Enabling complex biomass feedstock for biopower combustion and autothermal pyrolysis

[WBS 5.1.2.101/5.1.2.102/5.1.2.103]

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A multi-scale problem … A multi-lab solution

Acknowledgements

- Project Partners:
  - CPFD (Computational Particle Fluid Dynamics)
  - Babcock and Wilcox
  - Sacramento Municipal Utility District (SMUD)
  - McMinnville Electric System
  - POET
  - CanmetENERGY (Natural Resources Canada)

- Project Support:
  - U.S. Department of Energy Bioenergy Technologies Office (BETO)
  - BioPower Technology Manager:
    - Beau Hoffman
  - CCPC Technology Managers:
    - Trevor Smith, Andrea Bailey, and Jeremy Leong (now with DOE-AMO)

- We also acknowledge the Feedstock-Conversion Interface Consortium (FCIC) and fundamental science-based computational tools development R&D in FCIC that is being applied and utilized in this BioPower project
  - BETO Technology Managers: Beau Hoffman, Liz Moore, Mark Elles
  - Ed Wolfrum (FCIC PI) & Amie Sluiter (FCIC PM)

Project Overview

Lab Call for Biopower R&D (DE-LC-000L045):

- *“The Bioenergy Technologies Office (BETO), in the Office of Energy Efficiency and Renewable Energy, is pleased to issue a laboratory call for* ***early stage research and development projects to develop innovations in the use of biomass, municipally-derived biosolids, and sorted municipal solid waste to improve the economic potential of biopower production and use in the United States.“***

Project Objective:

- develop models and determine critical parameters to enable improved reactor design and optimal controls for more efficient and cost-effective biopower generation.

Challenges and Barriers:

- Lack of design tools that account for complex variations in biomass feedstocks
- Emissions impacts from combustion of biomass are not well understood
- Lack of information on primary products of biomass devolatilization and the mechanism of their low temperature oxidation.

Project began in FY2019 and is wrapping up in FY2021

- $1.5M DOE budget over (3) NLs + Iowa State Univ. (+15% cost share)

Focal Points of this Project

Biomass-to-Electricity

- **CanmetENERGY Fluidized Bed BioPower Combustor**
  - 50kW$_{th}$ reactor
  - NETL computational fluid dynamics (CFD) model has been validated with data from CanmetENERGY reactor

Biomass-to-Fuel

- **Iowa State University Autothermal Pyrolysis Fluidized Bed Reactor**
  - ~8 kg biomass/hr; reactor dimensions: ID=8.9cm, 83.0 cm length
  - NREL particle scale model advanced to account for char oxidation that is critical to autothermal pyrolysis; validation with ISU experimentalists
  - ORNL computational fluid dynamics (CFD) model of reactor for understanding effects of equivalence ratio and spatial location of exotherms

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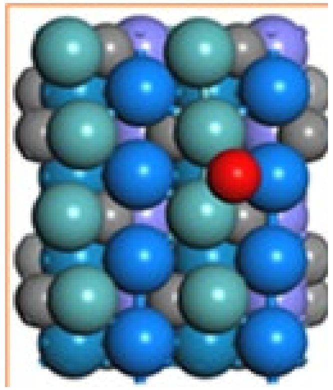
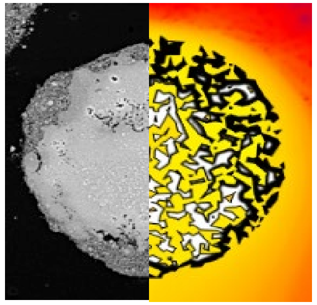
A Multi-Scale Approach to Computational Modeling of Complex Bioenergy Systems

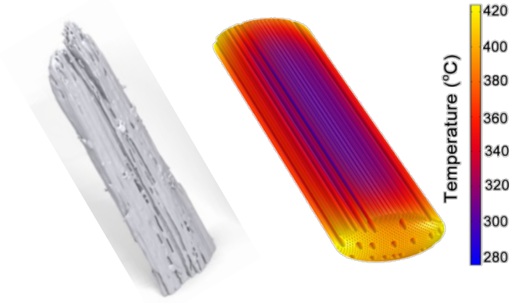
Catalysis Modeling at Atomic Scales



Investigating novel catalyst material combinations and understanding surface chemistry phenomena to guide experimentalists

Particle Modeling at Meso Scales

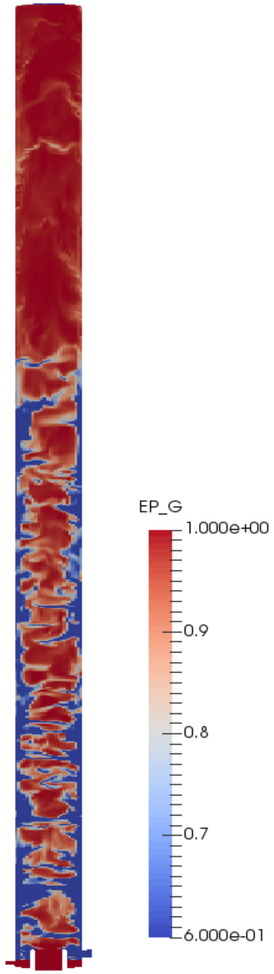




Understanding mass transport of reactants/products, heat transfer, reaction kinetics, and coking & deactivation processes

Conversion Modeling at Reactor Scales

Determining optimal process conditions for maximum yield and selectivity to desired products including high C efficient and commercially valuable products



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NREL
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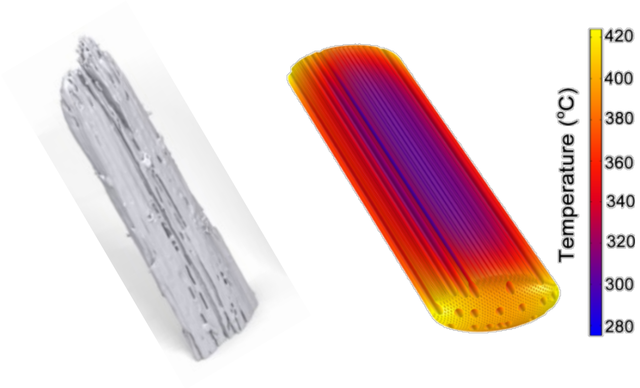
Project Expands Existing Meso- and Reactor-Scale Models in Pyrolysis of Biomass

Particle Modeling at Meso Scales



Particle shape, size, structure, and chemistry effects captured with Finite Element Models of individual biomass particles undergoing pyrolysis in reactor conditions

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Conversion Modeling at Reactor Scales

MFiX

Physics of feedstock flow, mixing, and residence times in reactor coupled with thermochemical conversion processes are captured with Computational Fluid Dynamics (CFD) models

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Project builds from foundational modeling toolset developed by CCPC in conjunction with the Feedstock-Conversion Interface Consortium (FCIC)

fcic
FEEDSTOCK-CONVERSION INTERFACE CONSORTIUM

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Project expands toolset with emphasis on:

(1) Adding char oxidation element to model toolset
(2) Developing models for new feedstocks (notably corn stover)

