Reaction engineering: a lost (and found) art for a decarbonized future

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April 19, 2024
Brown University National Laboratory Day, Providence, RI

Center for Integrated Mobility Sciences
Mechanical & Thermal Engineering Sciences Directorate
National Renewable Energy Laboratory, Golden, CO

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Introduction

- B.S. Chemical Engineering, Washington University in St. Louis, 2012
- Ph.D. Chemical Engineering, Northwestern University, 2017; *doctoral research sponsored by Dow Chemical*
  - Dissertation Title: "Understanding Silica-Supported Group 4 and 5 Metal Oxide Catalysts for Selective Oxidations with Hydrogen Peroxide and for Epoxide Activation"
- Former graduate intern at 3M, Corporate Research Materials Laboratory, 2015; *adhesive formulation R&D*
- ***Senior Reaction Engineer (and other roles) at the National Renewable Energy Laboratory, 2017–present***
- Adjunct Professor of Chemical Engineering, Colorado School of Mines, January 2024–present

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Transforming ENERGY
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NREL at-a-Glance

3,702

Workforce, including

205 postdoctoral researchers

179 graduate students

94 undergraduate students

World-class

facilities, renowned technology experts

More than 1000

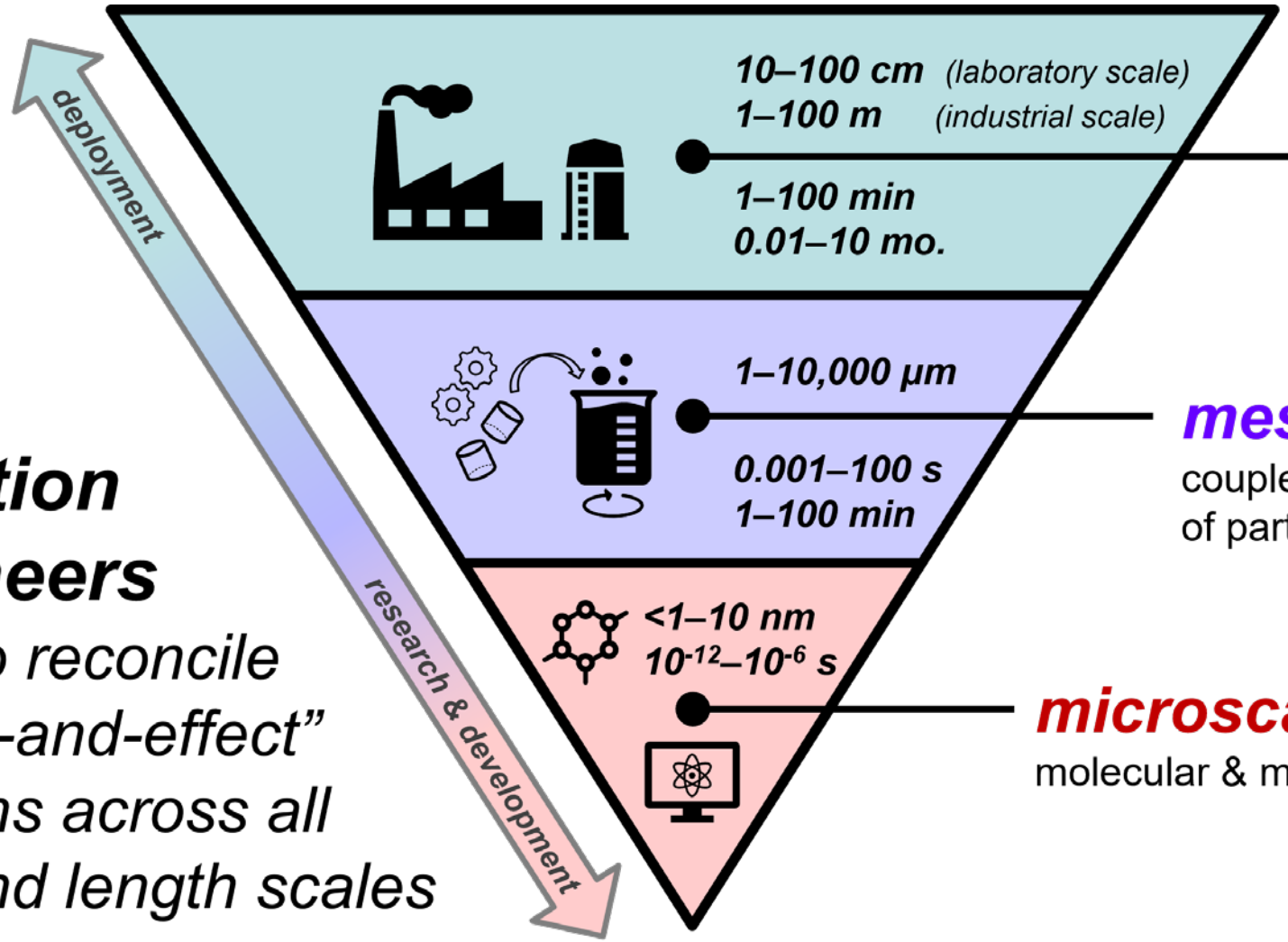
Partnerships

with industry, academia, and government

Campus

operates as a living laboratory

The reaction engineering discipline spans many time and length scales



macroscale
reactor design in the context of chemical process & plant design

mesoscale
coupled chemistry and physics of particles, droplets & interfaces

microscale
molecular & mechanistic levels of scrutiny

Reaction engineers *seek to reconcile "cause-and-effect" relations across all time and length scales*

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“But, like, isn’t reaction engineering… *old?!*”

(where the solid is used up in the reaction) are not further discussed in the present work.

Results of Calculations

Details of the calculations are given in a subsequent section, but the results will be presented here. The quantity to be determined is the ratio of the reaction rate with a given grain size to the reaction rate that would be observed if the composition of the fluid throughout the interior of the grain were the same as in the fluid surrounding the grain; in other words, it is desired to determine the reaction rate as a fraction of the rate that would be observed with the same amount of catalyst divided into infinitely small grains.

If the reaction is kinetically of the first order, the ratio in question depends on the dimensionless modulus, $x_s \sqrt{(c/kr)}$,

where x_s = some linear dimension fixing the grain size (for example, the radius of the equivalent sphere)
k = coefficient of diffusion of the reactants through the fluid
r = average area of pore cross section per unit length of perimeter of pore cross section (hydraulic radius of pores)
c = activity of the pore surface

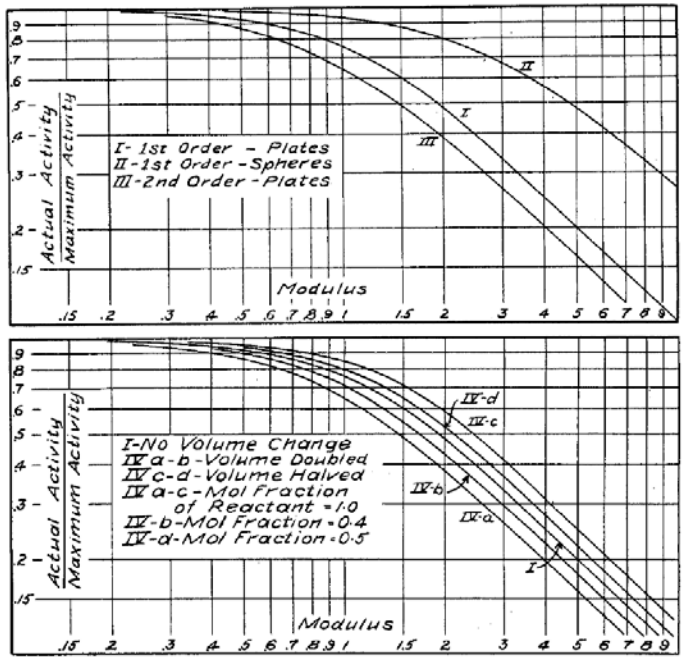
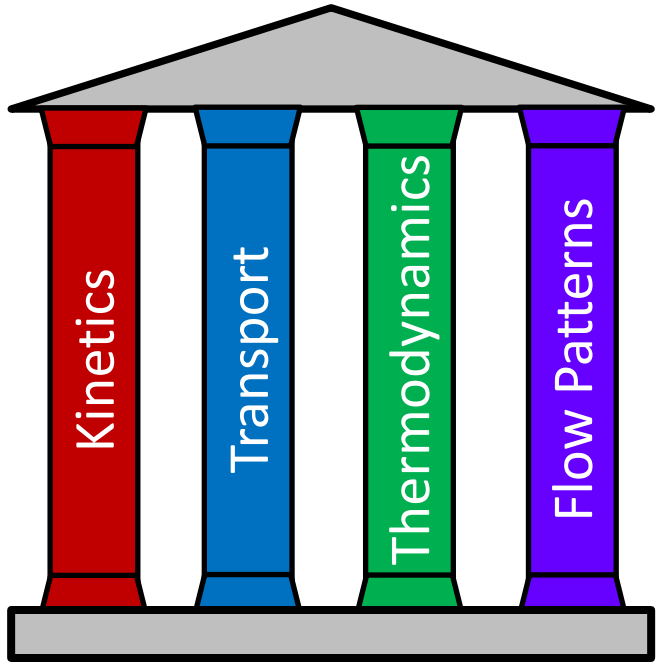


