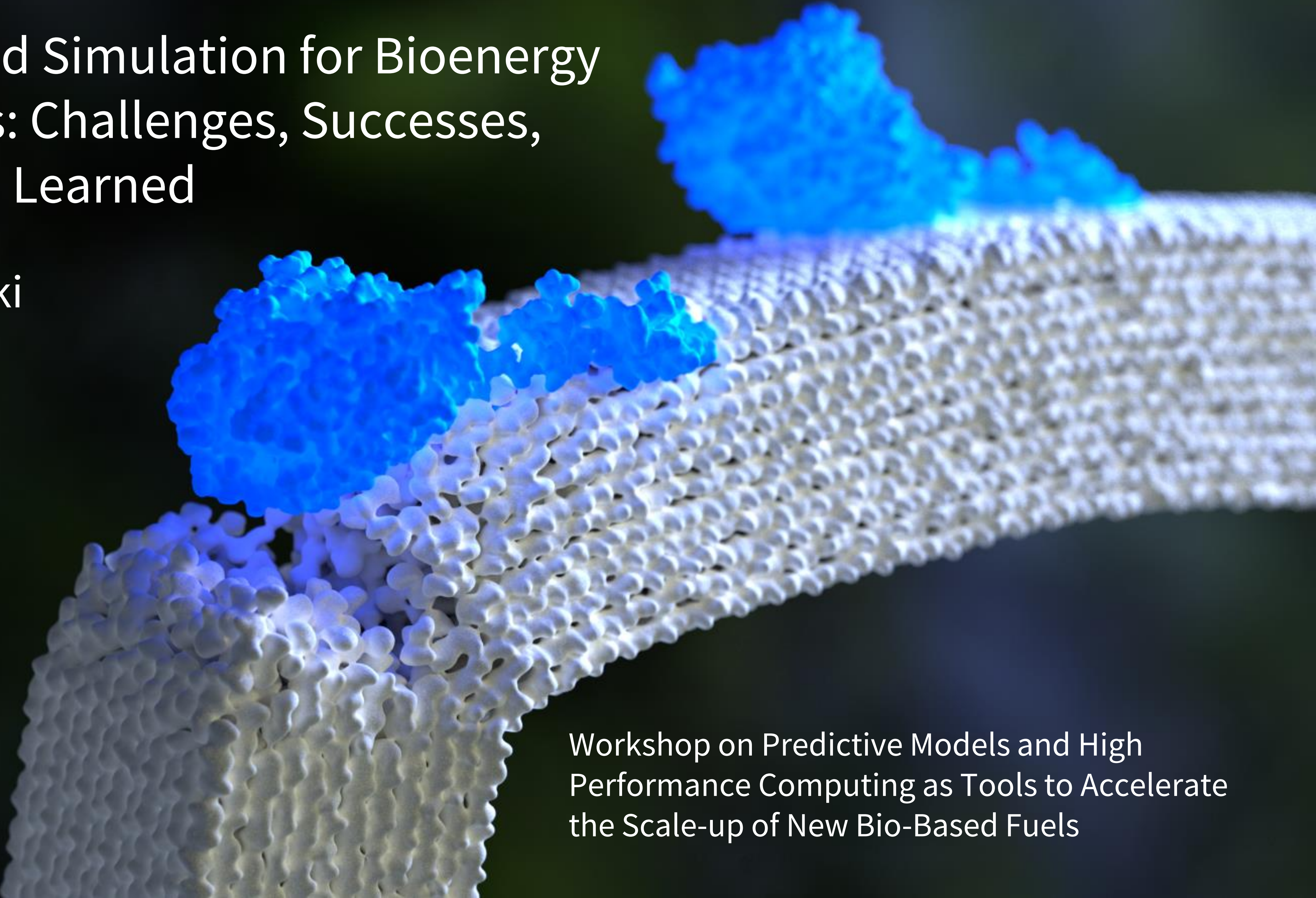
Modeling and Simulation for Bioenergy Applications: Challenges, Successes, and Lessons Learned

Peter Ciesielski
June 9th 2020



Workshop on Predictive Models and High Performance Computing as Tools to Accelerate the Scale-up of New Bio-Based Fuels

Challenges with predictive modeling and scaleup of bioenergy applications

What doesn't work…

$\not\approx$

Handling and comminution methods that were designed for other solid materials will work for biomass

NOPE

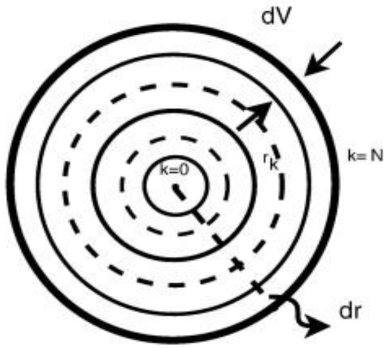
Modeling and simulation frameworks and engineering heuristics developed for other feedstocks will translate directly to biomass

Just stop!

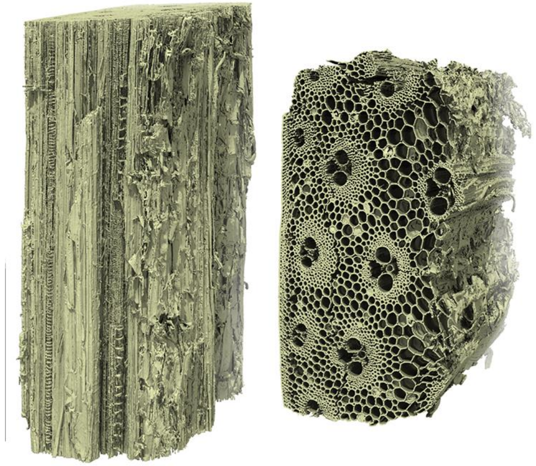
$\not\approx$

Pyrolysis oil

Petroleum



$\not\approx$

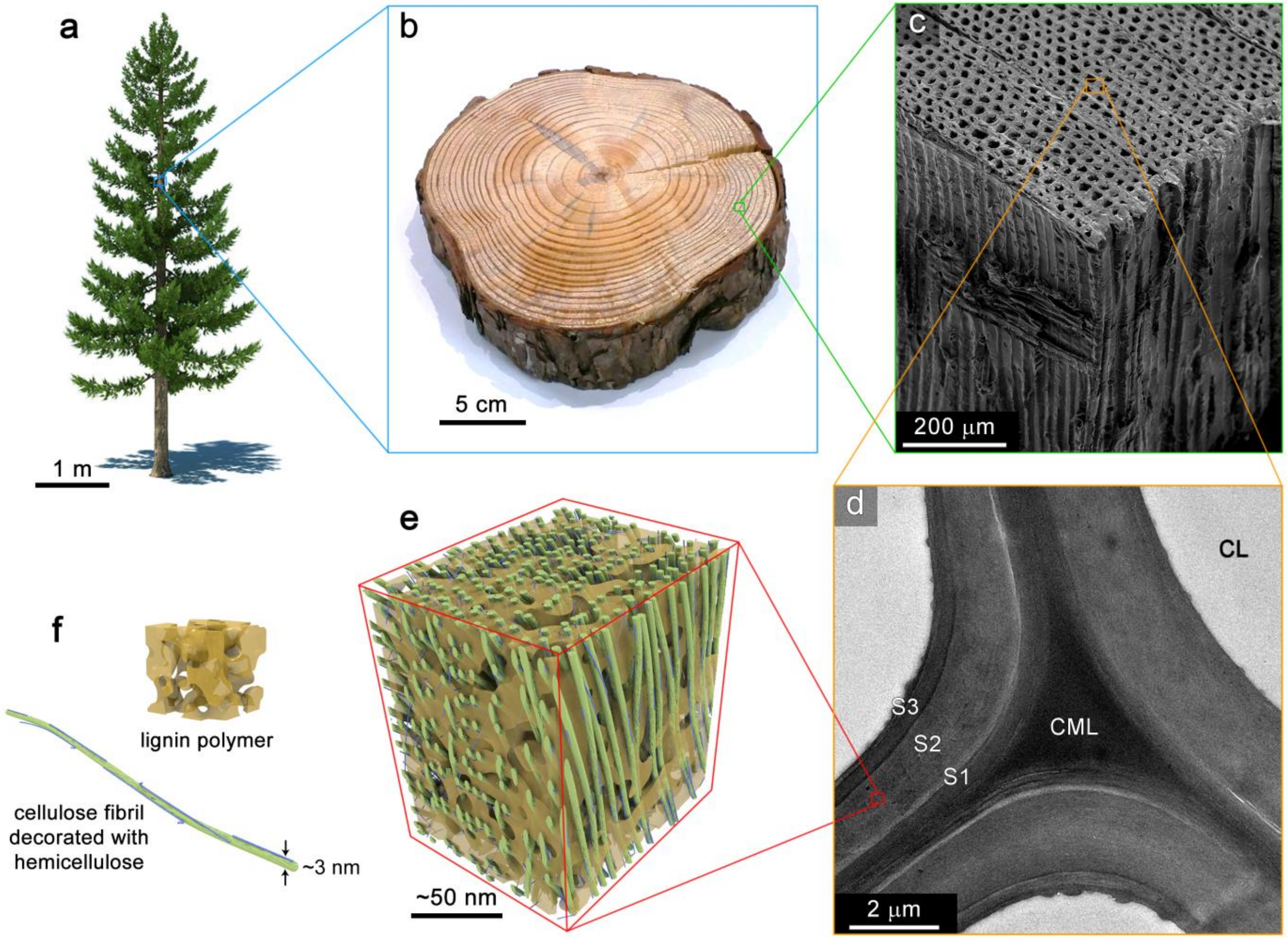


Upgrading and conversion technologies developed for petroleum feedstocks will also work for biomass-derived feedstocks

Wrong again

Challenges with predictive modeling and scaleup of bioenergy applications

Why is it so hard to get this right? **Hierarchical Structure** and **Variability**



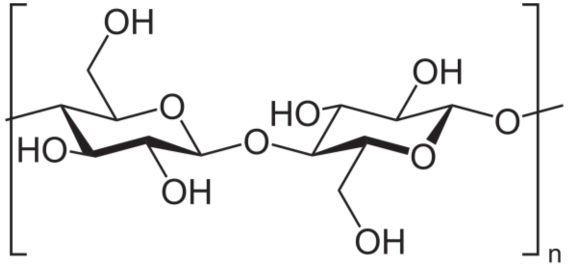
The **hierarchical structure** gives rise to **emergent properties** that dictate the behavior of biomass feedstocks in handling, pre-processing, and conversion operations.

Emergent properties are difficult or impossible to characterize by experiment or simulation performed at individual length/time scales.

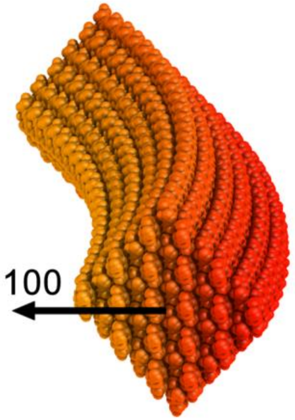
This makes scale-up particularly challenging!

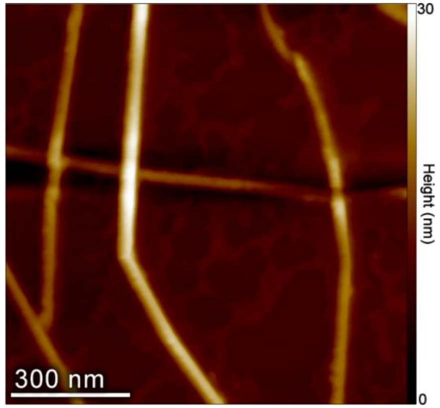
Zhu, H., Luo, W., Ciesielski, P.N., Fang, Z., Zhu, J.Y., Henriksson, G., Himmel, M.E. and Hu, L. *Chemical reviews*, **2016**.