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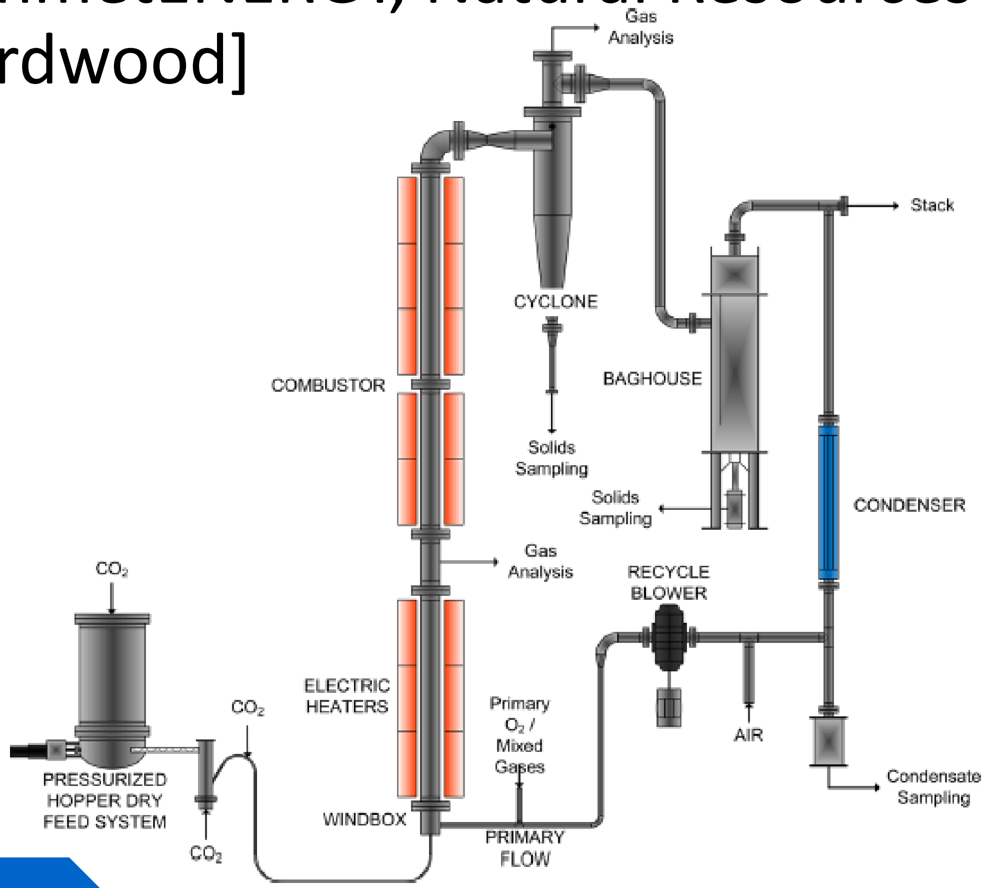
CanmetEnergy 50kW$_{th}$ CFB Combustor

- Bench-scale experimental facility designed, built, and operated at CanmetENERGY, Natural Resources Canada[1] (NRCan) [feedstock is torrefied hardwood]



Operating Conditions	
Inert material	Olivine sand, 273 µm, 3063 kg/m³
Biomass	Torrefied HW, 375 µm, 520 kg/m³
Initial mass of inert	9.0 kg
$\dot{m}$ of fluidizing gas (air)	15.6 kg/h
$\dot{m}$ of fuel feed gas (air)	3.06 kg/h
$\dot{m}$ of biomass	2.65 kg/h
Sidewall temperature	850°C
Fluidizing gas inlet temperature	120°C
Fuel feed gas inlet temperature	20°C

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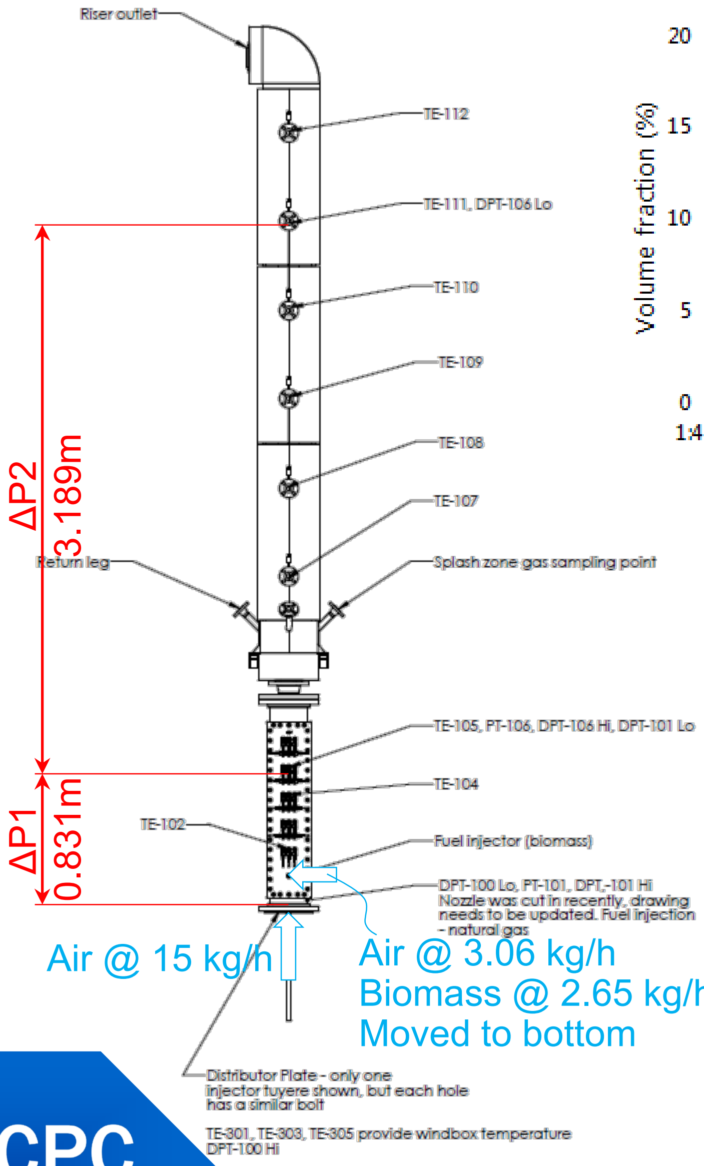
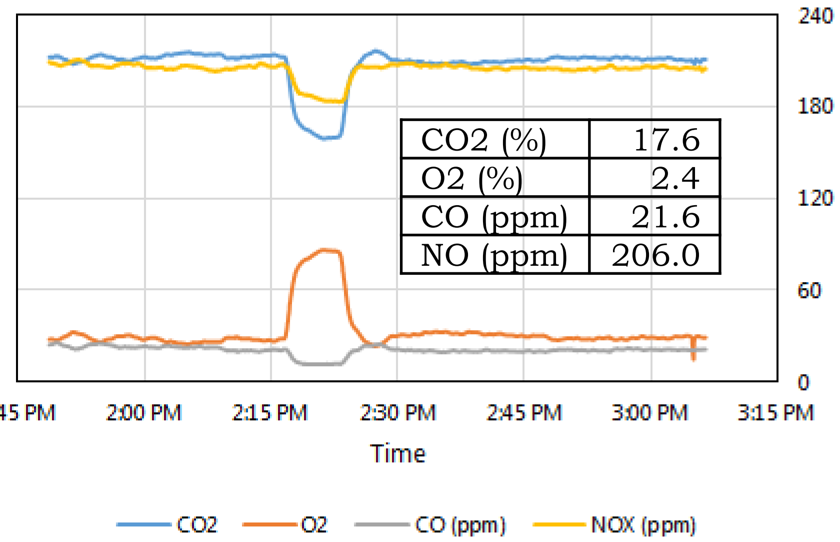
[1] Hughes, R.W. et al., 2015. Oxy-fluidized bed combustion using under bed fines fuel injection. In 22nd International Conference on Fluidized Bed Conversion. Turku, Finland, 2015.

