencheng Jin, Jonathan Stickel, Yidong Xia, Jordan Klinger. A review of computational models for the flow of milled biomass II: Continuum-mechanics models, *ACS Sustainable Chemistry & Engineering*, 8, No. 16 (2020): 6157-6172. https://pubs.acs.org/doi/abs/10.1021/acssuschemeng.0c00412



Constitutive model review



Application in milled biomass flow modeling



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Approach

Goal: Develop first-principles-based design tools that enable continuous, steady, trouble-free bulk flow transport through processing train to reactor throat.

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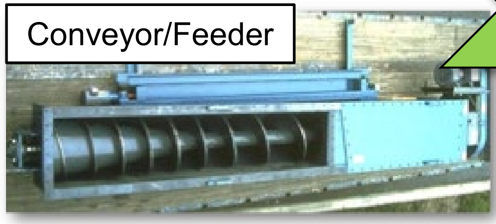
Process upsets in handling are a major challenge for lowering costs of biomass.

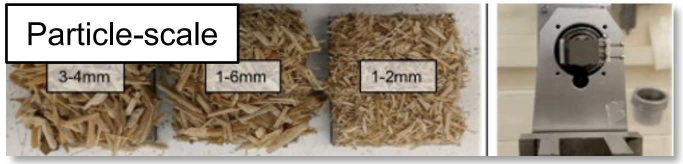
Hopper

Conveyor/Feeder

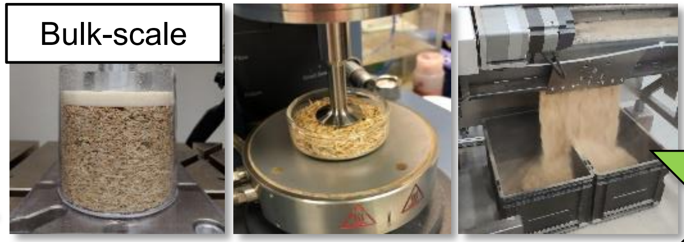


Experimental: multi-scale material characterization for state-of-the-art **knowledge** and **design charts**

Particle-scale



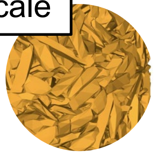
Bulk-scale



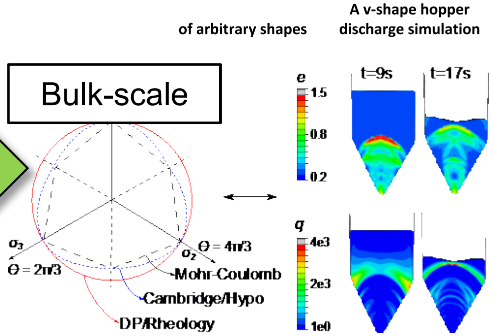
Pilot/demonstration-scale

Computational: experiment-validated multi-scale biomass mechanics & flow simulators as **open-source toolkits**

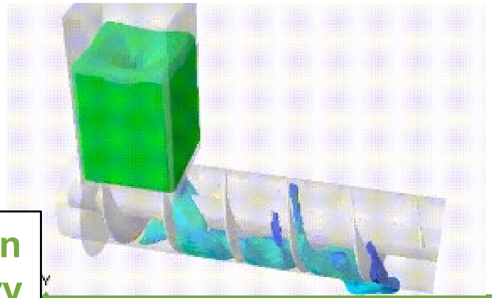
Particle-scale



Bulk-scale



Pilot/demonstration-scale



Outcome: efficient & effective design charts and simulators for bioenergy industries and other applicable areas

Preprocessing
CQAs (e.g., particle shape, PSD, feed rate)

CMAs & CPPs (e.g., particle shape, PSD, feed rate)
Material Handling
CQAs (controlled flow rate)

CMAs & CPPs (e.g., particle shape, PSD, feed rate)
Conversion
CQAs

CCPC Consortium for Computational Physics and Chemistry
U.S. DEPARTMENT OF ENERGY BIOENERGY TECHNOLOGIES OFFICE

FCIC Material Handling & Preprocessing Tasks are partners in BETO Consortium for Computational Physics and Chemistry

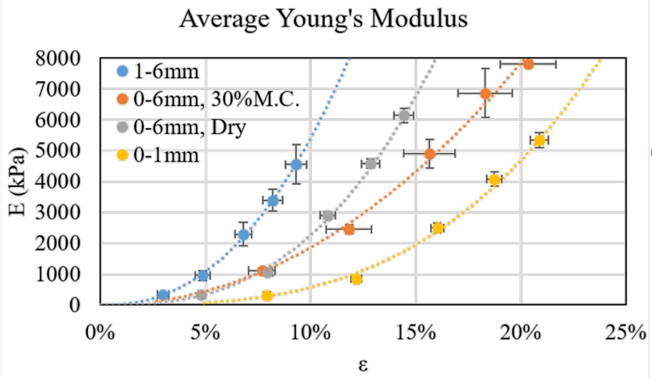
Approach (continued)

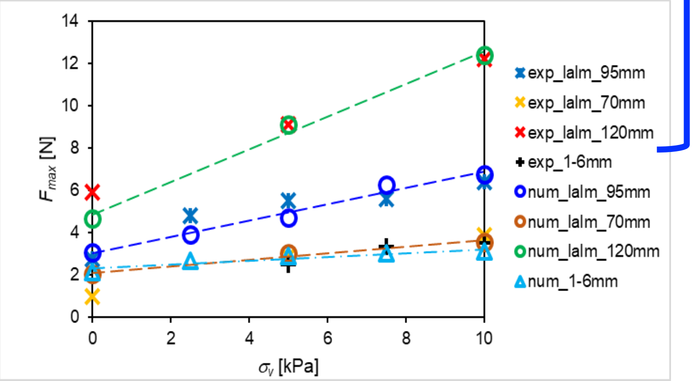
Metrics: 1) Operational reliability (e.g., design chart for consistent hopper flow at designed flow rate). 2) qualification of flow models (80% or higher agreement with experimental data.

Example: hopper design – experiment-validated modeling investigation of MA, PP influence on CQA

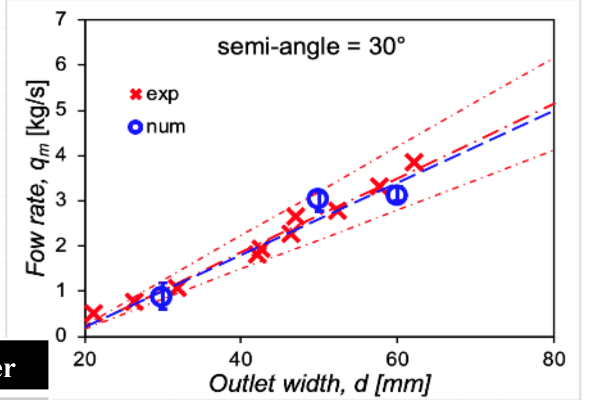
MA
Controllable attributes
Particle size distribution
Morphology (aspect ratio, shape, etc.)
Particle density/porosity
Surface energy
* Moisture content; * Ash content
Physical properties
Initial & critical state void ratio/density (bulk scale)
Critical state friction angle (bulk scale)
Elasticity (bulk scale)
Contact laws (particle scale)
* Time consolidation; * Scale-up effect

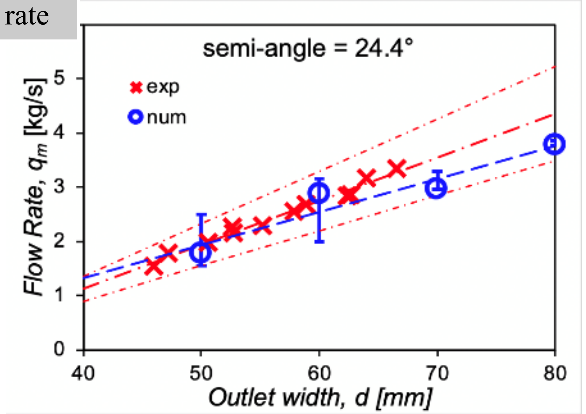
CPPs of Hopper
Feeding mass rate
Outlet mass rate
Depth
Side inclination angle
Outlet aperture size





CQAs of Hopper
Consistent flow at designed mass rate





Attributes denoted by * means not being currently studied in modeling

Figures from Wencheng Jin, Jordan Klinger et al. (2020)

Accomplishment and Progress – Material Handling

- Material Handling
  - Discrete particle models
    - A very brief overview
    - Biomass particle shape specification
    - A few DEM particle models that have been adopted in FCIC
  - Bulk flow models
    - A very brief overview
    - FEM hopper and conveyer flow model
    - FVM compressible-screw feeder model
    - FVM 1D pyrolysis screw-auger model

- **DEM**: Discrete Element Method
- **FEM**: Finite Element Method
- **FVM**: Finite Volume Method
- **CFD**: Computational Fluid Dynamics

Very Brief Overview of Discrete Particle Models

No one replaces another

Examples of biomass

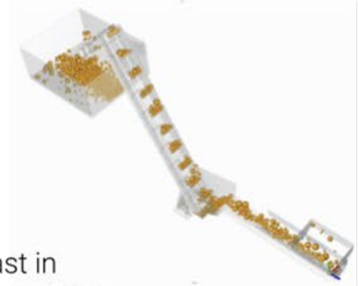
Loblolly pine

Corn stover

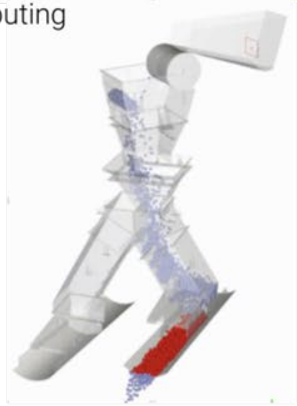
The evolving state-of-the-art of discrete element method (DEM) particle models

Mono-sphere model

Widely used in industry

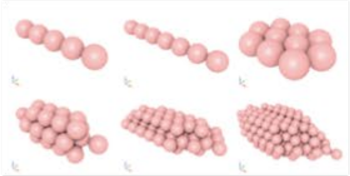


Fast in computing

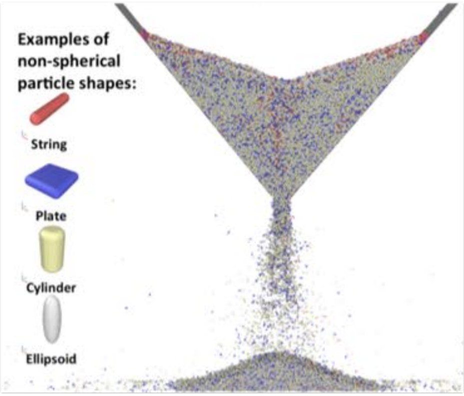


Clumped-sphere model

Bonded-sphere flexible clump

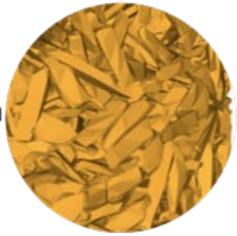


Multi-sphere rigid clump



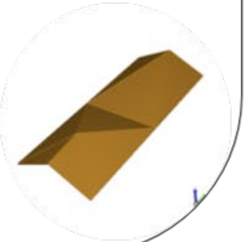
More advanced models ...

Custom arbitrary polyhedron



Flexible fiber

Flexible thin shell

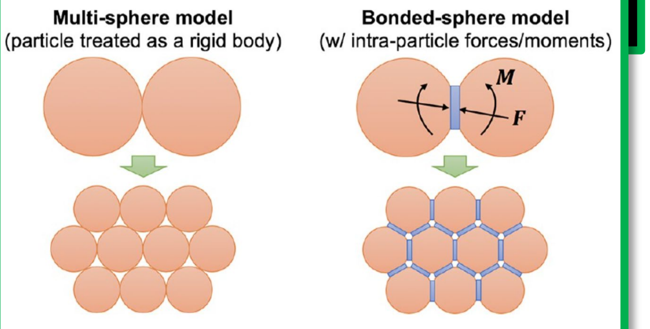


Cheng, Z., Leal, J., Hartford, C., Carson, J., Donohoe, B., Craig, D., Xia, Y., Daniel, R., Ajayi, O., Semelsberger, T. "Flow behavior characterization of biomass feedstocks", *Powder Technology*, 2021 (under review).

Early DEM Models for Biomass Particle Flow

Multi-sphere (rigid) and bonded-sphere (flexible) DEM particle models

- Advantages: simple surface contact detection
- Biomass applications: Pines (Xia et al, 2019) switchgrass (Guo et al. 2020)
- Limitation: (1) Limited shape complexity; (2) Expensive for certain shapes like long fiber-like particles, corn stover



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Yidong Xia, Zhengshou Lai, Tyler Westover, Jordan Klinger, Hai Huang, Qiushi Chen, "Discrete element modeling of deformable pinewood chips in cyclic loading test", *Powder Technology*, Vol 345, 1 March 2019, Pages 1-14. https://doi.org/10.1016/j.powtec.2018.12.072

Yuan Guo, Qiushi Chen, Yidong Xia, Tyler Westover, Sandra Eksioglu, Mohammad Roni, "Discrete element modeling of switchgrass particles under compression and rotational shear," Biomass & Bioenergy, Vol. 141, No. 105649, Oct. 2020. https://doi.org/10.1016/j.biombioe.2020.105649

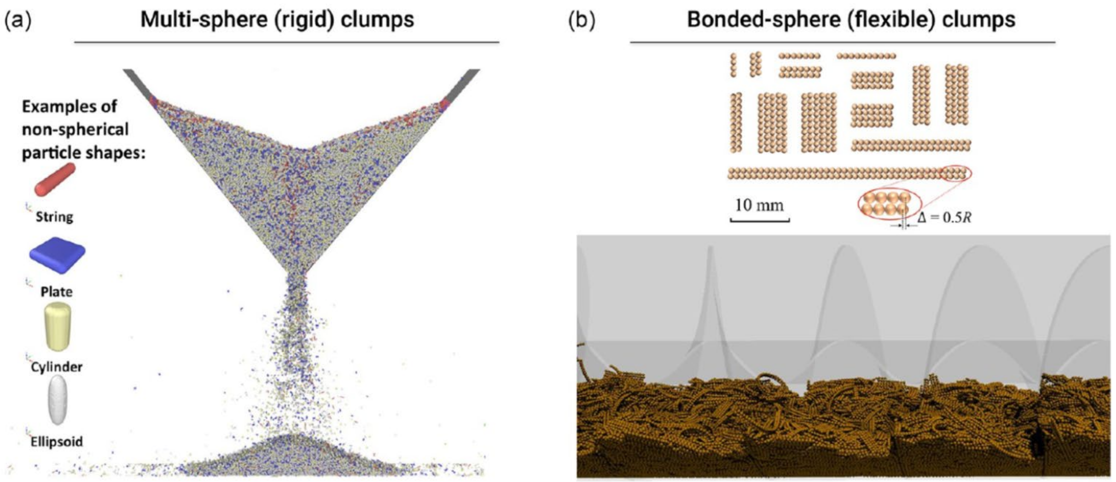


Figure 4. Composite-sphere models for milled biomass: (a) multisphere models for hard wood chips and (b) bonded-sphere models for flexible chopped switchgrass fragments.

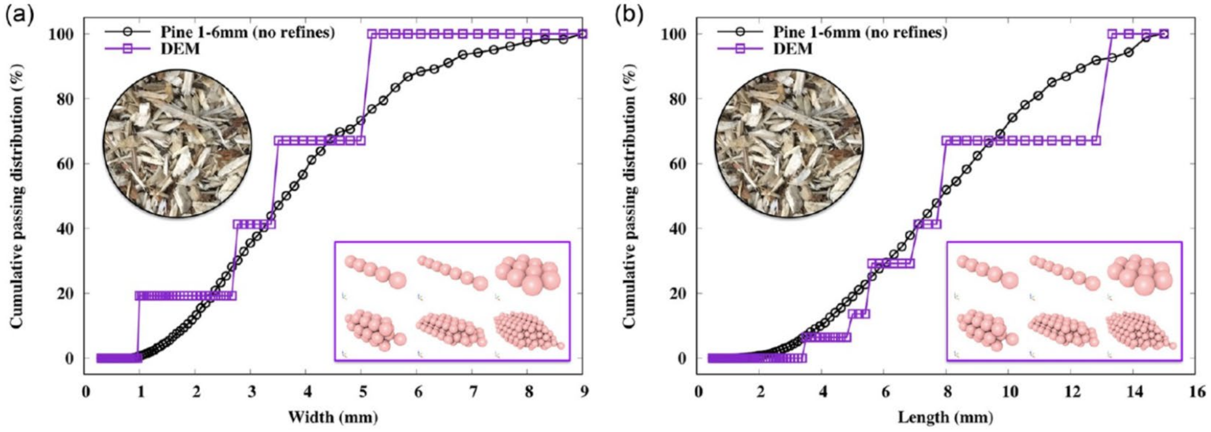
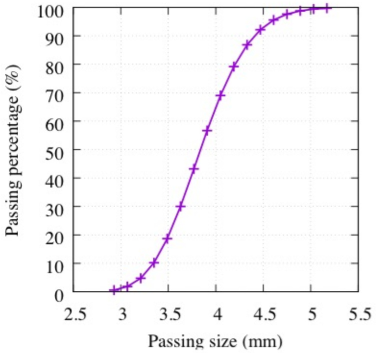


Figure 5. Approximation of (a) width and (b) length distributions of the physical loblolly pine particles (smooth curves) using the bonded-sphere DEM model with six shape templates and thus finite width and length distribution (staircase lines) (adapted with permission from Xia et al.,[45] Copyright 2019, Elsevier). Each bonded-sphere shape template represents real pine particles for a certain range of sizes. As a result, the cumulative distributions of the DEM particles show steps with each step corresponding to the size of a shape template.

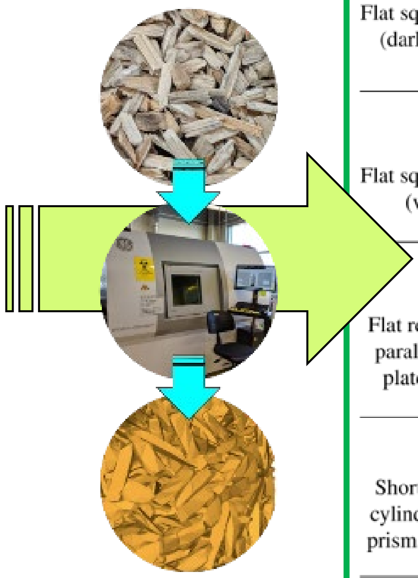
Shape Specification for Biomass Particles

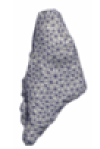
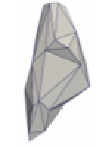
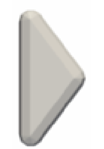
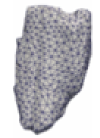
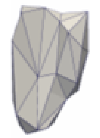
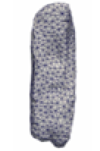
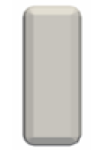
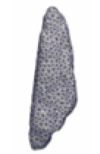
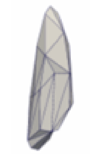
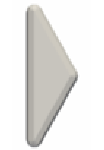
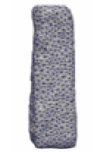
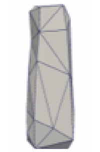
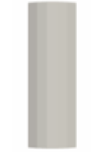
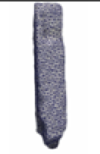
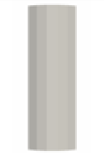
Tools



	Types	Shape description	No. of particles	% No. of particles
(a)		Flat square flakes (dark brown)	38	6.2%
(b)		Flat square flakes (white)	153	25.1%
(c)		Flat rectangular parallelepiped plates/flakes	116	19.0%
(d)		Short needles, cylinders, rods, prisms (4 faces)	171	28.1%
(e)		Medium needles, cylinders, rods, prisms (4 faces)	107	17.6%
(f)		Long needles, cylinders, prisms (4 faces)	24	3.9%

Nano-CT



Types	Example particle	EX-POLY	HIGH-POLY	LOW-POLY	SPHERO-POLY
(a) Flat square flakes (dark brown)	2.5 x 5.2 x 9,9 (mm^3)				
(b) Flat square flakes (white)	2.2 x 5.6 x 8.6 (mm^3)				
(c) Flat rectangular parallelepiped plates/flakes	2.5 x 3.8 x 11.6 (mm^3)				
(d) Short needles, cylinders, rods, prisms (4 faces)	2.6 x 4.8 x 14.1 (mm^3)				
(e) Medium needles, cylinders, rods, prisms (4 faces)	3.1 x 4.9 x 16 (mm^3)				
(f) Long needles, cylinders, prisms (4 faces)	3.6 x 4.6 x 18.7 (mm^3)				

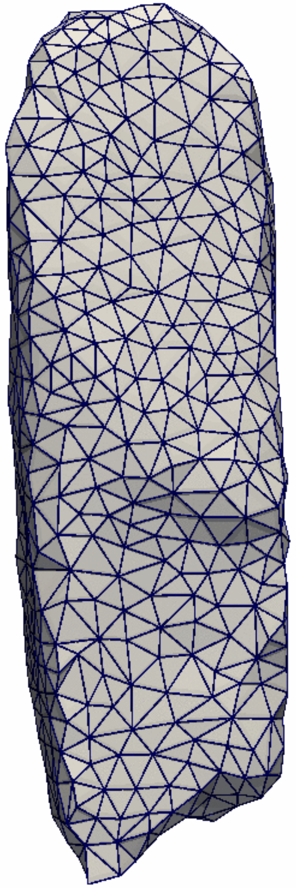
Yidong Xia, Feiyang Chen, Jordan Klinger, Joshua Kane, Tiasha Bhattacharjee, Robert Seifert, Oyelayo O. Ajayi, Qiushi Chen, "Assessment of a tomography-informed polyhedral discrete element modeling approach for complex-shaped granular woody biomass in stress consolidation", submitted to *Biosystems Engineering*, 2021 (under review).

A Closer Look at the Fractured Pine Particles

15 micrometer resolution

"Extreme"-resolution polyhedron

Coarse-graining for DEM modeling



"High"-resolution polyhedron

Polyhedral DEM for Pine Particle Physics

Tools

XCT-informed polyhedral DEM for fundamental flow physics of bulk fractured pine particles

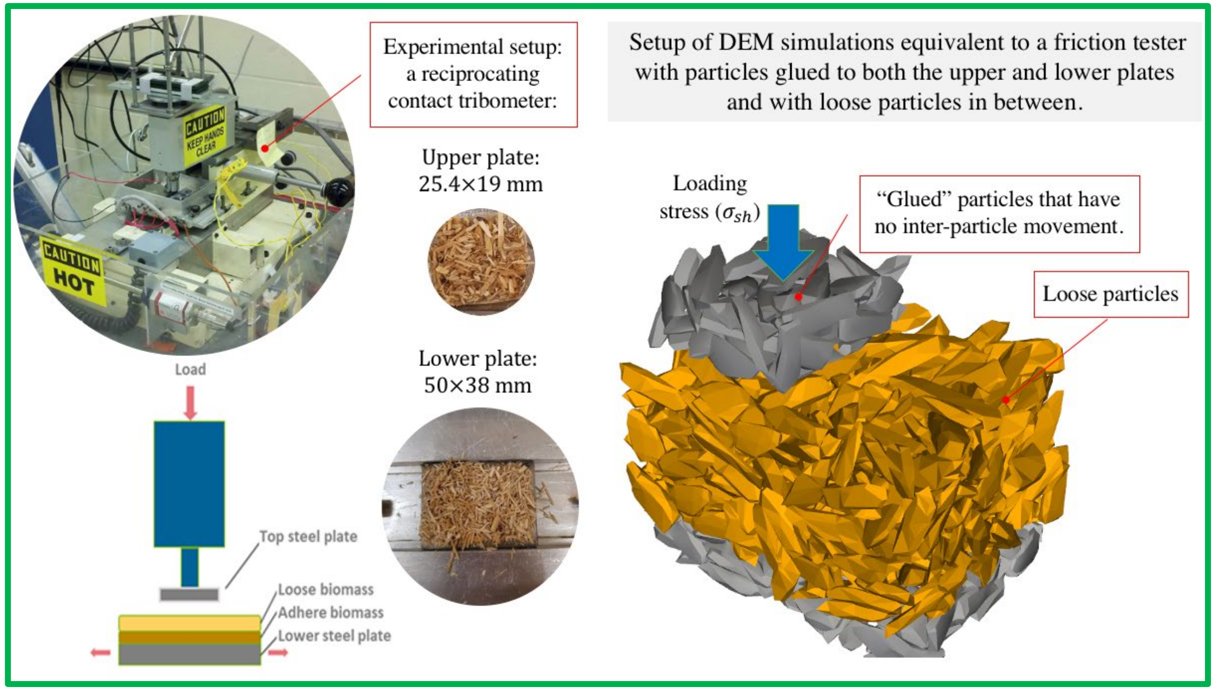
Description

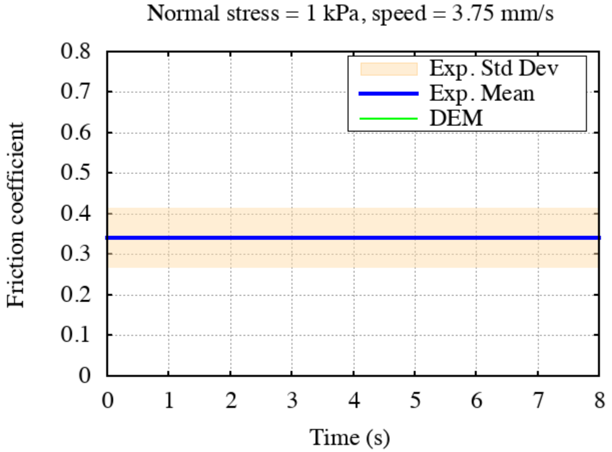
- For study of the influence of particle morphologies (shape, size, etc.) and contact force models as CMAs in stress consolidation.