Emergent property example: nanomechanics of cellulose

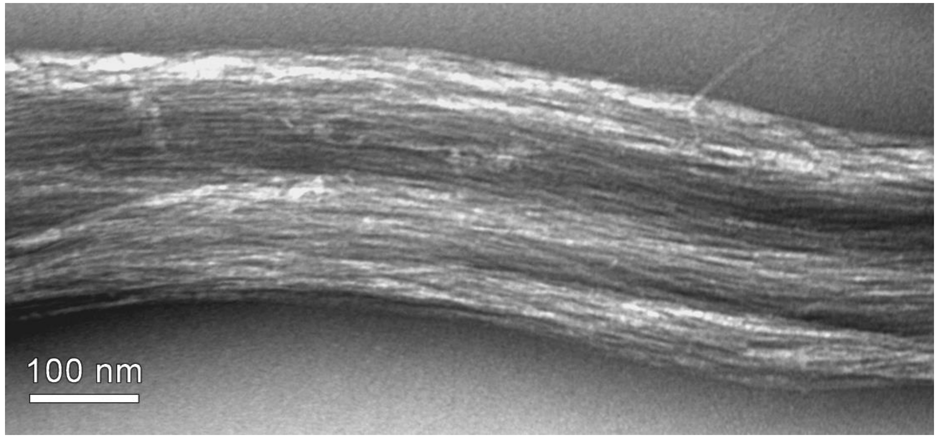


Molecular Structure

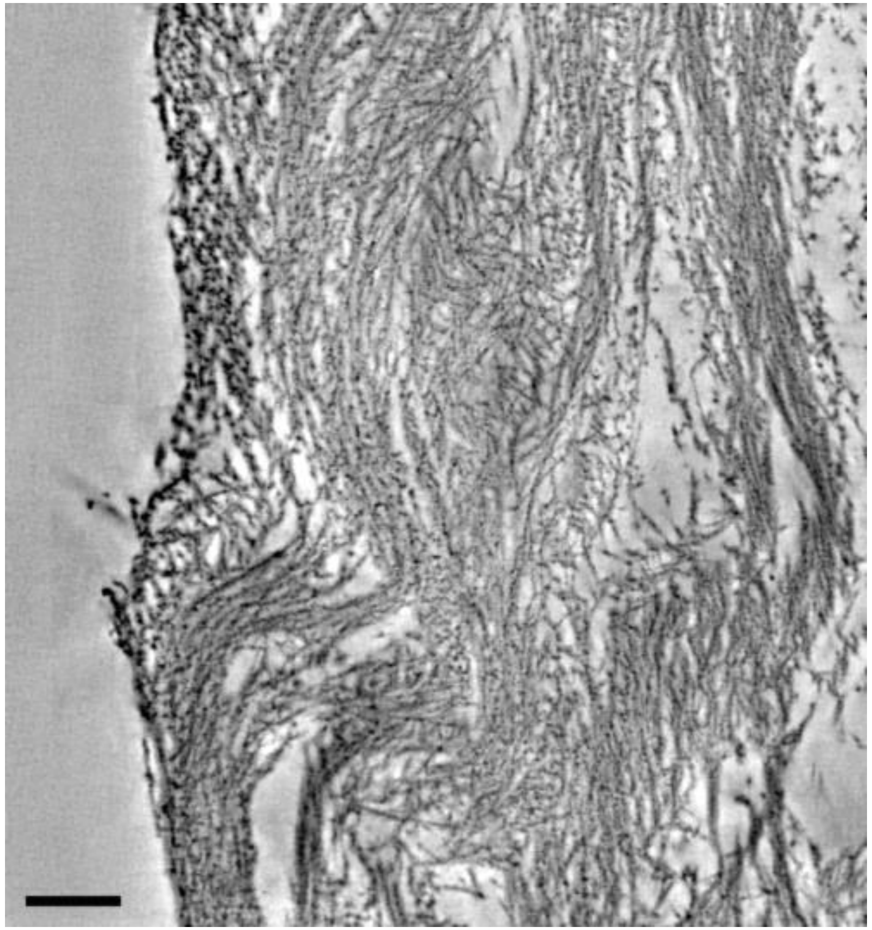




Nanostructure



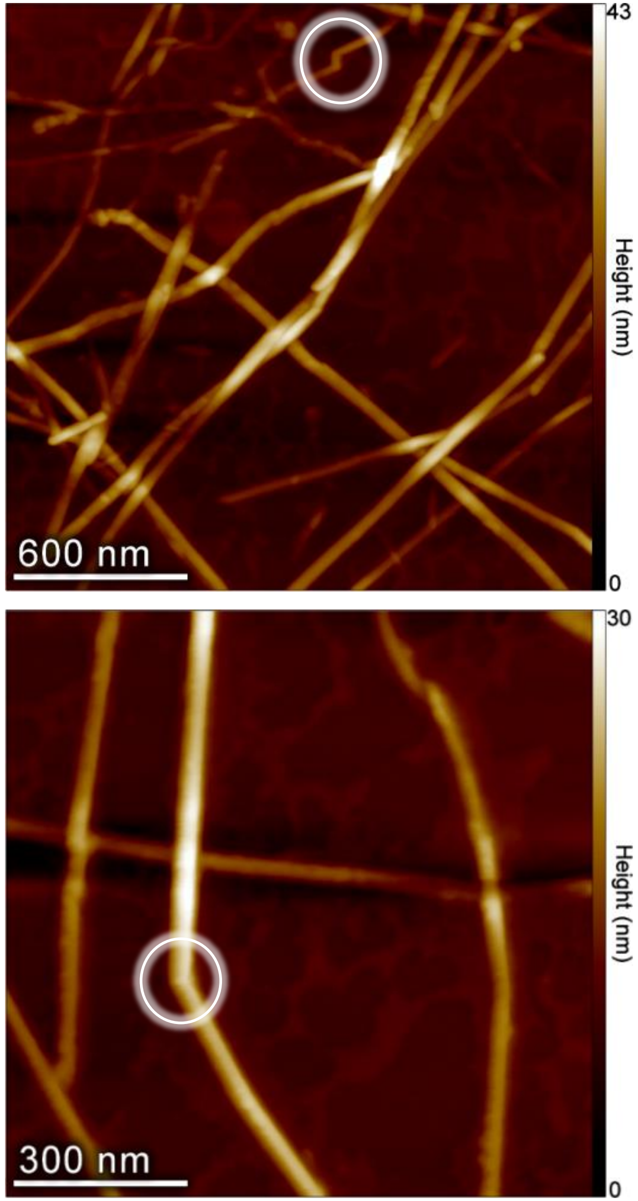
Microscale assemblies of nanofibrils



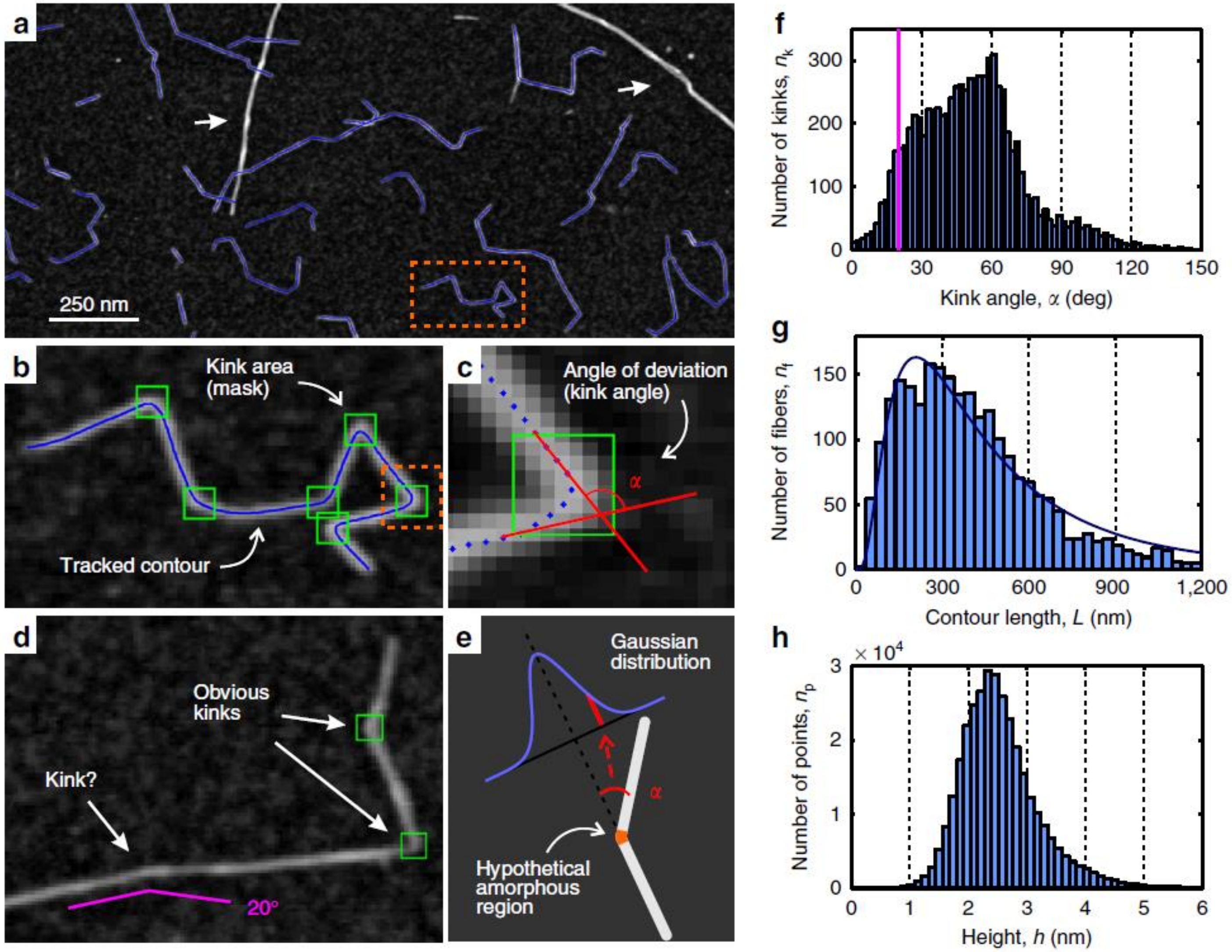
Higher-order assembly within the cell wall