Experimental Conditions and Results

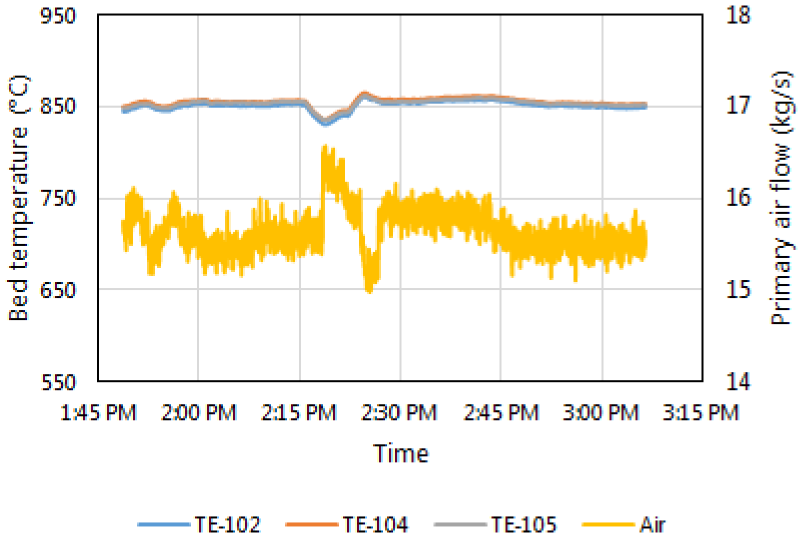


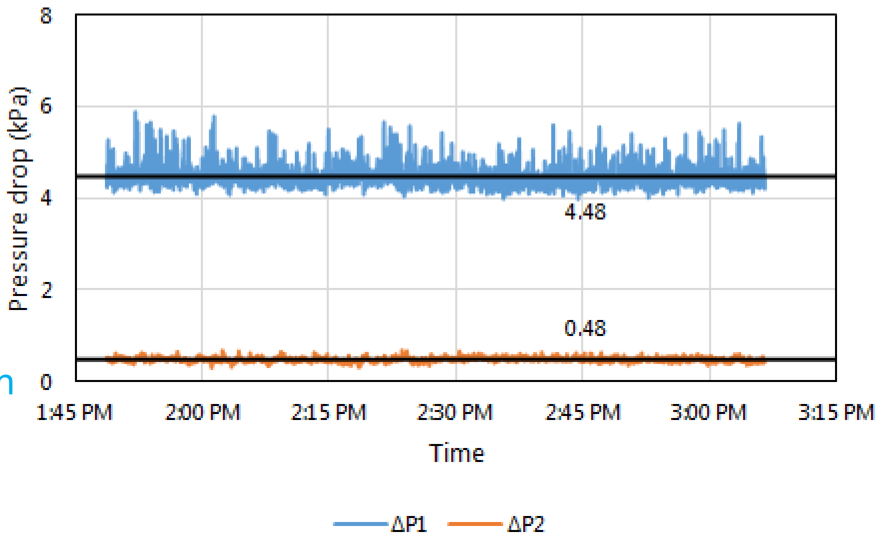
Air @ 15 kg/h

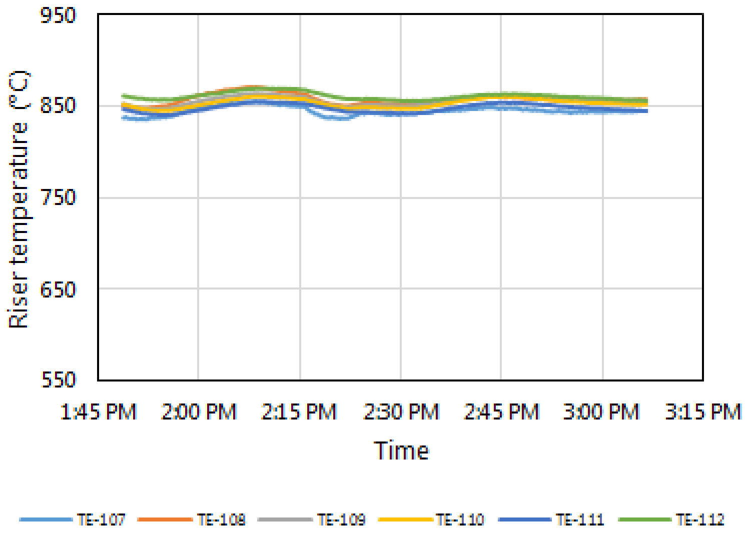
Air @ 3.06 kg/h
Biomass @ 2.65 kg/h
Moved to bottom



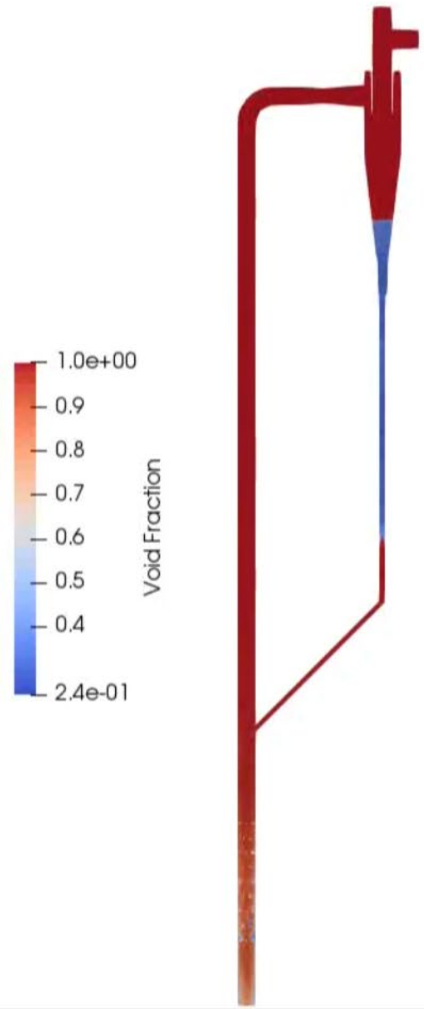
CO2 (%)	17.6
O2 (%)	2.4
CO (ppm)	21.6
NO (ppm)	206.0