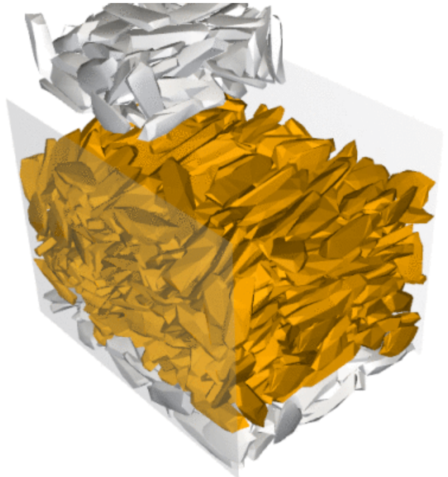
Value of new tool

- First-of-its-kind virtual laboratory for biomass particle mechanics.

Yidong Xia, Feiyang Chen, Jordan Klinger, Joshua Kane, Tiasha Bhattacharjee, Robert Seifert, Oyelayo O. Ajayi, Qiushi Chen, "Assessment of a tomography-informed polyhedral discrete element modeling approach for complex-shaped granular woody biomass in stress consolidation", *Biosystems Engineering*, 2021 (under review).

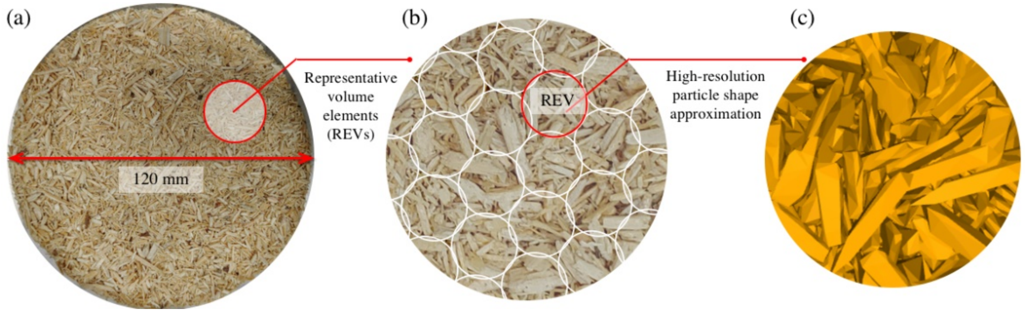


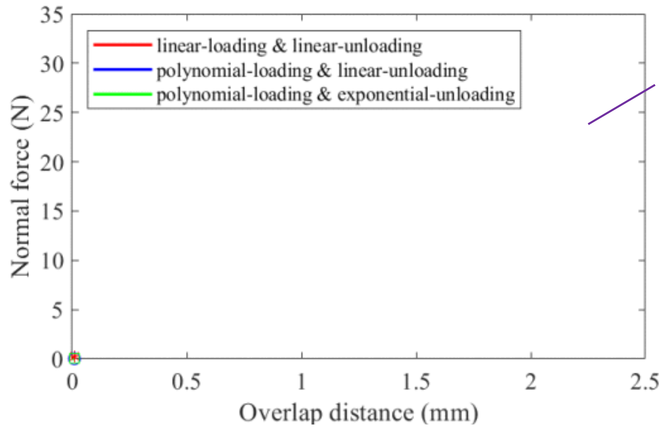




Coarse-grained DEM for Bulk Biomass Flow

Tools





--- Commercial DEM software
--- FCIC sponsored DEM codes
--- FCIC sponsored DEM codes

A coarse-grained DEM with hysteretic nonlinear force-displacement contact laws

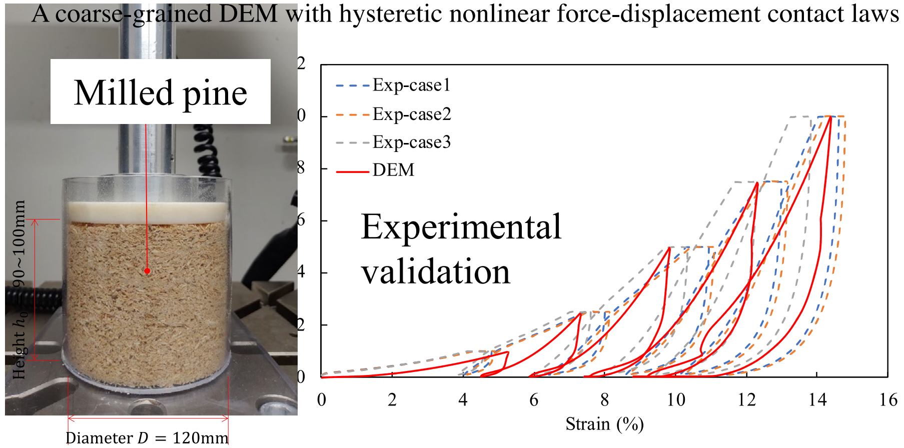
An HPC-enabled open-source coarse-grain DEM for bulk biomass flow

Description

- An HPC-enabled open-source DEM package with low-cost, semi-empirical mechanistic contact laws.

Value of new tool

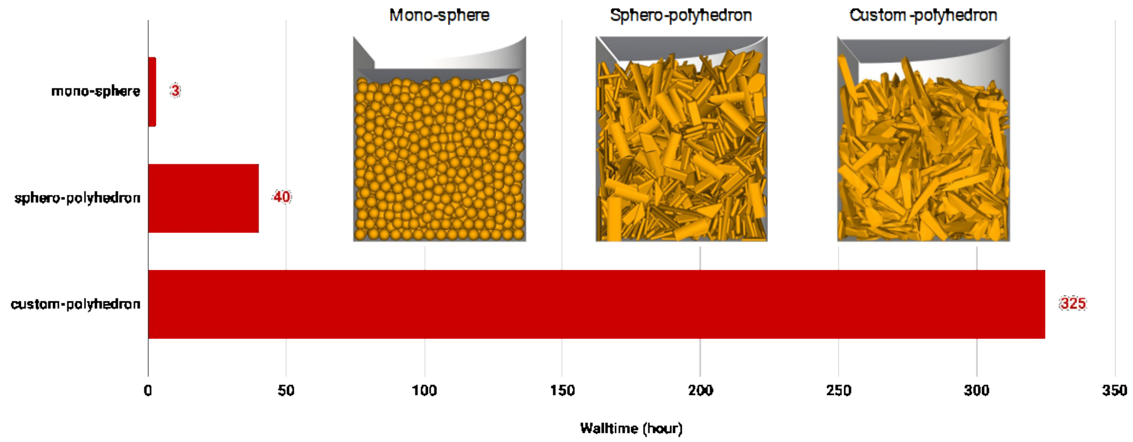
- First-of-its-kind virtual laboratory for biomass particle mechanics.
- Open-source strategy maximizes flexibility of DEM development.



DOE HPCs enable determination of DEM biomass particle model parameters with 100,000 simulations in parallel!

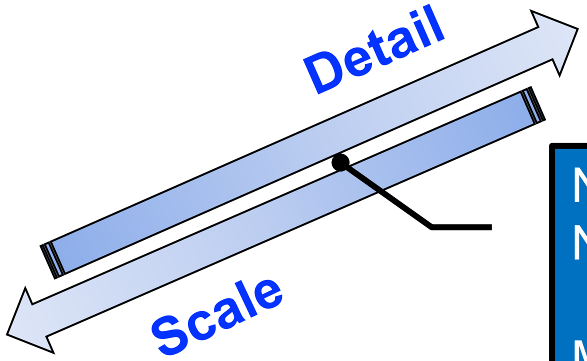
Xia, Y. Chen, F., Klinger, Bhattacharjee, Chen, Q. "A nonlinear hysteretic contact model for the discrete element modeling of strain hardening of woody biomass", 2021 (in preparation)

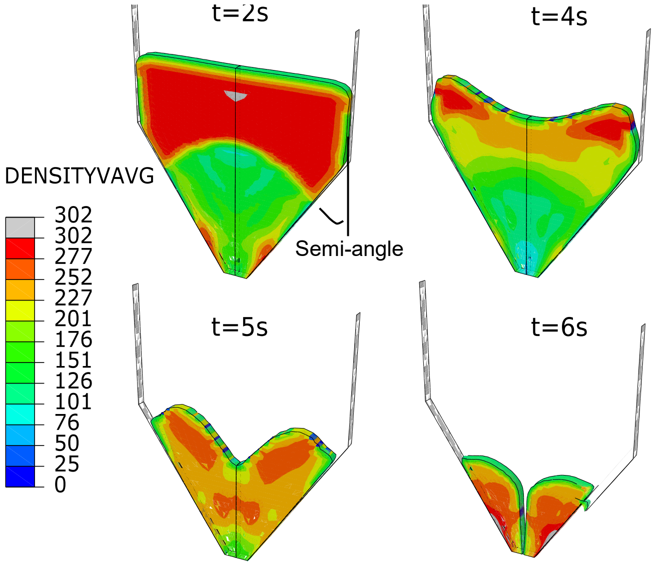
Limitations of Particle-based Models



DEM particle axial shear simulation:

- Size: ~50mm (~2000 particles)
- Resource: 4 CPU cores
- Cost: **300 hours** with polyhedral DEM model
- Cost: **3 hours with** coarse-grained DEM model





FEM pilot-scale hopper simulation
[Jin et al, 2020]:

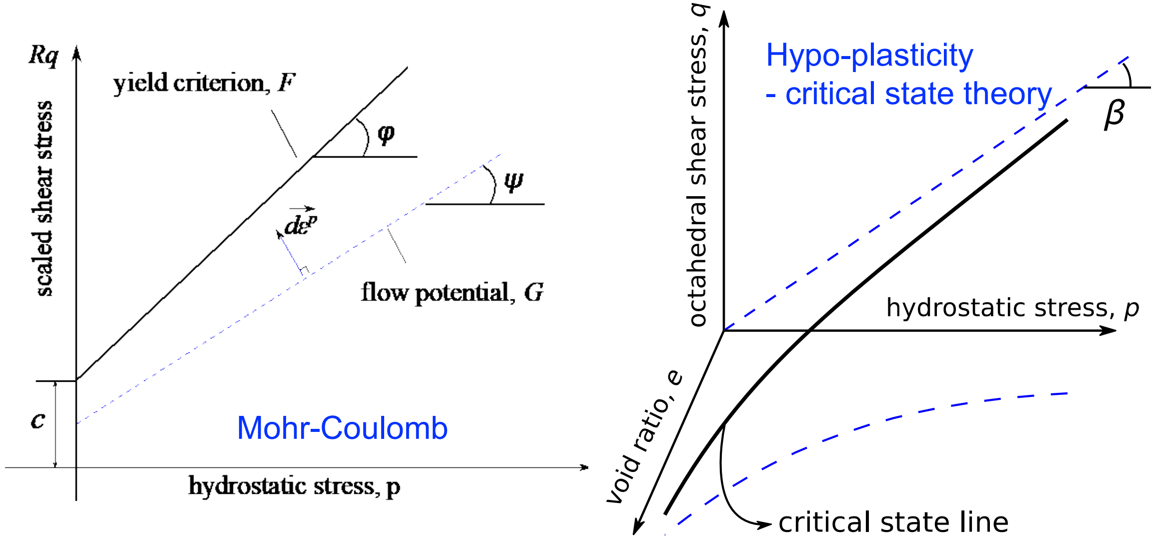
- Size: ~1000mm;
- Resource: 32 CPU cores
- **Cost: 2 hours**

No access to HPC?
Not a problem.

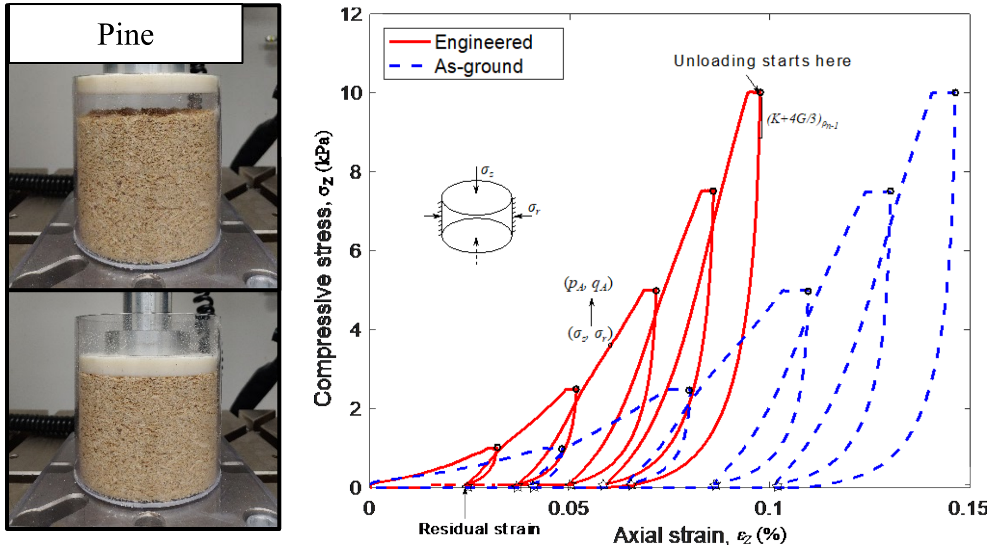
Most simulations shown here require only a good personal workstation to complete within a reasonable amount of time.

State-of-the-art Constitutive Models

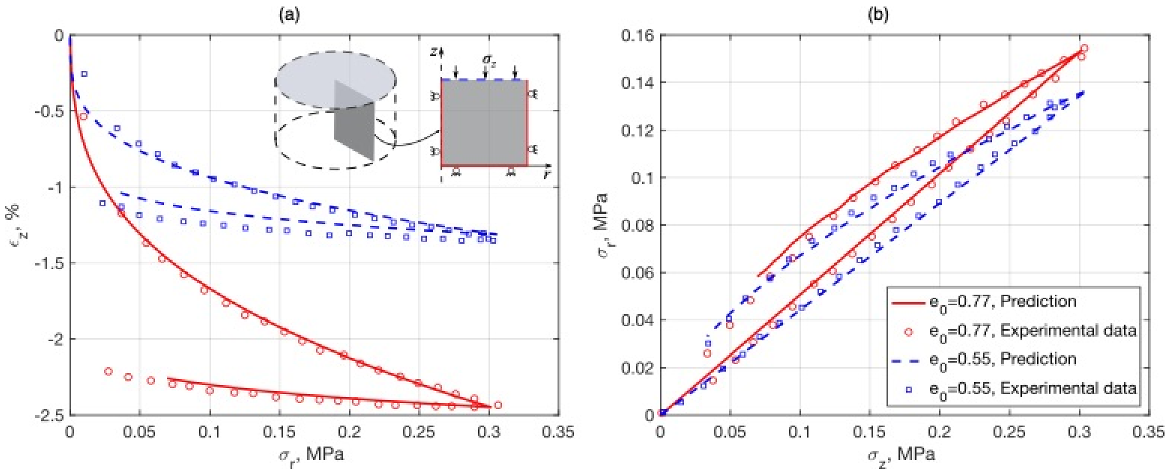
Observed Material Behavior	Mohr-Coulomb	Hypo-plasticity
Density & pressure dependent nonlinear elasticity	✗	✓
Critical state behavior	✗	✓
Stress dependent shear flow	✓	✓
Compaction induced hardening	✗	✓
Dilation induced softening	✗	✓
Shear rate dependency	✗	✗



Comparison of yield (flow) rule between Mohr-Coulomb and Hypo-plasticity



Lab test observed nonlinear elasticity



Hypo-plastic model predicted nonlinear elasticity

Continuum Flow Theories and Models

Knowledge

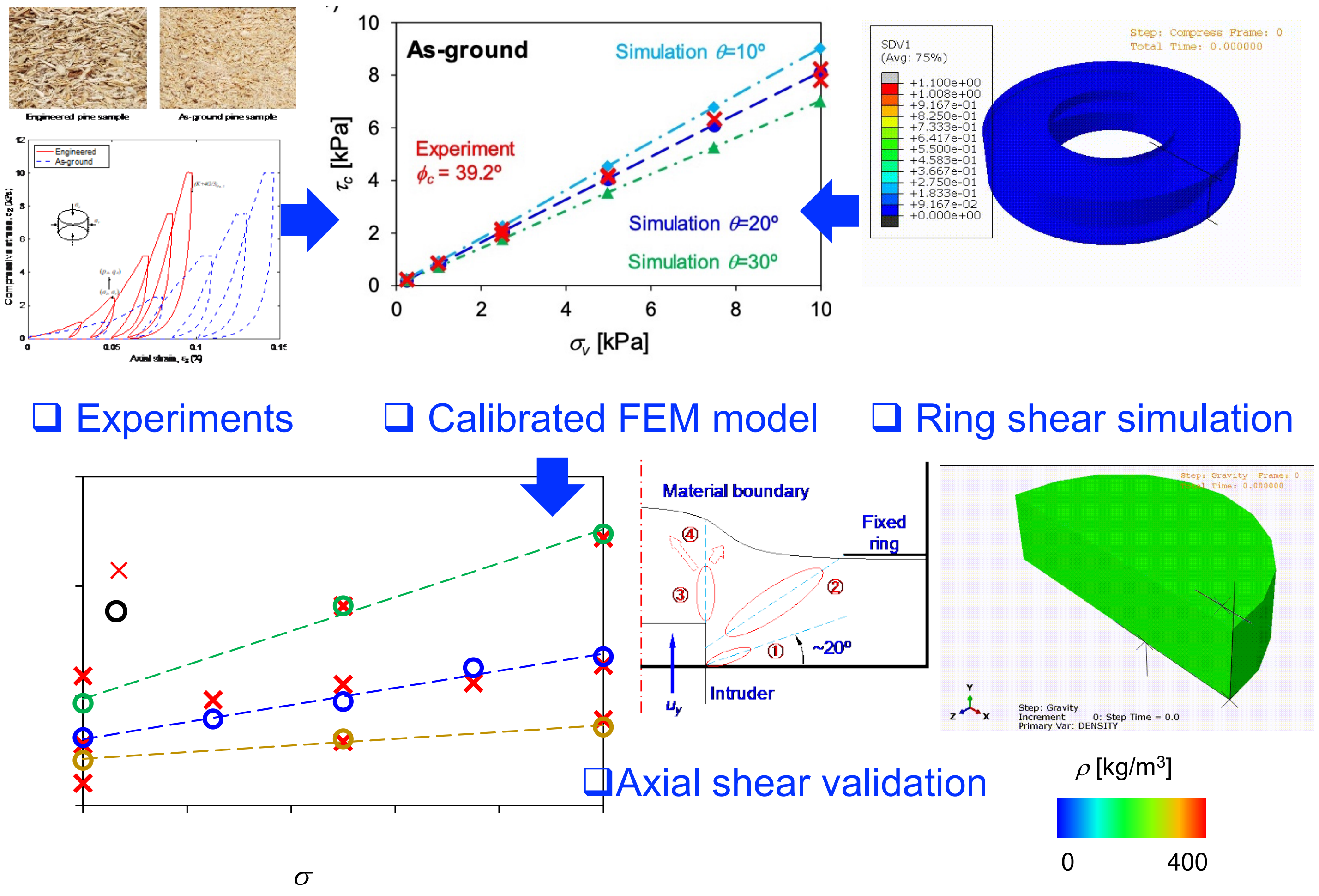
Advanced continuum particle flow theories & models to predict biomass in storage & slow flow conditions.

Current Knowledge Gap

- The state-of-the-art continuum flow models based on different theories & mathematical frameworks have not been evaluated for modeling biomass.
- Lab tests cannot provide direct measurement of constitutive model parameters due to the compressibility of particles

Achievement

- Established a work-flow to calibrate the model parameters by coupling standard laboratory tests with numerical simulations
- Implemented and evaluated four advanced continuum particle flow models for biomass granular material, and identified the hypoplastic model with critical state theory is the best one



W. Jin et al. A density dependent Drucker-Prager/Cap model for ring shear simulation of ground loblolly pine, *Powder Technology*, 368:45-58, 2020. https://doi.org/10.1016/j.powtec.2020.04.038

Continuum Model for Flow Design Guidance

Tools

Reformulated continuum particle flow models predict biomass & guide design of pilot-/industrial-scale hopper & conveyor.

Description

The validated hypoplastic model accurately capture the flow behavior in a pilot-scale hopper and capture flow behavior in the Acrison feeder at industrial-scale

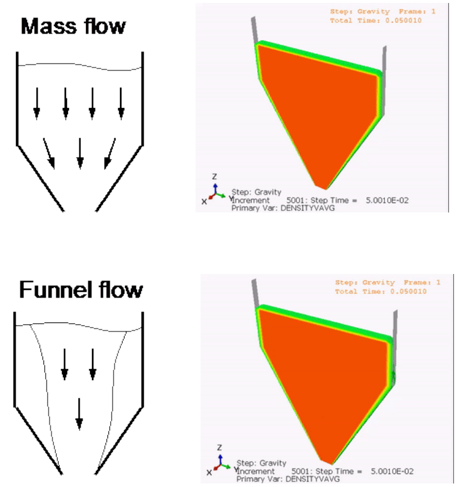
Value of new tool

Industry-scale simulation using the constitutive model will identify the CMAs that control material flow and provide a tool to optimize equipment design and to guide equipment operation for biorefinery engineers

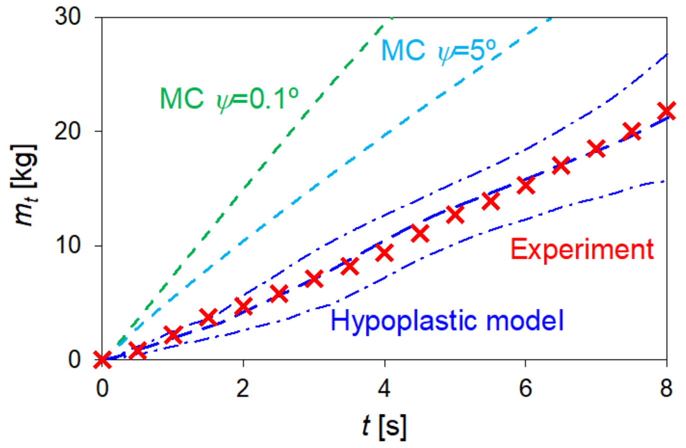
Sensitivity analysis using the constitutive model will provide CMAs working envelops for conventional flow equipment as a tool and the tool will guide biomass preprocessing steps

Y., Lu, W. Jin, J. Klinger, T. Westover, S. Dai. Flow characterization of compressible biomass particles using multiscale experiments and a hypoplastic model, *Powder Technology* (2021). https://doi.org/10.1016/j.powtec.2021.01.027

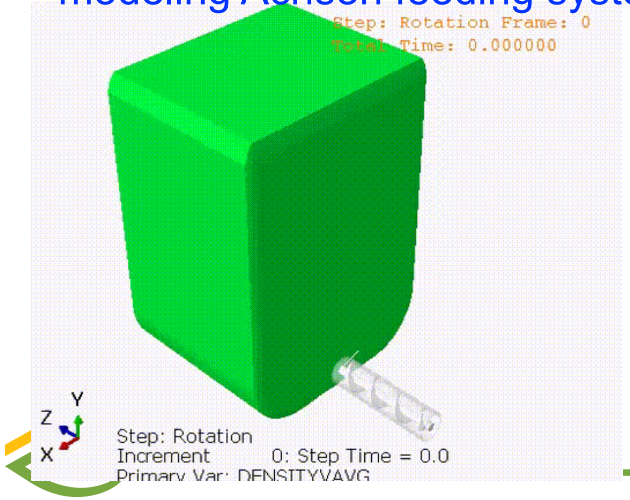
- Hopper flow pattern prediction



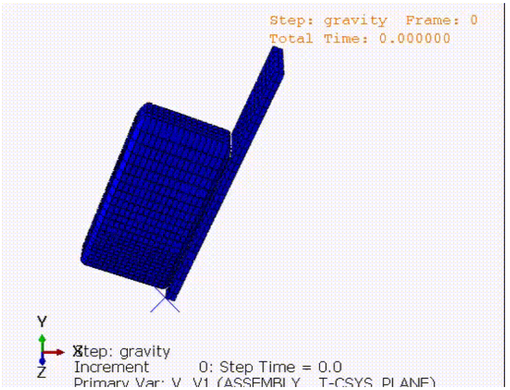
- Quantitative flow rate validation



- Engineering Application - modeling Acrison feeding system



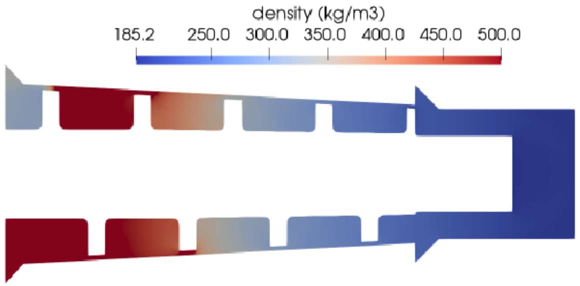
- Inclined plate flow modeling

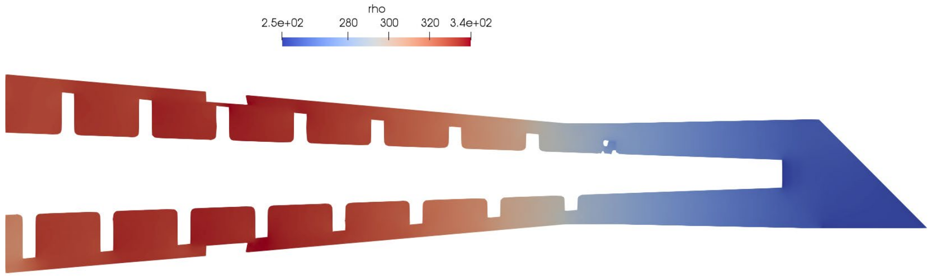


CFD Model of Compression-Screw Feeders

Tools

Computational fluid dynamics (CFD) model developed for the dynamic flow of milled lignocellulosic biomass in compression-screw feeders





This work was performed jointly between the FCIC and a competitively awarded project, "Integrated Computational Tools to Optimize and De-Risk Feedstock Handling & High- Pressure Reactor Feedings Systems,"

Description

- Experiment-based novel models are necessary for resolving the deformation behavior of the biomass material
- Simulated torque of wood chips or corn stover being compressed and transported through pilot-scale feeders quantitatively agreed with experimental measurements.