Ciesielski, et al. *ACS Nano, 2013*

Emergent property example: nanomechanics of cellulose

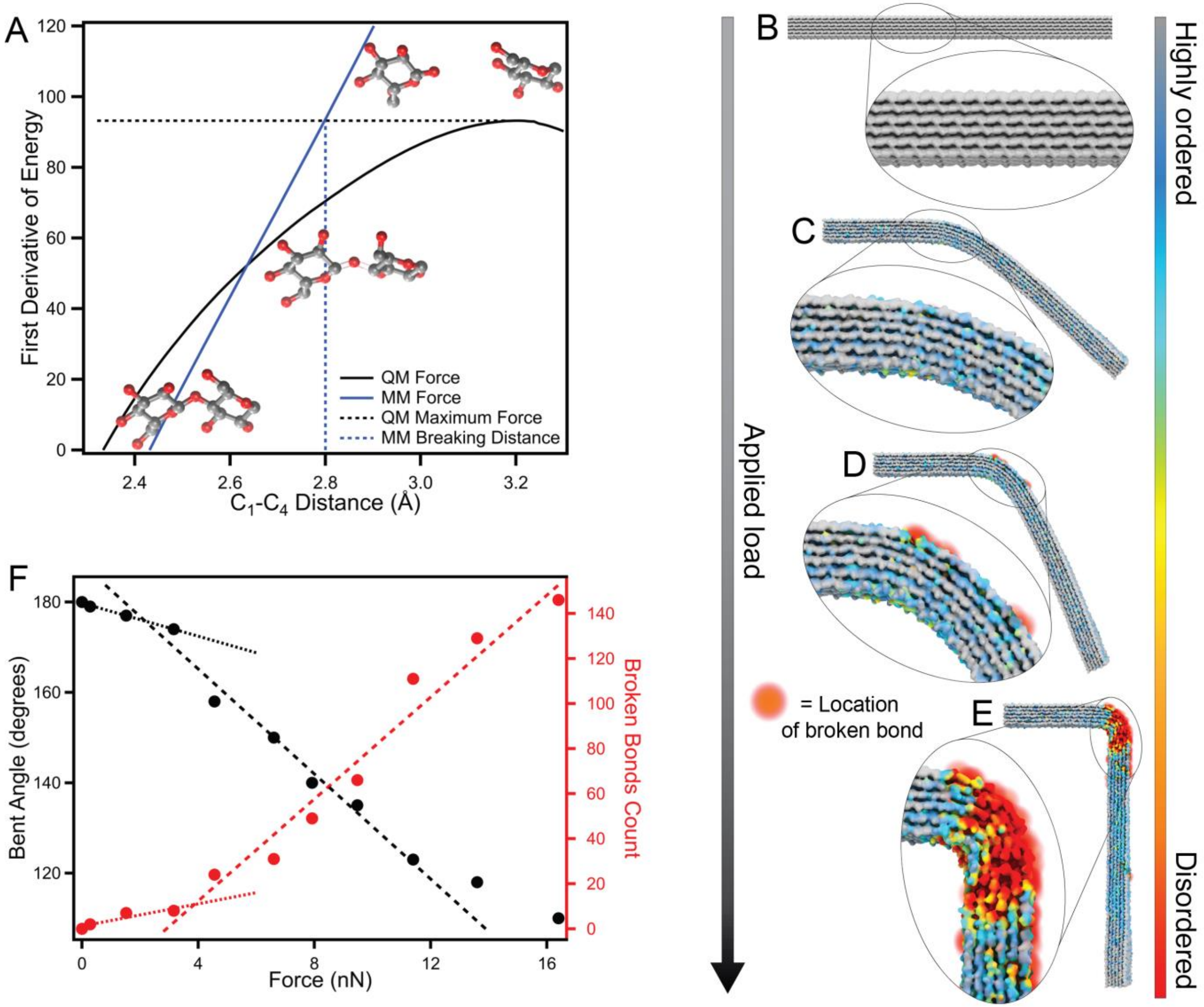


P. Ciesielski, NREL BSCL



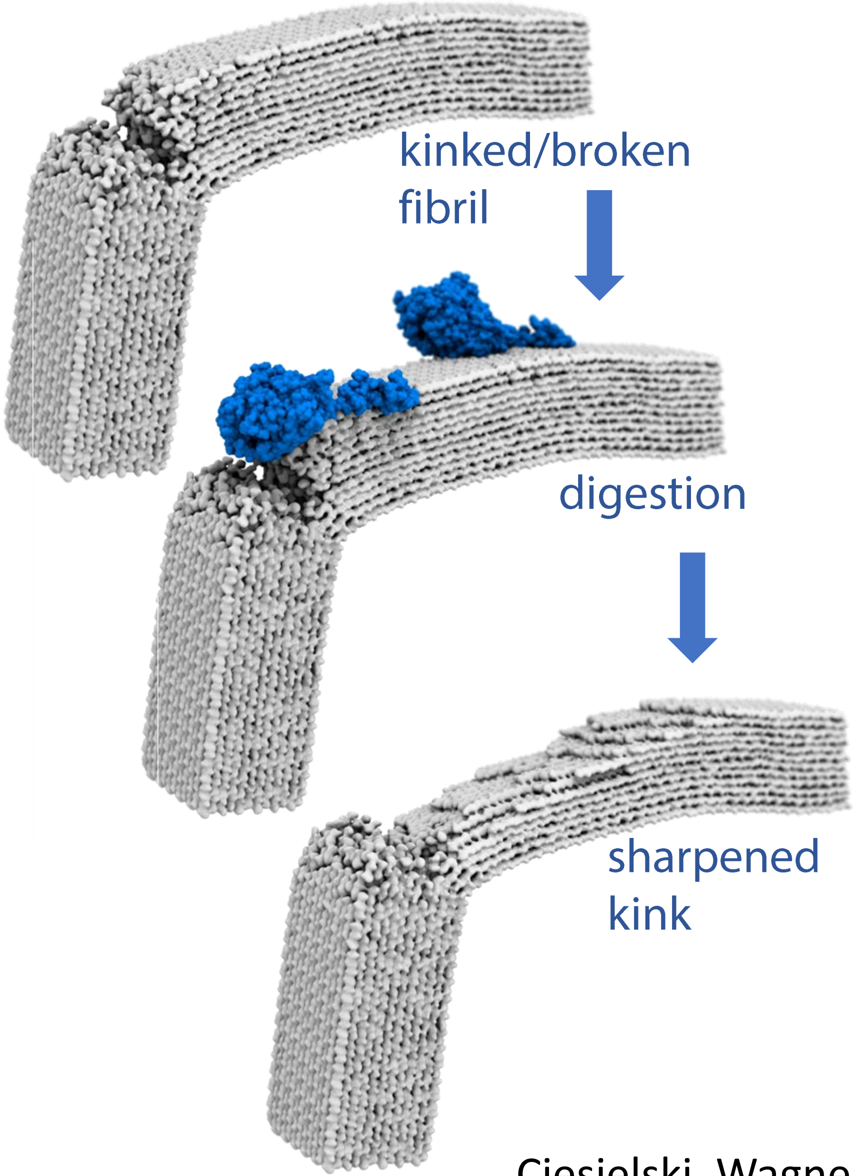
Usov et al. Nature Communications, 2015

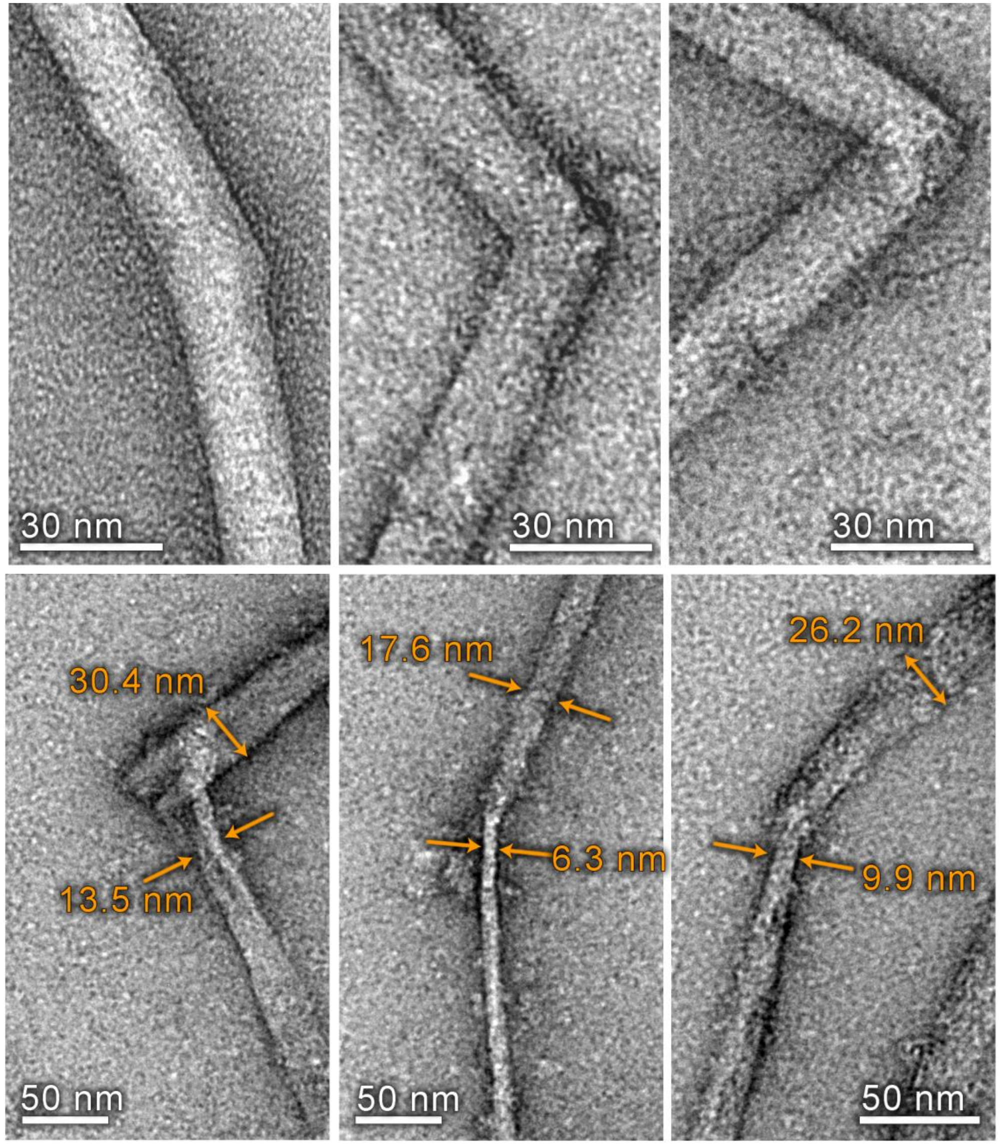
Pseudo-reactive simulations combine quantum results with classical MD predict strain-induced bond breakages accompany kink defects



Ciesielski, Wagner, Bharadwaj, Killgore, Mittal, Beckham, Decker, Himmel, Crowley. PNAS, 2019

Sharpening will occur in the direction of the reducing end (in the case of digestion by R-end acting Cel7A)

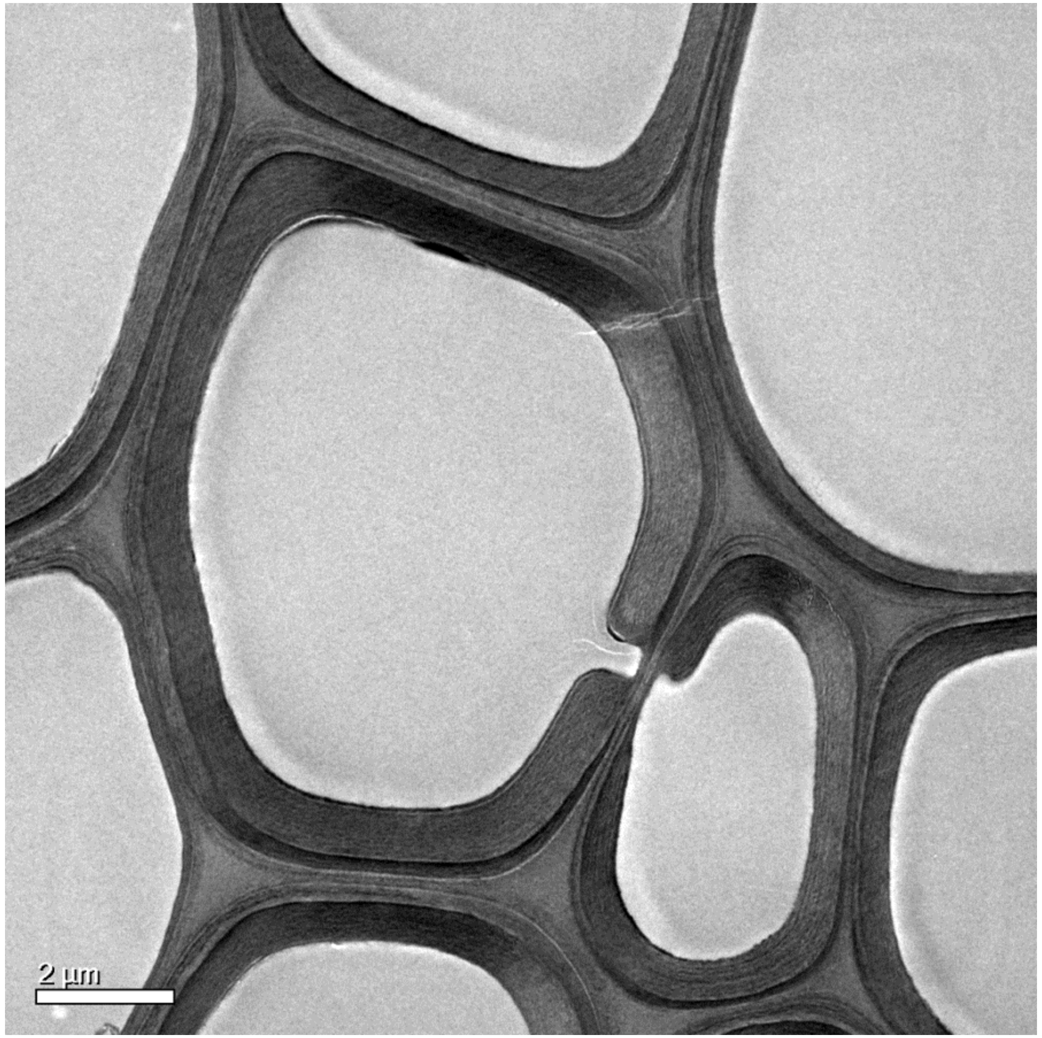




Ciesielski, Wagner, Bharadwaj, Killgore, Mittal, Beckham, Decker, Himmel, Crowley. PNAS, 2019

These findings provide new fundamental insights to evaluate the impacts of pre-processing and pretreatments

Untreated corn stover cell walls



21.5 % cellulose converted
after 96 h of enzymatic digestion

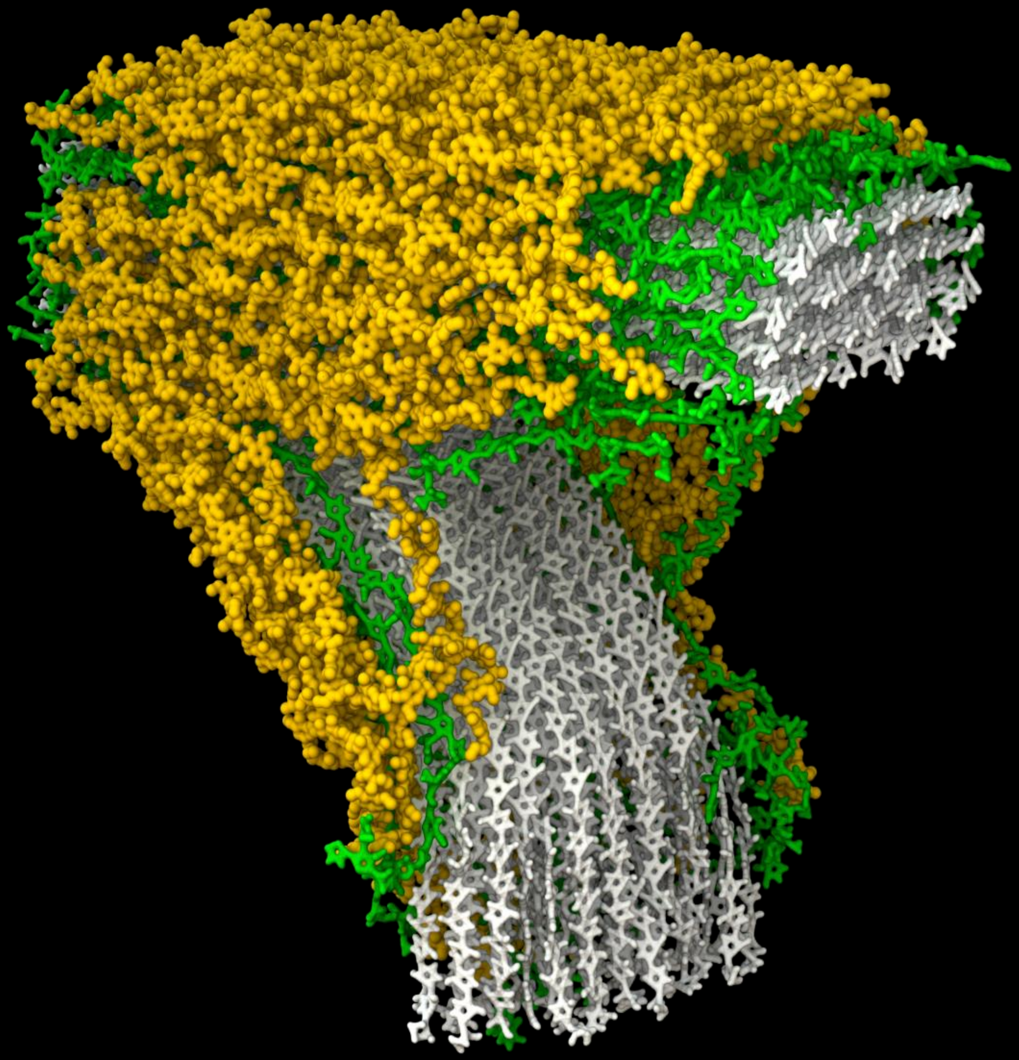
Steam exploded corn stover cell walls

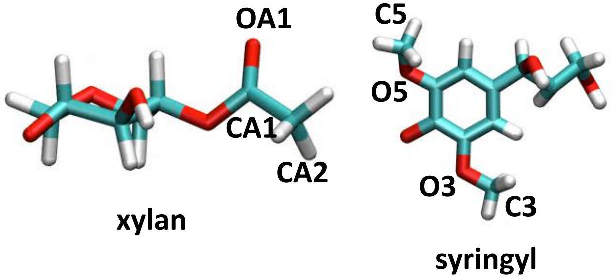
88.0 % cellulose converted
after 96 h of enzymatic digestion

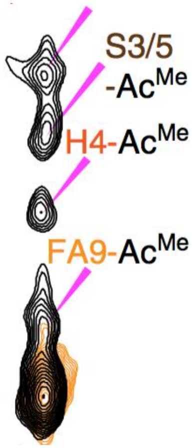
Ciesielski, et al. (2014).