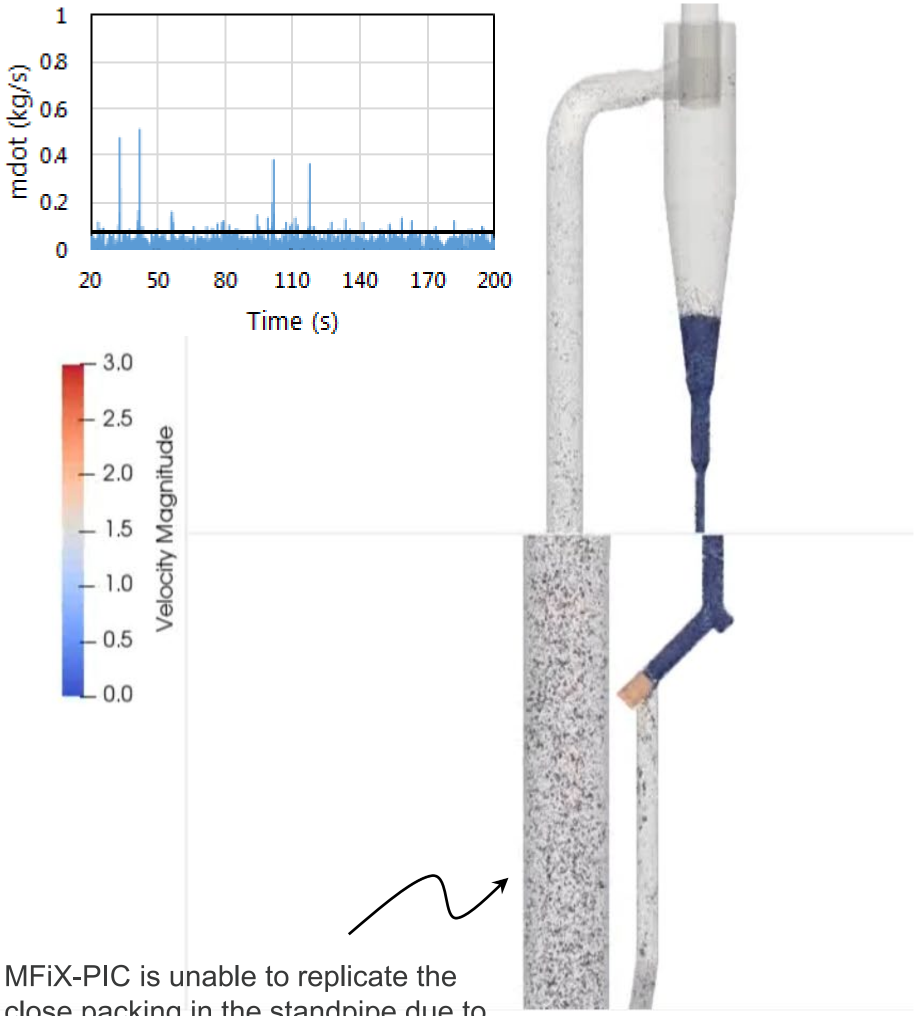




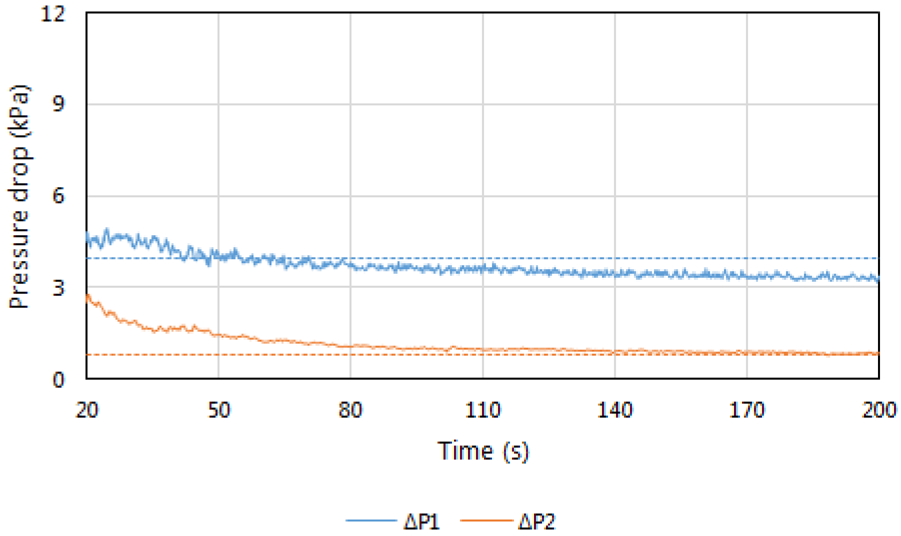


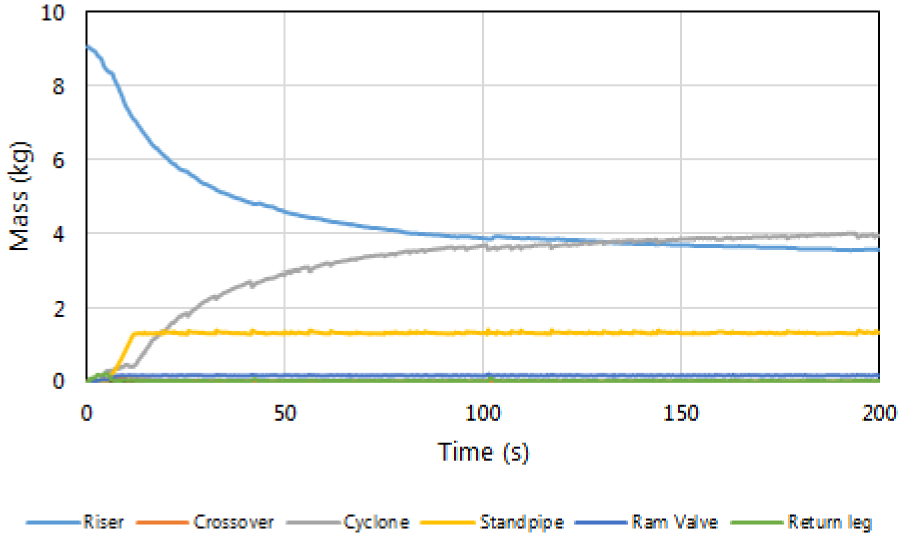
Hydrodynamics Validation with Cold Flow Simulation





MFiX-PIC is unable to replicate the close packing in the standpipe due to lack of a collisional damping model, so an artificial valve stroke is implemented to approximate the dense packing and appropriate residence time in the standpipe





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Combustion Scheme

- For combustion simulations, the volatile gases are lumped into a single pseudospecies[1] $CH_{2.274}O_{0.9392}$ based on the proximate and ultimate analysis of the fuel
- The simplest reaction mechanism to model the volatile matter combustion is the global one-step reaction[2,3] with the rate interpolated from Westbrook & Dryer[4]

$$\mathrm{CH}_x\mathrm{O}_y + \left(1 + \frac{x}{4} - \frac{y}{2}\right)\mathrm{O}_2 \rightarrow \mathrm{CO}_2 + \frac{x}{2}\mathrm{H}_2\mathrm{O}$$

$$k = 4.94 \cdot 10^{11} \cdot \exp(-1.510 \cdot 10^4/T) \cdot [\mathrm{CH}_x\mathrm{O}_y]^{0.25} \cdot [\mathrm{O}_2]^{1.5}$$

Pyrolysis	$\mathrm{Volatiles}_{(s)} \rightarrow \mathrm{Volatiles}_{(g)}$	$r_1 = 2 \times 10^{19}\, e^{\frac{-212180}{8.314 T_b}} \frac{m_b}{MW_b}$
Char combustion	$\mathrm{Char}_{(s)} + \mathrm{O}_2 \rightarrow \mathrm{CO}_2$	$r_2 = \frac{p_{O_2} S_{char}}{MW_{O_2}[1/k_{film} + 1/k_{reaction}]}$
Volatile combustion	$\mathrm{Volatiles} + 1.099017 \cdot \mathrm{O}_2 \rightarrow \mathrm{CO}_2 + 1.137212 \cdot \mathrm{H}_2\mathrm{O}$	$r_3 = 4.94 \cdot 10^{11} e^{\frac{-15100}{T_g}} c_{\mathrm{O}_2}^{1.5} c_{\mathrm{Volatiles}}^{0.25}$

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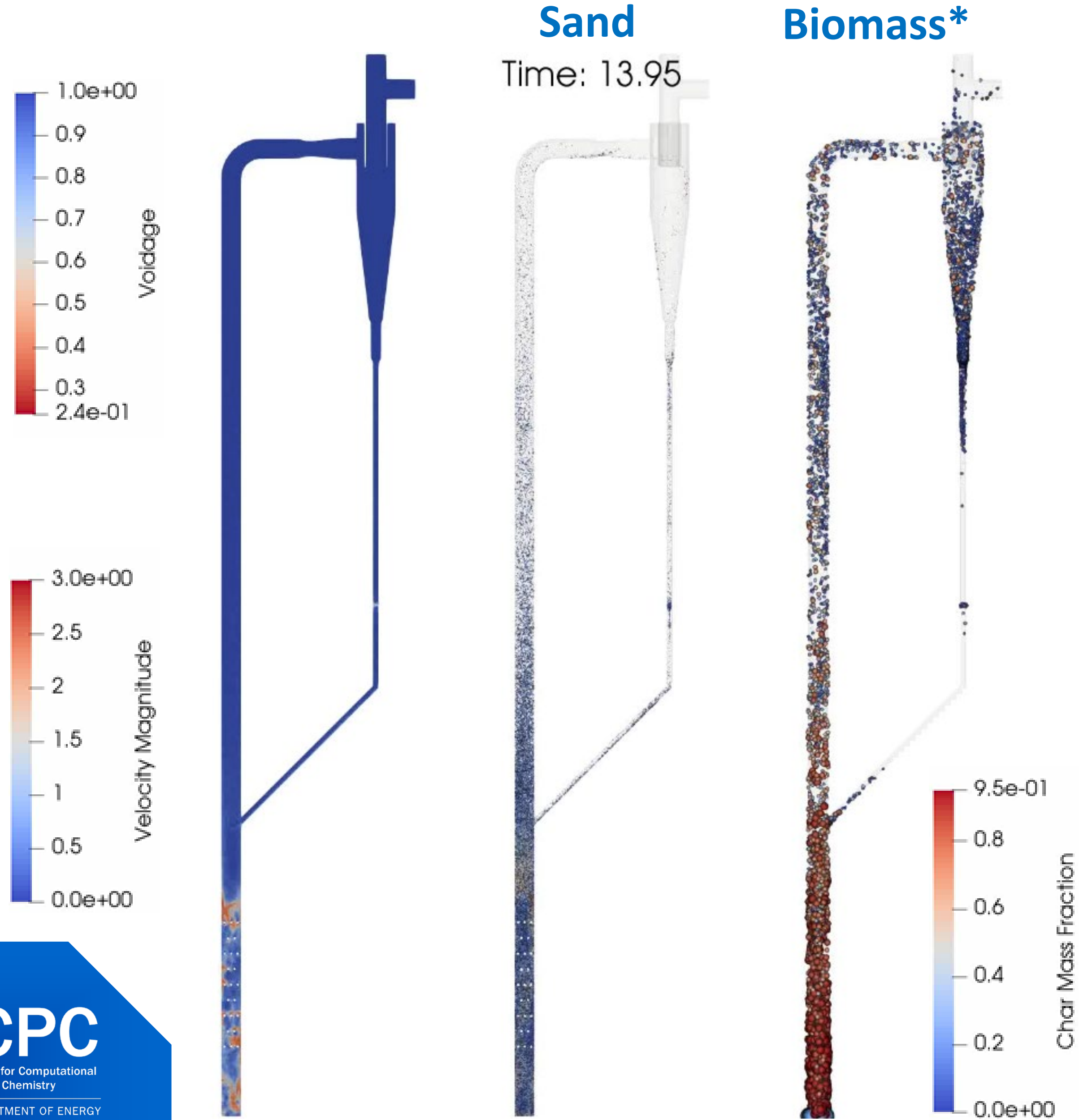
[1] Marangwanda, G.T., Madyira, D.M. & Babarinde, T.O. (2020) Combustion models for biomass: A review. *Energy Reports*, 6, pp. 664–672.