Value of new tool

- Engineering calculation dependent design and operation of compression-screw feeders poorly predicts process upsets
- The CFD models can be used to evaluate feeder performance for different operating conditions and to study upset dynamics.

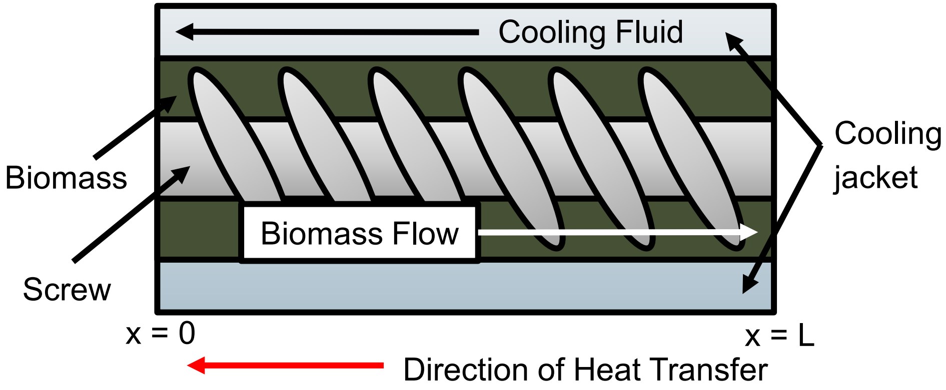
Outreach Plan

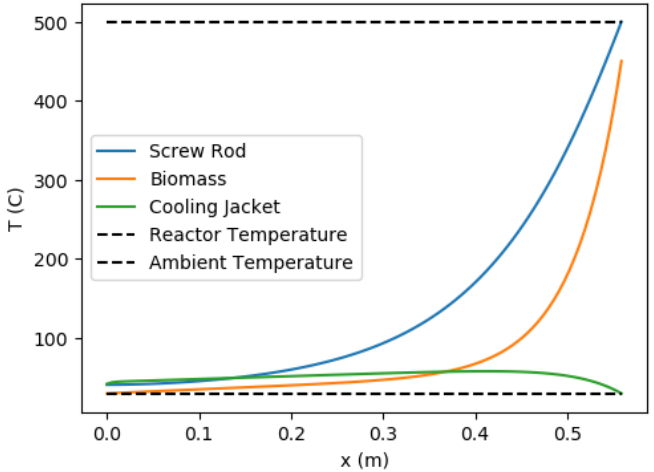
- Models made available via open-source models offered for public use and CRADA projects between industry and labs to enable simulations on HPC

Temperature Modeling of Pyrolysis Feeder

Tools

1D convection and heat transfer models predict the temperature of biomass in pyrolysis screw-auger feeders





Description

- Elevated temperatures can result in premature reaction and plugging of the feeder, as has been observed in NREL's 2FBR pyrolysis-reactor system
- Coupled 1D temperature models of each component in the feeder system provide a low-fidelity but computationally efficient prediction of biomass temperature.

Value of new tool

- Model predictions can suggest feeder designs and operating conditions that improve the biomass temperature profile.

Outreach Plan

- Model was made available to NREL engineers via a Jupyter notebook (simple GUI).
- Notebook will be shared publicly via GitHub repository after the model is validated against feeder temperature measurements.

Accomplishment and Progress – Preprocessing

- **Preprocessing**
  - DEM model for knife milling
  - DEM-CFD model for air classification
  - DEM model for biomass fracture mechanics
  - DEM model for biomass microstructure mechanics

- **DEM**: Discrete Element Method
- **FEM**: Finite Element Method
- **FVM**: Finite Volume Method
- **CFD**: Computational Fluid Dynamics

Preprocessing – An JRS Knife Milling Model

Tools

Crosscut: technique developed in FCIC Material Handling Task & applied and/or extended to Preprocessing Task

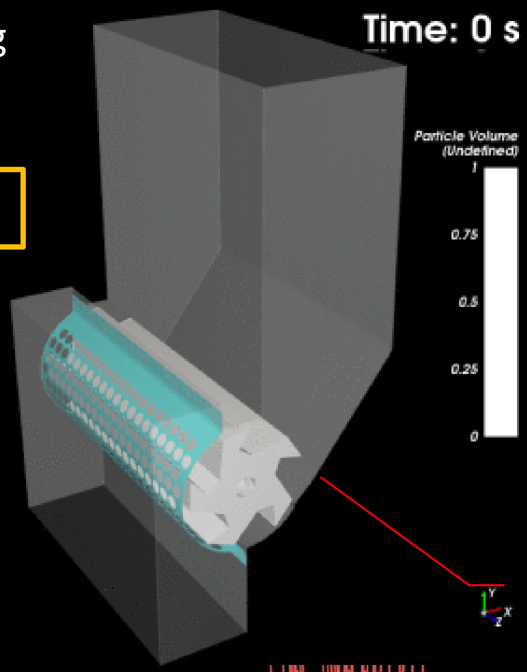
Experiment-informed knife-milling model

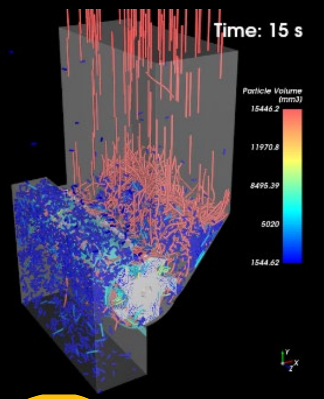
Description

- Supporting ***Quality-by-Design (QbD).***

Value of new tool

- Part of the first-of-its-kind virtual lab
- Fast testing and real-time diagnosis of knife milling Critical Processing Parameters (CPPs) & Critical Quality Attributes (CQAs).





Application example: JRS knife milling of corn stalks

Modeling facilitates massive testing for QbD

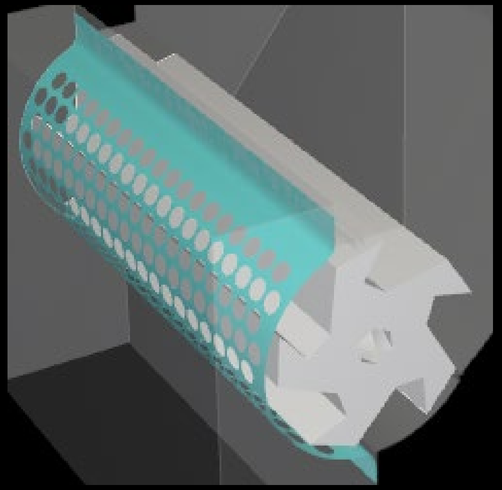
- **CMA:** input PSD, particle shapes, etc.
- **CPP:** rotor speed, blade angle, input mass rate.
- **CQA:** output PSD, output mass rate etc.

Applications

- Biomass
- MSW (papers, plastics, etc.)

CPP of JRS knife mill:

- input mass rate
- rotor speed
- blade angle
- screen sieve size
- etc.



Preprocessing – An Air Classification Model

Tools

Crosscut: technique developed in FCIC Material Handling Task & applied and/or extended to Preprocessing Task

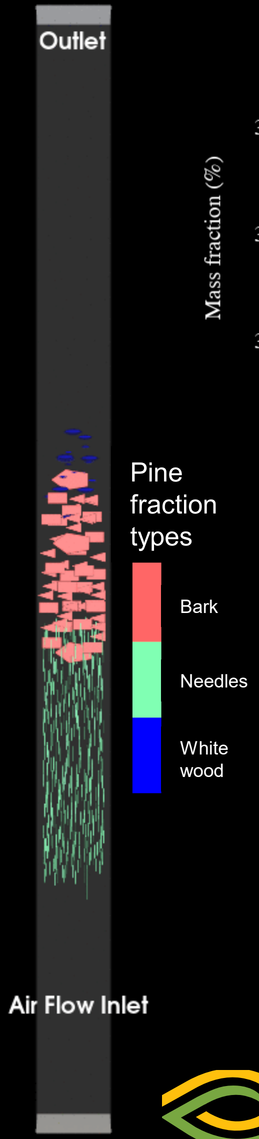
Experiment-validated air separation model

Description

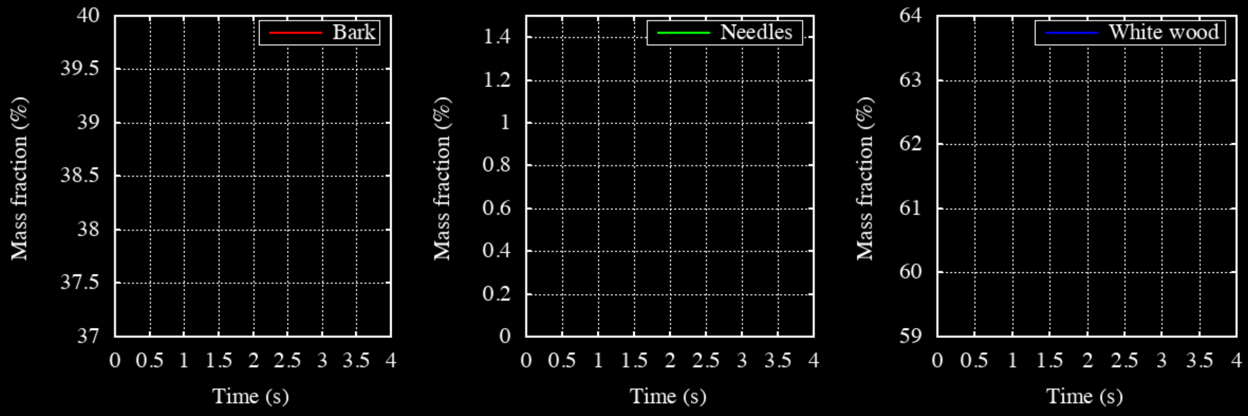
- Supporting ***Quality-by-Design (QbD).***

Value of new tool

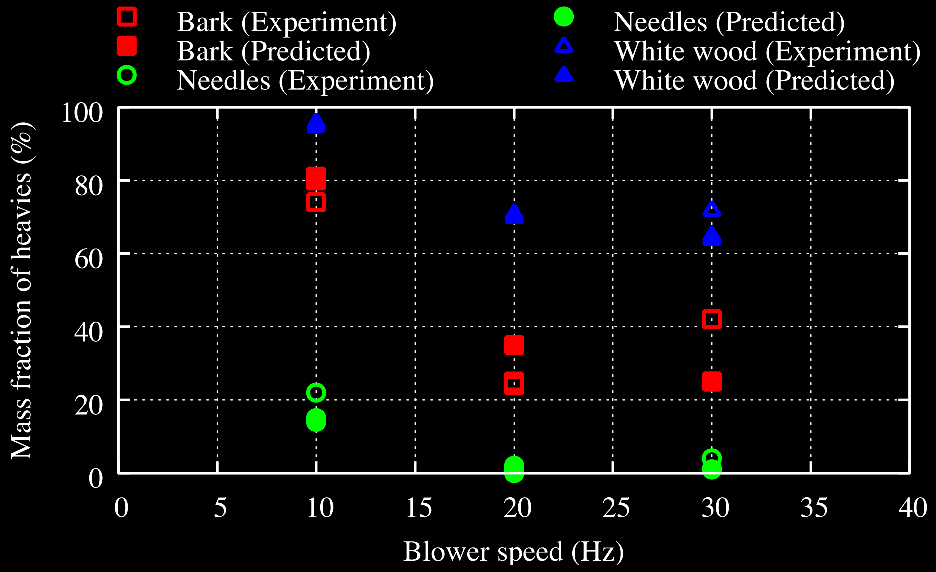
- Part of the first-of-its-kind virtual lab
- Fast testing and real-time diagnosis of processing parameters (blower speed, feeding mass rate, etc.) and quality attributes (heavy fractions mass rate, output particle size distribution, etc.).



Modeling enables real-time diagnosis for QbD



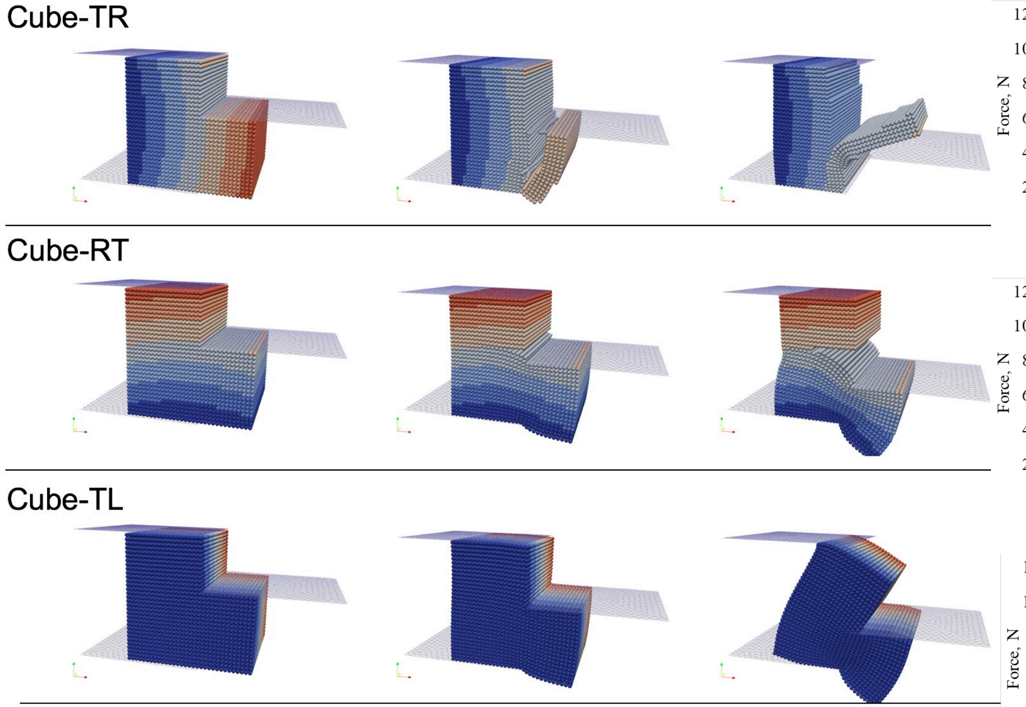
Experimental validation for modeling

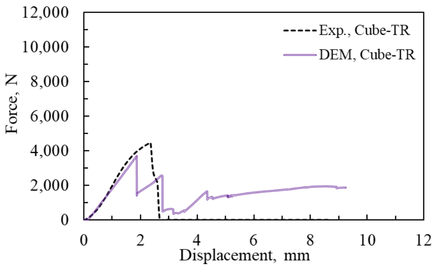


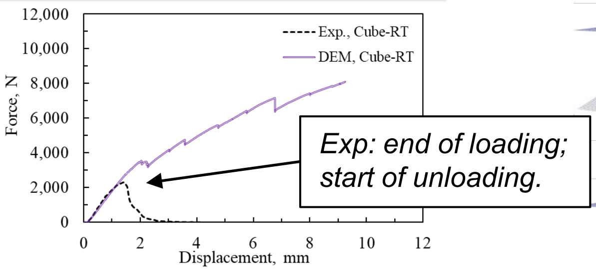
Deconstruction Mechanism Theory & Model

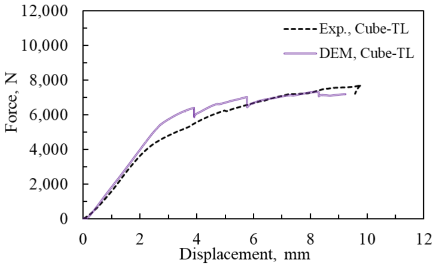
Tools

Developed experiment-validated open-source macroscale DEM model for pine structural deformation & deconstruction

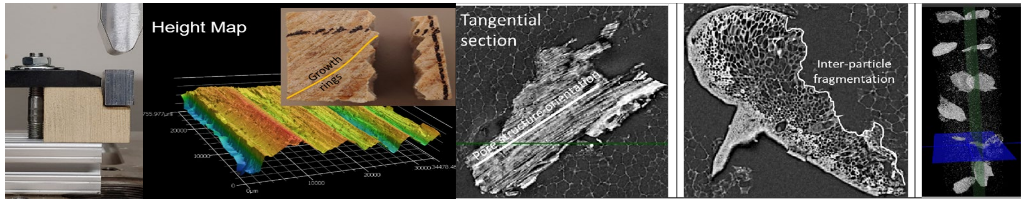


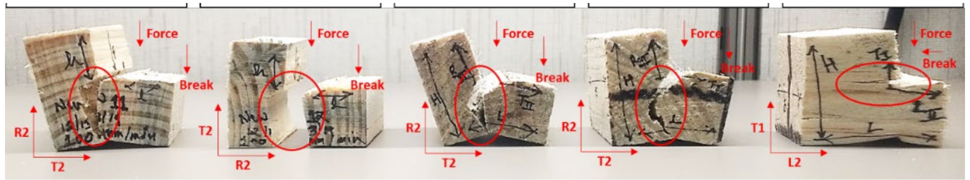




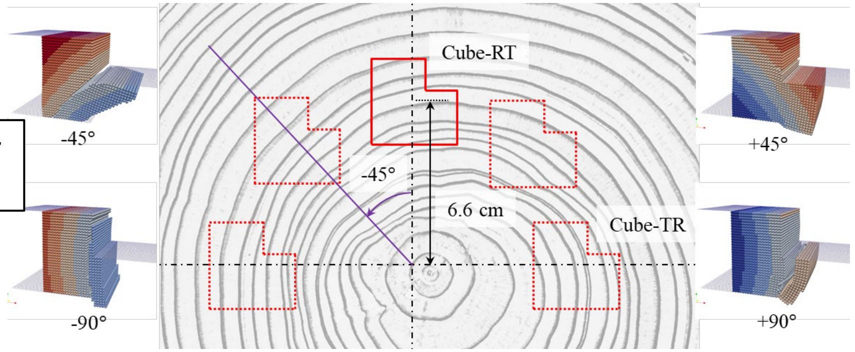


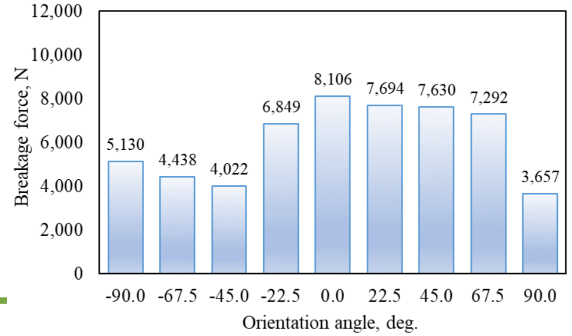
Y. Guo, Q. Chen, Y. Xia, J. Klinger, V. Thompson, “A nonlinear elasto-plastic bond model for the discrete element modeling of woody biomass particles,” *Powder Technology*, 2021 (revision under review)





11 (R2 R2) 12 (T2 T2) 13 (R2 R2) 14 (R2 R2) 15 (T1 L2)

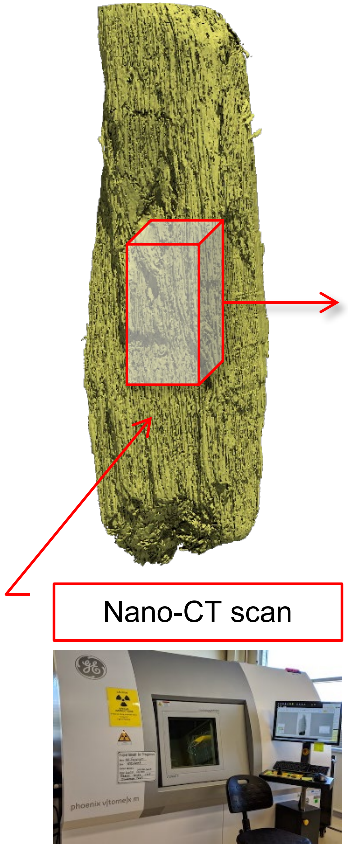


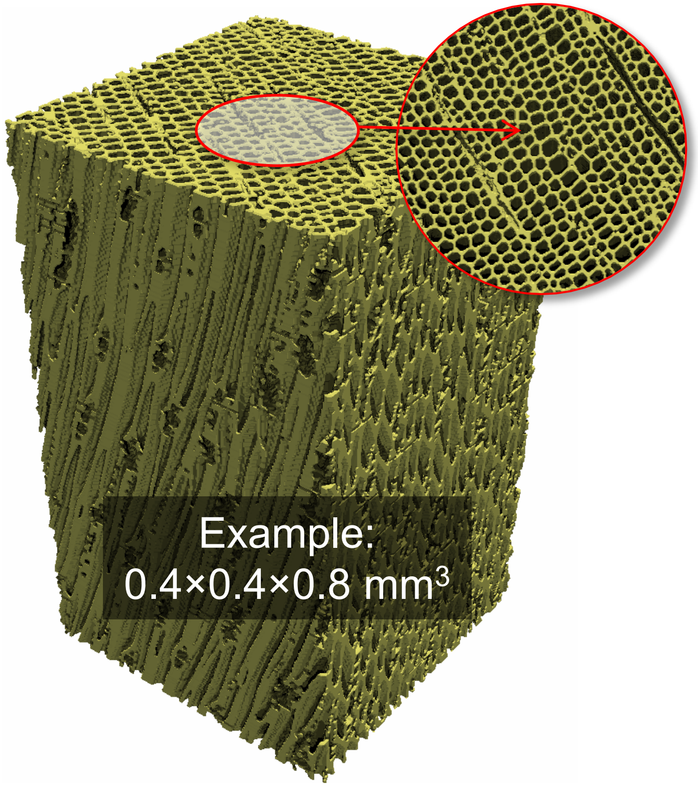


Enabling Microstructural Fracture Modeling

Tools

Developed XCT-informed loblolly pine 3D microstructural topology reconstruction workflow for fracture physics & models

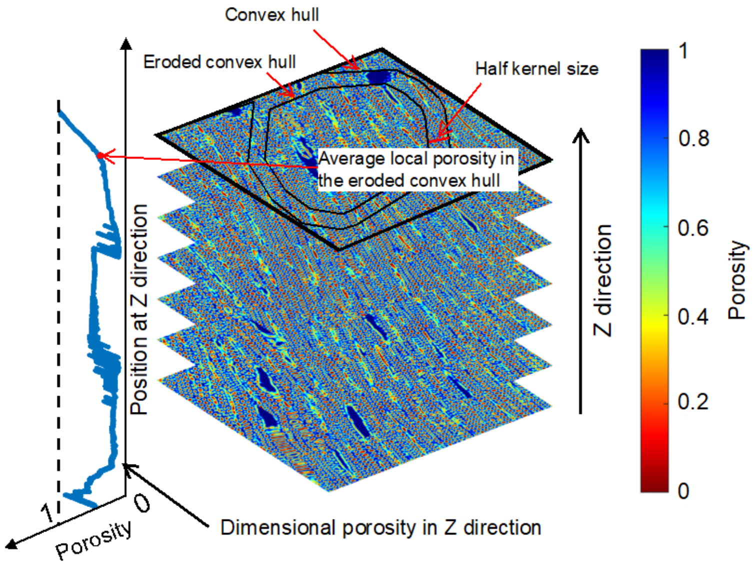


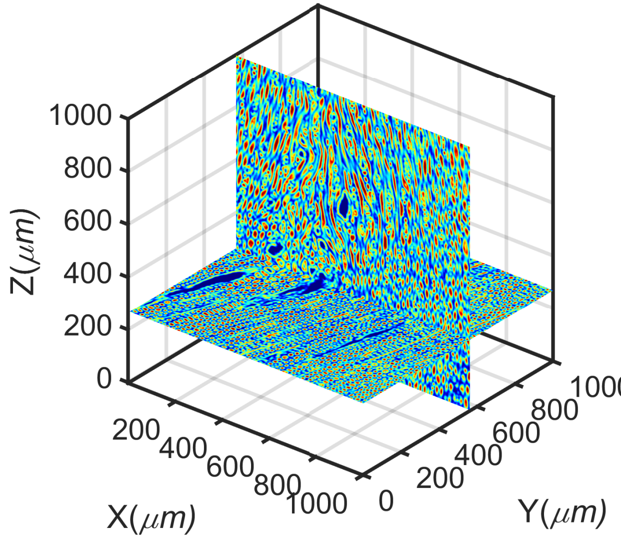


Reconstructed 3D microstructure

Value of new tool

- First-of-its-kind virtual laboratory for biomass micromechanics
- Microstructural mechanics DEM model will be open-source
- An intermediate-scale model links mesoscale model and macroscale model in the multis-scale model plan (NREL/INL)