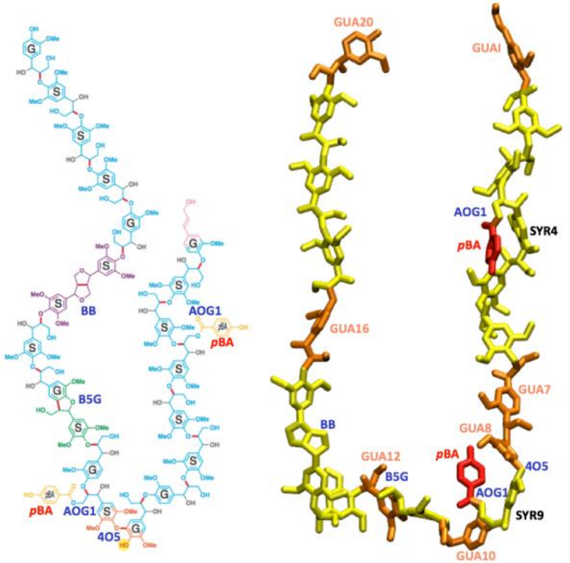
How do hemicellulose and lignin impact mechanics of lignocellulose assemblies?

Atomistic model informed by NMR









ss-NMR: Ac^{Me}-S3/5 (xylan acetyl with syringyl $–CH_3$)
Kang et. al Nat. Commun. 2019

Zhang et al. *Chem. Sus. Chem.* 2020
Ralph et al. *Current Opin. Biotechnol.* 2019

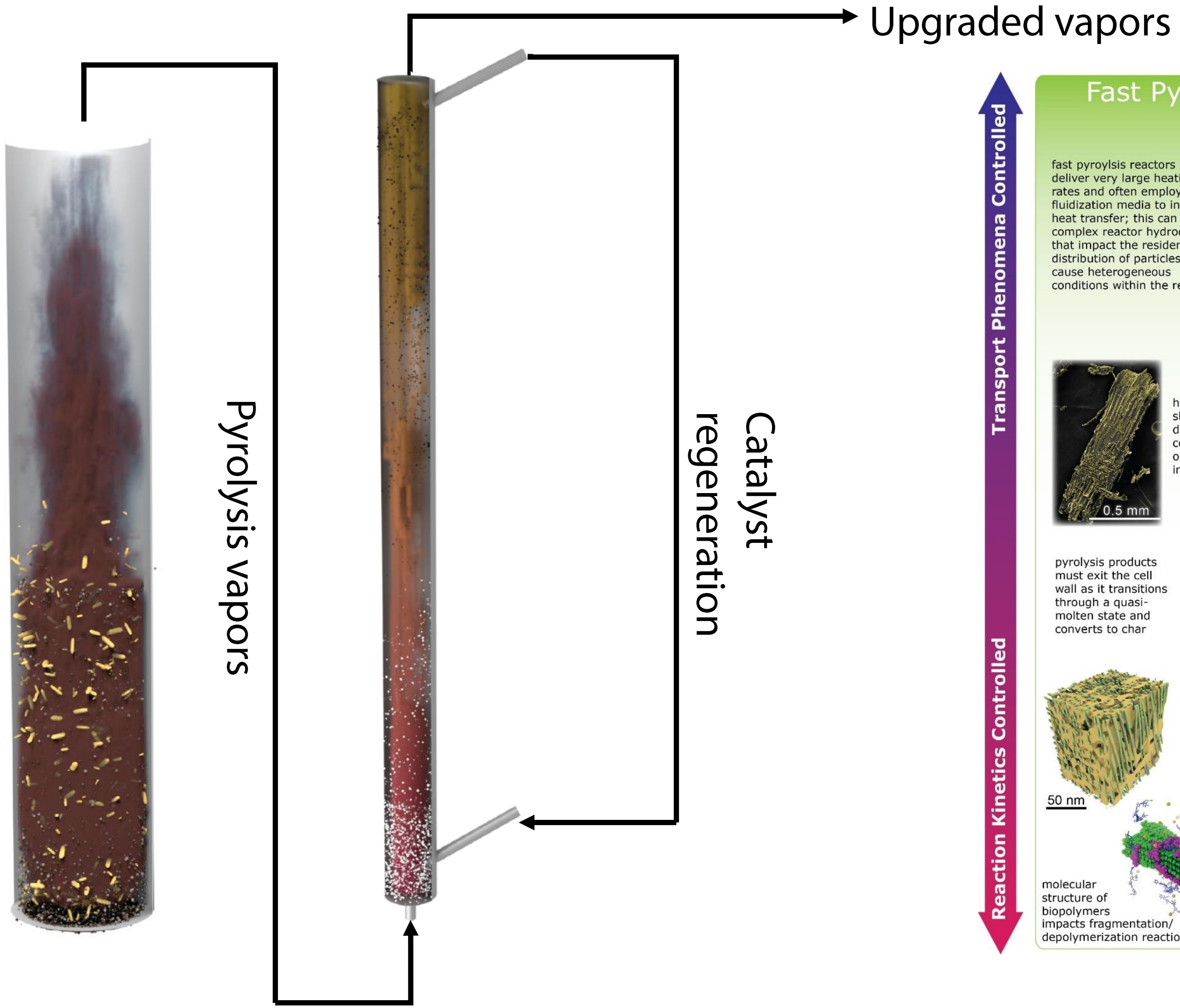
	Experimental Composition	Experiment ratio	DP	Simulation ratio
cellulose	41.1%	1.88	40	1.89
hemicellulose	21.9%	1.00	40	1.00
lignin	27.0%	1.23	20	1.23

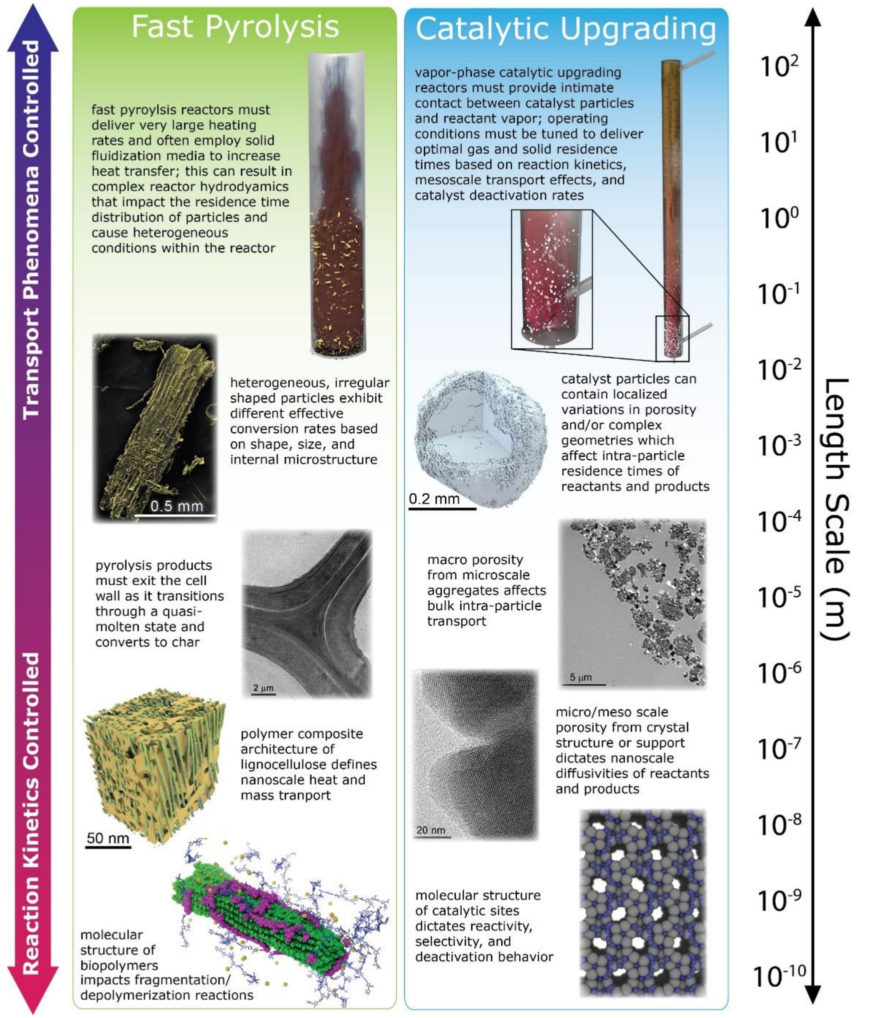
L. Bu, M. Crowley, B. Addison, M. Crowley, P. Ciesielski

A thermochemical conversion example: catalytic fast pyrolysis

Pyrolysis vapors exit reactor and go on to catalytic upgrading or condensation

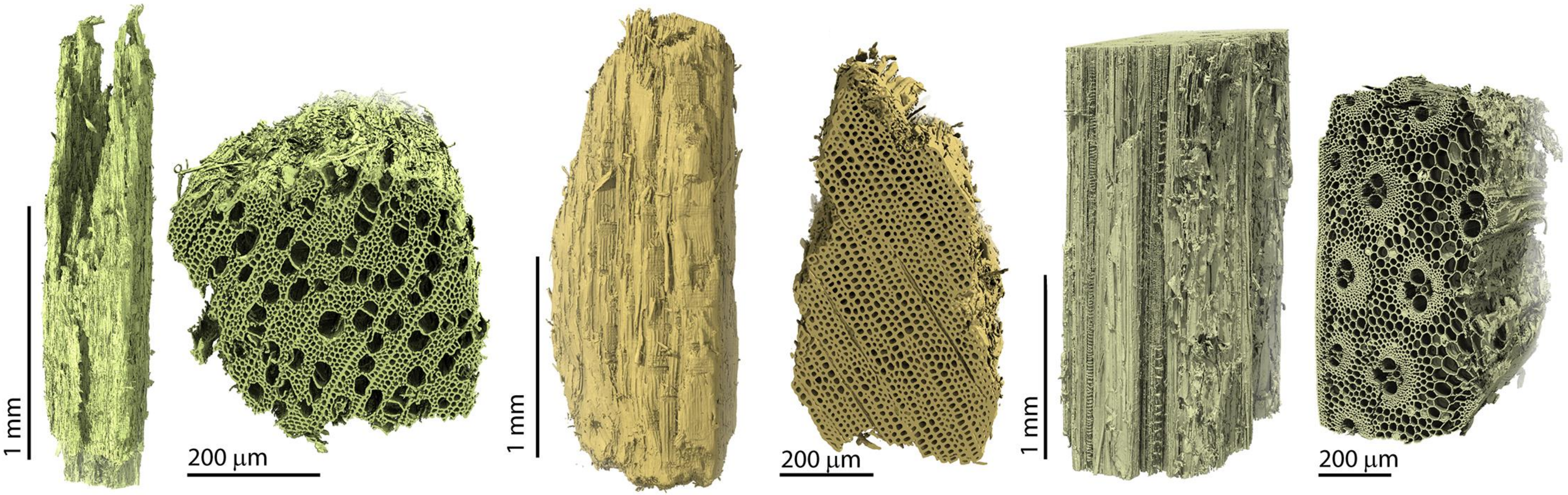
Biomass mixes with hot sand to increase heat transfer





Ciesielski, Pecha, Bharadwaj, Mukarakate, Leong, Kappes, Crowley, Kim, Foust, and Nimlos. "Advancing catalytic fast pyrolysis through integrated multiscale modeling and experimentation: Challenges, progress, and perspectives." *Wiley Interdisciplinary Reviews in Energy*, **2018**

A thermochemical conversion example: catalytic fast pyrolysis



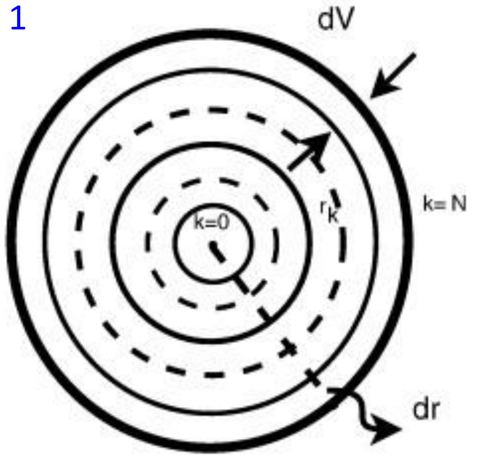
Poplar Pine Corn stover

- Biomass feedstocks are highly variable
- The species-specific microstructure dictates intraparticle heat and mass transfer
- Particle size and shape impacts required conversion times, fluidization behavior, and flowability

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

The critical question for biomass models: if the feedstock attributes change, how does the model change?