[2] Ma, L., Jones, J.M., Pourkashanian, M. & Williams, A. (2007) Modelling the combustion of pulverized biomass in an industrial combustion test furnace. *Fuel*, 86, 1959–1965.

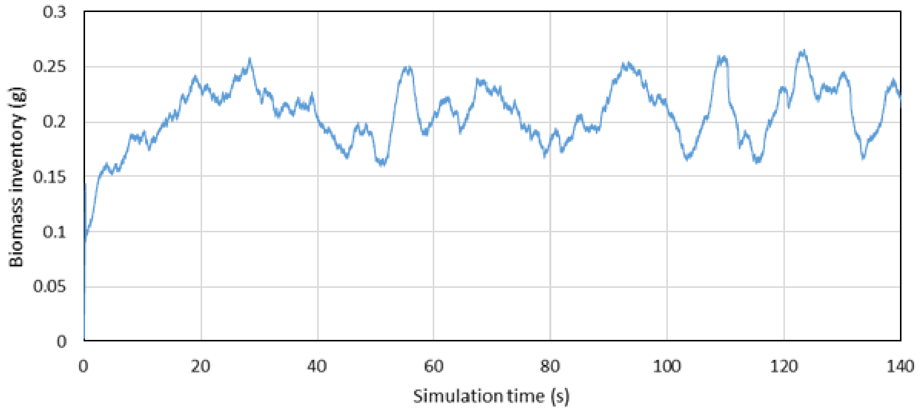
[3] Álvarez, L., Yin, C., Riaza, J., Pevida, C., Pis, J.J. & Rubiera, F. (2014) Biomass co-firing under oxy-fuel conditions: A computational fluid dynamics modelling study and experimental validation. *Fuel Process. Technol.*, 120, pp. 22–33.

[4] Westbrook, C.K. & Dryer, F.L. (1981) Simplified reaction mechanisms for the oxidation of hydrocarbon fuels in flames. *Combust. Sci. Technol.*, 27, pp. 31–43.

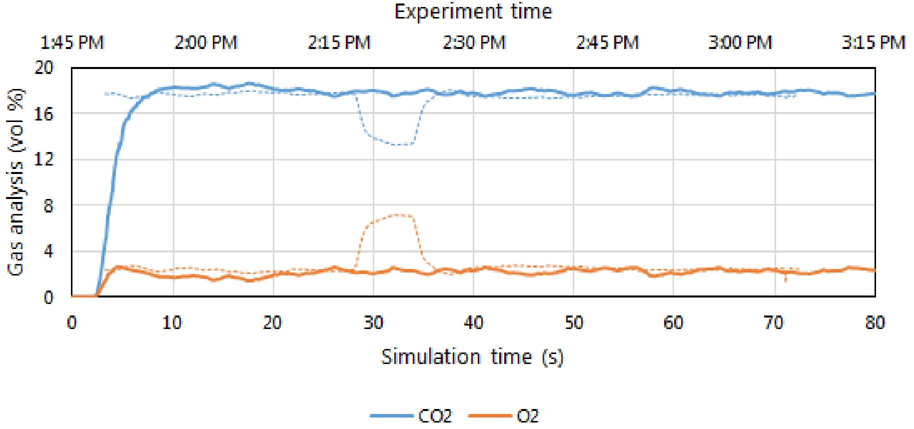
Model Results and Validation with Experimental Data



Total biomass inventory increases initially and then remains steady around 0.2g



The compositions of CO_2 and O_2 show excellent match with experimental results (dashed lines) validating the simplified combustion scheme

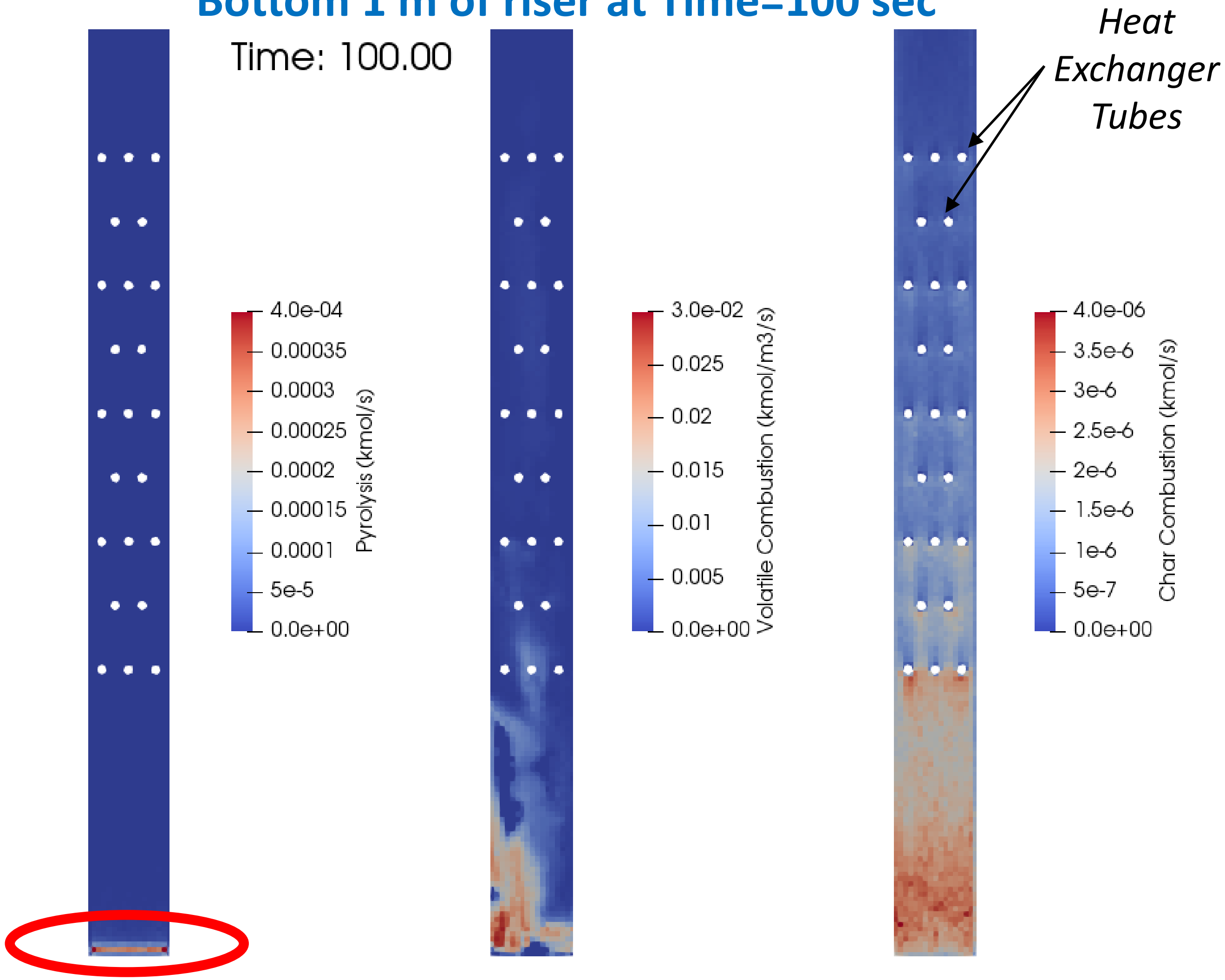


Biomass particles enlarged 50x for visualization of diameter change

Combustion Zone Details

- Bottom 1 m of riser magnified to highlight combustion zone
- Pyrolysis is near instantaneous at 850°C and occurs to completion near the inlet
- Next, pyrolysis vapors are combusted in the bottom bed region near the inlet
- Char combustion rates are highest in the stagnation zones around the heat exchanger tubes