FIGURE 1



REACTION ENGINEERING THEORY **REACTION ENGINEERING PRACTICE**

6-1 **E. W. Thiele**, *Industrial & Engineering Chemistry* 31 916-920 (**1939**)

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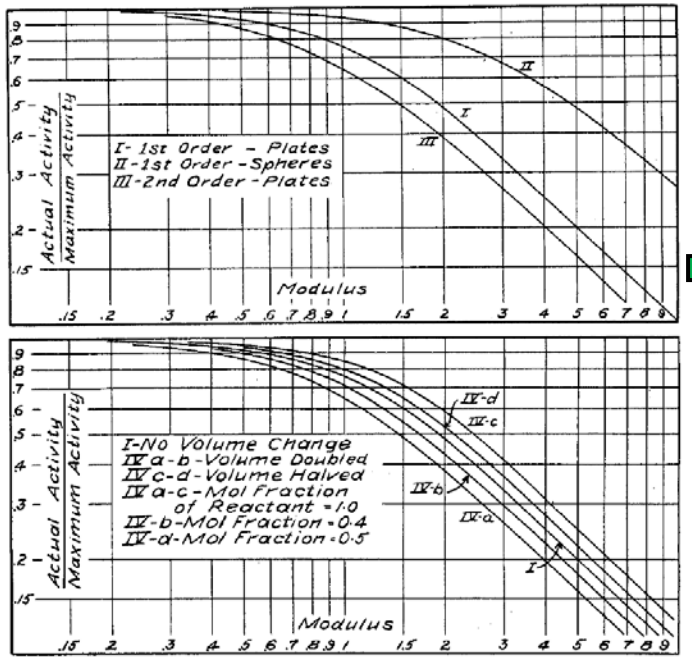
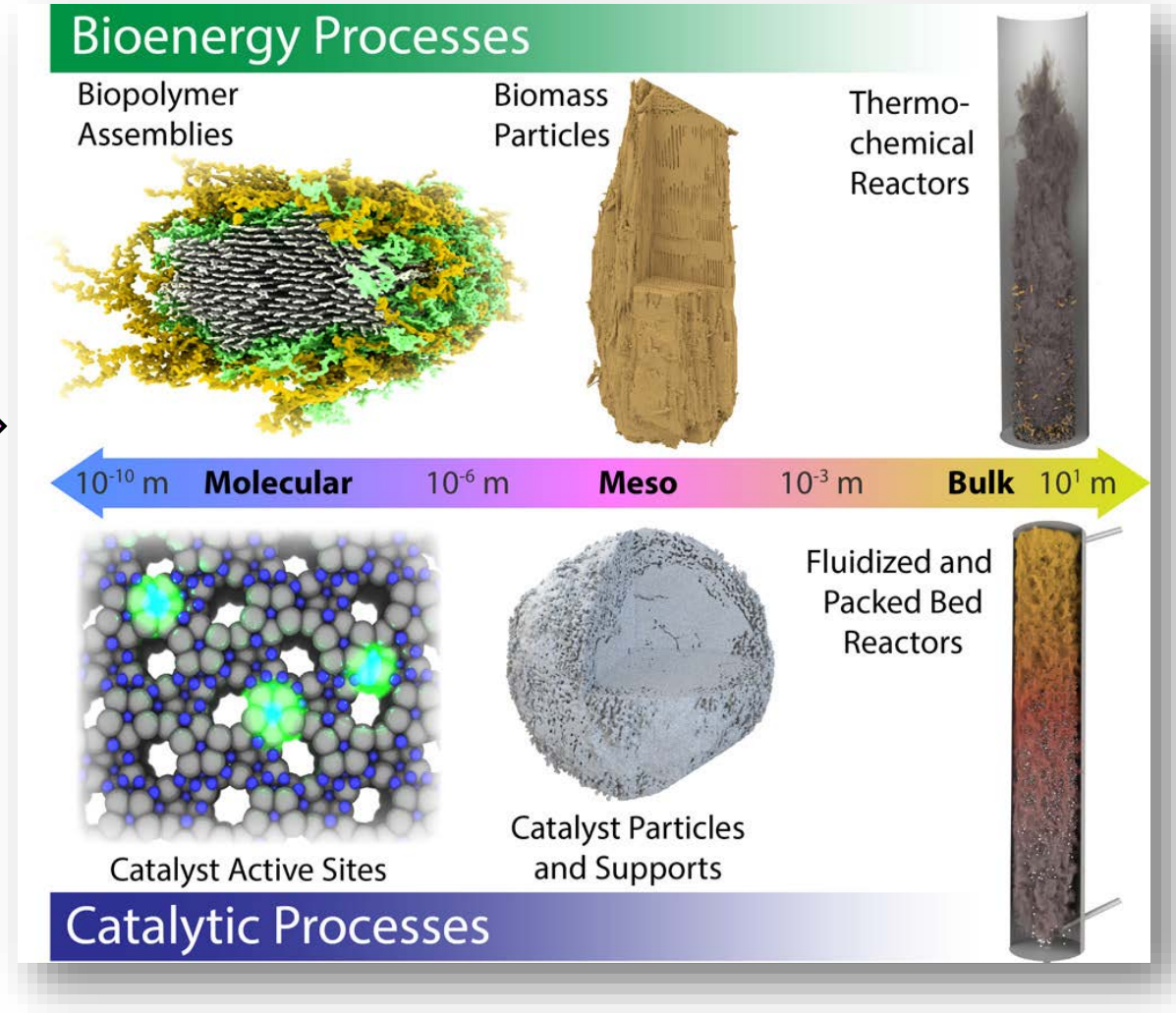


FIGURE 1

Remarkably, modern chemical engineering curricula still utilize these historical theories and practices to teach students!

However…“new” problems require referenda on “old” theories to advance sustainable energy and chemical product solutions.



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7-1 **E. W. Thiele**, *Industrial & Engineering Chemistry* 31 916-920 (**1939**)
7-2 P. N. Ciesielski, M. B. Pecha, N. E. Thornburg, M. F. Crowley, X. Gao, O. Oyedeji, H. Sitaraman, N. Brunhart-Lupo, *Energy & Fuels* 35 14282-14400 (2021)

VIGNETTE #1: grand challenges in biofuels—ghosts of past and present

Elegant concept, but several technical and economic failures at commercial scale… why??

- HUGE challenges with the biomass itself!
  - Challenges at the commercial scale with ***feedstock variability*** and ***handling***

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Left image from Google Images. Accessed 16 April 2019.
Right image courtesy of Idaho National Laboratory.