1



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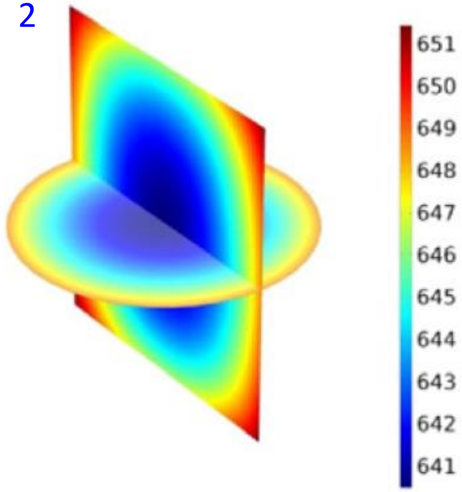
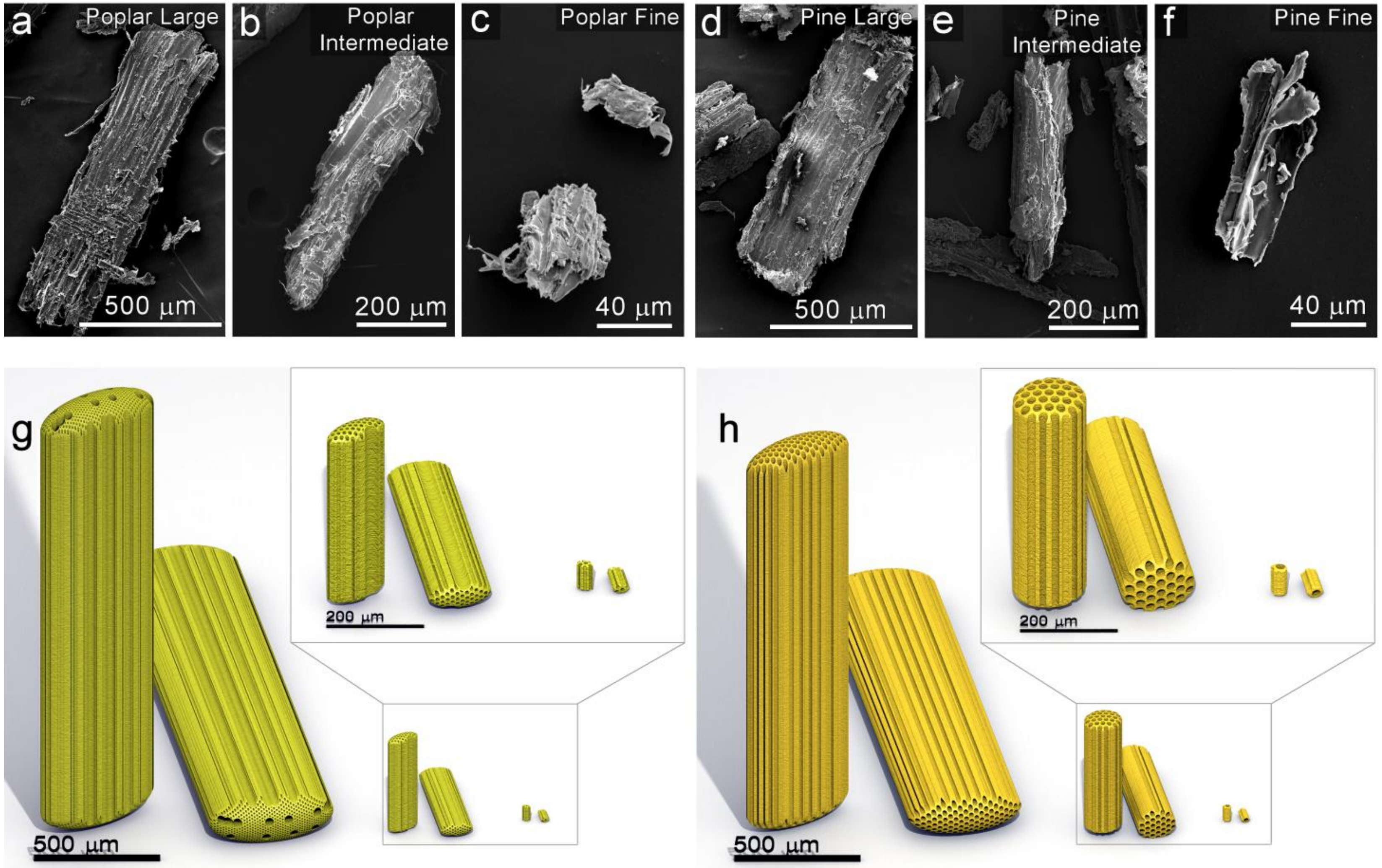
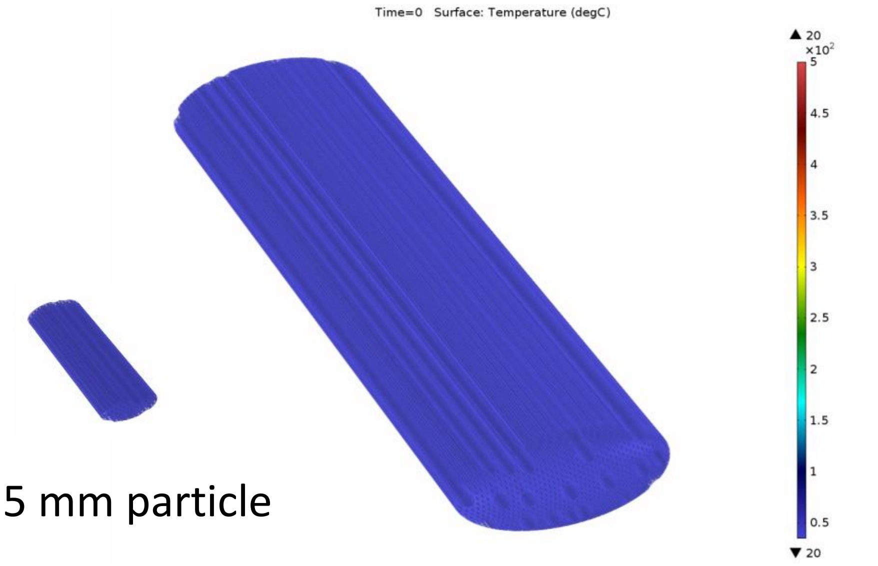




[1] Papadikis, *et al.* Application of CFD to model fast pyrolysis of biomass. *Fuel Process Technol* **2009,** *90* (4), 504-512
[2] Shi, X., *et al.* Finite element modeling of intraparticle heterogeneous tar conversion during pyrolysis of woody biomass particles. *Fuel Process Technol* **2016**, 148, 302-316.

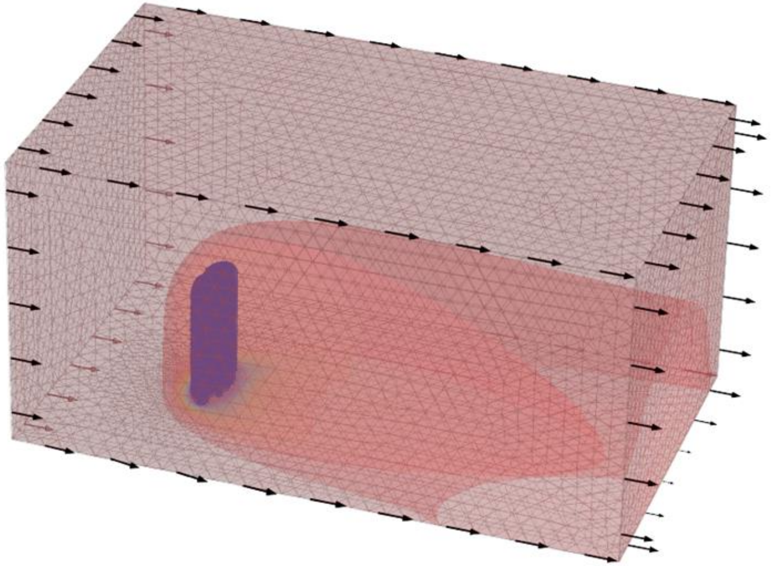
Ciesielski, *et al.* Biomass Particle Models with Realistic Morphology and Resolved Microstructure for Simulations of Intra-Particle Transport Phenomena. *Energy and Fuels,* **2015**.

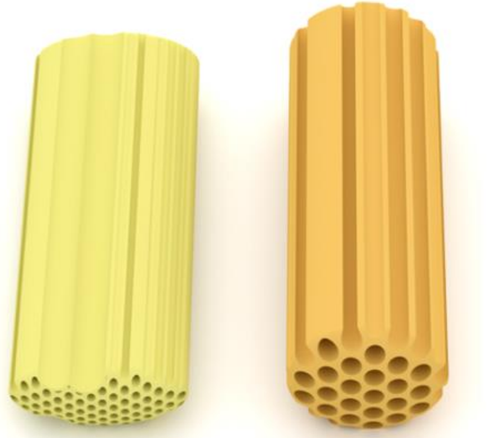
Finite element simulations of conjugate heat transfer

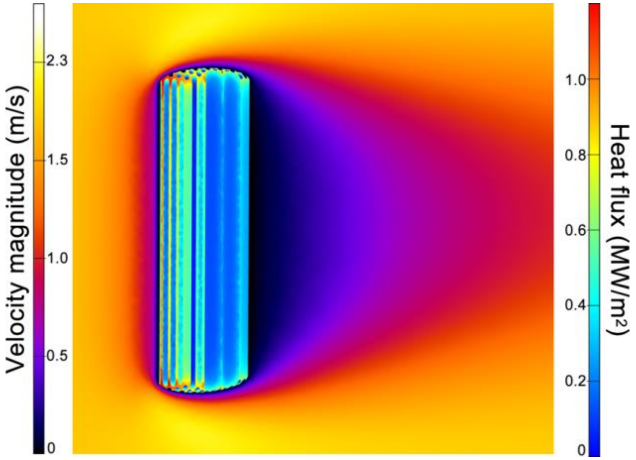


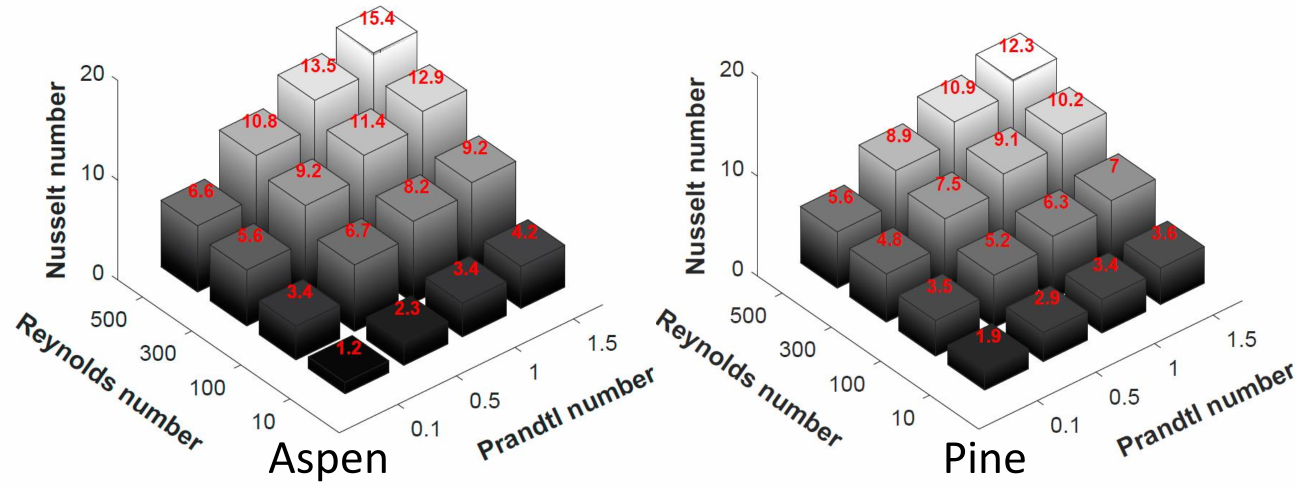
0.5 mm particle

2 mm particle









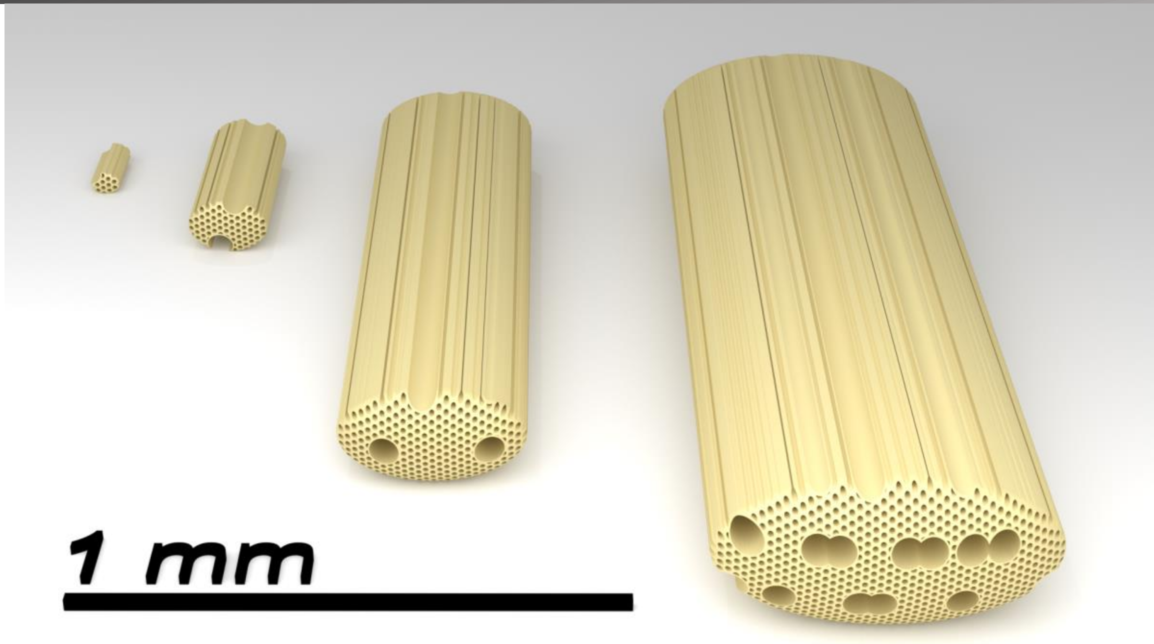
Pecha, M. Brennan, Manuel Garcia-Perez, Thomas D. Foust, and Peter N. Ciesielski. "Estimation of Heat Transfer Coefficients for Biomass Particles by Direct Numerical Simulation Using Microstructured Particle Models in the Laminar Regime." *ACS Sustainable Chemistry & Engineering* (**2016**).