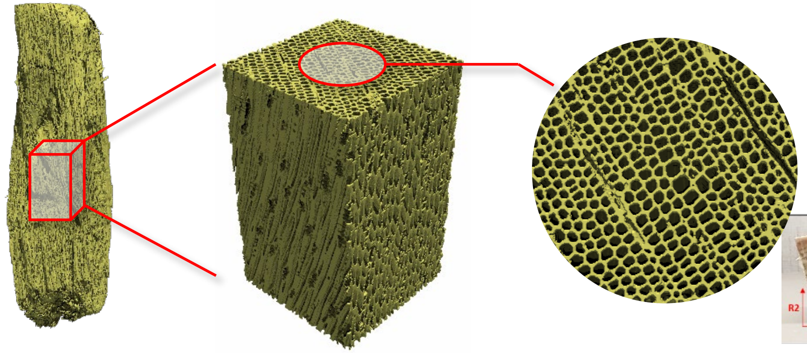
Advanced 3D analysis model reveals heterogeneous porosity distribution in pines (for the first time)

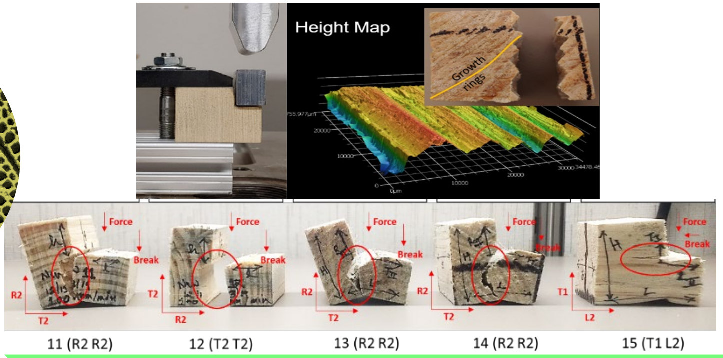
Q. Sun, Y. Xia, Q. Chen, J. Klinger, V. Thompson, "3D tomography-informed porosity analysis for woody biomass," (in preparation)

Virtual Laboratory for Preprocessing

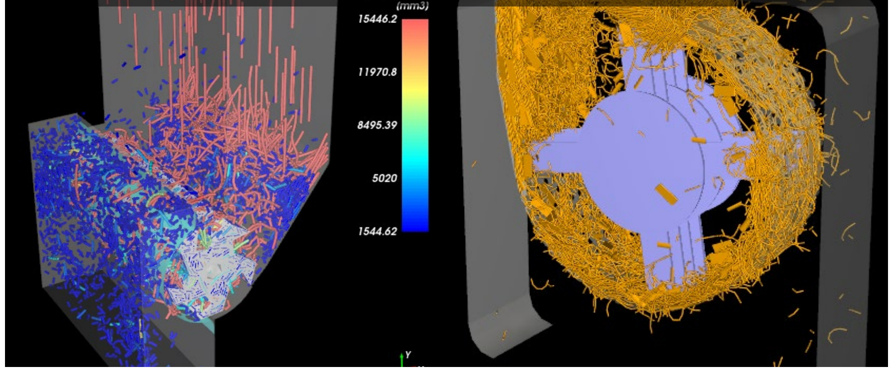
Tools

XCT-informed microstructural deconstruction model and upscaling



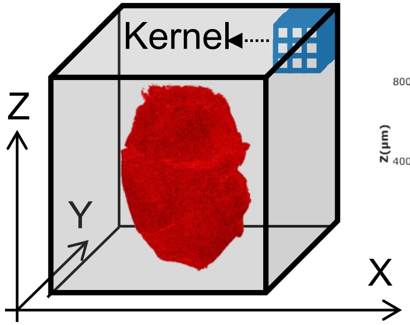


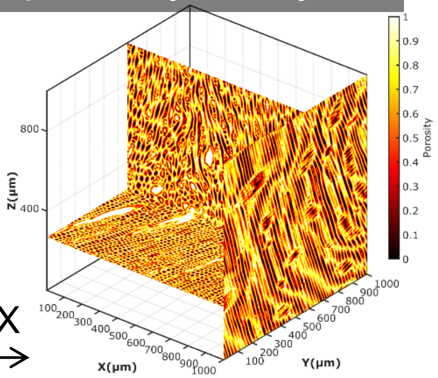
Modeling of various milling techniques

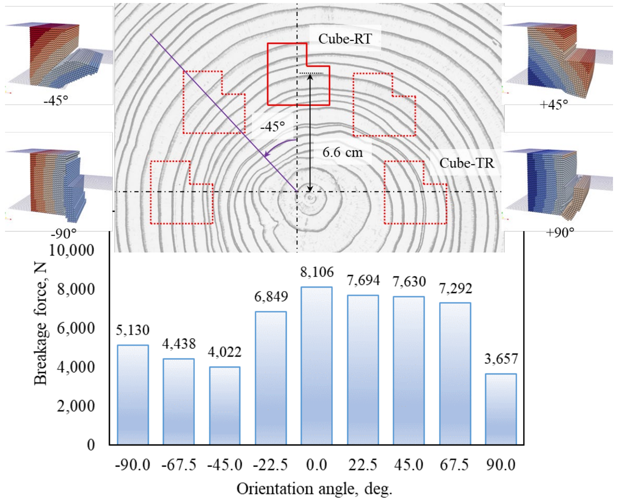


Microscale (um) → **Laboratory scale (cm)** → **Pilot scale (m)**

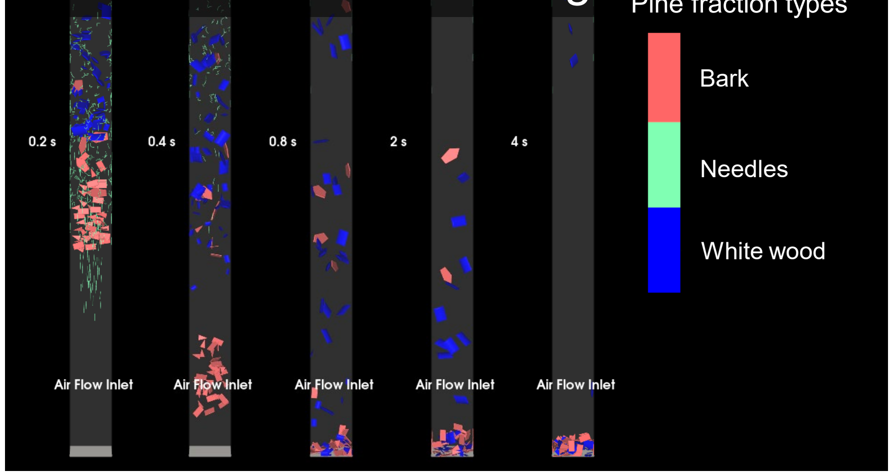
Advanced micro-porosity analysis



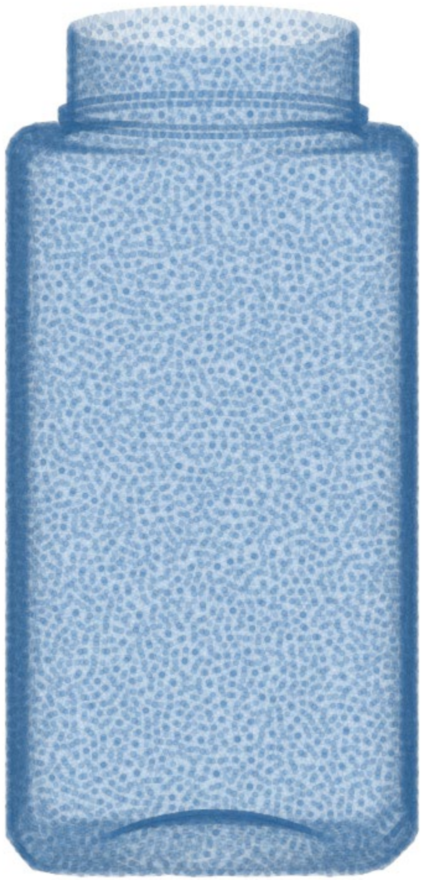


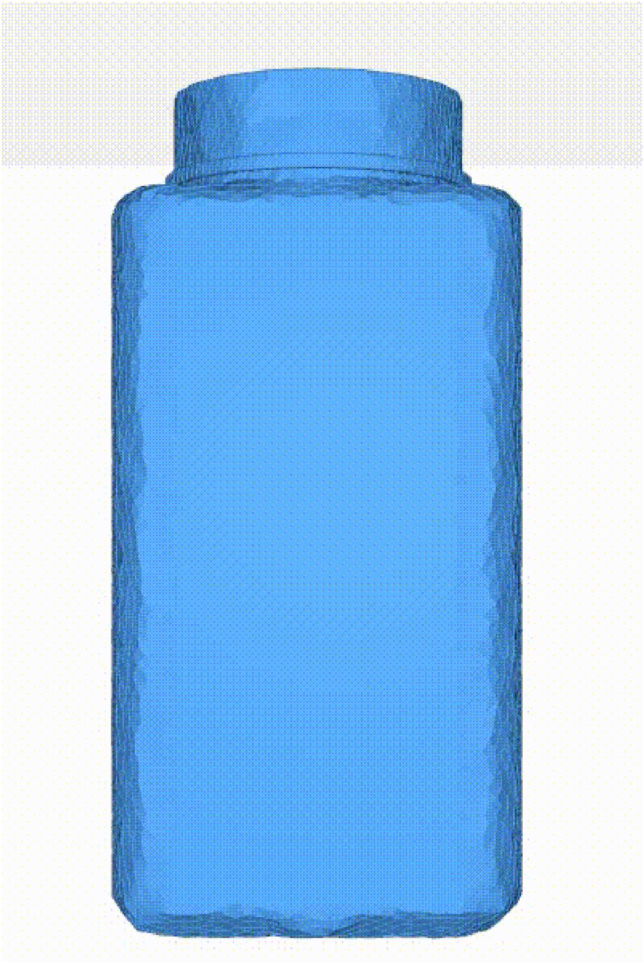


Air classification modeling



Readying Capabilities for the Emerging Needs



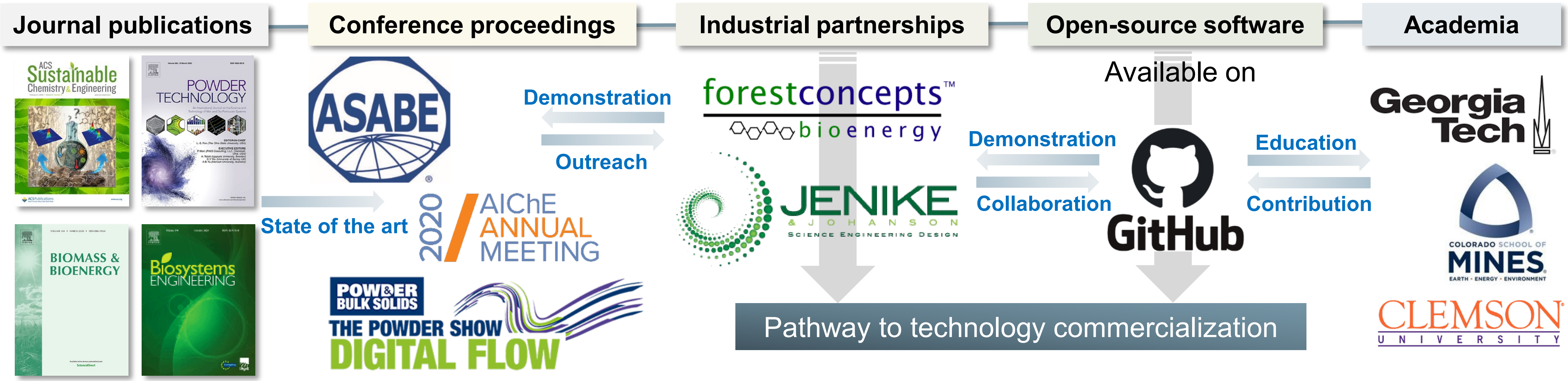


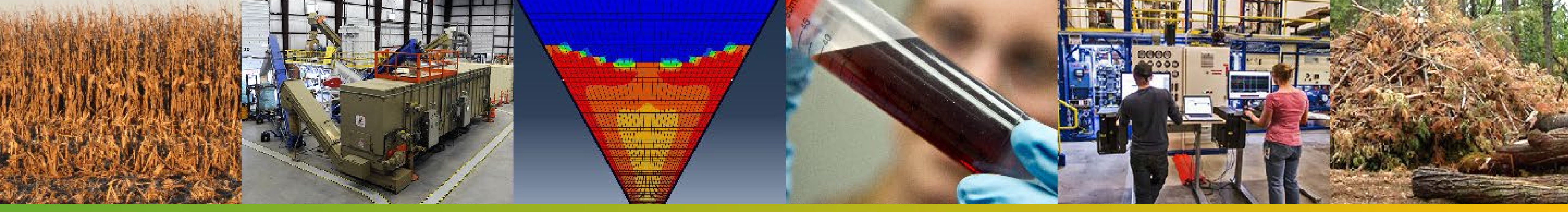
Impact

Impact: Provide biomass industry with suitable & predictive design tools to effectively assist design of feedstock processing & handling equipment, including

- ❑ Reliable working envelope of CMAs & CPPs for achieving CQAs (i.e., design charts for consistent flow),
- ❑ Open-source biomass flow modeling software packages/moduli available to public.

Dissemination





Thank you

energy.gov/fcic

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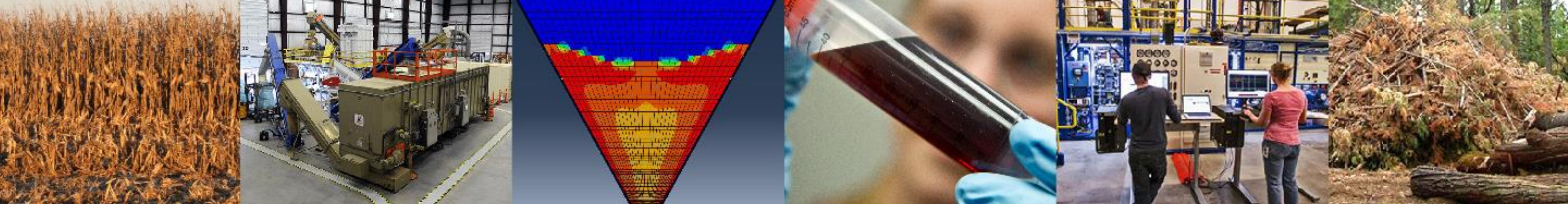
FEEDSTOCK-CONVERSION
INTERFACE CONSORTIUM



Transforming Fundamental Knowledge to Actionable Insight:

Elucidating Relationships Between Molecular Features and Bulk Behavior in Handling and Conversion Processes

Peter N. Ciesielski, National Renewable Energy Lab
February 11th, 2021

CCPC
Consortium for Computational Physics and Chemistry
U.S. DEPARTMENT OF ENERGY
BIOENERGY TECHNOLOGIES OFFICE

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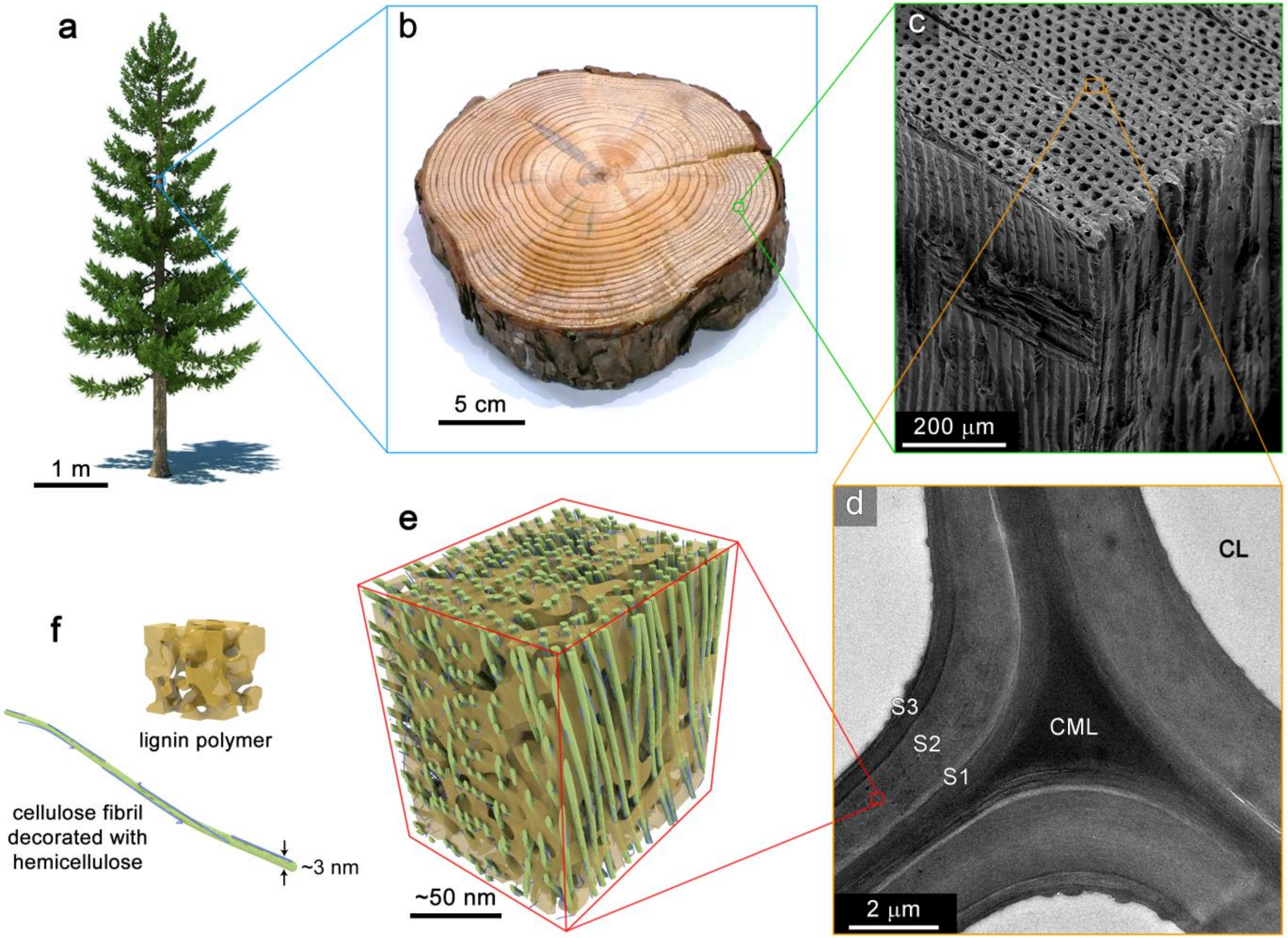
The Hierarchal Nature of Biomass



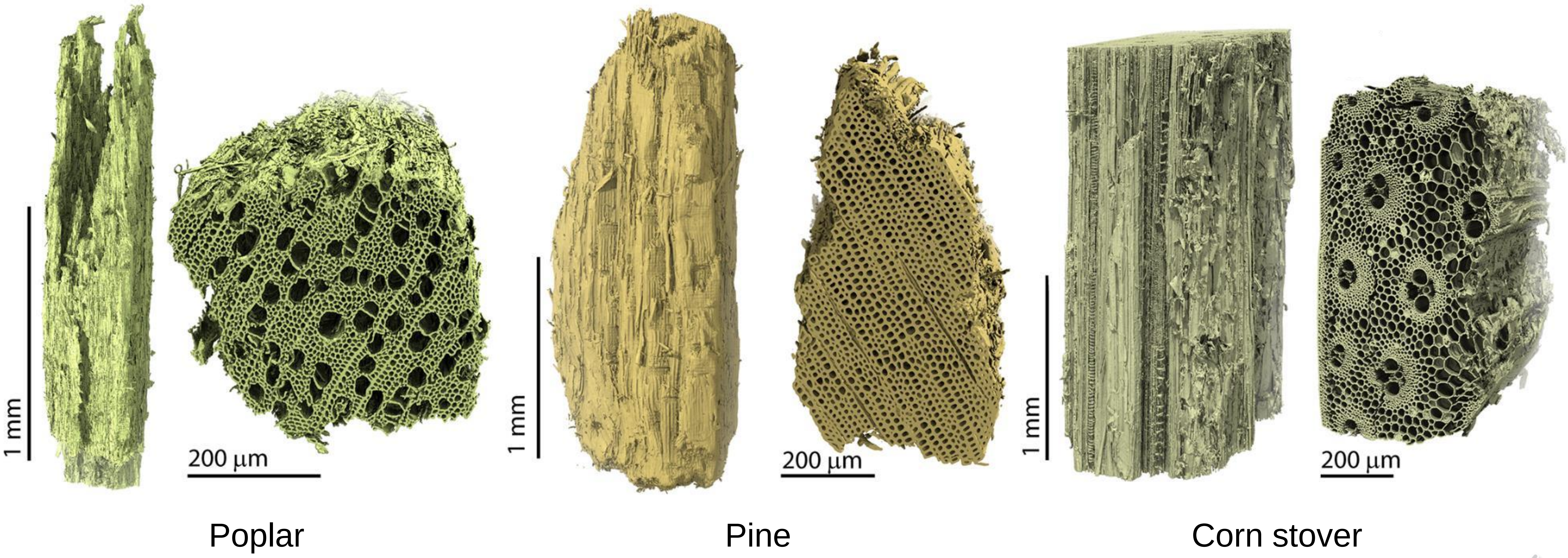
- The properties of biomass that influence its performance in processing scenarios arise from structural features that span many length scales.

- These **Emergent Properties** are difficult or impossible to characterize by experiment or simulation performed at individual length/time scales.

Zhu, H., Luo, W., Ciesielski, P.N., Fang, Z., Zhu, J.Y., Henriksson, G., Himmel, M.E. and Hu, L. *Chemical reviews*, **2016**.