VIGNETTE #1: grand challenges in biofuels—ghosts of past and present

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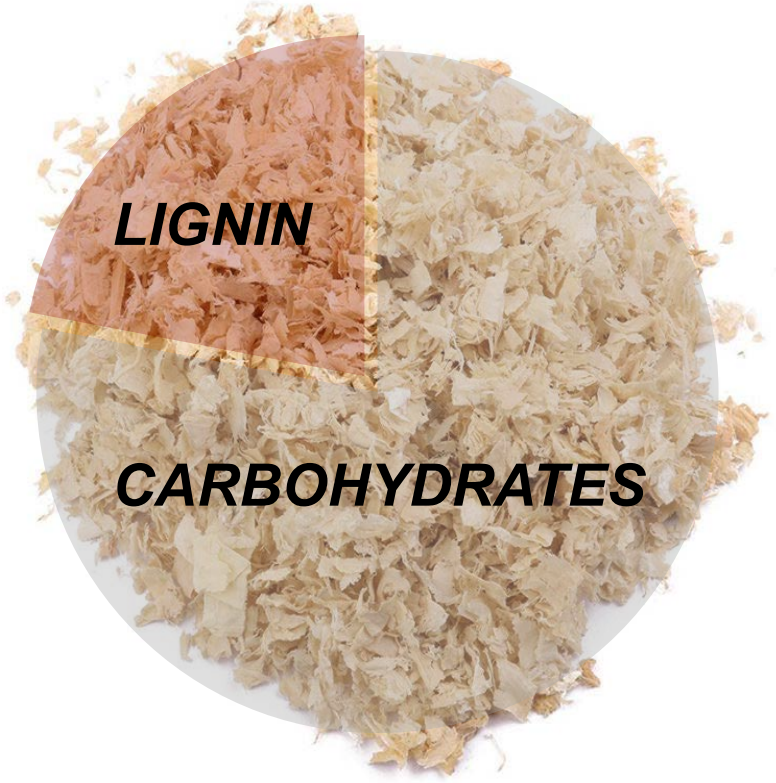
- HUGE challenges with the biomass itself!
  - Challenges at the commercial scale with ***feedstock variability*** and ***handling***
  - Plants are very complex at a molecular level… and ***certain things (acetate, lignin) get in the way*** of making cellulosic fuels



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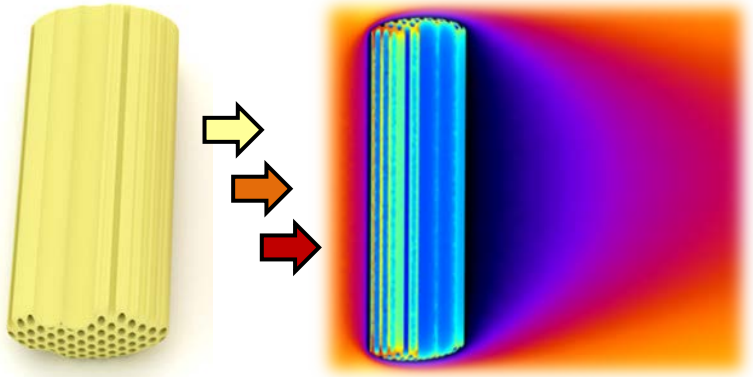
Images from Google Images. Accessed 16 April 2019.

It began with the mesoscale in lignin R&D: much ado about (almost) nothing

Studying the kinetics of decomposition of lignin *model compounds*, to…

- Understand the reactivities of key bonds in native lignin
- Optimize (heterogeneous) catalyst performance through rapid screening and mechanistic studies
- Develop molecular-level insights in (relatively) clean systems



Studying *particle-scale* reaction engineering and transport phenomena, to…

- Pose fundamental questions about biomass deconstruction in multiphase systems
- ➢ **Understand the trade-off between kinetics and mass transfer limitations**
- Extend particle phenomena to practical engineering systems (e.g., flow through a packed bed of biomass)

Studying the (catalytic) depolymerization of lignin from *real biomass*, to…

- Develop performance trends by 'turning the knobs' (e.g., varying *T*, *P*, reaction time, solvent, pH, biomass/catalyst loadings, etc.)
- Enhance overall yields and/or selectivities by introducing catalysts and/or additives
- Understand practical limitations of real feedstocks and catalysts

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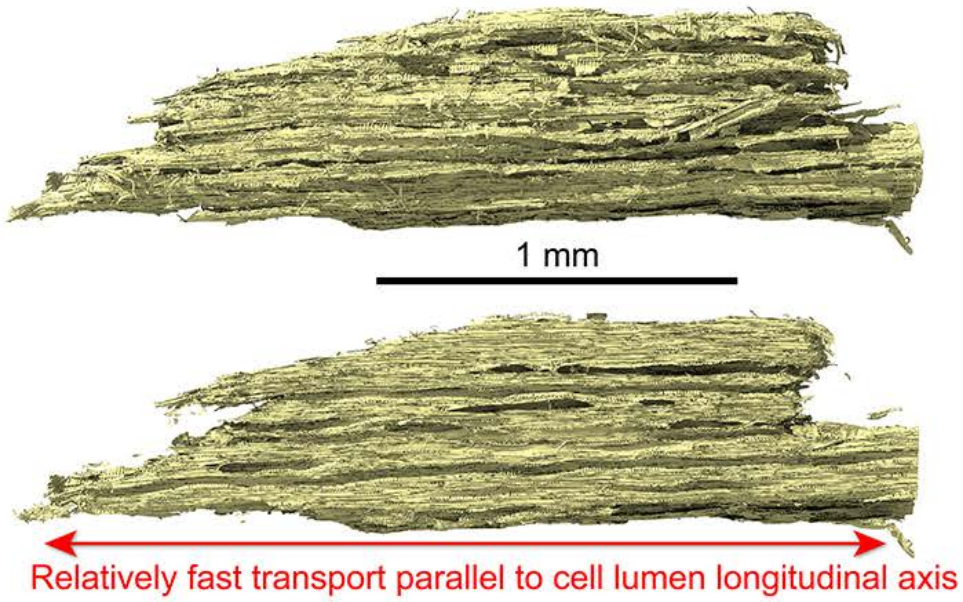
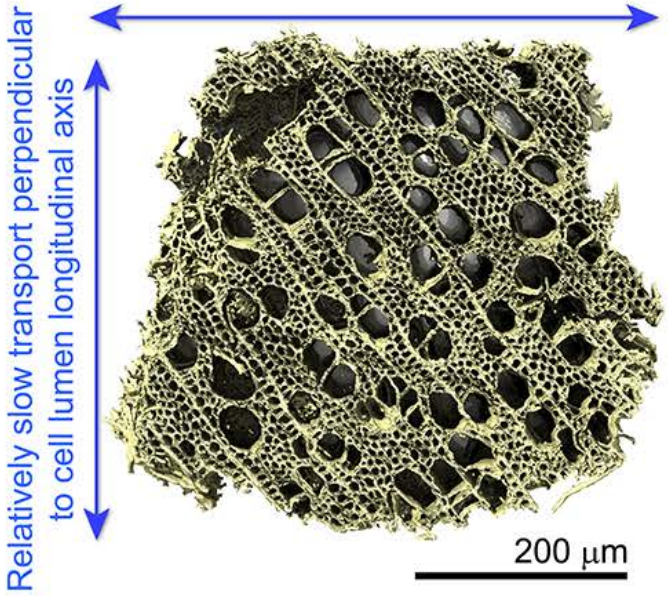
10-1 J. Lu, M. Wang, X. Zhang, A. Heyden, F. Wang, *ACS Catalysis* 6 5589-5598 (2016)