Finite element simulations of reaction/diffusion process for lignin extraction

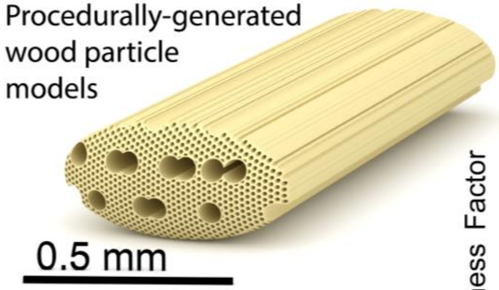
ChemSusChem
Full Papers
doi.org/10.1002/cssc.202000558

Mesoscale Reaction–Diffusion Phenomena Governing Lignin-First Biomass Fractionation

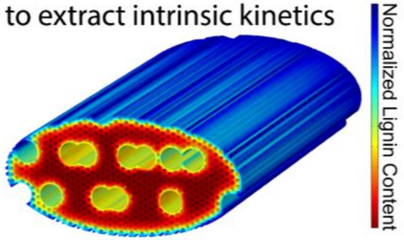
Nicholas E. Thornburg,[a] M. Brennan Pecha,[b] David G. Brandner,[a] Michelle L. Reed,[b] Josh V. Vermaas,[b] William E. Michener,[b] Rui Katahira,[a] Todd B. Vinzant,[b] Thomas D. Foust,[a] Bryon S. Donohoe,[b] Yuriy Román-Leshkov,[c] Peter N. Ciesielski,*[b] and Gregg T. Beckham*[a]

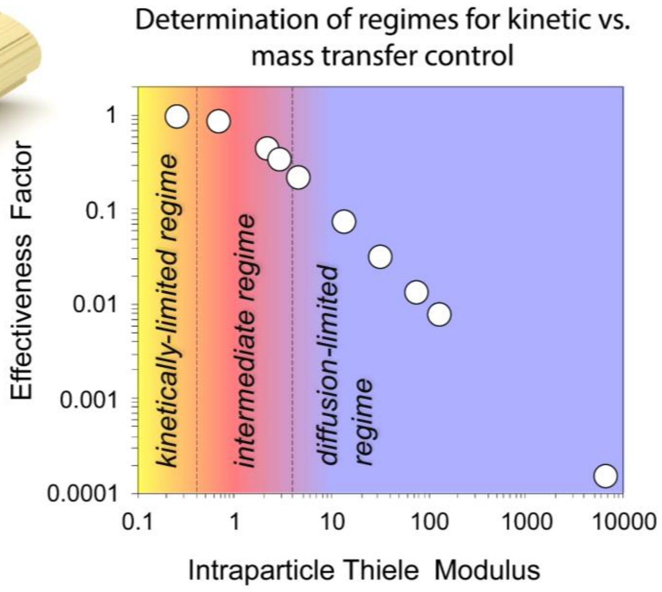


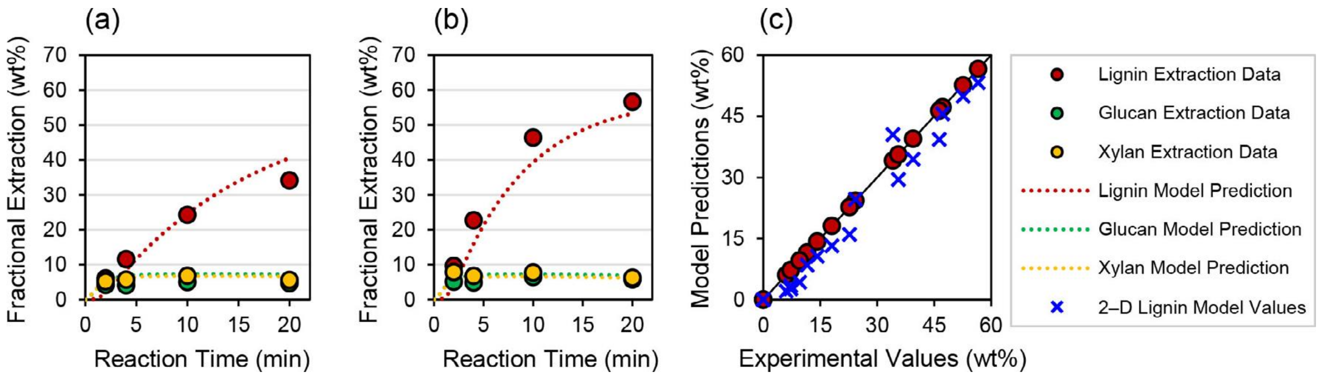
Procedurally-generated wood particle models



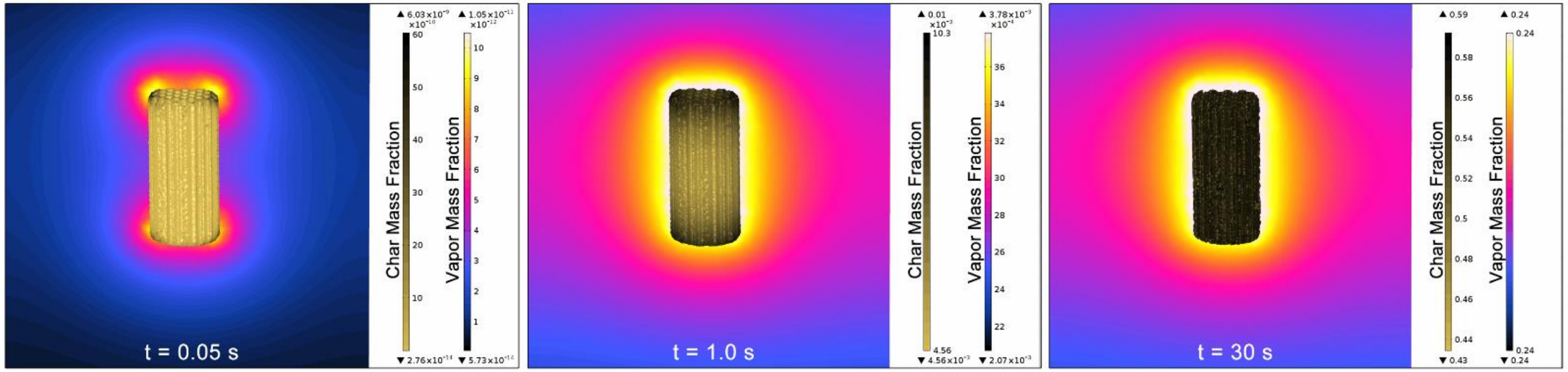
Reaction-diffusion simulations to extract intrinsic kinetics

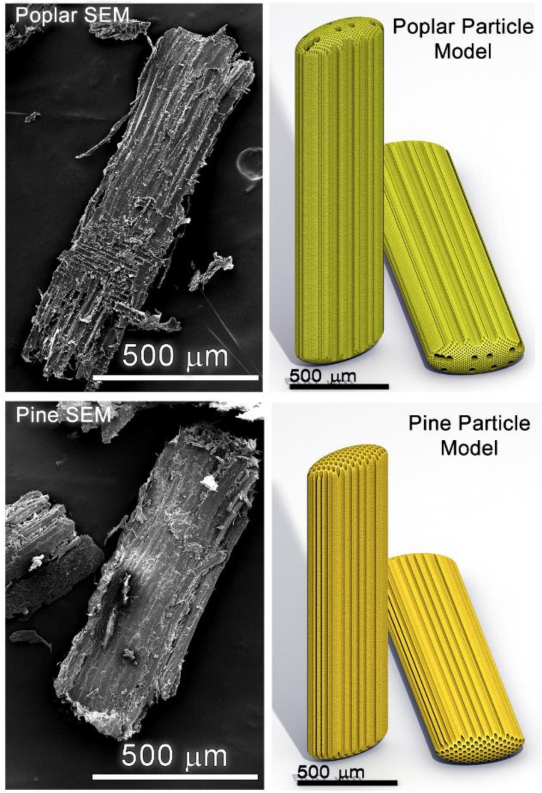


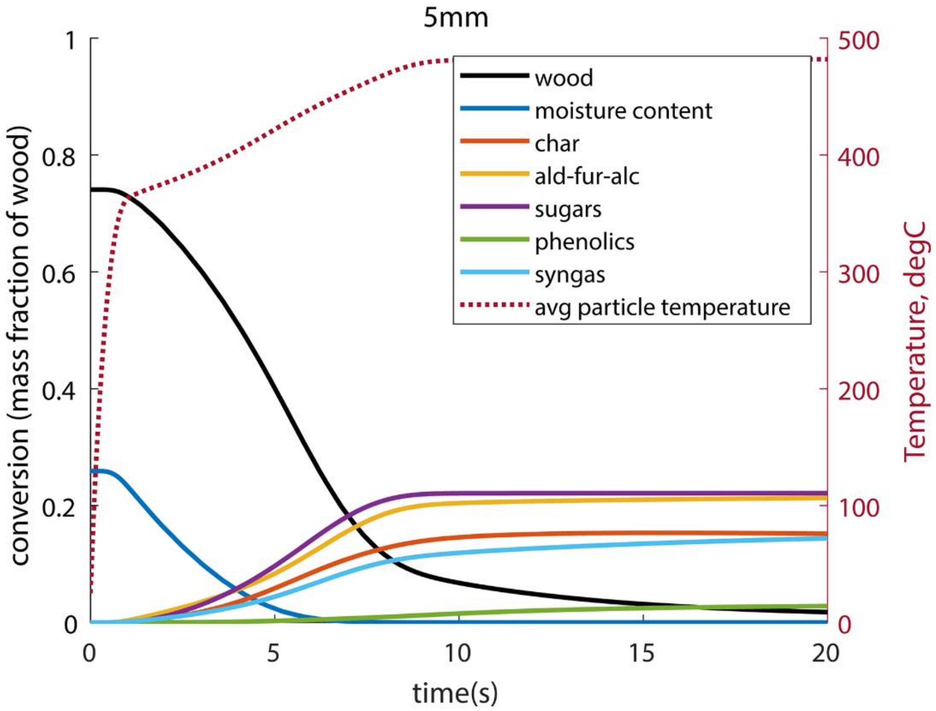




Pyrolysis simulations

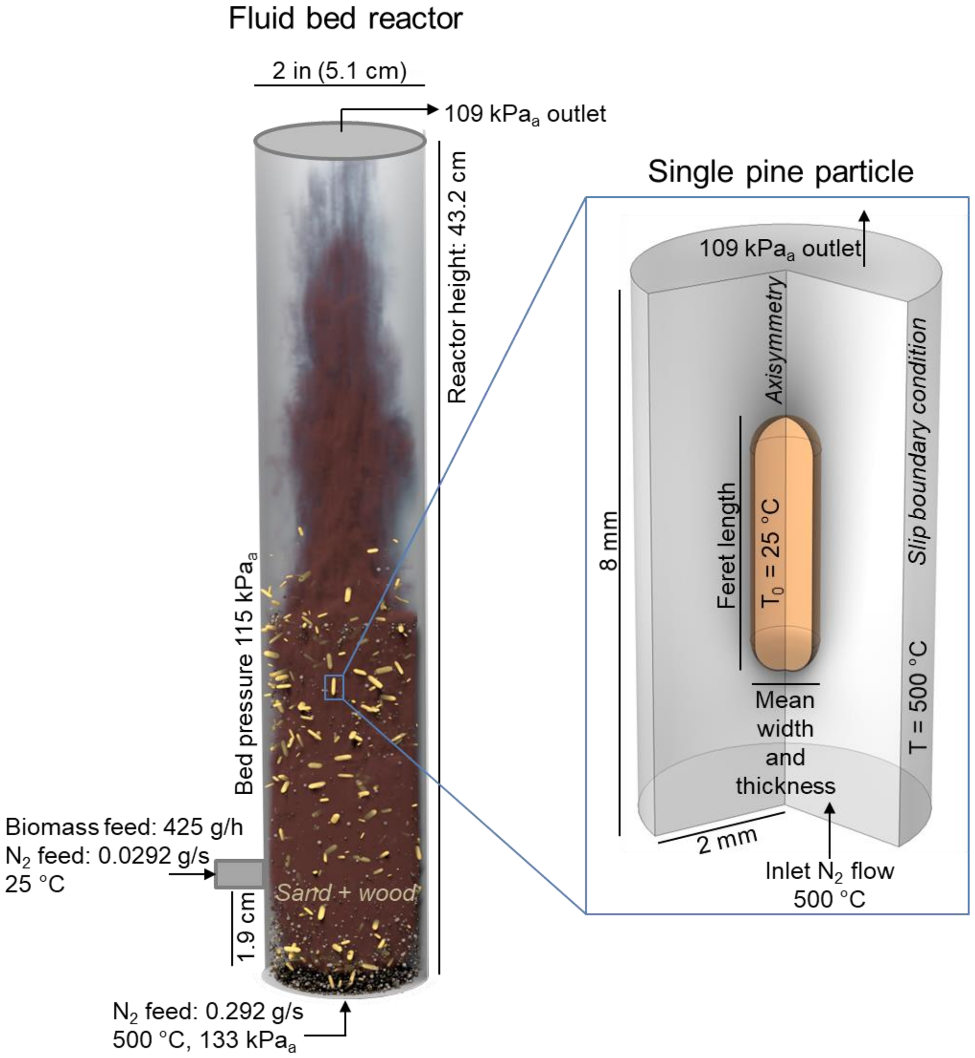






Detailed particle models enable prediction of yield, product distribution, and required conversion times as a function of feedstock attributes including particle size, shape, microstructure, and composition