Variability of Biomass is Inherent and Impactful

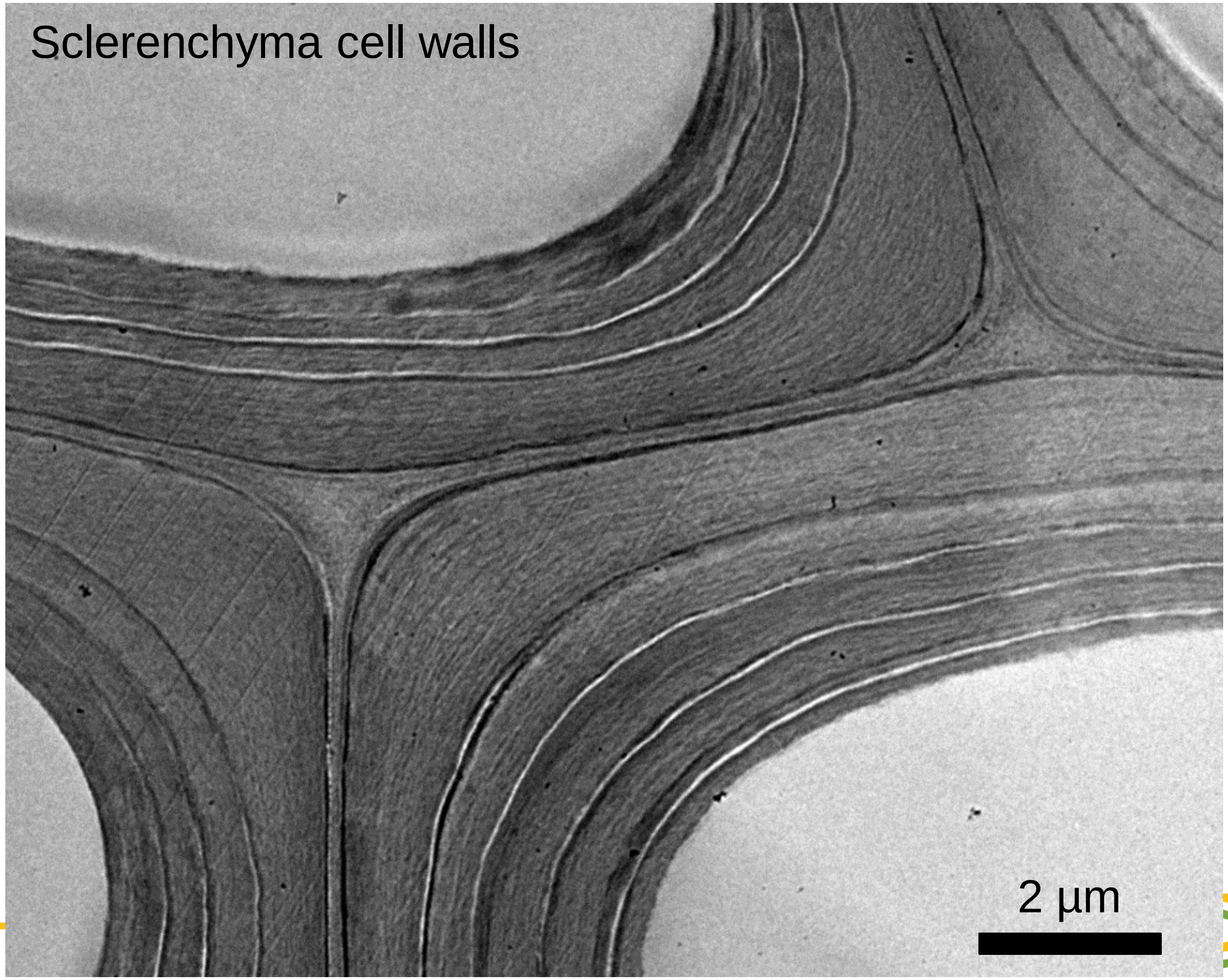
Example 1: At the tissue scale, biomass **structure** varies due to species of origin, which impacts **bulk mechanical properties, permeability, density, and thermal conductivity**

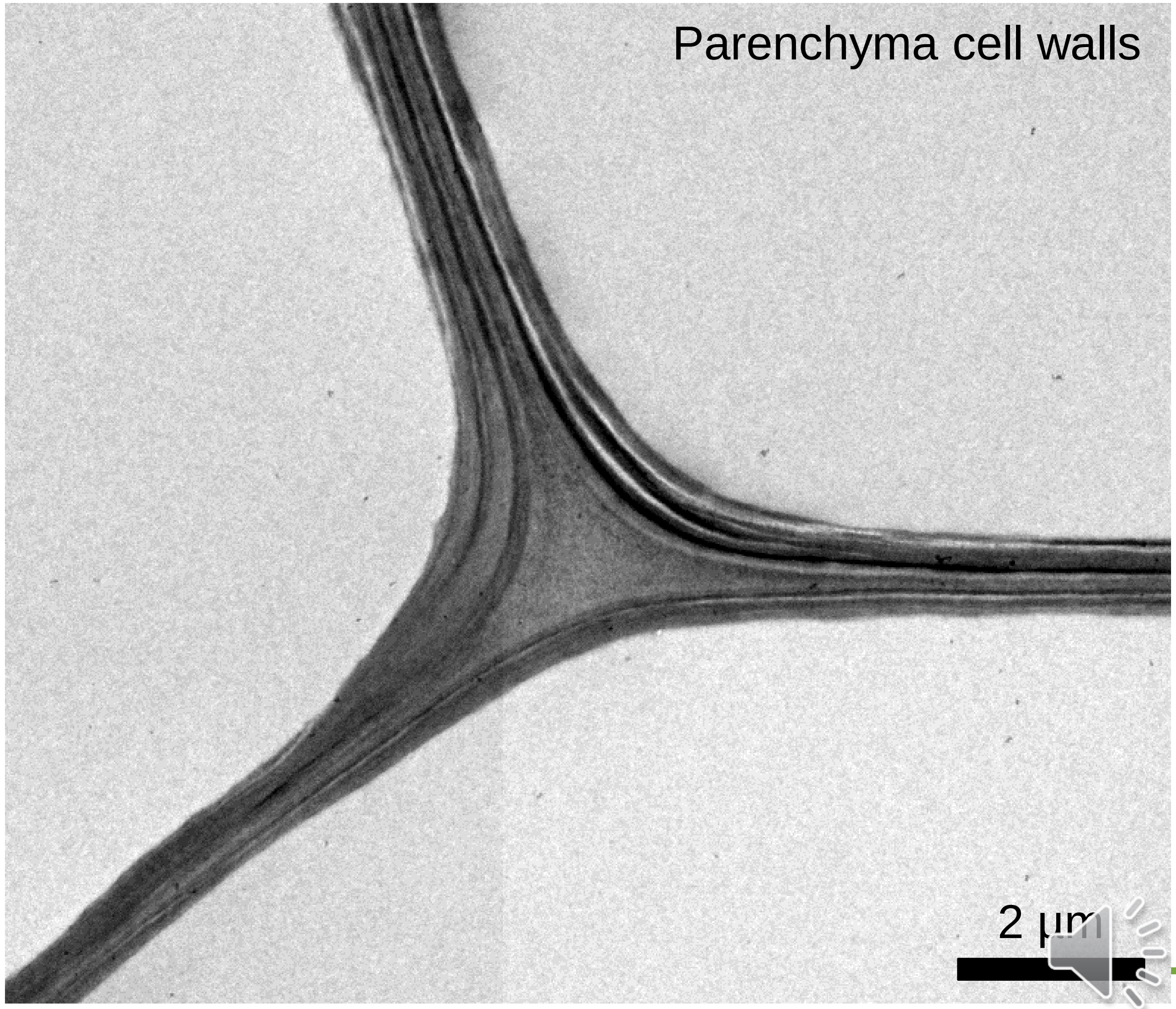


Ciesielski, Pecha, Lattanzi, Bharadwaj, Crowley, Bu, Vermaas, Steirer, Crowley. “Advances in Multiscale Modeling of Lignocellulosic Biomass.” *ACS Sustainable Chemistry and Engineering*. **2020**

Variability of Biomass is Inherent and Impactful

Example 2: At the cell wall scale, lignocellulose **architecture and composition** varies based on tissue type, which impacts **micromechanical properties** and **reactivity in (bio)chemical processing**





Images: P. Ciesielski, NREL BSCL

Variability of Biomass is Inherent and Impactful

Example 3: At the cell wall scale, lignocellulose **composition** can vary due to **genetic manipulation**, which impacts behavior in **chemical and enzymatic processing** scenarios

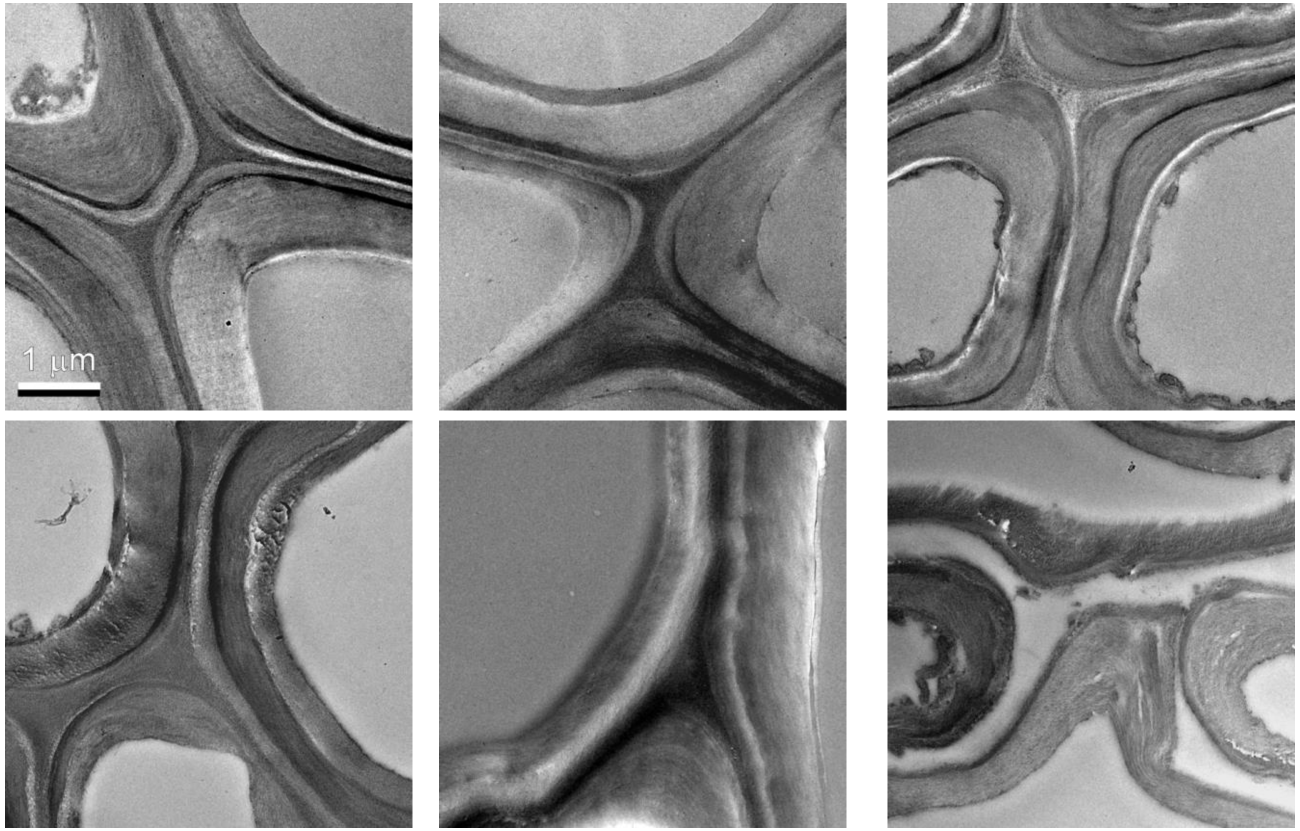
WT: 70% S, 30% G

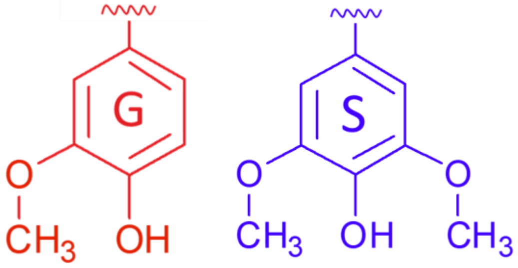
100% G

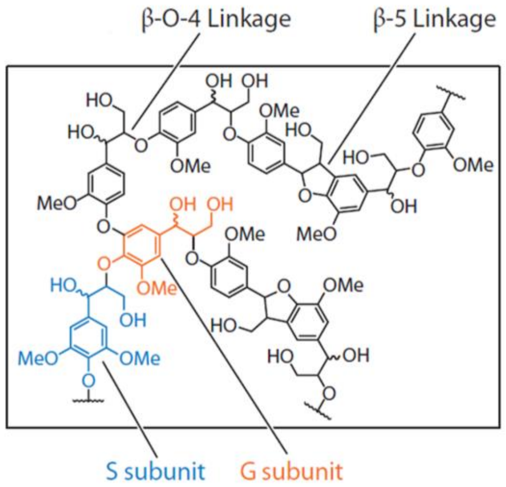
100% S

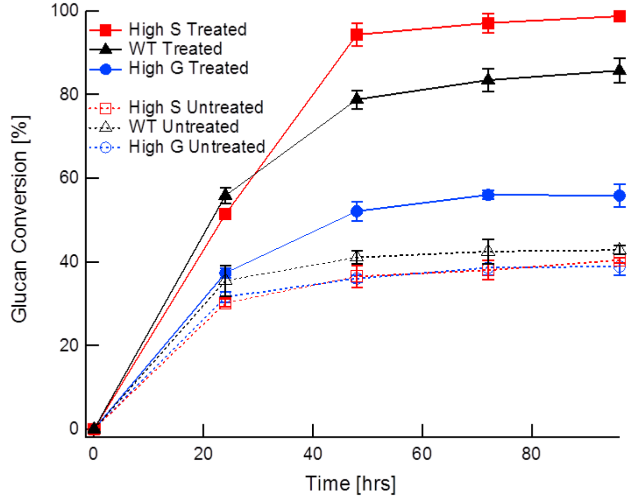
Untreated

Acid Treatment





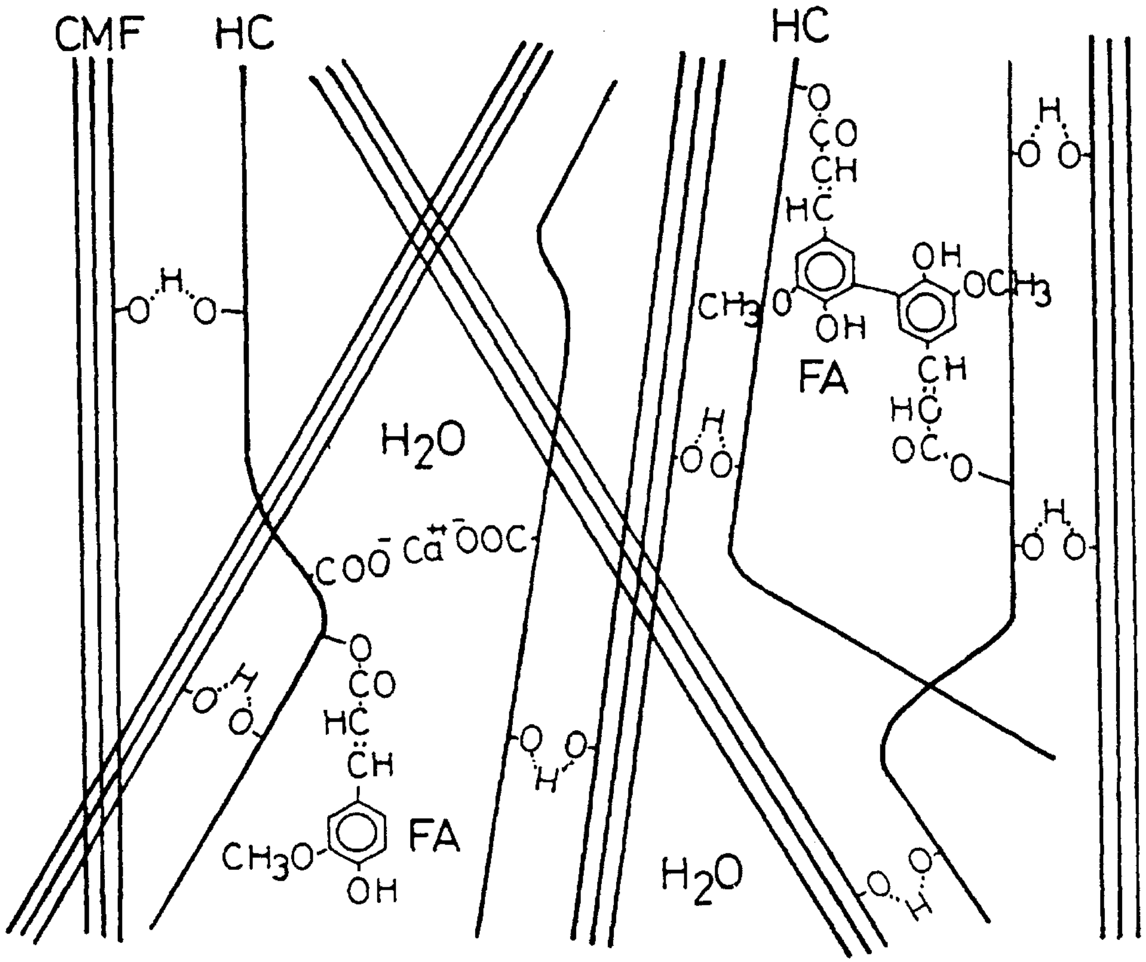




Ciesielski, P.N., M.G. Resch, B. Hewetson, J.P. Killgore, A. Curtin, N. Anderson, A.N. Chiaramonti, D.C. Hurley, A. Sanders, M.E. Himmel, C. Chapple, N. Mosier, and Donohoe, B.S. *Engineering plant cell walls: tuning lignin monomer composition for deconstructable biofuel feedstocks or resilient biomaterials. Green Chemistry,* ***2014.***

Plant cell wall models

- **Qualitative** models provide a framework to understand the nature of lignocellulose at a fundamental level.
- They attempt to articulate relationships between molecular composition, biopolymer interactions, and nanoscale architecture that give rise to the



N. Terashima, et al, 1993

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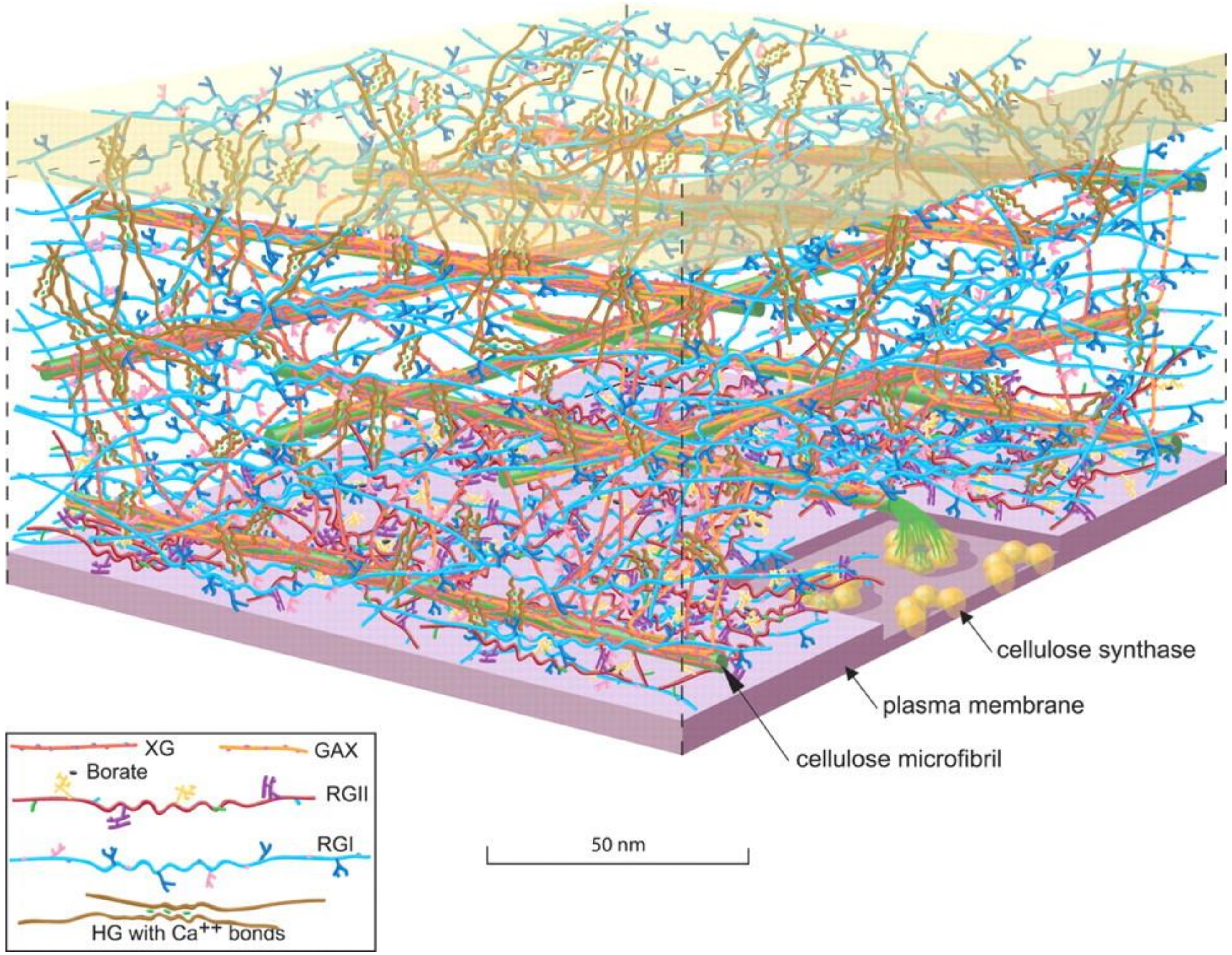

Sommerville, et al., *Science*, 2004

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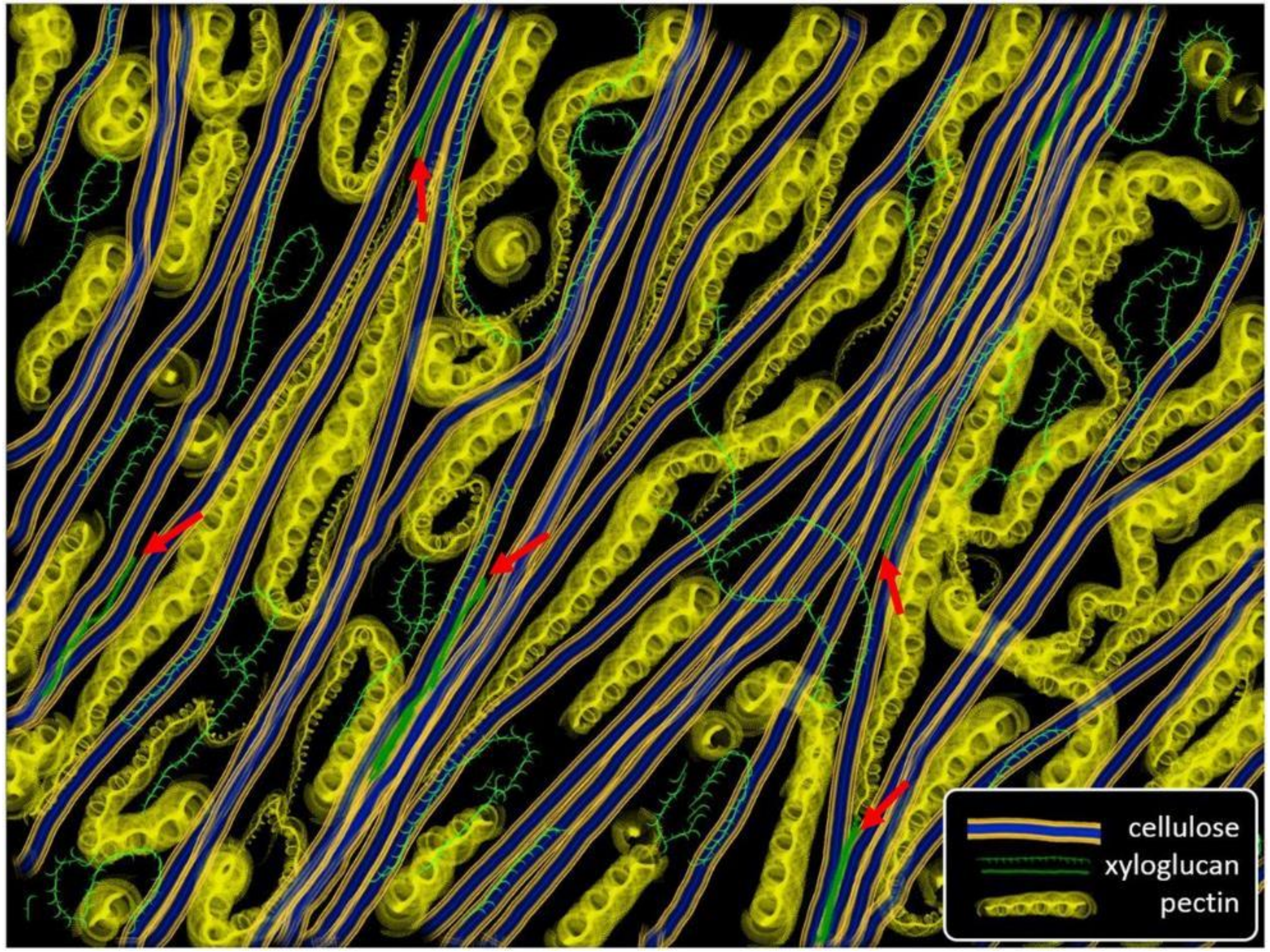
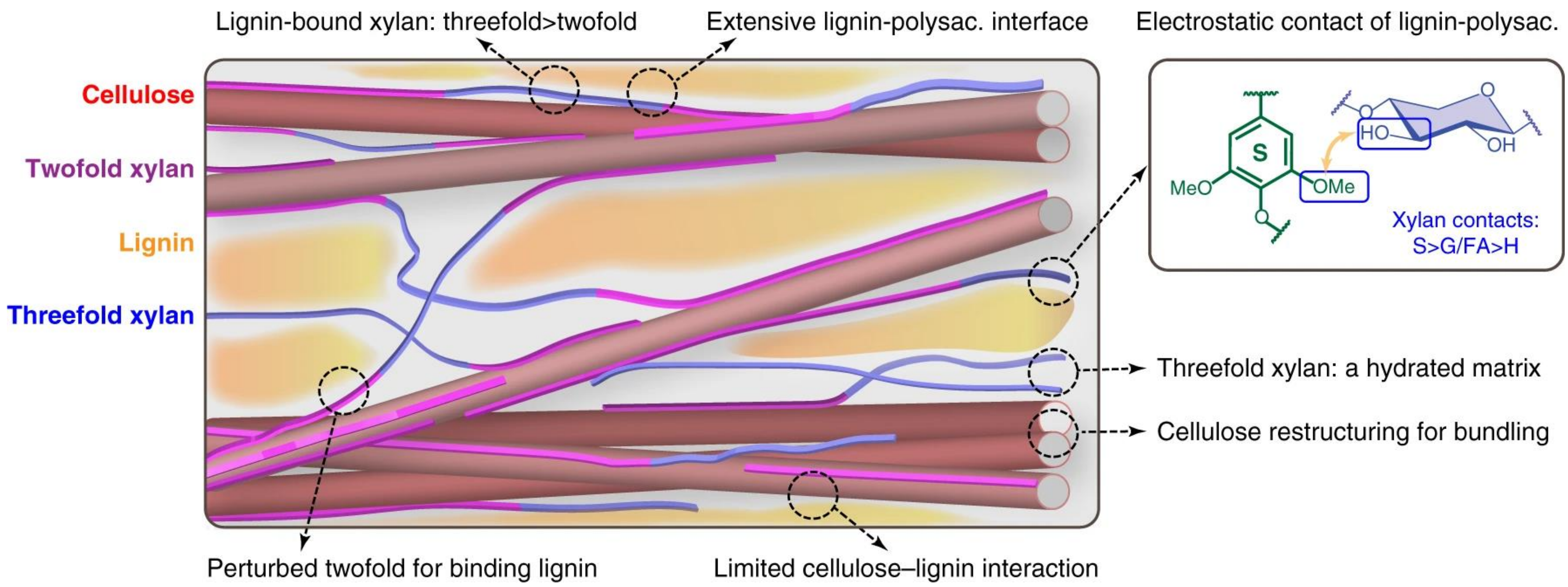