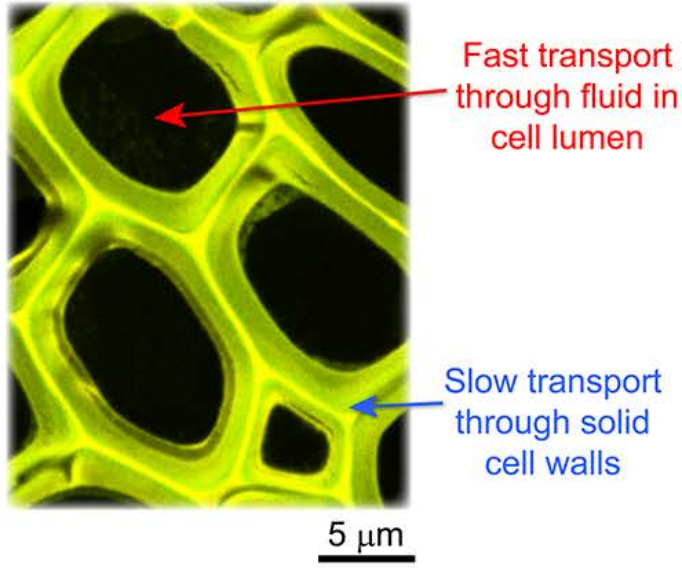
10-2 M. B. Pecha, M. Garcia-Perez, T. D. Foust, P. N. Ciesielski, *ACS Sustainable Chemistry & Engineering* 5 1046-1053 (2017)

10-3 T. Renders, S. Van den Bosch, T. Vangeel, T. Ennaert, S.-F. Koelewijn, G. Van den Bossche, C. M. Courtin, W. Schutyser, B. F. Sels, *ACS Sustainable Chemistry & Engineering* 4 6894-6904 (2016)

Wood is a highly anisotropic material with multiple modes of transport







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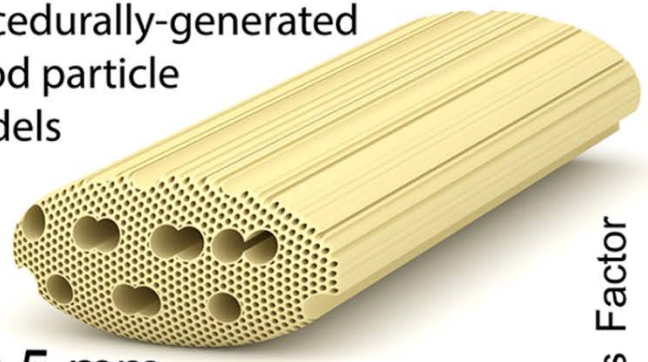
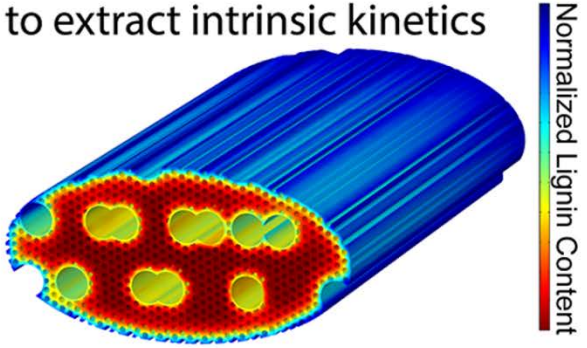
With Peter Ciesielski.

It began with the mesoscale in lignin R&D: much ado about (almost) nothing

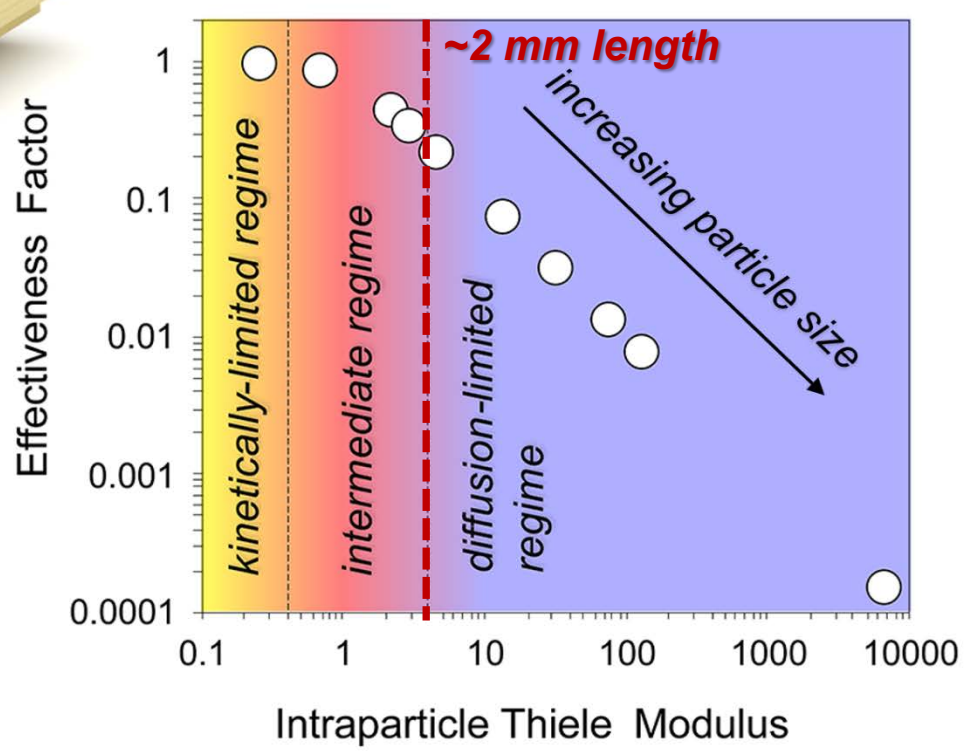
Procedurally-generated wood particle models



Reaction-diffusion simulations to extract intrinsic kinetics



Determination of regimes for kinetic vs. mass transfer control



Mass transfer resistance plays a dominant role in lignin reactive extraction from hardwoods. Lab- and pilot-scale R&D must heed.

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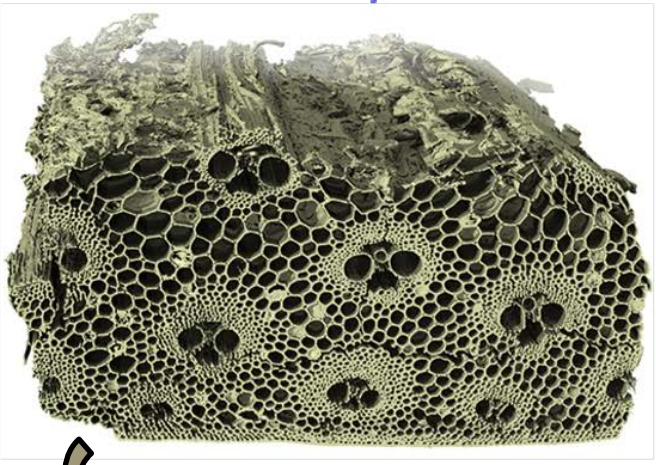
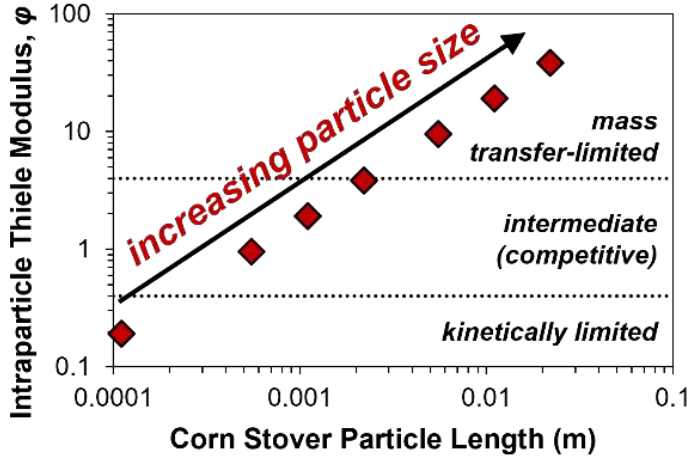
12-1 N. E. Thornburg, M. B. Pecha, D. G. Brandner, M. L. Reed, J. V. Vermaas, W. E. Michener, R. Katahira, T. B. Vinzant, T. D. Foust, B. S. Donohoe, Y. Román-Leshkov, P. N. Ciesielski, G. T. Beckham, *ChemSusChem* 13 4495–4509 (2020)