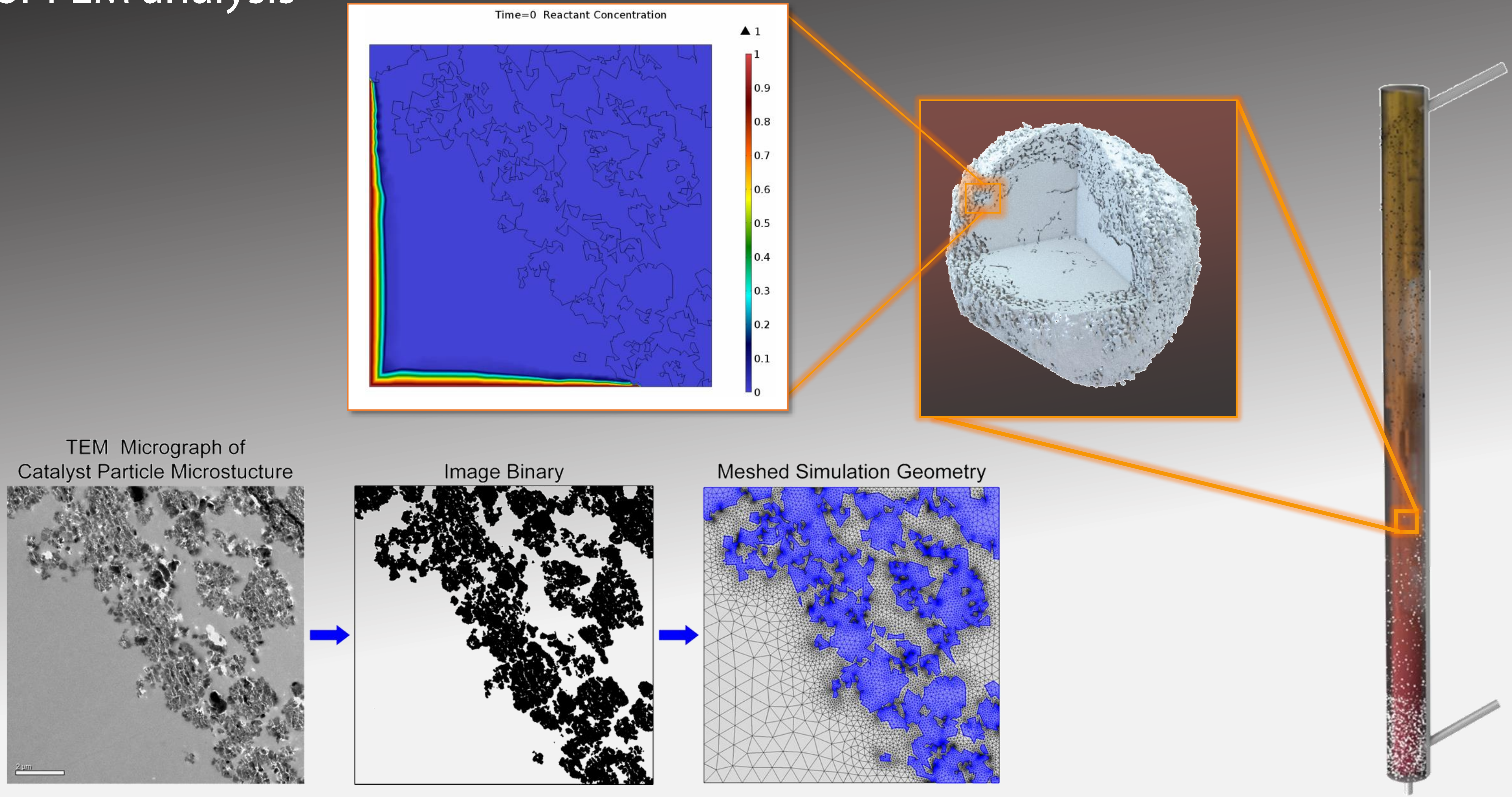
Coupling to reactor simulations and ensemble calculations enables highly accurate, predictive reactor models



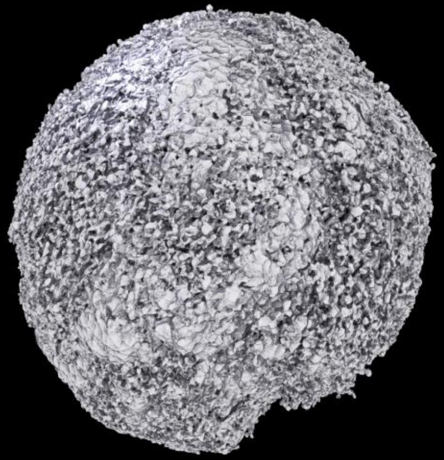
- Reactor scale simulations account for hydrodynamics and are used to estimate residence time distributions
- Particle-scale simulations are used to account for feedstock-specific effects and calculate conversion
- These simulations predict the product yield from NREL's 2" FBR within 1-2%

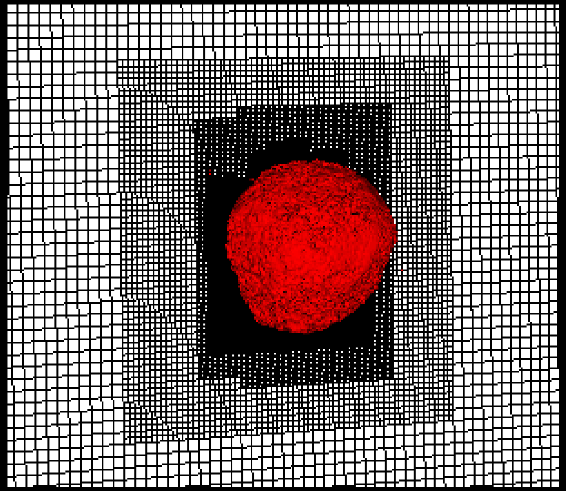
Pecha, Ramirez, Wiggins, Carpenter, Kappes, Daw, and Ciesielski. *Energy & Fuels,* **2018**

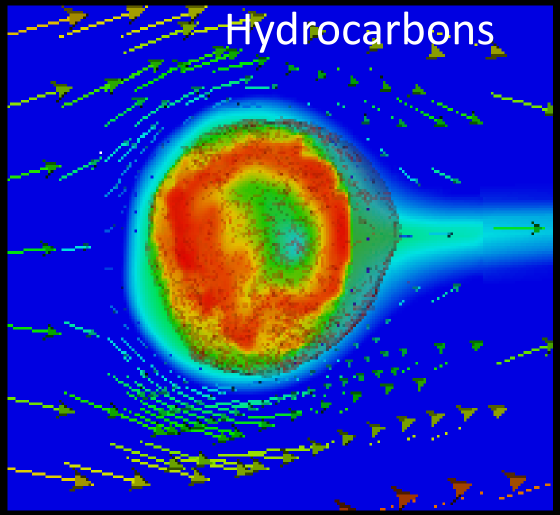
Catalytic upgraind: Direct import of complex 3D geometries for FEM analysis



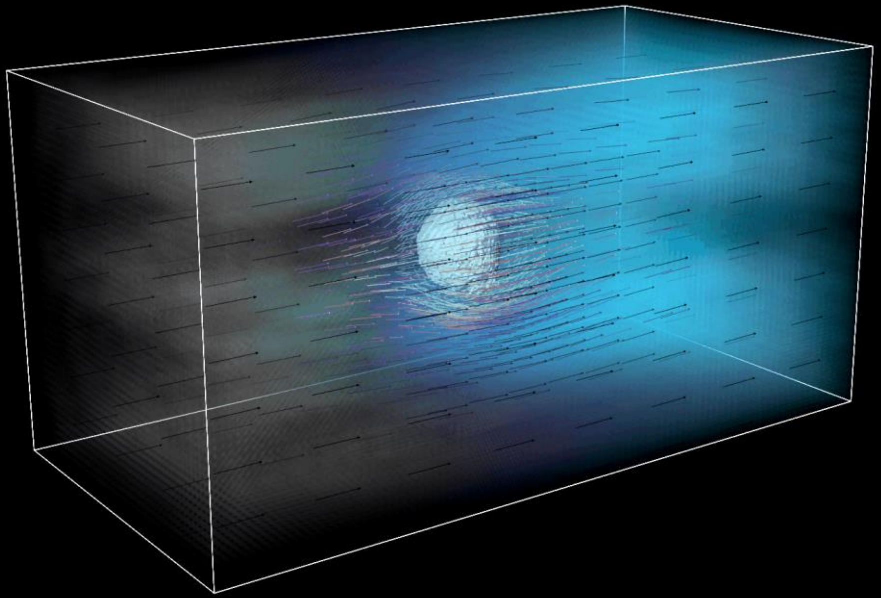
Direct import of complex 3D geometries for FEM analysis

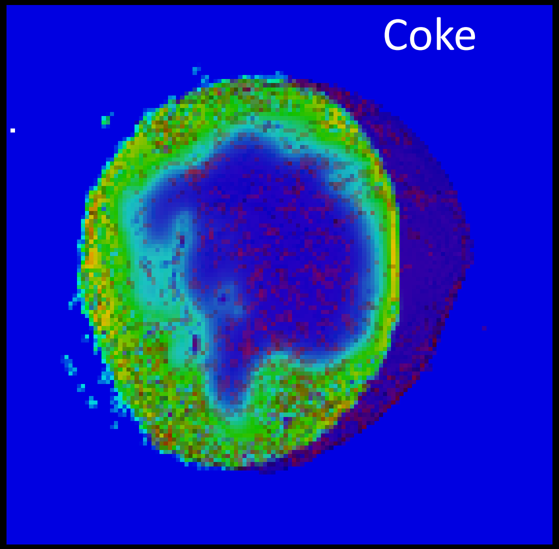


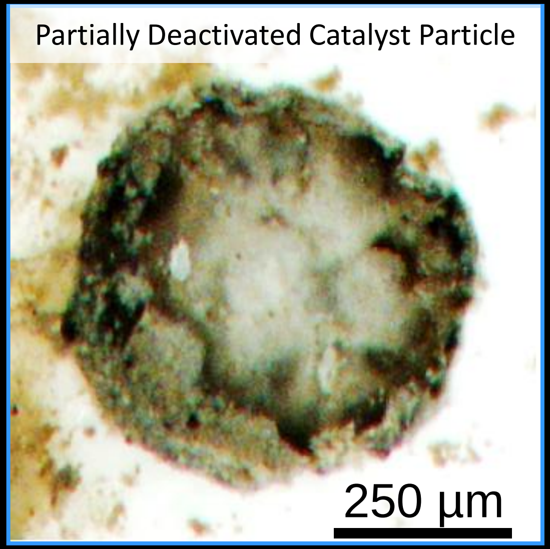




Primary Vapors
Hydrocarbons
Oxygenates



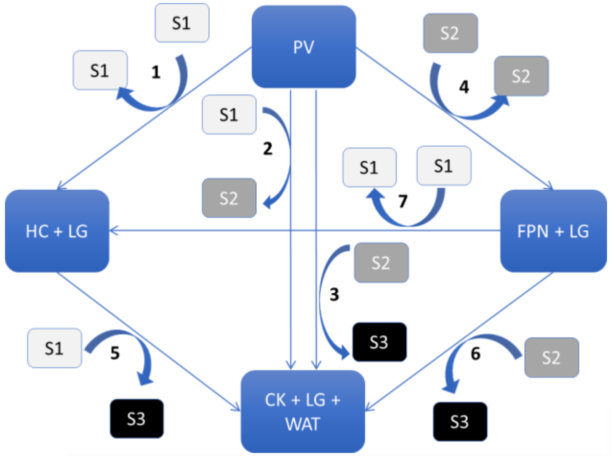




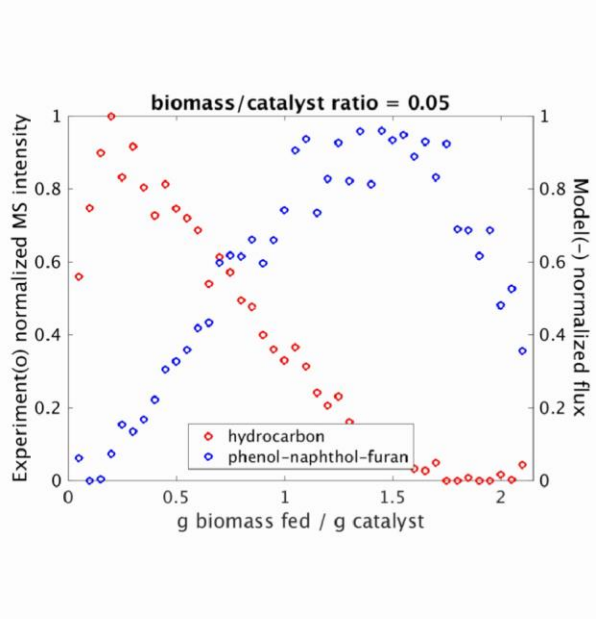
Hariswaran Sitaraman, NREL

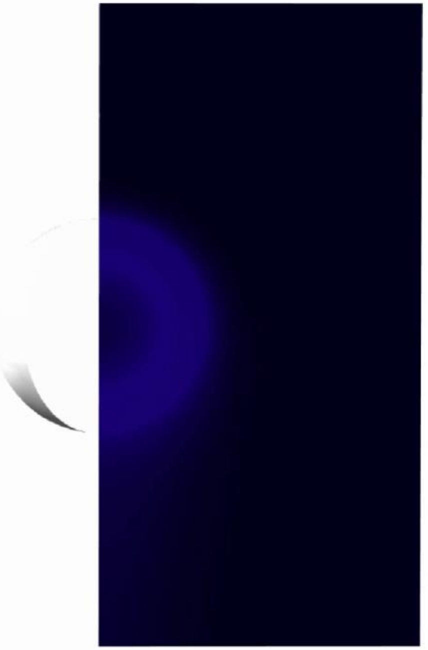
Development of reduced order models enables extraction of intrinsic kinetics from experimental data