Bottom 1 m of riser at Time=100 sec



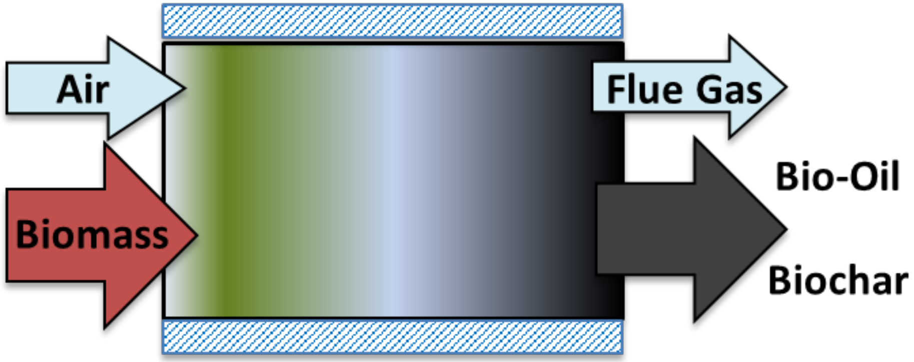
Pyrolysis **Volatile Combustion** **Char Oxidation**

Autothermal Pyrolysis

Part of the biomass and/or pyrolysis products are oxidized to provide energy for endothermic pyrolysis reactions

- Advantages
  - Heat transfer no longer bottleneck
- Challenge
  - Preserve organic yields of bio-oil under partial oxidative conditions

Autothermal Pyrolyzer (adiabatic)



Air

Biomass

Flue Gas

Bio-Oil

Biochar

$$\phi = \frac{Air}{Air_{Stoich}}$$

Autothermal Pyrolysis
$0.04 \le \phi \le 0.10$

Gasification
$0.15 \le \phi \le 0.35$

Pyrolysis
$\phi = 0.00$

Combustion
$\phi > 1.0$

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Char oxidation added to continuum particle modeling for pyrolysis

Model description

Particle model: pyrolysis + oxidation

Char oxidation reaction scheme: *Corn stover*

$$\frac{0.64 Char_{mass}}{MW_C} + \left(1-\eta/2+\alpha/4-\beta/2\right)O_2 \rightarrow \eta CO + \left(1-\eta\right)CO_2 + \frac{\alpha}{2}H_2O$$

$$\eta = \frac{12\exp\left(-3300/T\right)}{1+12\exp\left(-3300/T\right)}$$

$$r_{char}\left[\frac{g_{char}}{s.m^3}\right] = A_{ox}\exp\left(-E_{ox}/RT\right)P_{O_2}\frac{S_{Macro}}{V_{part}}\frac{C_{char}}{C_{char,\max}}$$

$$\frac{dChar_{mass}}{dt} = -r_{char}$$

$$\frac{dO_2}{dt} = -\left(1-\eta/2+\alpha/4-\beta/2\right)r_{char}\frac{0.64}{MW_C}$$

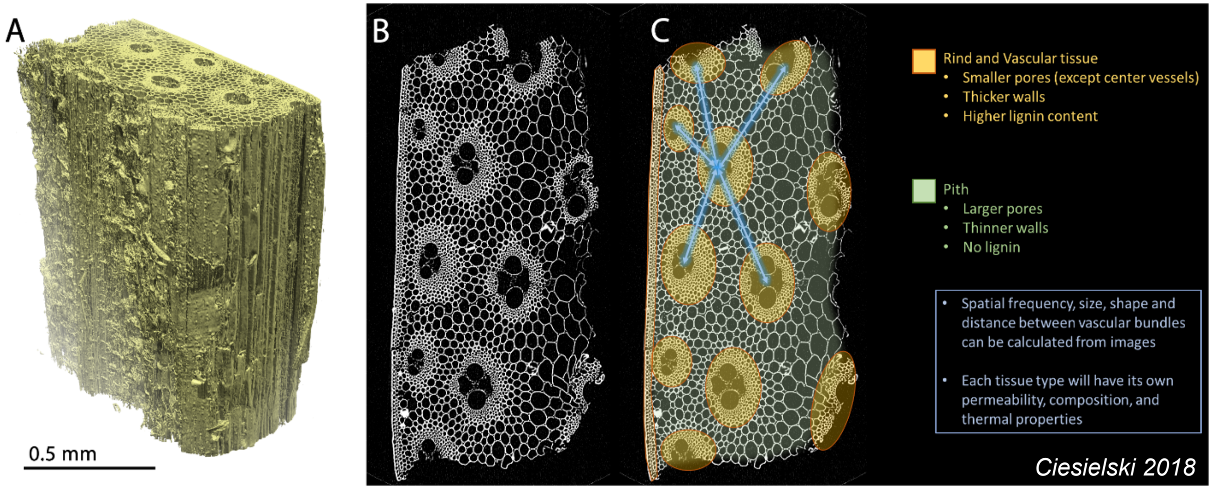
$$\frac{dCO}{dt} = \eta r_{char}\frac{0.64}{MW_C}$$

$$\frac{dCO_2}{dt} = \left(1-\eta\right)r_{char}\frac{0.64}{MW_C}$$

$$\frac{dH_2O}{dt} = \frac{\alpha}{2}r_{char}\frac{0.64}{MW_C}$$

$$\Delta H_{reaction} = \left(\Delta H_{CO_2}\left(1-\eta\right)+\Delta H_{CO}\eta\right)r_{char}\frac{0.64}{MW_C}$$

XCT data: *Corn stover*



- Spatial frequency, size, shape and distance between vascular bundles can be calculated from images
- Each tissue type will have its own permeability, composition, and thermal properties

Ciesielski 2018

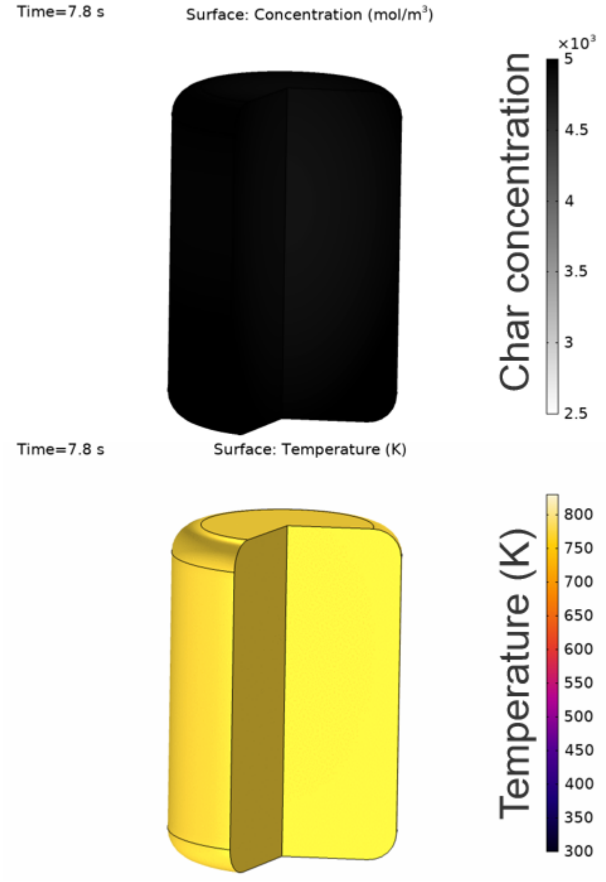
XCT extracted parameter	Value
Outer perimeter particle	6.50 mm
Total perimeter (outer + inner walls)	73.2 mm
void fraction	0.59
total surface area	87.8 mm^2
length particle	1.2 mm
width particle	1.1 mm
thickness particle	0.5 mm
volume particle	0.66 mm^3
surface area/volume	133.1 mm^2/mm^3

Anca-Couce, A. and R. Scharler, *Modelling heat of reaction in biomass pyrolysis with detailed reaction schemes.* Fuel, 2017. **206**(Supplement C): p. 572-579.
Evans, D.D. and H.W. Emmons, Combustion of wood charcoal. Fire Safety Journal, 1977. 1(1): p. 57-66