Cosgrove, *Plant Physiology*, 2018

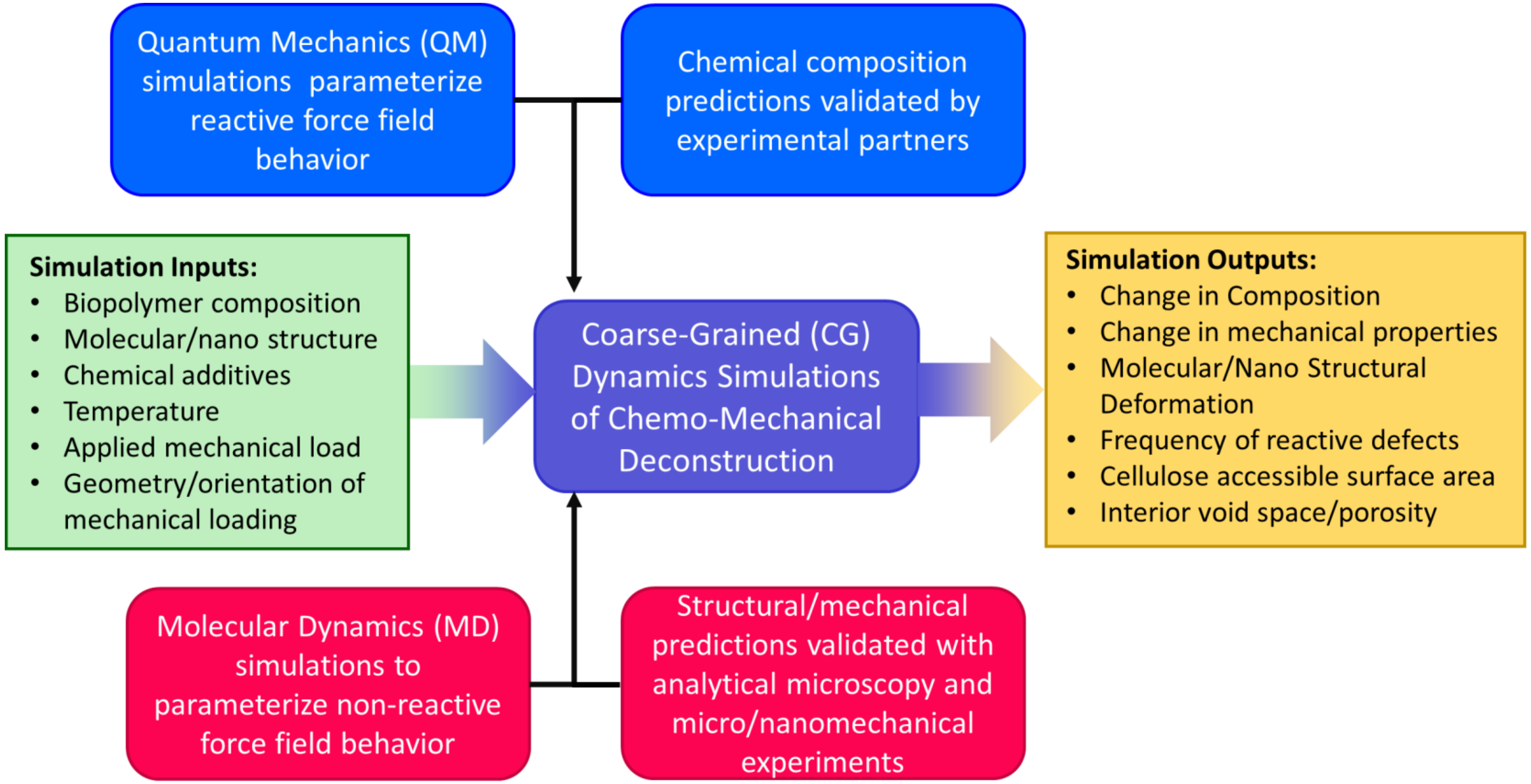
Plant cell wall models



Kang, et al., *Nature Communications*, 2019

FCIC Modeling Objective and Approach

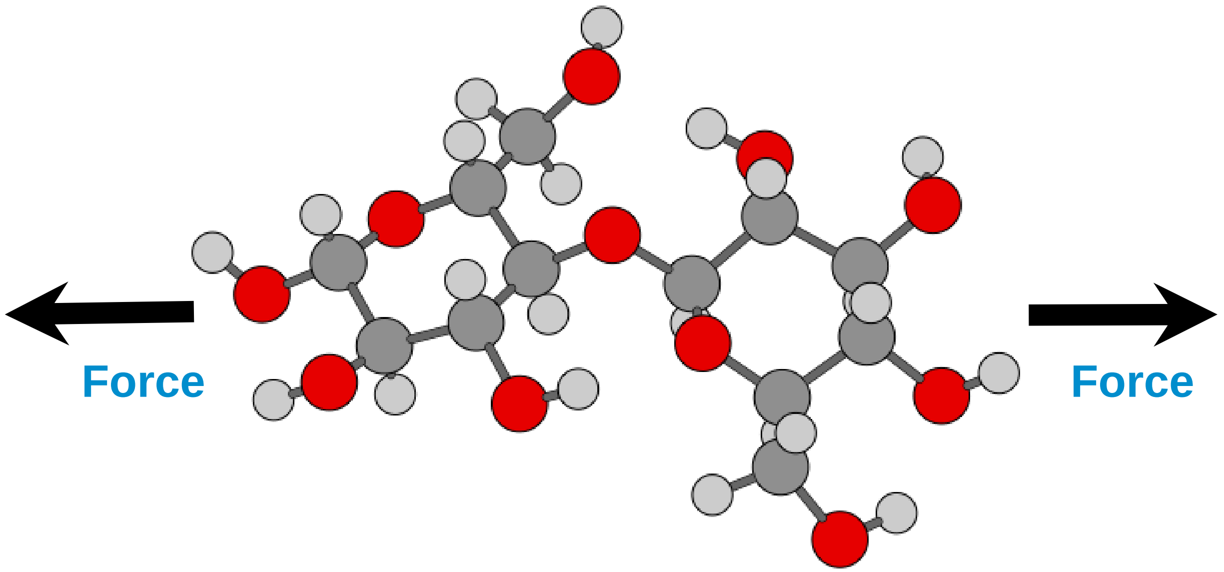
Articulate **state-of-the-art, fundamental knowledge** about the molecular composition and nanoscale architecture of the plant cell wall into a **computational tool** that can be used to provide **quantitative predictions** about the behavior of biomass in handling and conversion processes



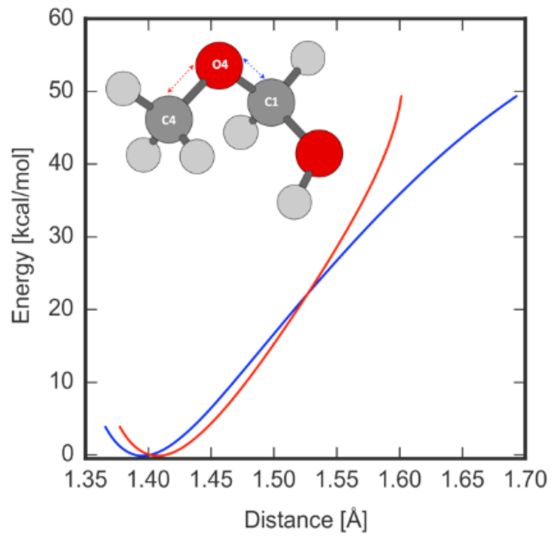
Translate what we know and what we can measure about biomass into predictions of its properties and behavior

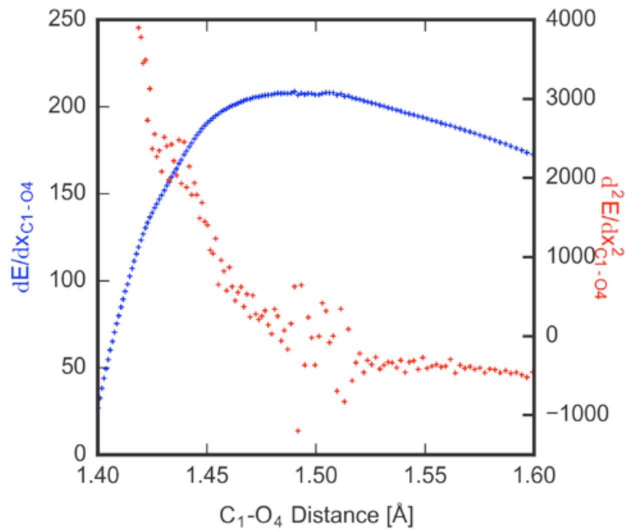
First, model the biopolymer components

Quantum Mechanical Properties of Cellulose:
How far can a glycosidic bond stretch before it breaks?



Answer: Until the C1-O4 bond length reaches 1.5 Å

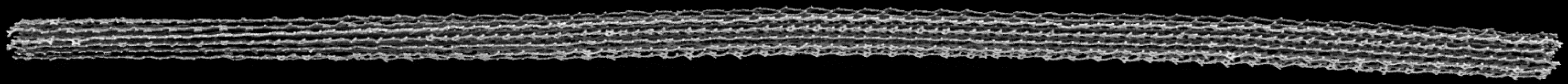




First, model the biopolymer components

Macromolecular Mechanical Properties of Cellulose:

How much stress does it take to break a cellulose nanofibril?

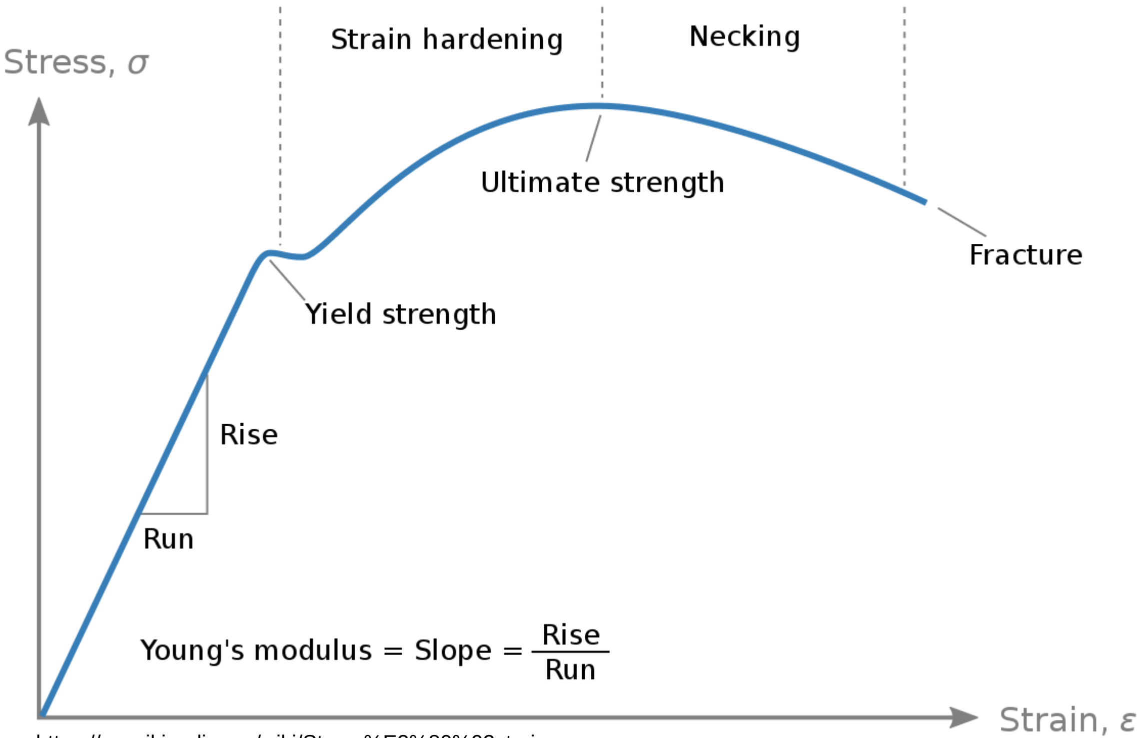


Meagan Crowley, Michael Crowley, Peter Ciesielski

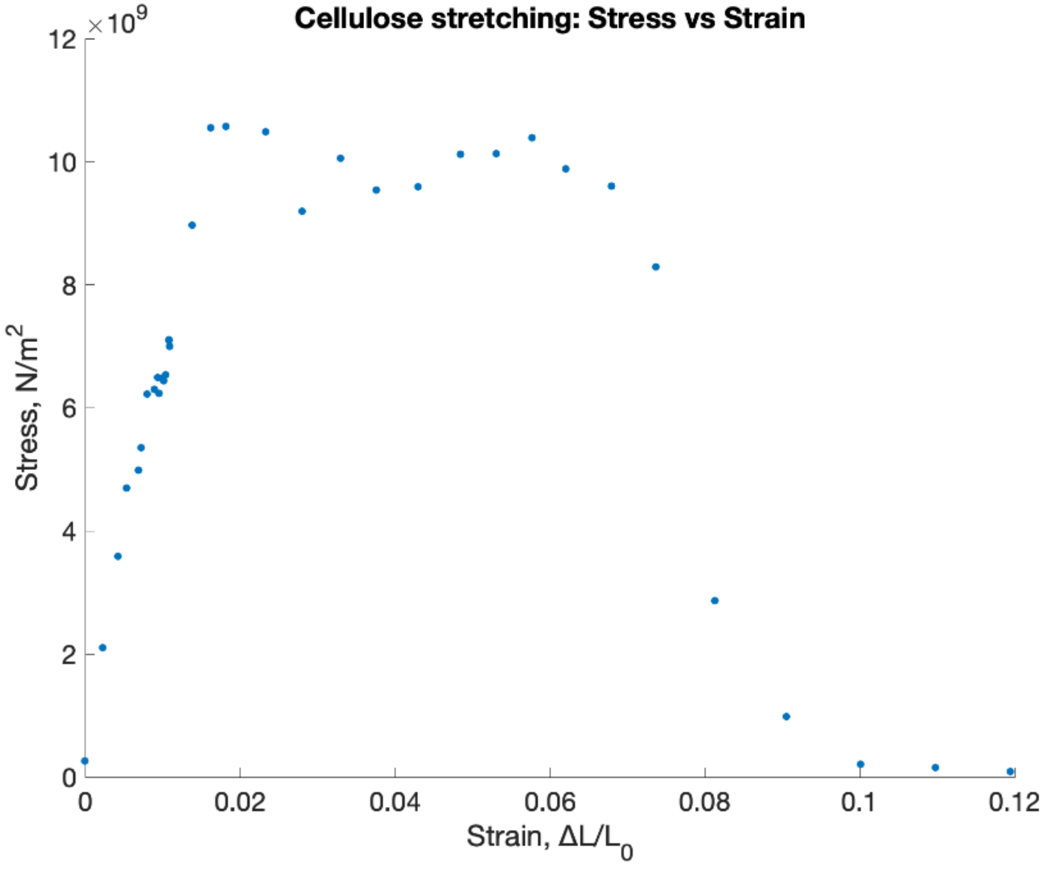
First, model the biopolymer components

Macromolecular Mechanical Properties of Cellulose:

How much stress does it take to break a cellulose nanofibril? Answer: much less than bulk cellulose!



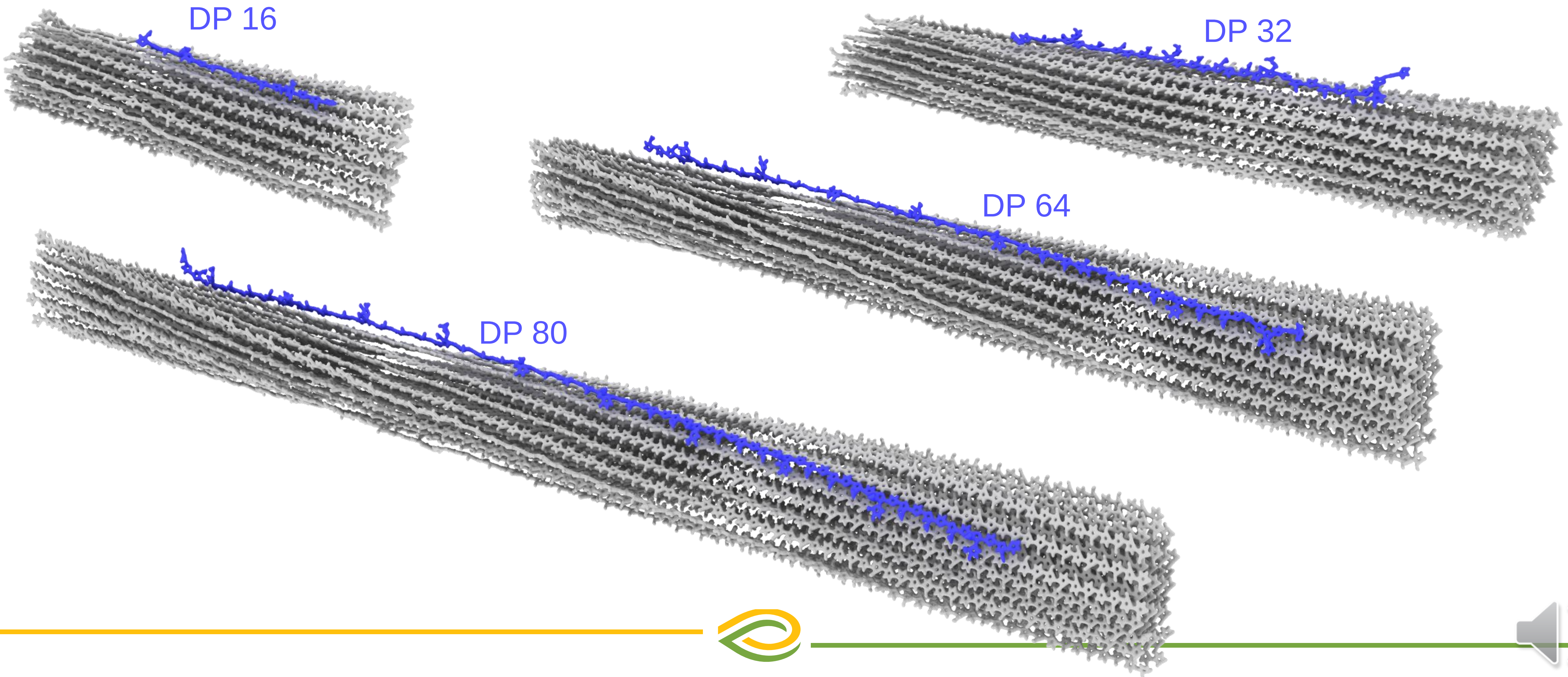
https://en.wikipedia.org/wiki/Stress%E2%80%93strain_curve



Meagan Crowley, Michael Crowley, Peter Ciesielski

Next, model the biopolymer interactions

Macromolecular Interactions of Cellulose and Hemicellulose:
How does the molecular structure of hemicellulose affect its binding to cellulose?



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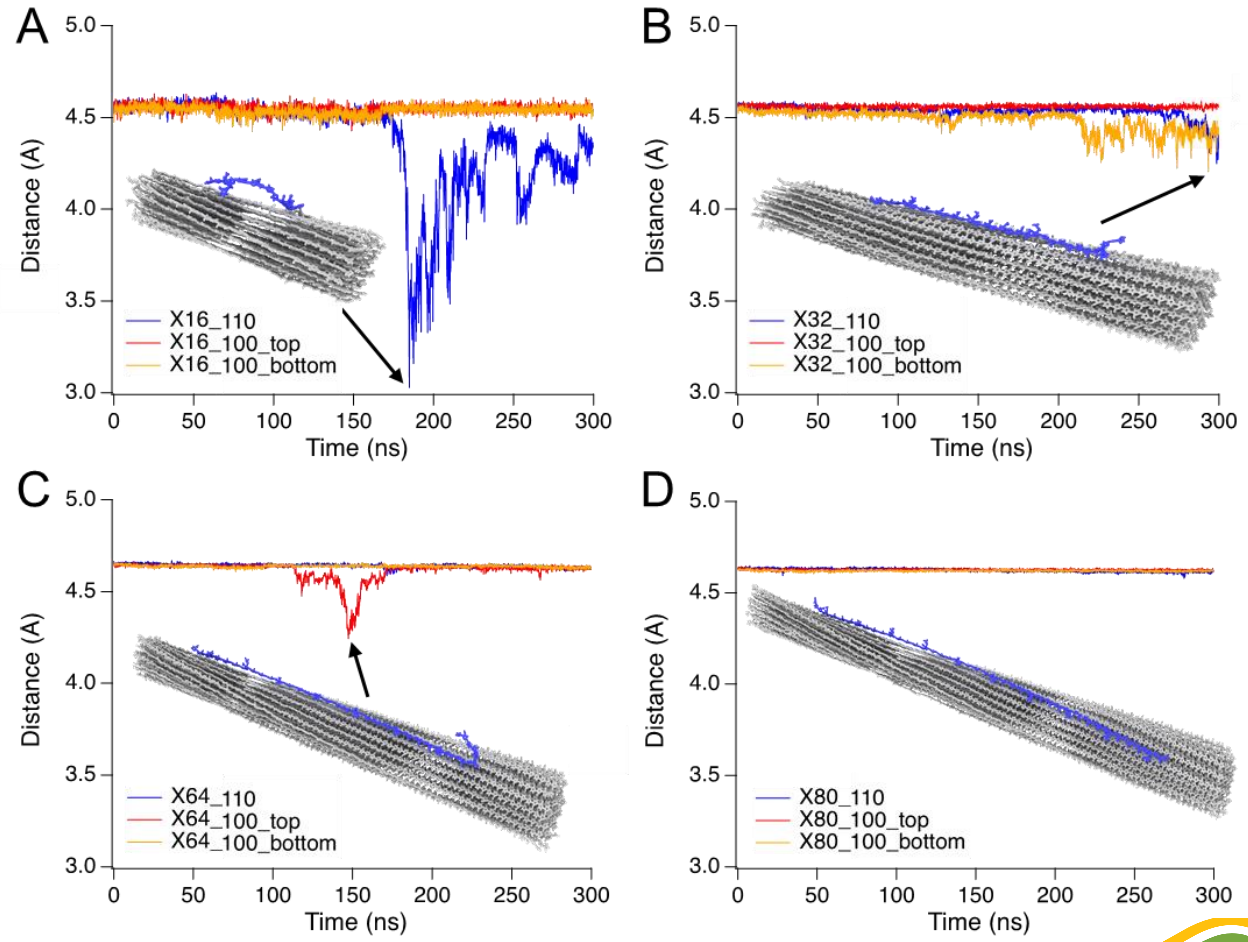


Energy (kcal/mol)	X16	X32	X64	X80
(110)	-6.8 ± 2.7	-8.4 ± 0.8	-9.3 ± 0.6	-9.4 ± 0.4
(100)	-12.2 ± 1.0	-12.4 ± 0.5	-12.1 ± 0.5	-12.5 ± 0.3

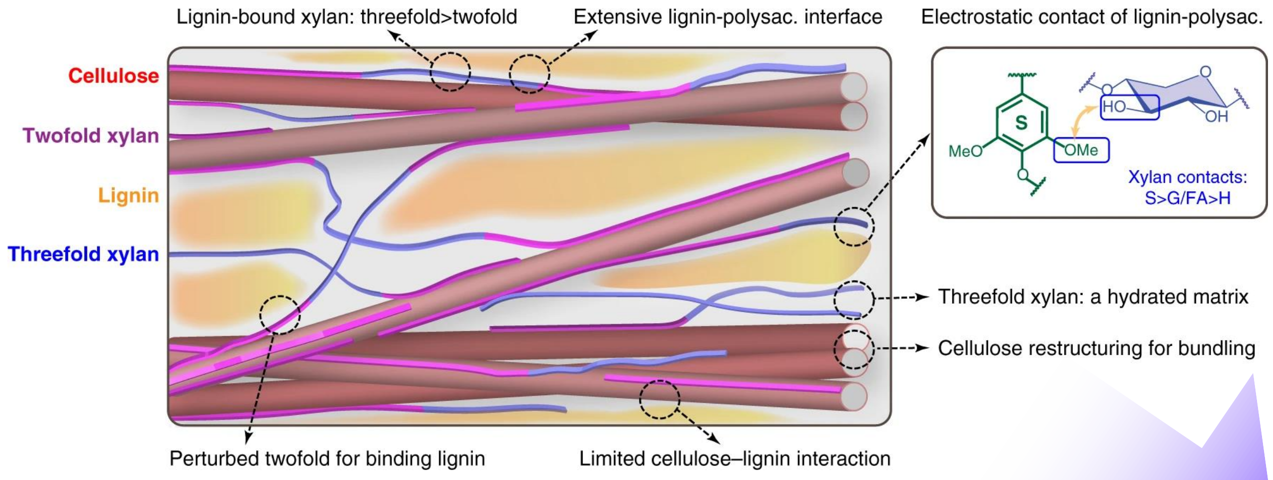
Answer:

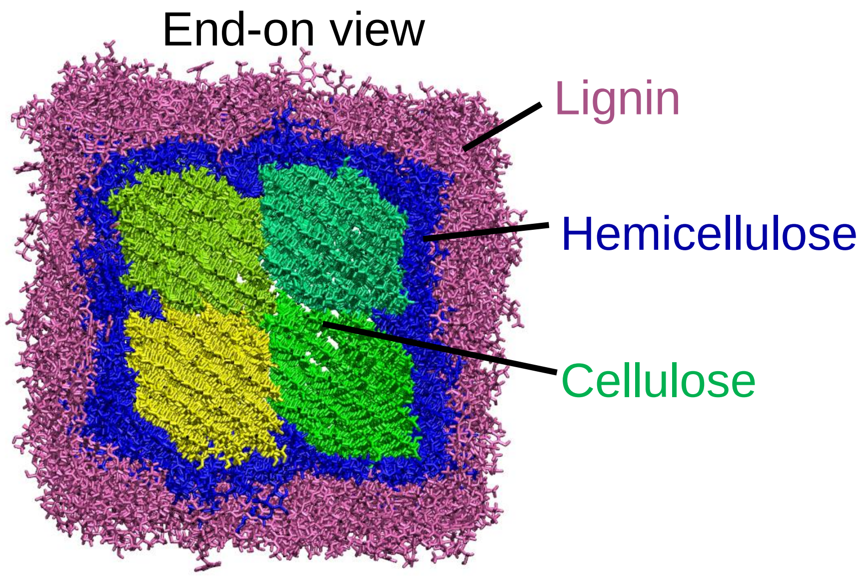
- Xylan with DP < 32 will readily dissociated from the fibril in an aqueous environment
- Xylan with DP > 32 remains firmly bound

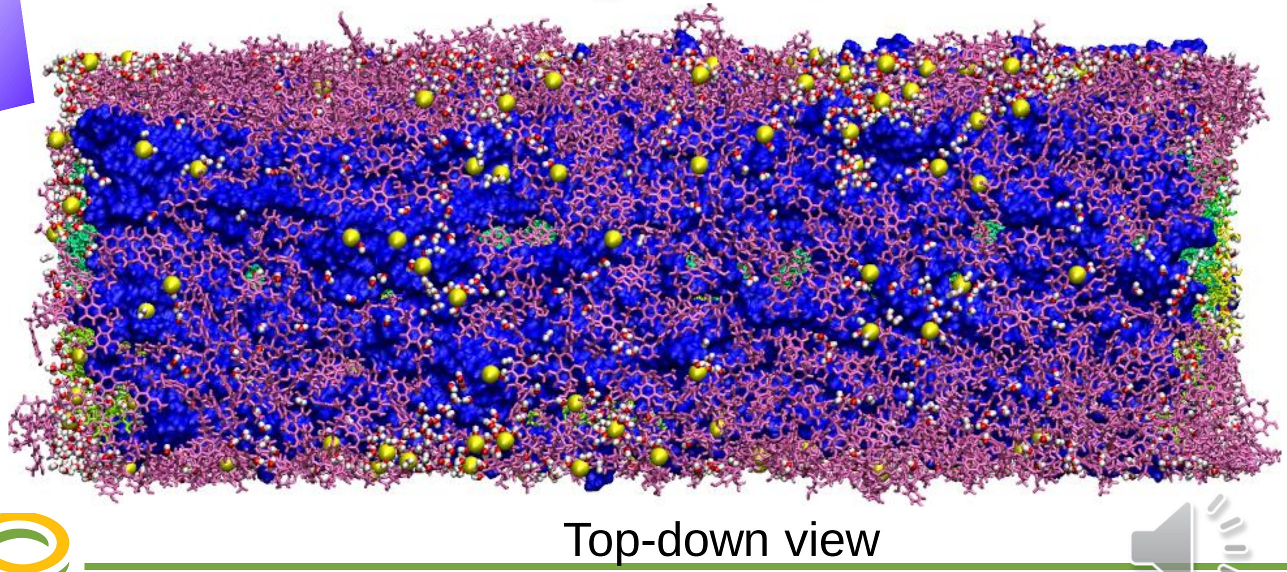
Actionable Insight: In order to effectively fractionate xylan from cellulose, you must reduce it's DP below ~32

L. Bu, C. S. Pereira, V. Bharadwaj,[1] M. F. Crowley,[1] B. S. Donohoe, M. E. Himmel, M. S. Skaf, P. N. Ciesielski, and M. F. Crowley. *In preparation.*

Building the lignocellulose assembly





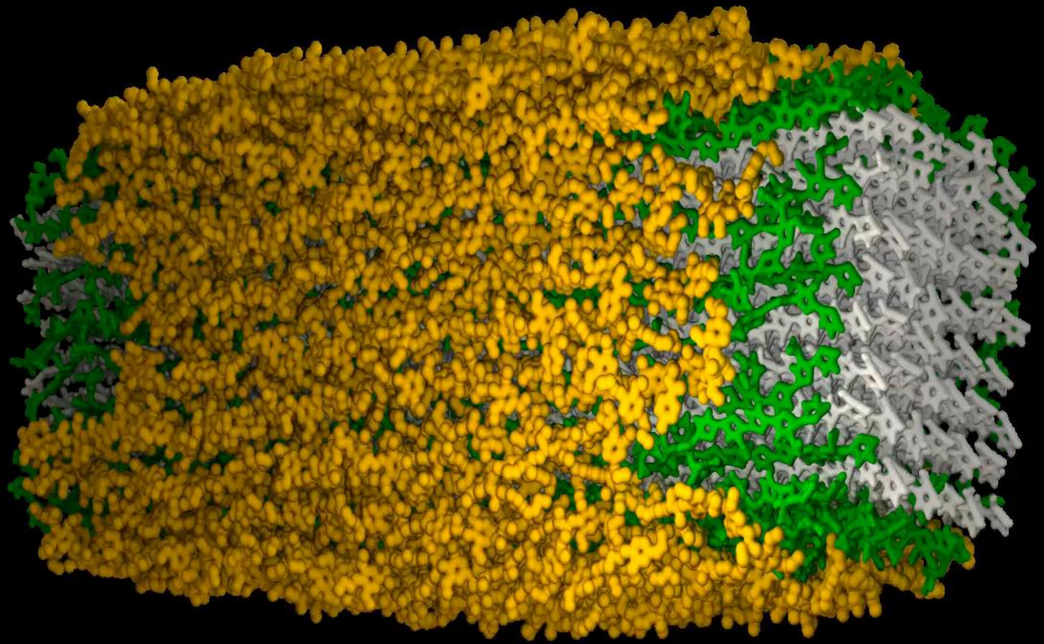


Best available structural data are articulated into an atomistic model

- Recent results suggest that lignin is rarely in direct contact with cellulose (Kang et al, *Nat. Comm*. 2019)
- Elementary cellulose fibrils are thought to contain 18 chains which aggregate into larger bundles (Li et al., *PNAS*, 2016; Stephaphong & Haigler, et al. *PNAS*, 2013)

L. Bu, B. Addison, V. Bharadwaj, M. F. Crowley, M. F. Crowley, Y. Bomble, and P. N. Ciesielski, *In preparation.*

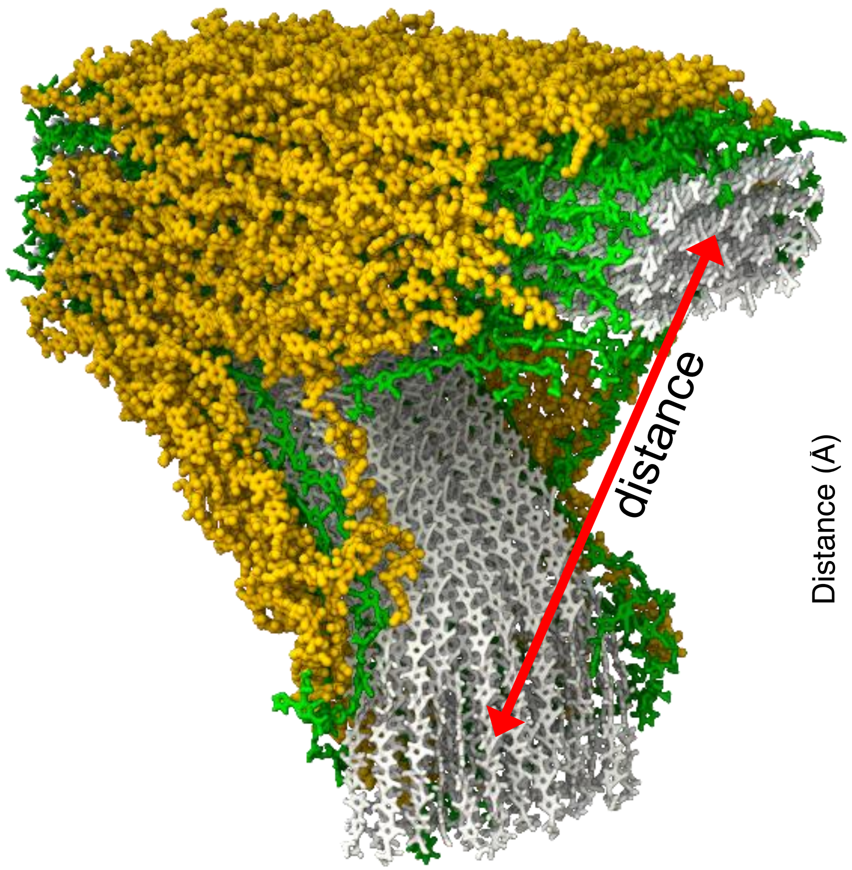
… And ripping it apart

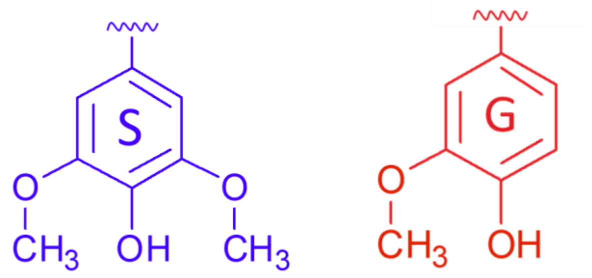


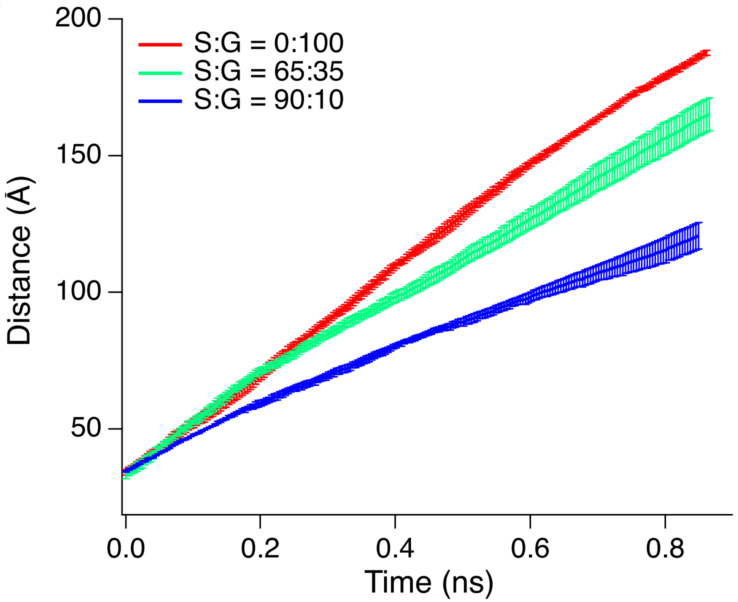
Mapping molecular structure to macromolecular properties

Macromolecular Mechanical Properties of Lignocellulose:

How does lignin monomer composition affect mechanical properties?







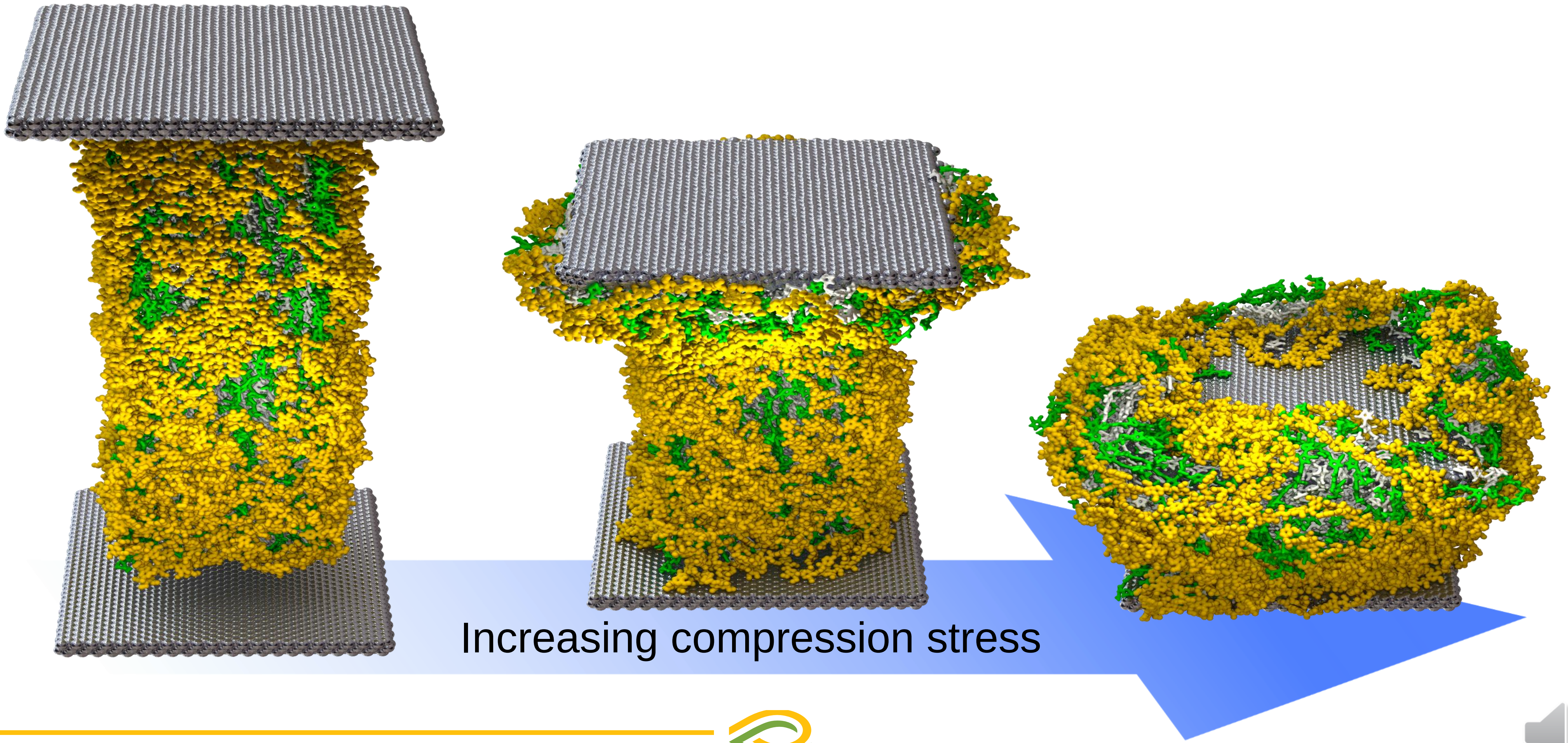
Answer:

- Lignin polymers with a higher content of S-type subunits increase the mechanical integrity of the lignocellulose assembly

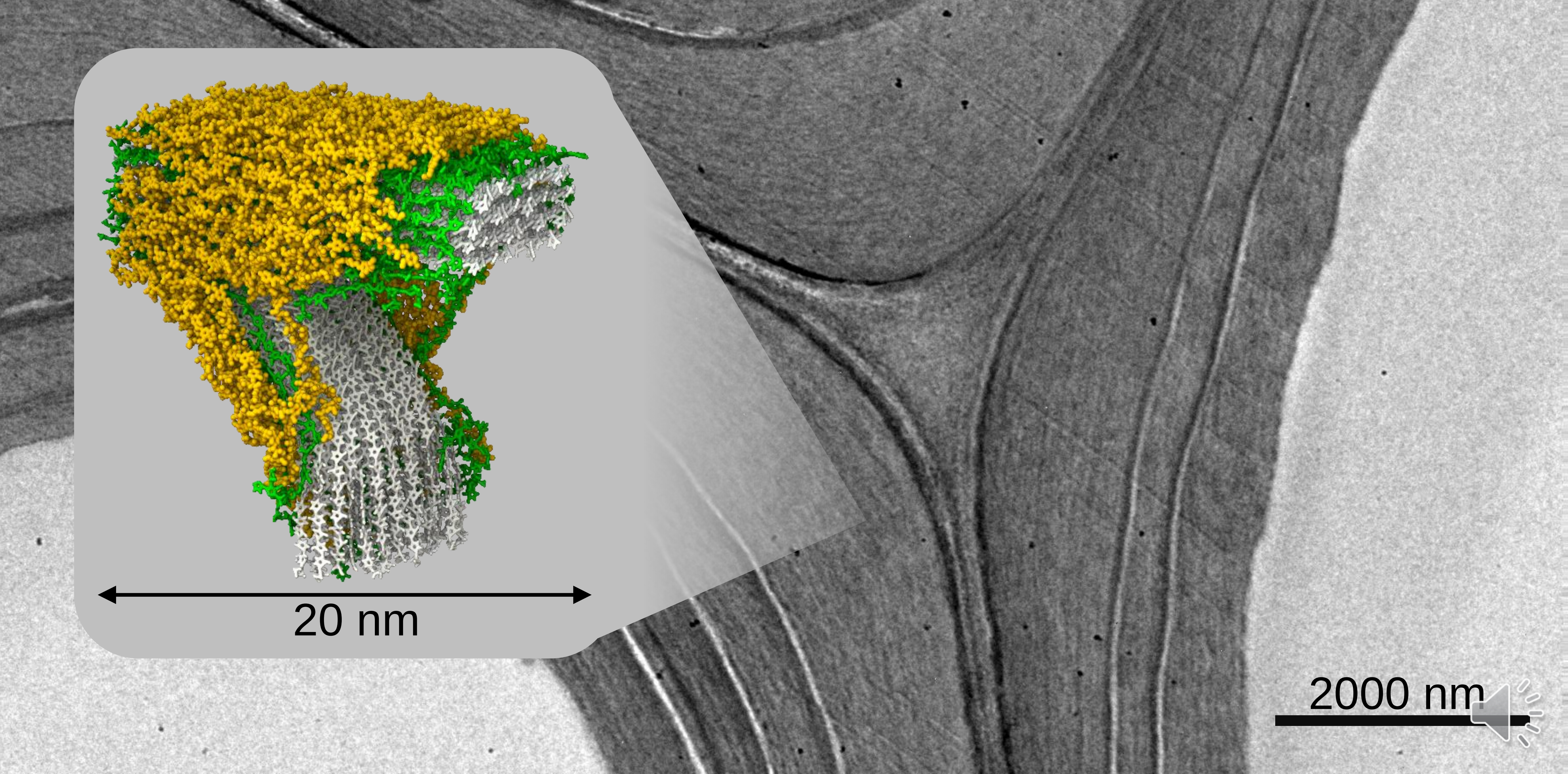
Actionable Insight: This tool could guide genetic modification strategies to specific mechanical properties for materials applications, or tune mechanical comminution processes for optimal performance on a given feedstock

L. Bu, B. Addison, V. Bharadwaj, M. F. Crowley, M. F. Crowley, Y. Bomble, and P. N. Ciesielski, *In preparation.*

Measuring Compression Modulous



We need to go bigger!

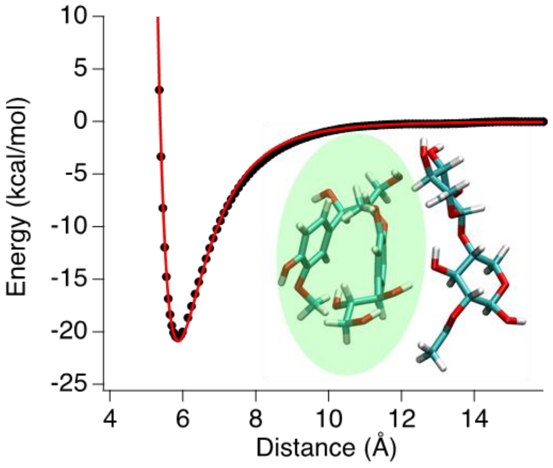


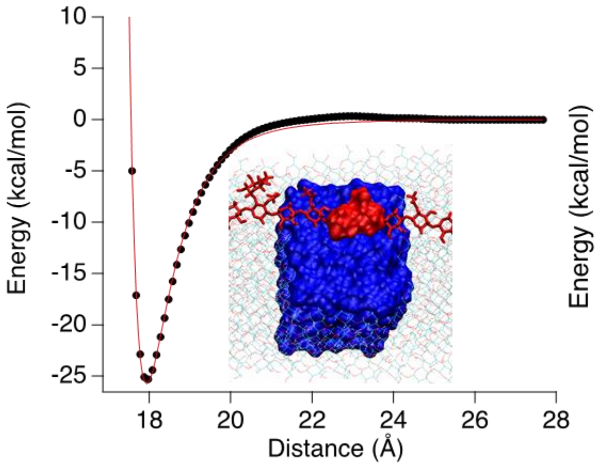
Coarse-graining strategy

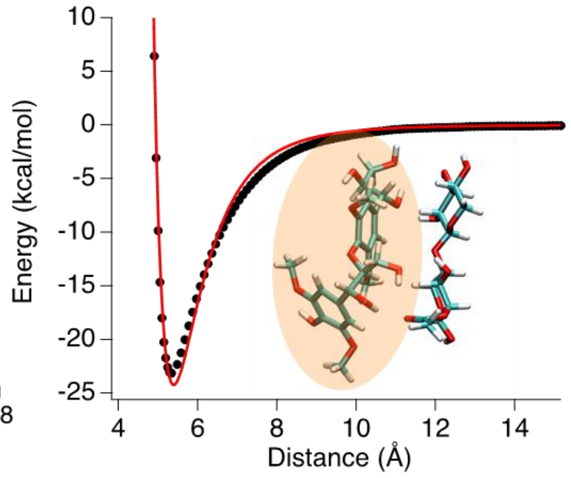
Classical molecular dynamics is used to develop coarse-grained force field parameters

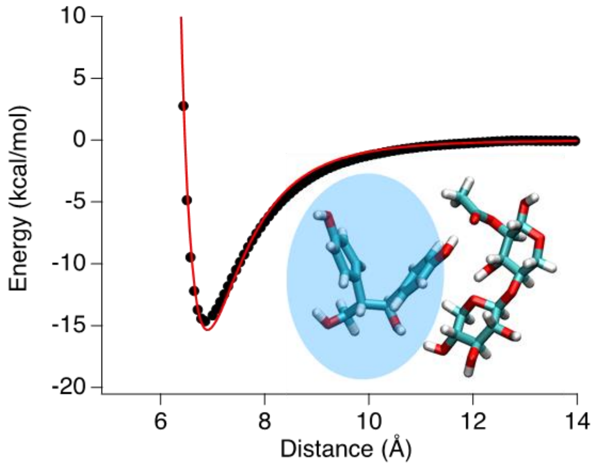
Cellulose: 18chain, DP4 segment → 1 CG Unit

Hemicellulose, Lignin: 1 residue → 1 CG Unit







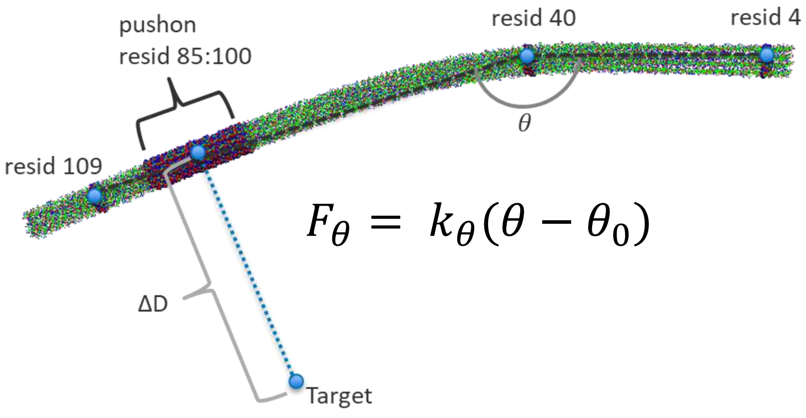


L-J potential	cell/ xylan	xylan/ xylan	xylan/ s-lig	xylan/ g-lig	xylan/ h-lig	s-lig/ s-lig	g-lig/ g-lig	h-lig/ h-lig
ε (kcal/mol)	25.76	20.32	24.27	20.91	15.35	24.10	22.00	17.31
r_m (Å)	3.52	2.93	4.13	4.53	3.95	4.76	3.43	4.49
r_0 (Å)	14.42	3.36	1.27	1.34	2.95	2.23	2.39	2.64

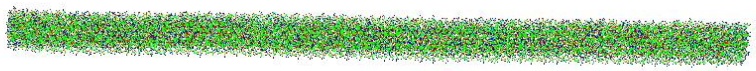
Actionable Insight: Increasing methoxy groups on lignin monomers results in stronger interactions will all other biopolymer subunits