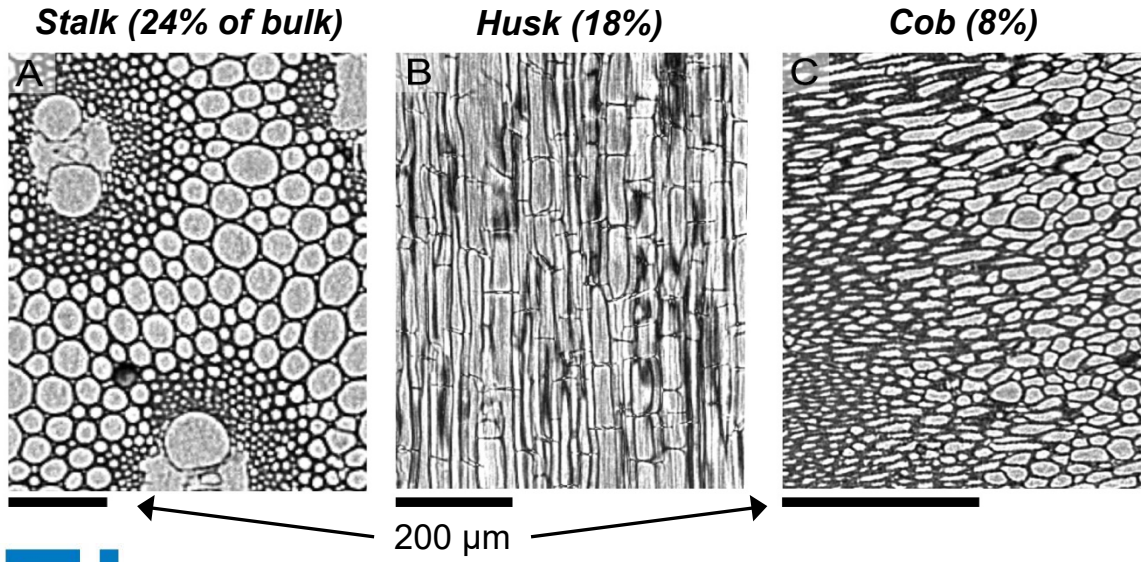
Extension of reaction–diffusion models to other biomass processing hurdles

Anatomically-specific reaction–diffusion models of biomass pretreatments…





…and their mesoscale transport limitations.



Model validation via targeted pilot plant campaigns enabled the identification of anatomically-specific feedstock limitations and practical feed preparation solutions.

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With Peter Ciesielski and Meagan Crowley. Simulations performed in COMSOL Multiphysics 5.6. See doi.org/10.3389/fenrg.2022.841169 for details.
Pilot plant photograph from https://www.nrel.gov/bioenergy/ibrf.html. Accessed 12 April 2024.

VIGNETTE #2: *Pulses to Pellets to Packed Beds*—propane dehydrogenation

The world's largest Catofin plant for alkane dehydrogenation, Dalian, China (2019).

Aspects of the Catofin process for propane dehydrogenation (PDH) developed by Clariant and Lummus

- ***Reactor*** Horizontal Fixed Bed
- ***Catalyst*** CrO_x/Al_2O_3
- ***Temperature*** 560–650 °C
- ***Pressure*** 0.2–0.5 bar
- ***WHSV*** <2.0 h^{-1}
- ***Operating Period*** 15–25 min
- ***Catalyst Lifetime*** Up to 5 years
- ***Conversion*** ~45%
- ***Selectivity*** ~90%

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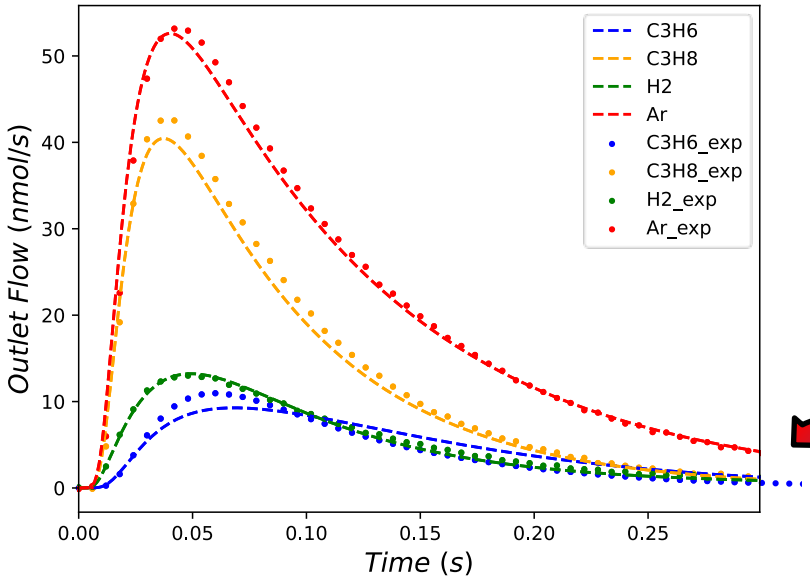
Image from Google Images. Accessed 12 April 2024.

PULSES: reduced-order PDH reaction mechanisms derived from pulse data

- Several potential reaction mechanisms were tested on transient PDH experimental data
- ***Proposed seven-step mechanism*** involving reactant/product adsorption and desorption, hydrogen cleavage from propane and a simplified coke formation mechanism best matched the data
- Although we do not extract elementary processes, **a high level of detail may be gleaned from a relatively brief experiment**



*The **optimized model below** was used to **simulate a set of experimental PDH pulses***

Reaction Step	k_f	k_b
$C_3H_8 + * \leftrightarrow C_3H_8*$	1.43e-5 [cm^3/nmol s]	2.22e-7 [1/s]
$C_3H_8* + * \leftrightarrow C_3H_6* + H_2*$	1.31e0 [cm^3/nmol s]	0.00e0 [cm^3/nmol s]
$C_3H_6* \leftrightarrow C_3H_6 + *$	3.75e2 [1/s]	2.46e-5 [cm^3/nmol s]
$H_2* \leftrightarrow H_2 + *$	4.20e2 [1/s]	1.36e-5 [cm^3/nmol s]
$C_3H_8* + * \longrightarrow C_2H_5* + CH_3*$	5.49e-8 [cm^3/nmol s]	--
$C_3H_6* + * \longrightarrow C_2H_5* + CH*$	2.96e-6 [cm^3/nmol s]	--
$H_2* + * \leftrightarrow 2\ H*$	2.40e-5 [cm^3/nmol s]	1.48e0 [cm^3/nmol s]