Char oxidation varies with particle geometry and O_2

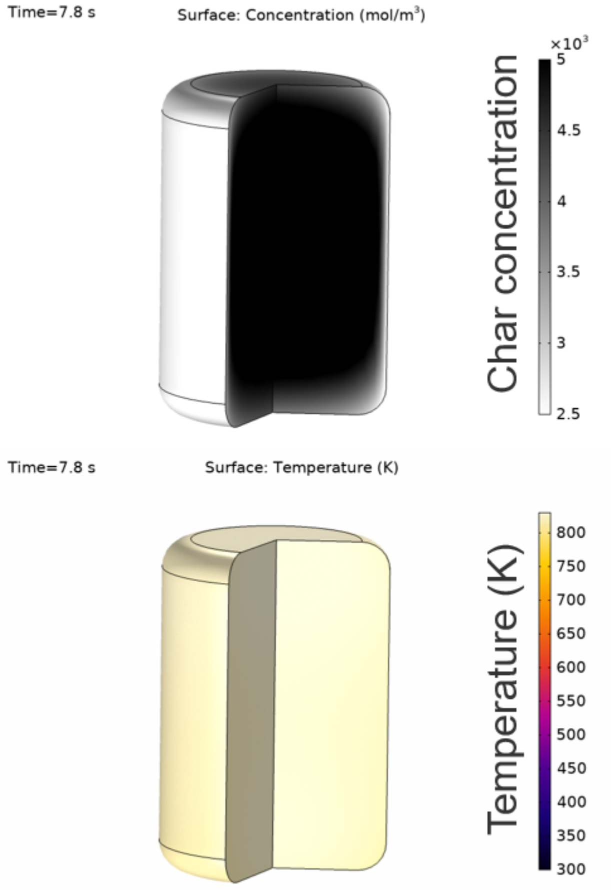
Pyrolysis

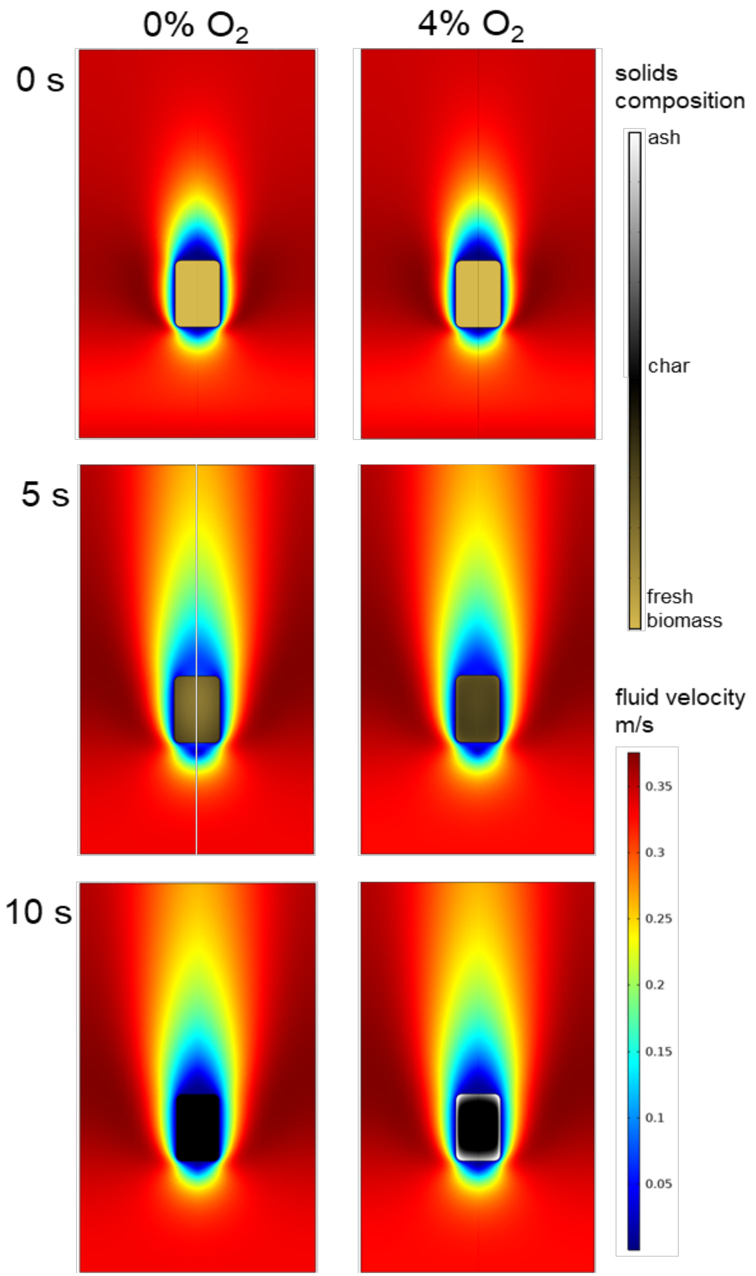
0% O_2



Pyrolysis + Oxidation

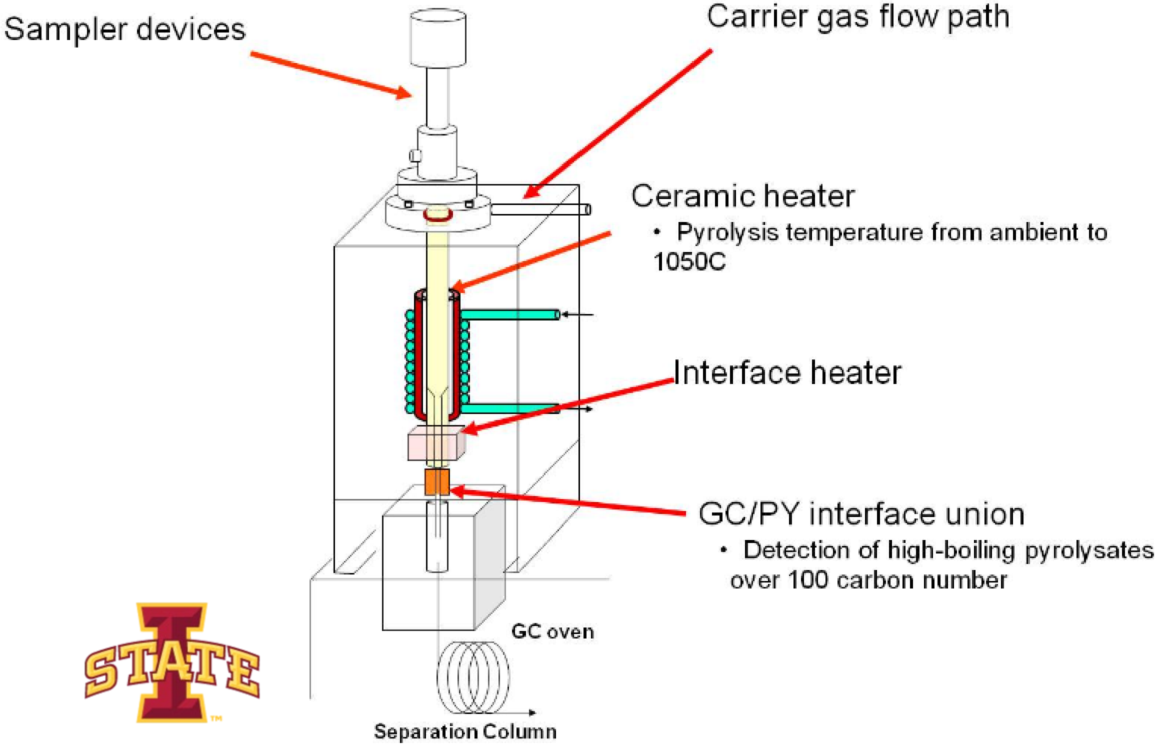
4% O_2



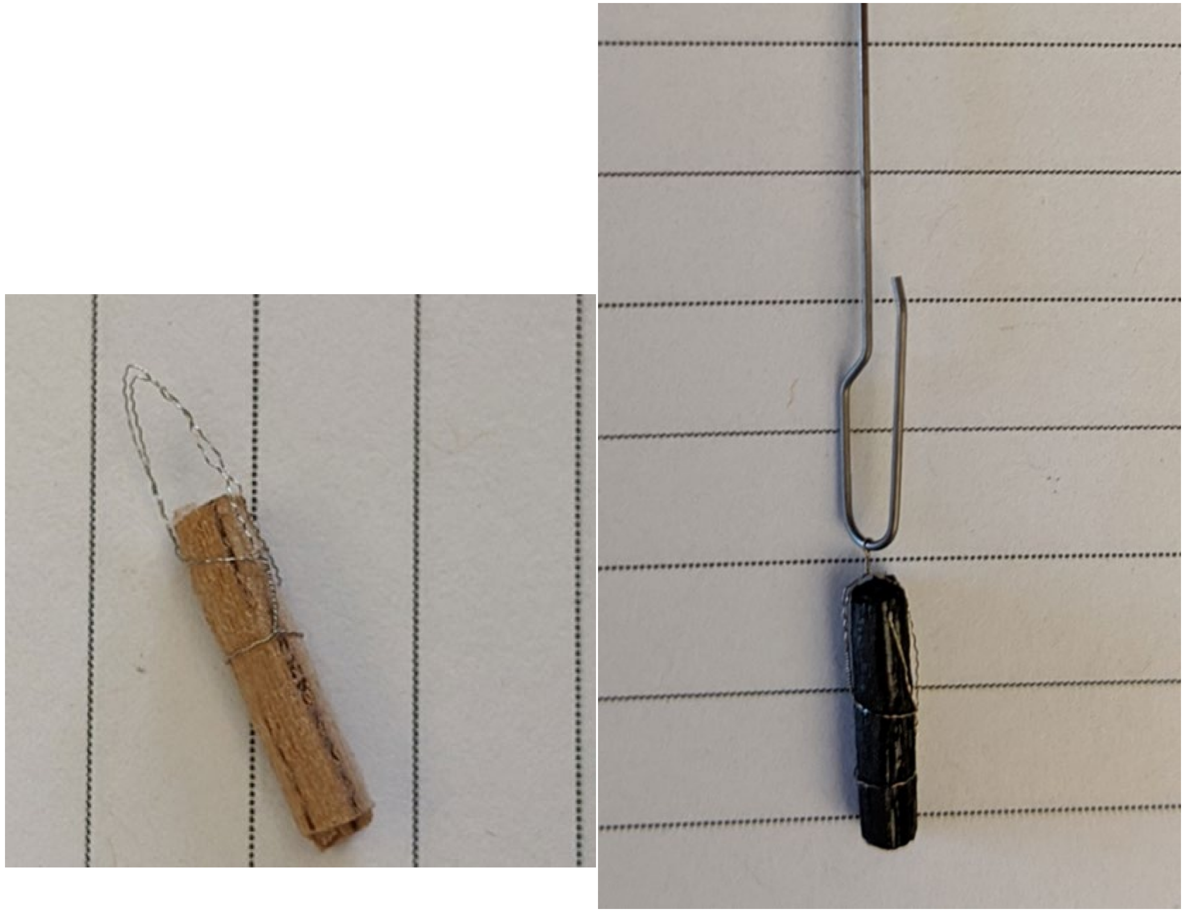


Experimental validation with ISU (oak feedstock)

- Dried oak dowels (3 mm x 12 mm)
- 0, 3, 6 % O_2 in He



- Pyrolysis temperature from ambient to 1050C
- Detection of high-boiling pyrolysates over 100 carbon number

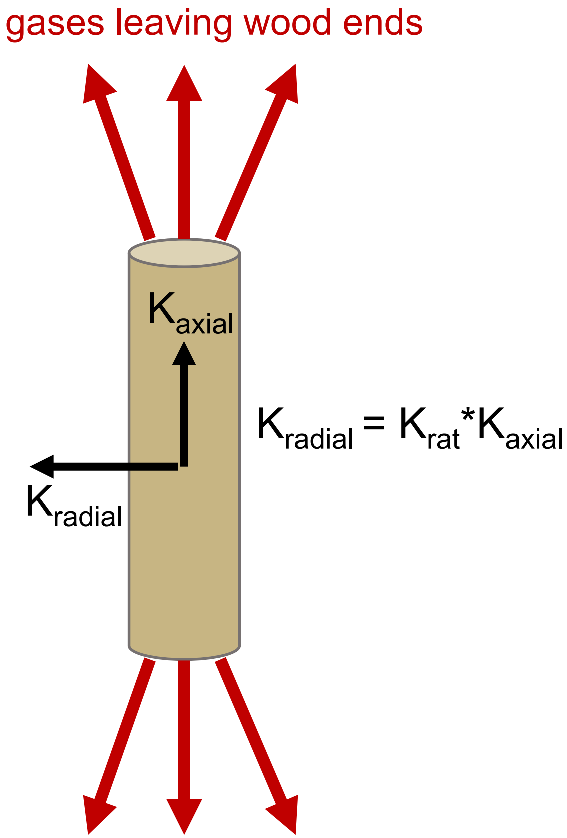