Pyrolysis vapor upgrading over ZSM5



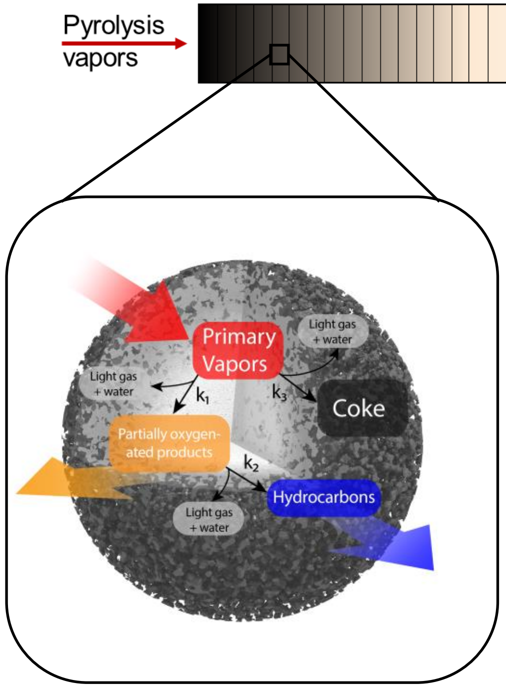
No.	Reaction	k[m³/(mol.s)] @ T=450⁰C	k[m³/(mol.s)] @ T=500⁰C	k[m³/(mol.s)] @ T=550⁰C
1	PV + S1 → HC + S1	0.0066	2.5728	3.4127
2	PV + S1 → CK + S2	0.3983	0.4561	1.2097
3	PV + S2 → CK + S3	0.0348	0.1523	0.1245
4	PV + S2 → FPN + S2	0.0031	2.9039	1.3198
5	HC + S1 → CK + S3	0.6676	0.5073	0.0110
6	FPN + S2 → CK + S3	0.0059	0.006	0.0003
7	FPN + S2 → HC + S2	0.0795	0.0509	0.2824



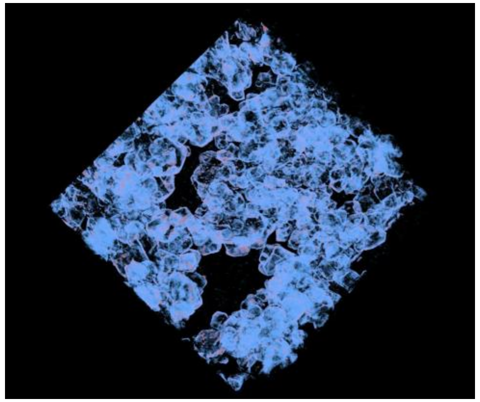


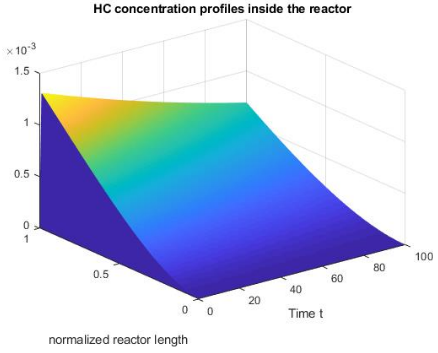
Bharadwaj, et al. *In preparation*

Pyrolysis vapor upgrading over Pt/TiO2 in a Packed Bed

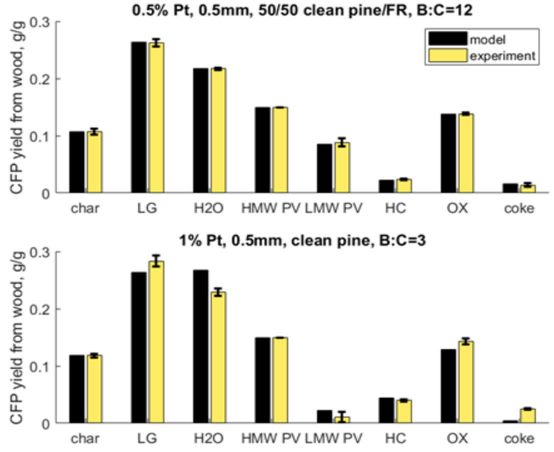


Particle models are informed by 3D EM



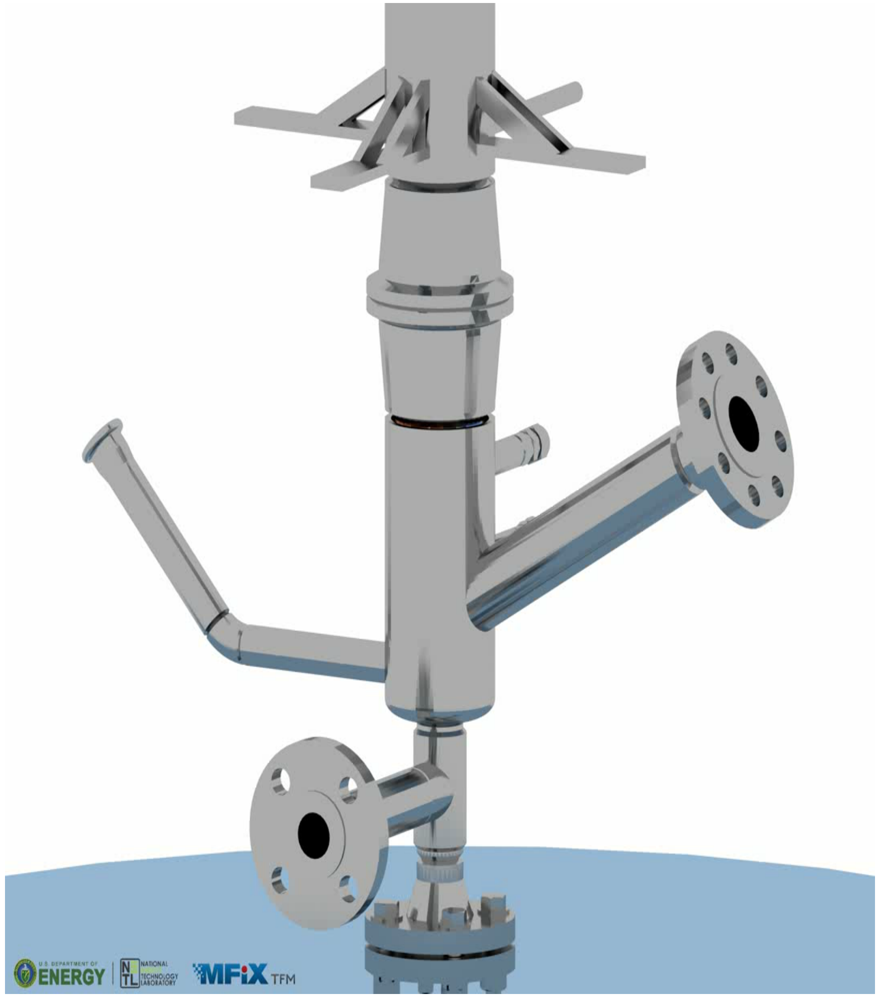


Yields from dry wood for pyrolysis + VPU



Pecha, et al. *In preparation*

Intrinsic kinetics enable process-scale models that investigate reactor designs and operating conditions



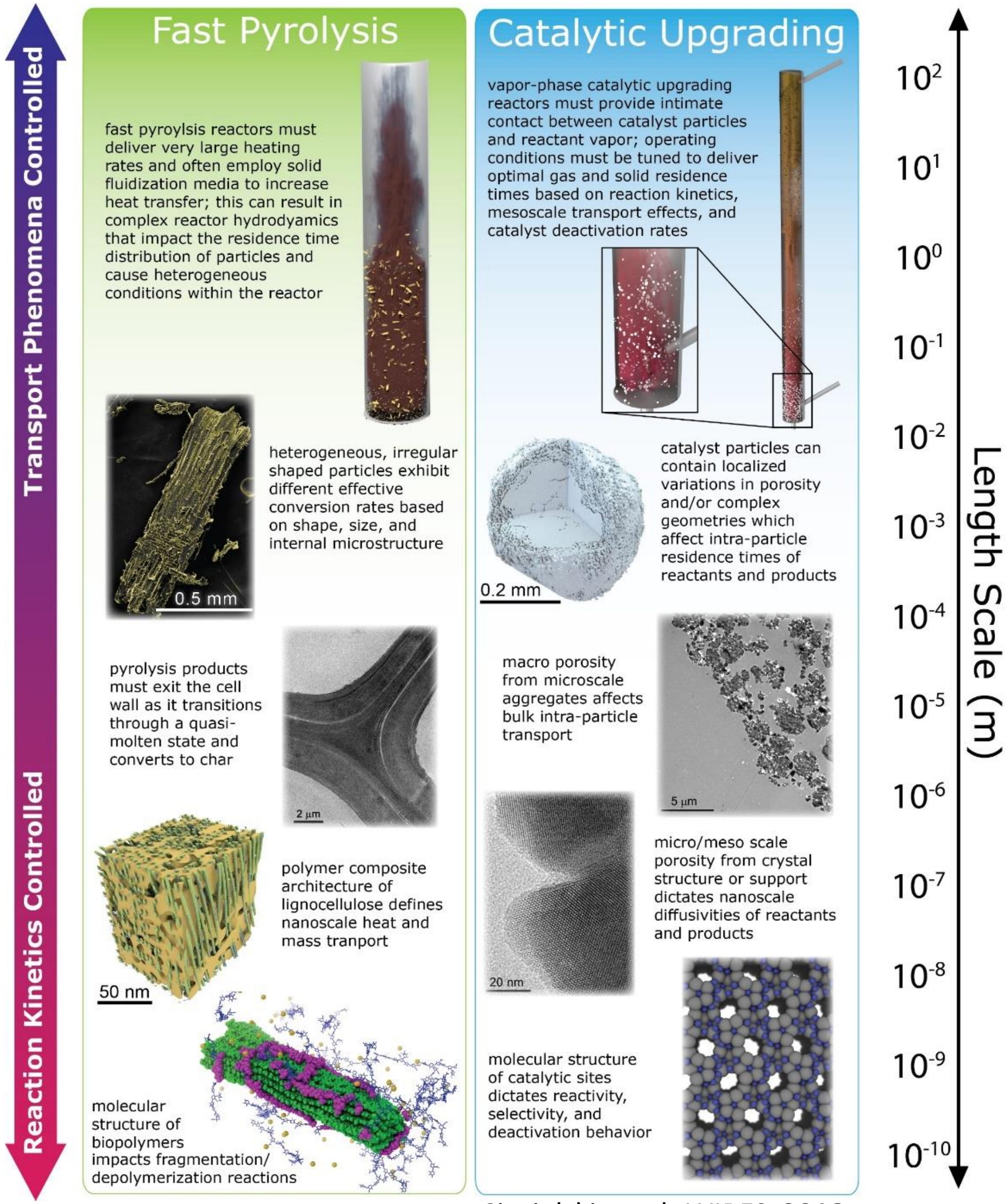
Biomass pyrolysis vapor phase upgrading (VPU) simulation in circulating fluidized reactor

- Computational fluid dynamics simulation is used to accelerate the design and scale-up of CCPC catalytic Vapor Phase Upgrading (VPU) circulating fluid bed systems for upgrading biomass pyrolysis vapor.
- MFIX two fluid model was developed and validated to simulate the multiphase flow hydrodynamics, temperature fields at different operating conditions in the VPU riser.
- The validated model has been used to predict the residence time distribution and provided input data for the development of the reduced order model.
- The validated R-cubed riser model has been coupled with the VPU kinetics to guide the reacting flow experimental tests at NREL.

X. Gau, B. Rodgers, NETL

Conclusions, guiding principles and lessons learned (the hard way)

- **Start by modeling the feedstock itself, not the process**
  - Helps avoid embedded assumptions (e.g. black box with arrows)
  - Models are generally applicable to many processes
- **Start from scratch and use measurements and data to parameterize the model**
  - Models are rooted in reality rather than assumptions or convenient math (e.g. spherical cow)
- **Appreciate biocomplexity**
  - Yes, it's difficult and there aren't plug and play tools available. Stop whining and start coding.
- **Model variability distributions, not averages**
  - One particle model is not representative of the entire feedstock
  - Ensemble calculations are critical



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