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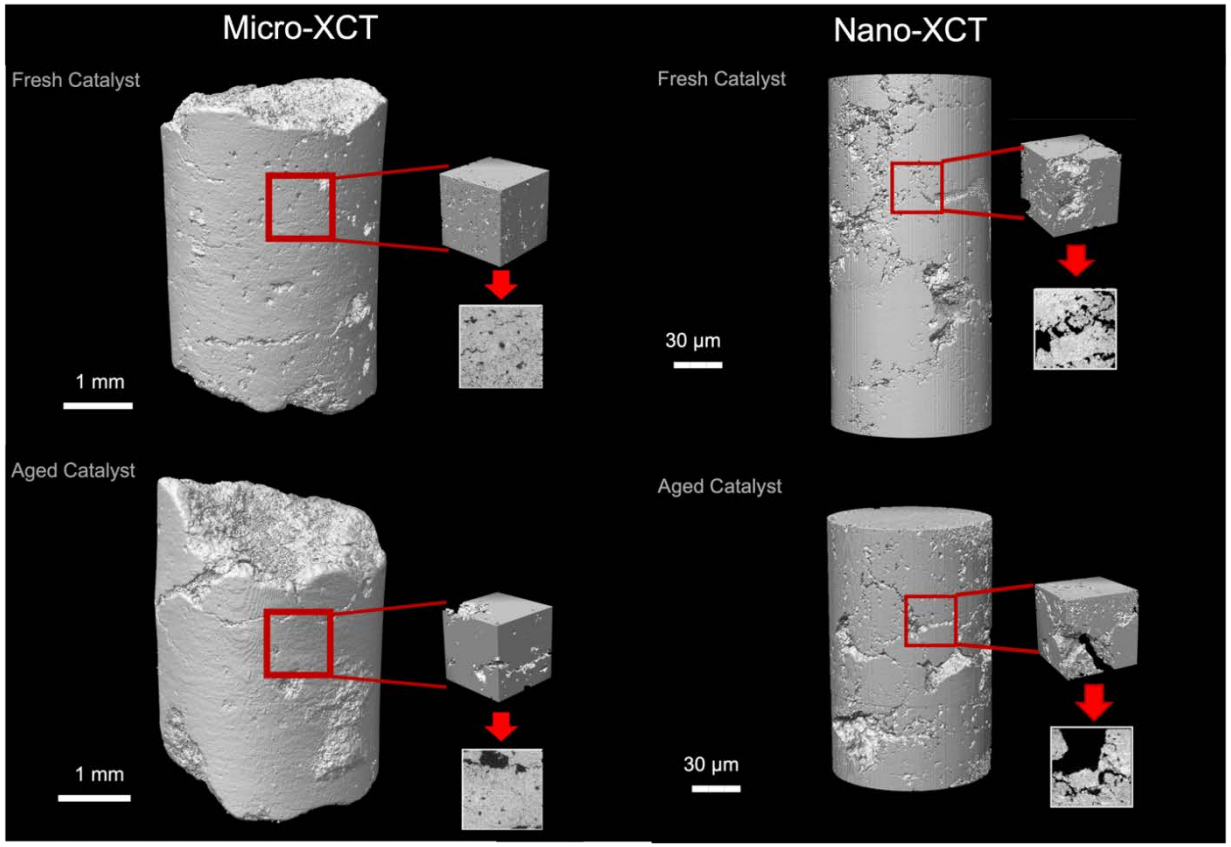
With Adam Yonge, A. J. Medford and Rebecca Fushimi.

PELLETS: XCT geometries leveraged to study deactivation via reactive CFD

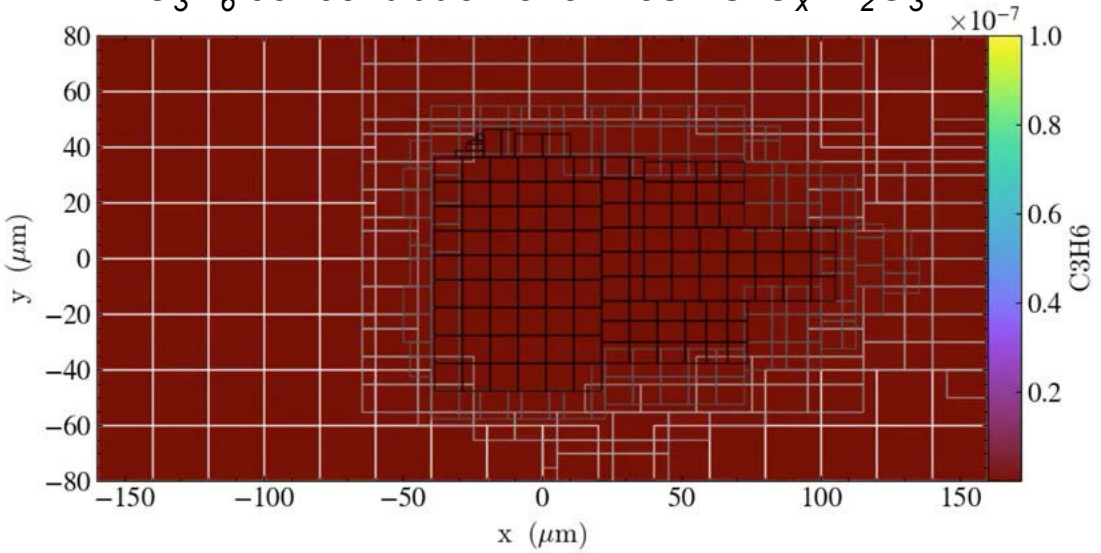


- MicroCT (Colorado School of Mines) using a Zeiss 520 Versa CT are used in preliminary CFD simulations to validate physics
- NanoCT (NREL) using the Zeiss 810 Ultra informs pore structure below 2 µm microCT resolution limit; CFD simulations underway

Introducing *mesoflow* for reactive physics CFD

- Continuum-scale simulation tool for modeling transport-coupled chemistry at the mesoscale (i.e., particle-/pellet-scale)
- Features ***adaptive mesh refinement*** to resolve complex surface morphologies obtained via XCT
- Enables direct calculation of **permeability tensors**
- Advection–diffusion–reaction case to be validated

C_3H_6 concentration over fresh CrO_x/Al_2O_3



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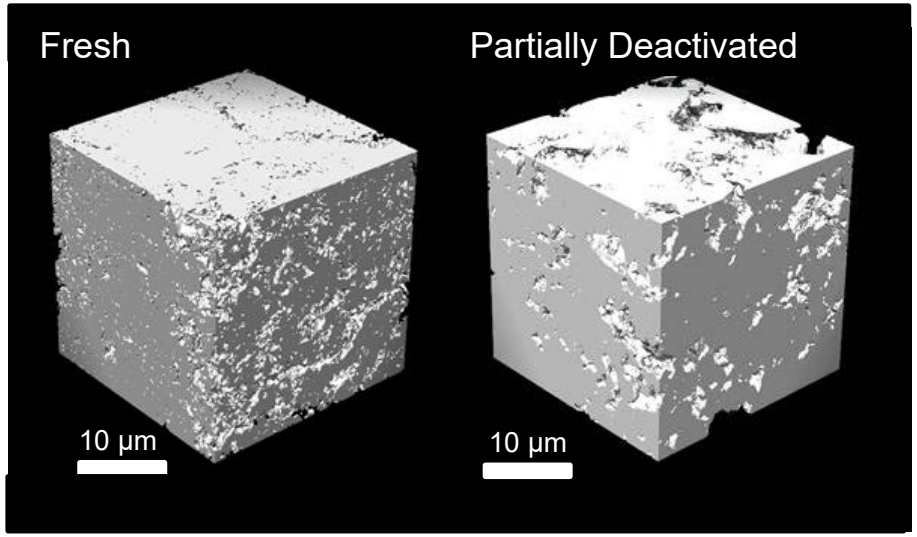
16-1 H. Sitaraman, P. N. Ciesielski, M. F. Crowley, M. B. Pecha, N. E. Thornburg, M. F. Crowley, V. Bharadwaj, *"mesoflow"* computer software invention (2022), developed under U.S. DOE Laboratory Directed Research & Development (LDRD) Program *https://www.osti.gov//servlets/purl/1873470*