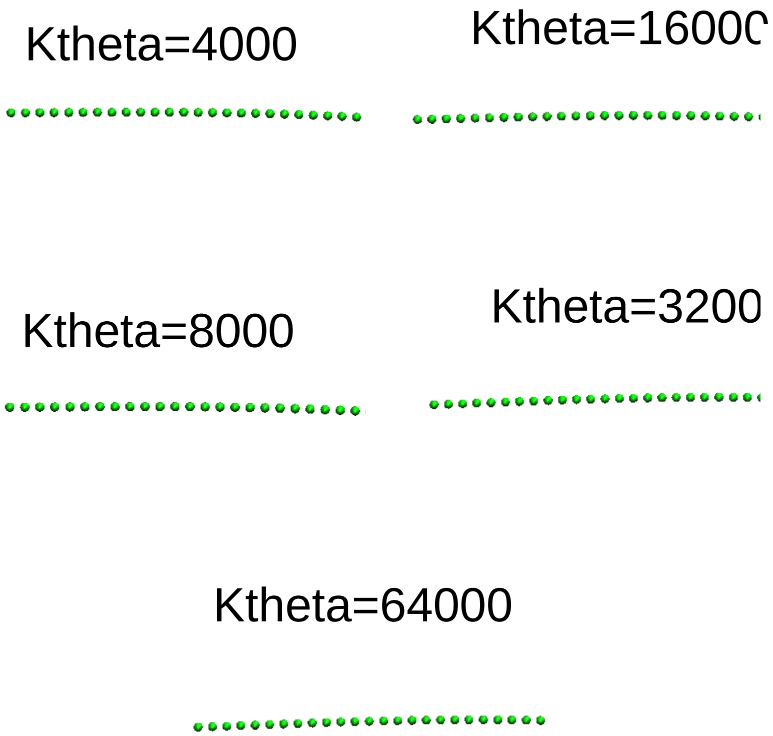
Coarse-graining strategy

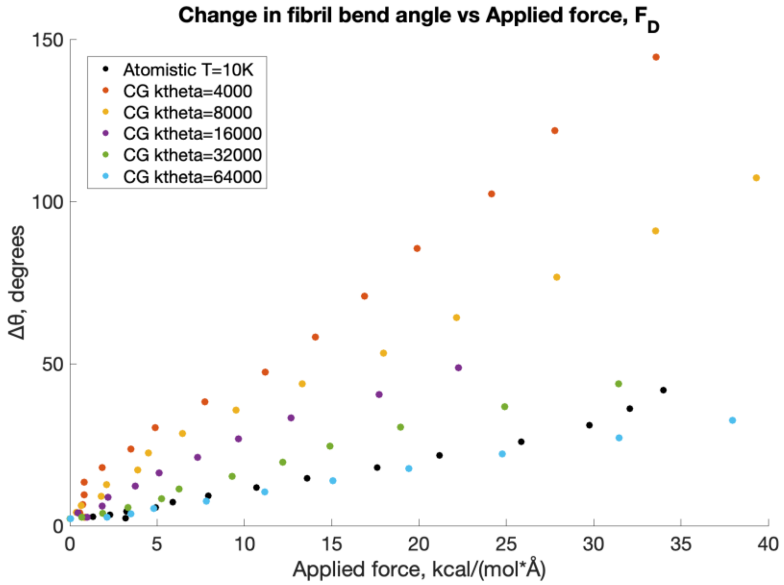
The “stiffness” of cellulose nanofibrils (force field angle term) is also calculated by fitting parameters in CG simulations to behavior of atomistic simulations



$$F_\theta = k_\theta(\theta - \theta_0)$$

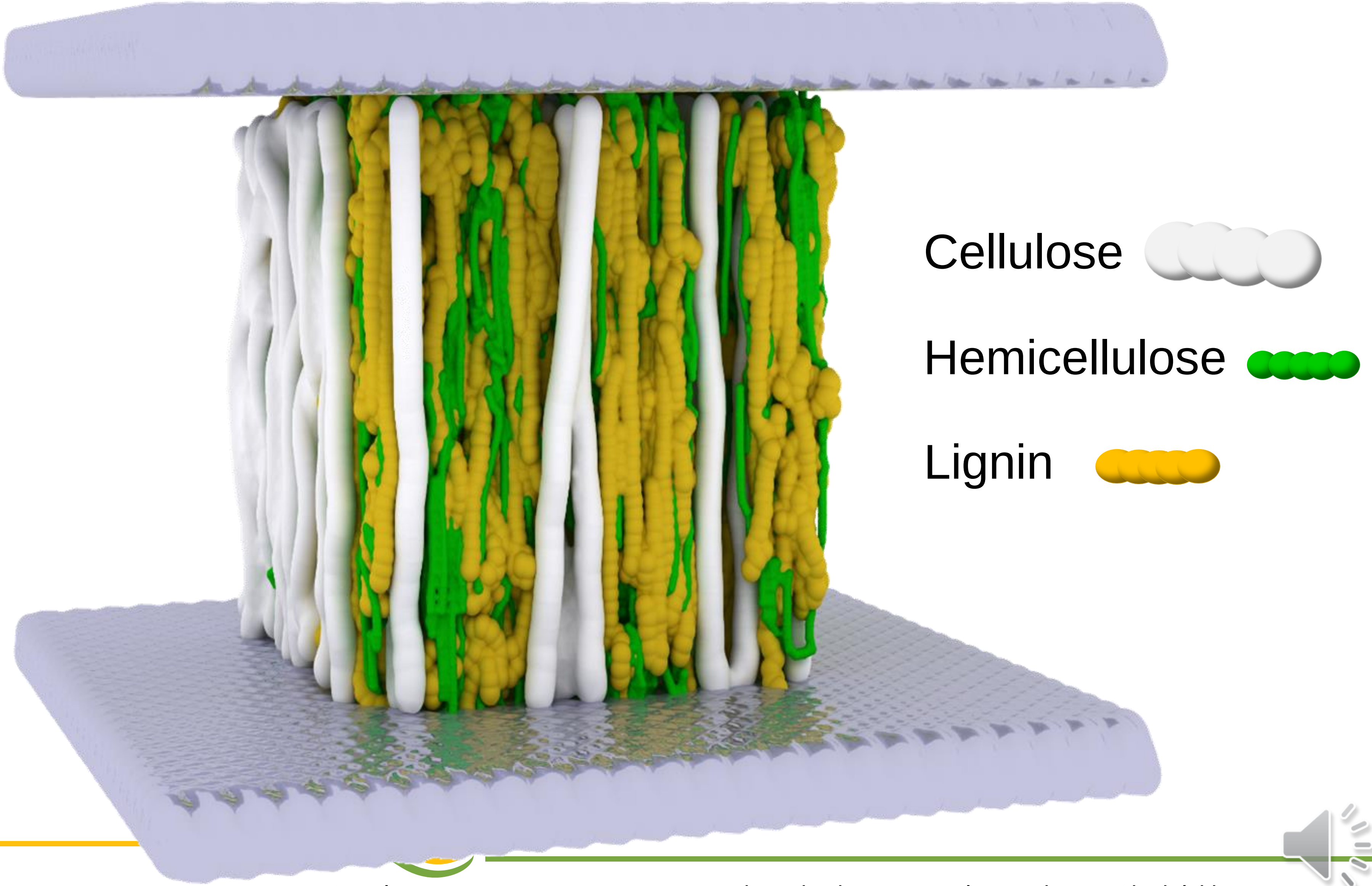






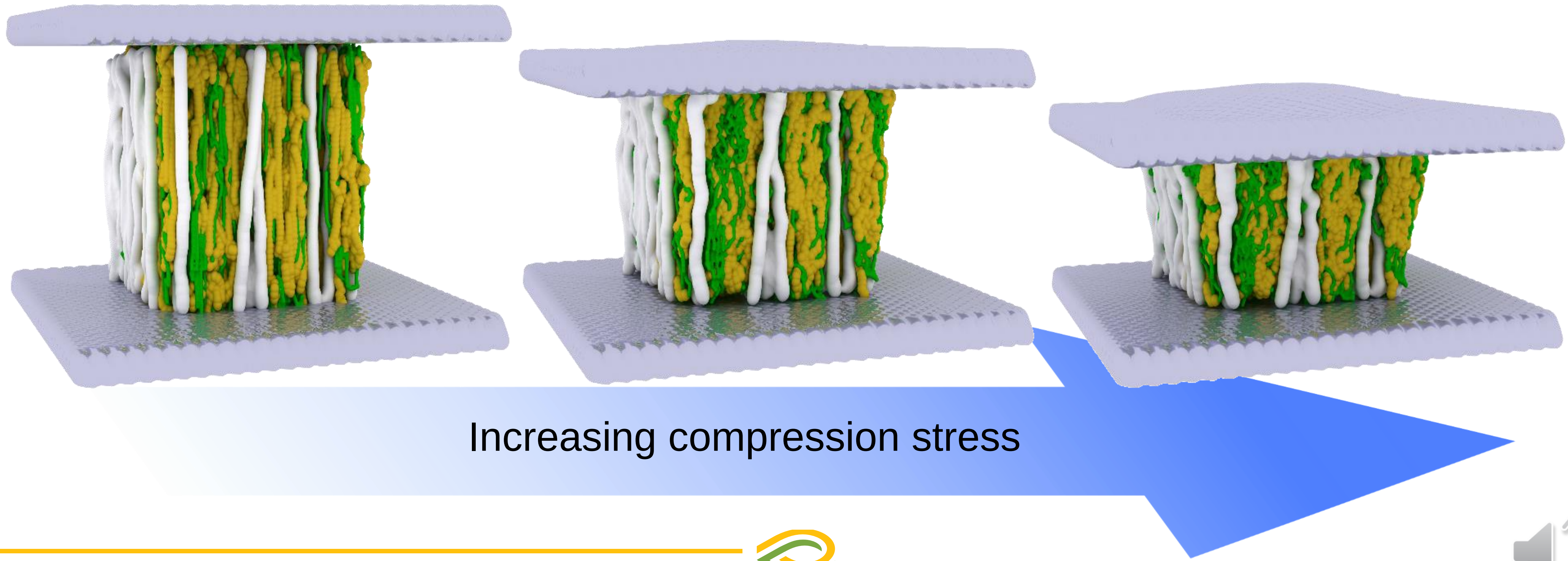
New Coarse-Grained Model for Lignocellulose!

- Particle coarse grain ratio of **~1700 for cellulose, ~20-30 for hemicellulose and lignin**
- **Procedurally generated** nanoscale architecture based on geometric rules derived from experimental studies
- **Can vary biopolymer composition**, including lignin monomer composition
- Built in CHARMM, will be released as open-source after publication

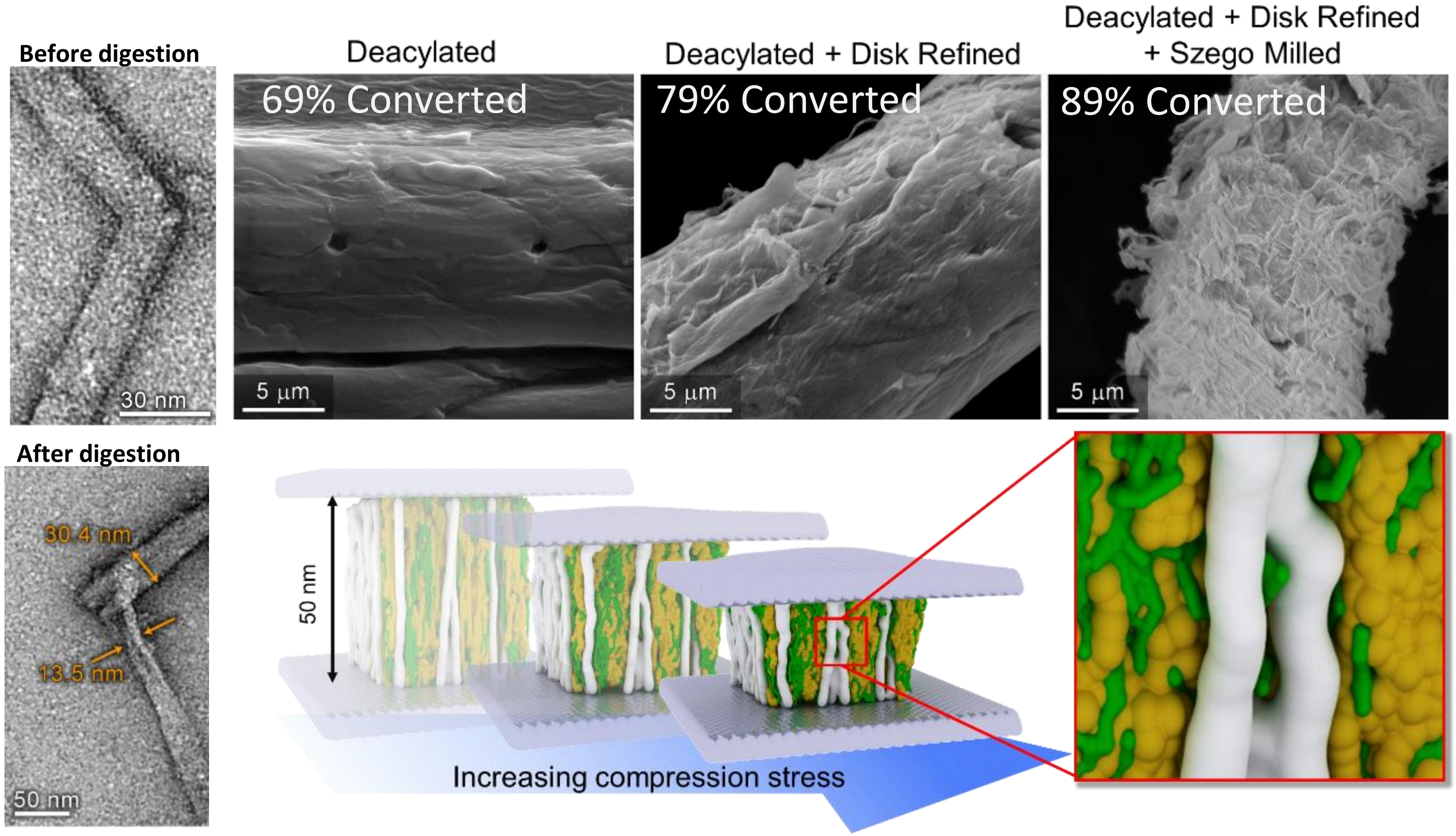


Crowley, M. F., L. Bu, J. Vermaas, V. Bharadwaj, M.F. Crowley, and P. N. Ciesielski, *In preparation.*

Coarse-grained Compression Simulation



Biomass that surfaces that exhibit kink defects are much more amenable to enzymatic hydrolysis

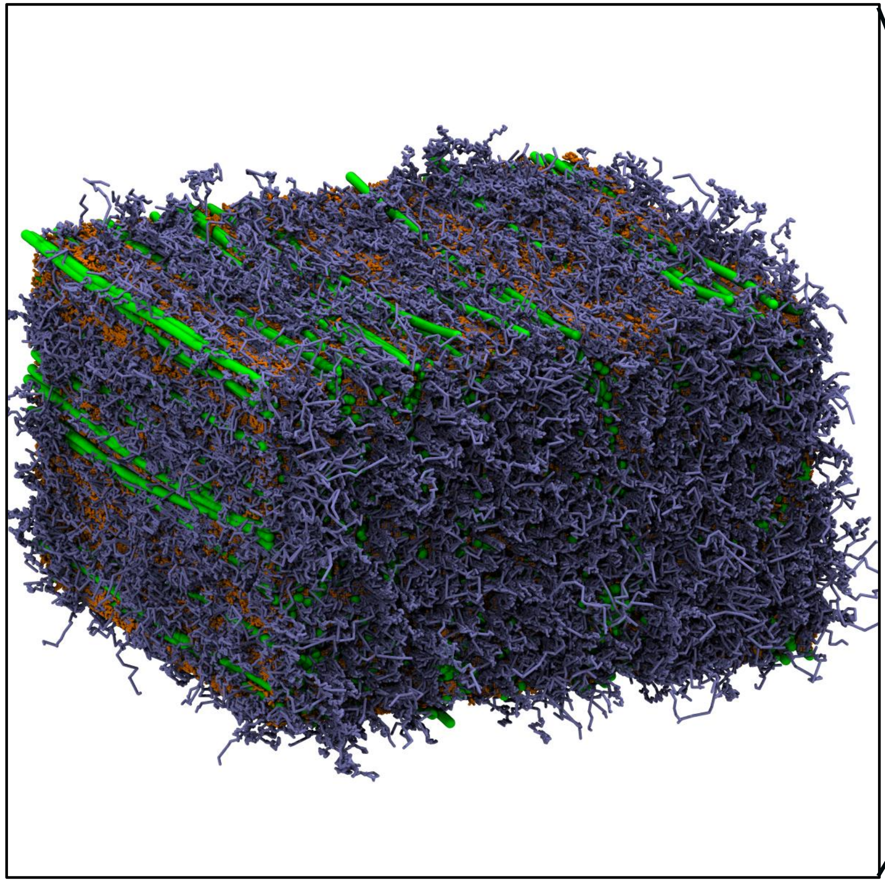


- Enzymes initiate hydrolysis at macromolecular kink defects[1]
- Mechanical treatments that produce biomass surfaces with "kinky" cellulose produce highly digestible biomass[2]
- Our coarse-grained simulation predicts formation of kink defects in lignocellulose when nanomechanical stress exceeds a certain threshold

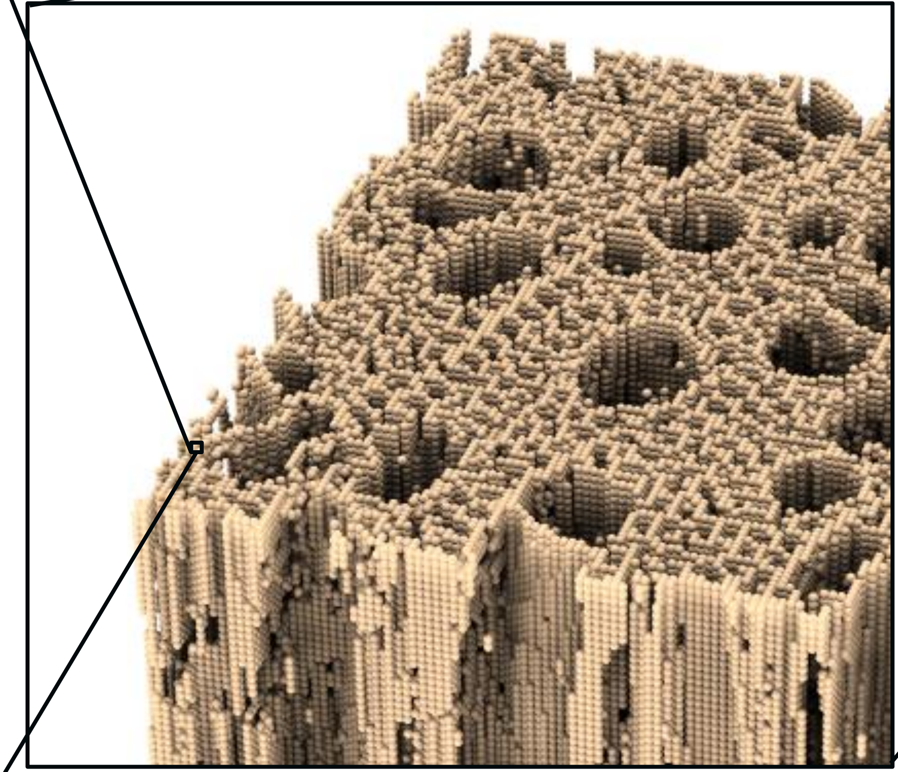
Coarse-grained simulation is being used to identify modes of mechanical processing that maximize formation of "reactive defects" while minimizing energy requirements

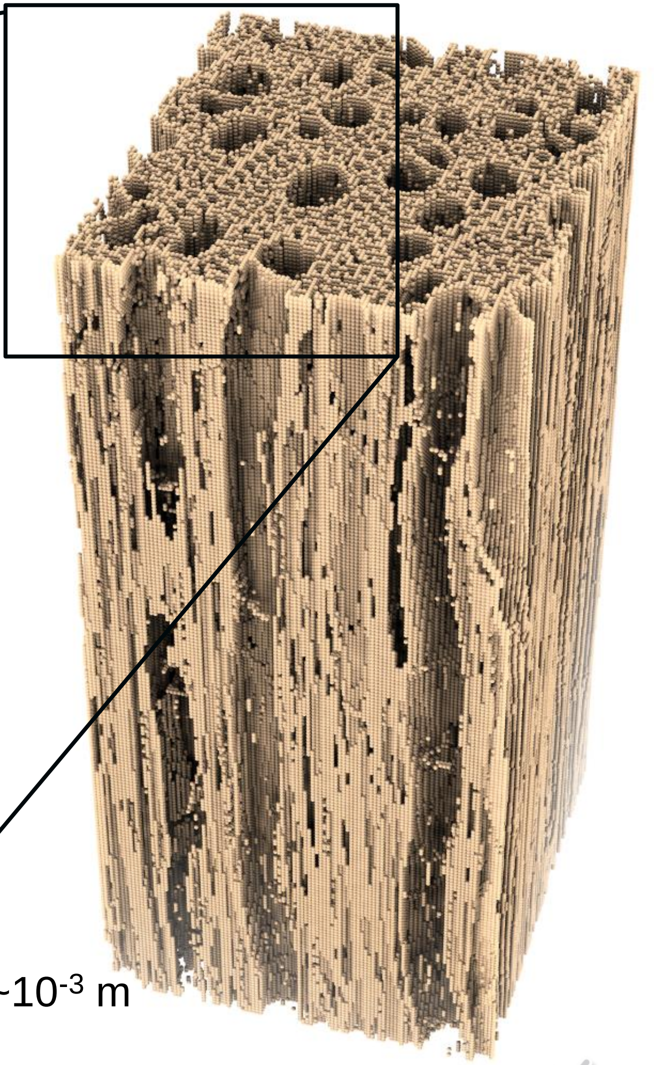
[1]Ciesielski, et al. PNAS, 2019; [2]Chen, et al. ACS Sus. Chem. Eng., 2016

Multiscale Homogenization Strategy



Atomistic-Derived CG lignocellulose model ~10^{-7} m
(NREL)





XCT-Derived Tissue Scale Lattice Model ~10^{-3} m
(INL)

Summary and Conclusions

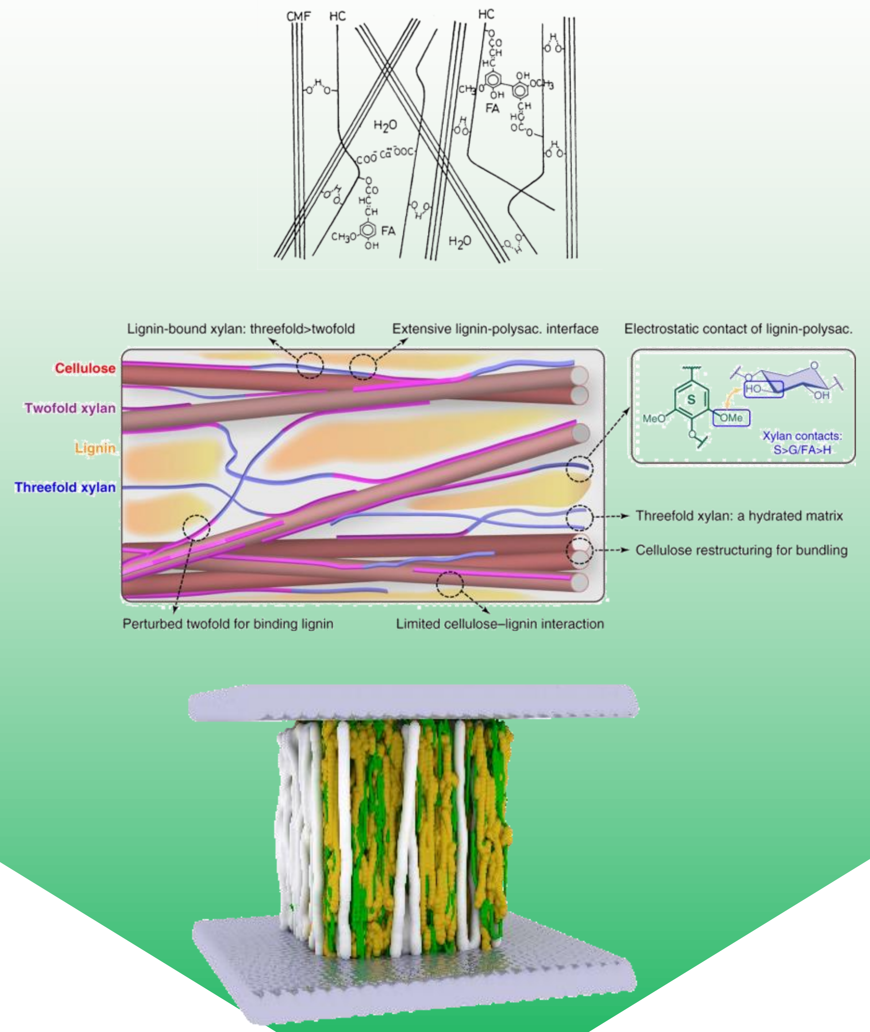
- These FCIC modeling efforts are focused on developing tools that **translate fundamental knowledge into quantitative, actionable information**

- Major capability gaps that we are addressing are **multiscale integration and robust representation of lignocellulose variablity**

- This is a **daunting problem**, and what was presented today is a **just work in progress**, but we **are generating valuable insight along the way**

- These toolsets for multiscale modeling of polymer assemblies are readily extensible to other systems, **like waste plastics, synthetic composites, etc.**

- **FCIC/CCPC modeling efforts continue to advance the state of the art!**



Acknowledgments

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