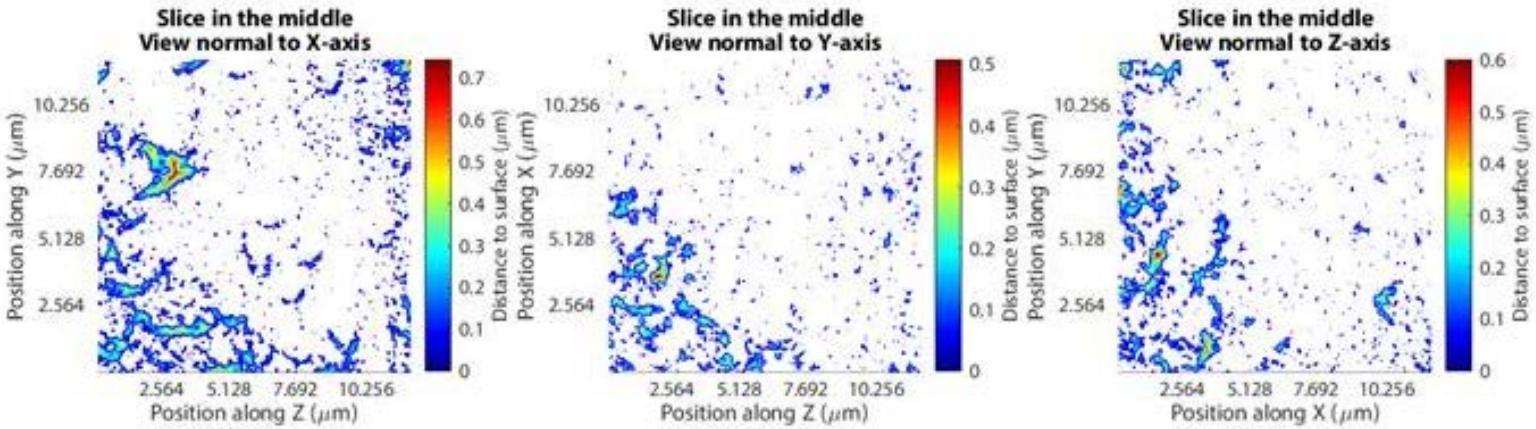
PELLETS: NanoCT scans of real fresh and partially deactivated CrO_x/Al_2O_3



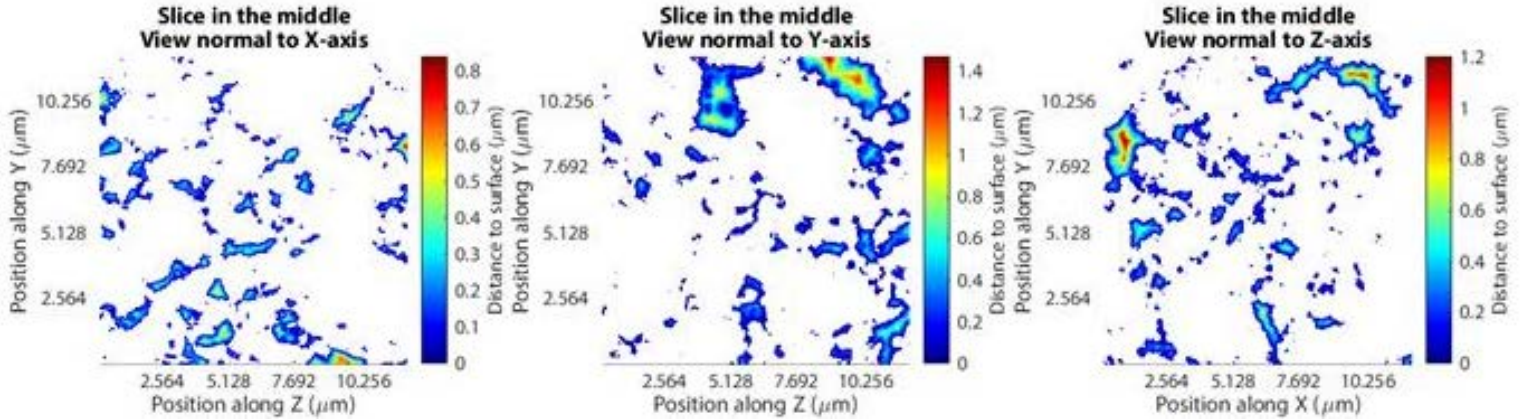
Catalyst State	Void Fraction	Radial Tortuosity	Mean Pore Dia. (μm)
Fresh	0.228	5.34	0.114
Partially Deactivated	0.339	3.06	0.292

Due to the 64-nm resolution limit of NanoCT, we will impose continuum mesoporosities via BET physisorption.

Fresh



Partially Deactivated



- **GOAL:** Direct calculation of void fraction from high-res. NanoCT scans will (help) define solid phase transport descriptors of current MicroCT catalyst pellets missing voids <2 μm
- Distance to surface plots produced in MATBOX, an NREL microstructural analysis toolbox

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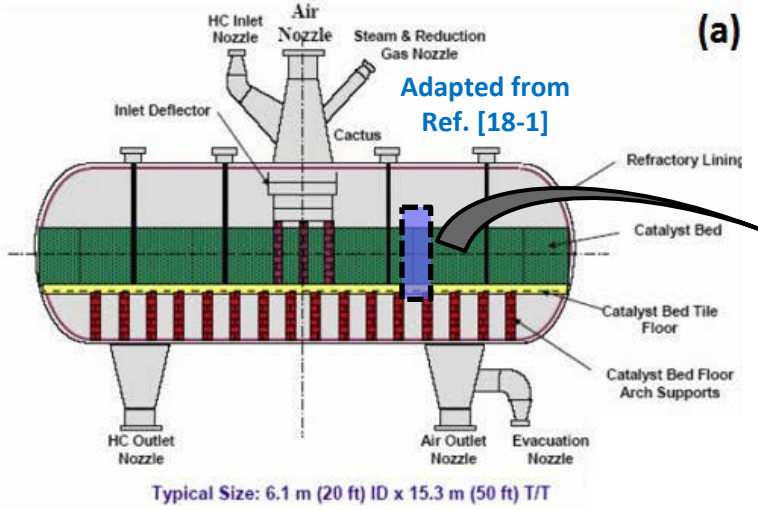
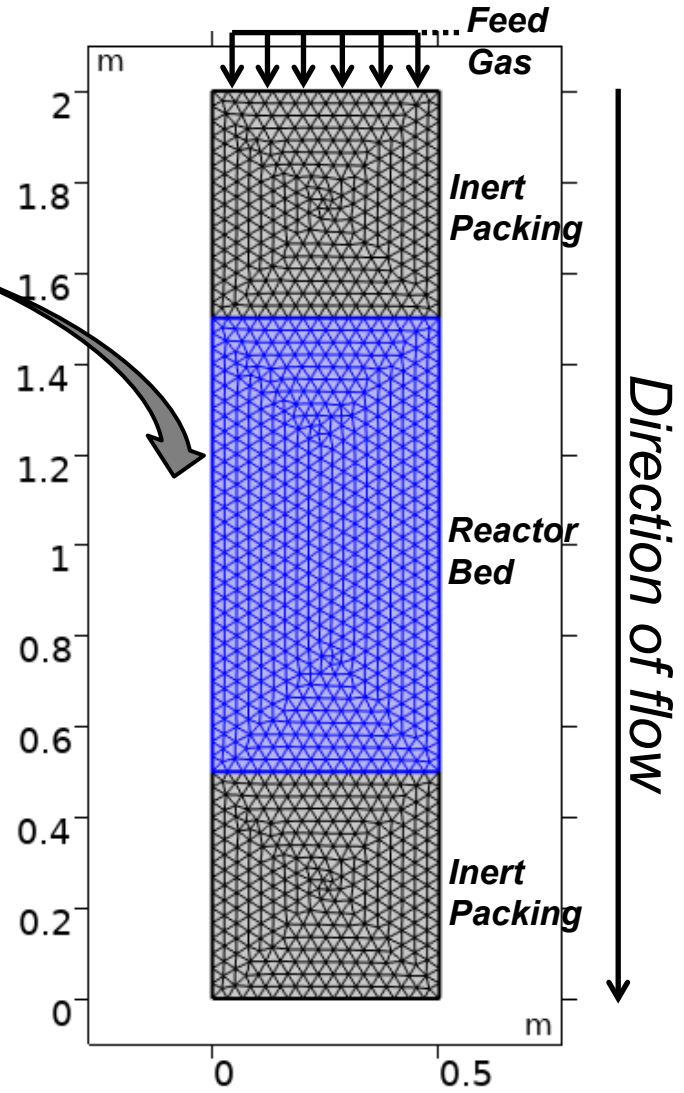
17-1 F. L. E. Usseglio-Viretta, P. Patel, E. Bernhardt, A. Mistry, P. P. Mukherjee, J. Allen, S. J. Cooper, J. Laurencin, K. Smith, *SoftwareX* 17 100915 (2022)

PACKED BEDS: reactor model development for Lummus-type Catofin geometry

- Parameterization of a 2D cross-section of a commercial PDH packed bed reactor for **adiabatic operation** (i.e., heat flux **q** = 0)
  - COMSOL Multiphysics 6.1 model features gas–solid plug flow, intra-/inter-particle reactive transport, heat transfer and a transient numerical solver
  - Kinetics incorporated from **seven-step, reduced-order mechanism** fitted to TAP reactor data by TAPsolver



Adapted from Ref. [18-1]



Darcy's Law – Reaction and Diffusion inside of Pellet

$$\frac{\partial(\varepsilon_P c_i)}{\partial t} + \nabla\cdot\left(-D_{e,i}\nabla c_i\right) = R_i \qquad D_{e,i} = \frac{\varepsilon_P}{\tau} D_{F,i}$$

Heat Transfer inside of Pellet and Bed

$$(\rho C_P)_{\text{eff}} \frac{\partial T}{\partial t} + \rho_f C_{P,f}\mathbf{u}\cdot\nabla T + \nabla\cdot\mathbf{q} = \Sigma Q$$

Reaction and Diffusion in Fluid Phase

$$\frac{\partial c_i}{\partial t} + \nabla\cdot\left(-D_{F,i}\nabla c_i\right) = R_i$$

Advection in Fluid and Pellet Phases

$$\rho\frac{\partial \mathbf{u}}{\partial t} + \rho(\mathbf{u}\cdot\nabla)\mathbf{u} = \nabla\cdot[-P\mathbf{I} + \mathbf{K}] + \mathbf{F}$$

$$\frac{\partial \varepsilon_P \rho}{\partial t} + \nabla\cdot(\rho\mathbf{u}) = 0$$

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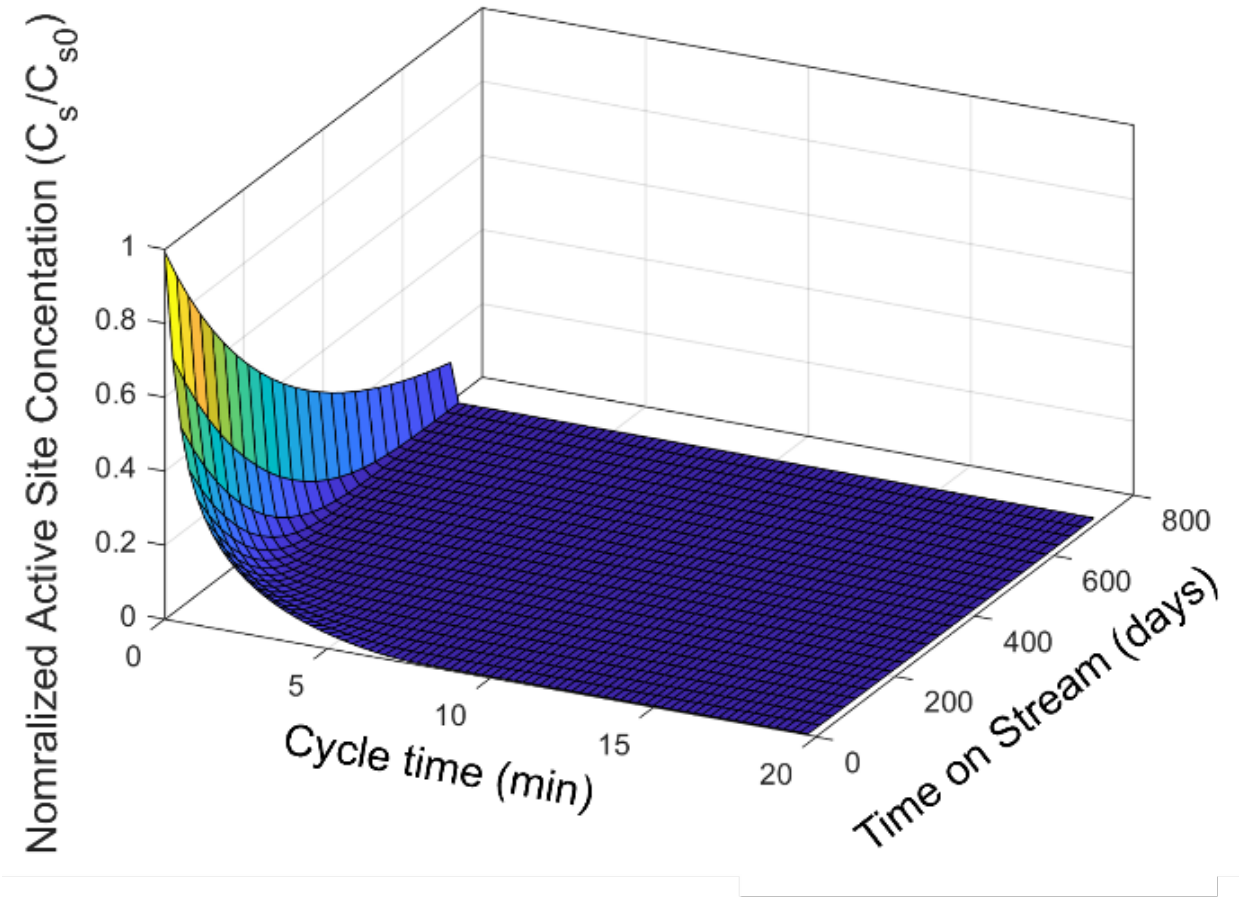
18-1 H. A. Maddah, *ASRJETS* 45 49–63 (2018), Figure 3(a) [*Catofin reactor drawing*]

With Peter Ciesielski, Adam Yonge and Meagan Crowley.

Reaction Conditions: T_0 = 1000°F, P = 0.5 bar, $d_{p,avg}$ = 0.3 cm (ε_p = 0.25), [S] = 1752 mol m^{-3} (i.e., 11.3 wt% Cr), 1.34 mol s^{-1} C_3H_8 feed (i.e., LHSV = 3.0 h^{-1})

PACKED BEDS: reactor model predicts rapid in-cycle & long-term deactivation



- Dimensionless fraction of Cr active sites exhibits steeply declining profiles along the reaction coordinate of both individual PDH cycles (*xz* plane) and along the entire 720-day simulated catalyst lifetime (*yz* plane)
- Long-time-on-stream deactivation profiles are initially benchmarked from published CrO_x/Al_2O_3 plant data
- Eyring-derived kinetic temperature dependencies predict ~55 K maximum temperature drop in the first PDH cycle
- Takeaway: reasonable deactivation profiles may be predicted over typical PDH cycle times and catalyst lifetimes

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19-1 V. Fridman, R. Xing, *Ind. Eng. Chem. Res.* 56 (28) 7937–7947 (2017)

With Peter Ciesielski, Adam Yonge and Meagan Crowley.

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Acknowledgement

National Renewable Energy Laboratory

- Peter N. Ciesielski
- Brennan M. Pecha
- Meagan F. Crowley
- Adam C. Yonge
- Hariswaran Sitaraman
- David G. Brandner
- Gregg T. Beckham

Others

- Rebecca Fushimi (*INL*)
- Jason P. Malizia (*INL*)
- A. J. Medford (*Georgia Tech*)
- Lars C. Grabow (*U. Houston*)
- Rong Xing (*Clariant Corporation*)
- Mingyong Sun (*Clariant Corporation*)
- Yuriy Román-Leshkov (*MIT*)

N.E.T. acknowledges funding from the U.S. Department of Energy Bioenergy Technologies Office (BETO) and Industrial Efficiency and Decarbonization Office (IEDO) under Contract DE-AC36-08GO28308 with the National Renewable Energy Laboratory.

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