Validation of 3-d cylindrical model for oak autothermal pyrolysis

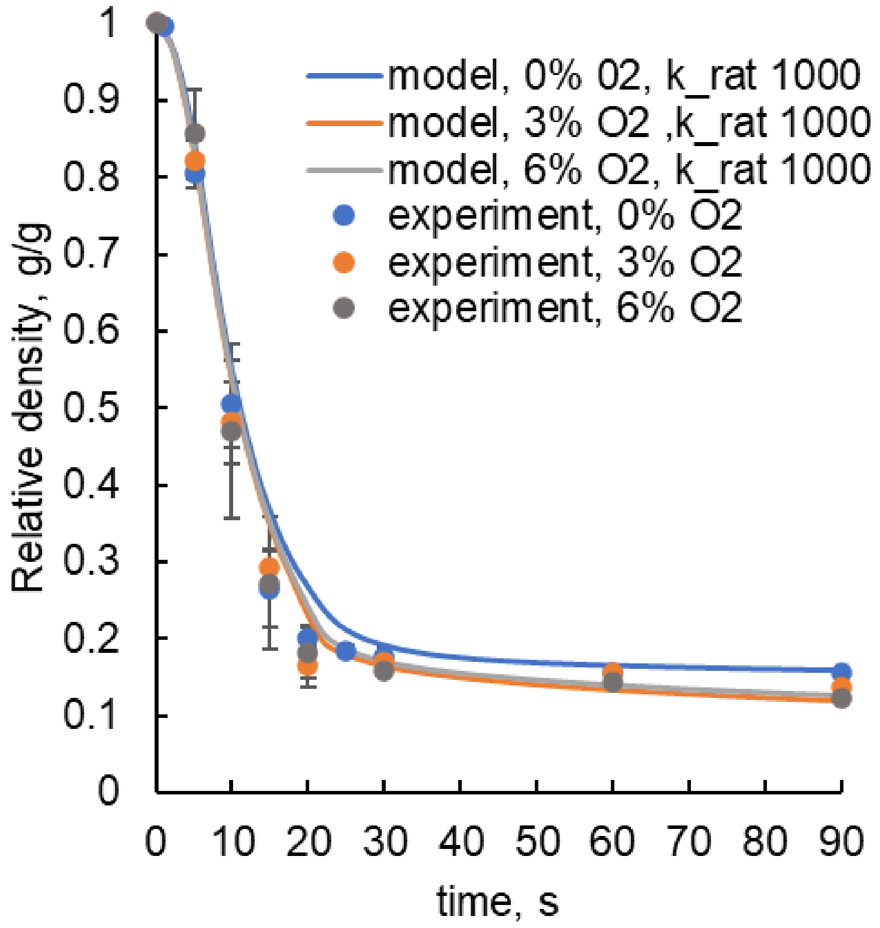
- 3-d cylindrical model for oak autothermal pyrolysis parameterized to ISU particle reactor

- *Model very sensitive to anisotropic properties like permeability (K)*
- K_{axial} varies from 5.9E-11 m^2 for wood to 1.5E09 m^2 for char
- Krat = ratio of axial : radial permeability and diffusion

- ***Model built from measured CMAs was able to accurately capture autothermal carbon mass loss***



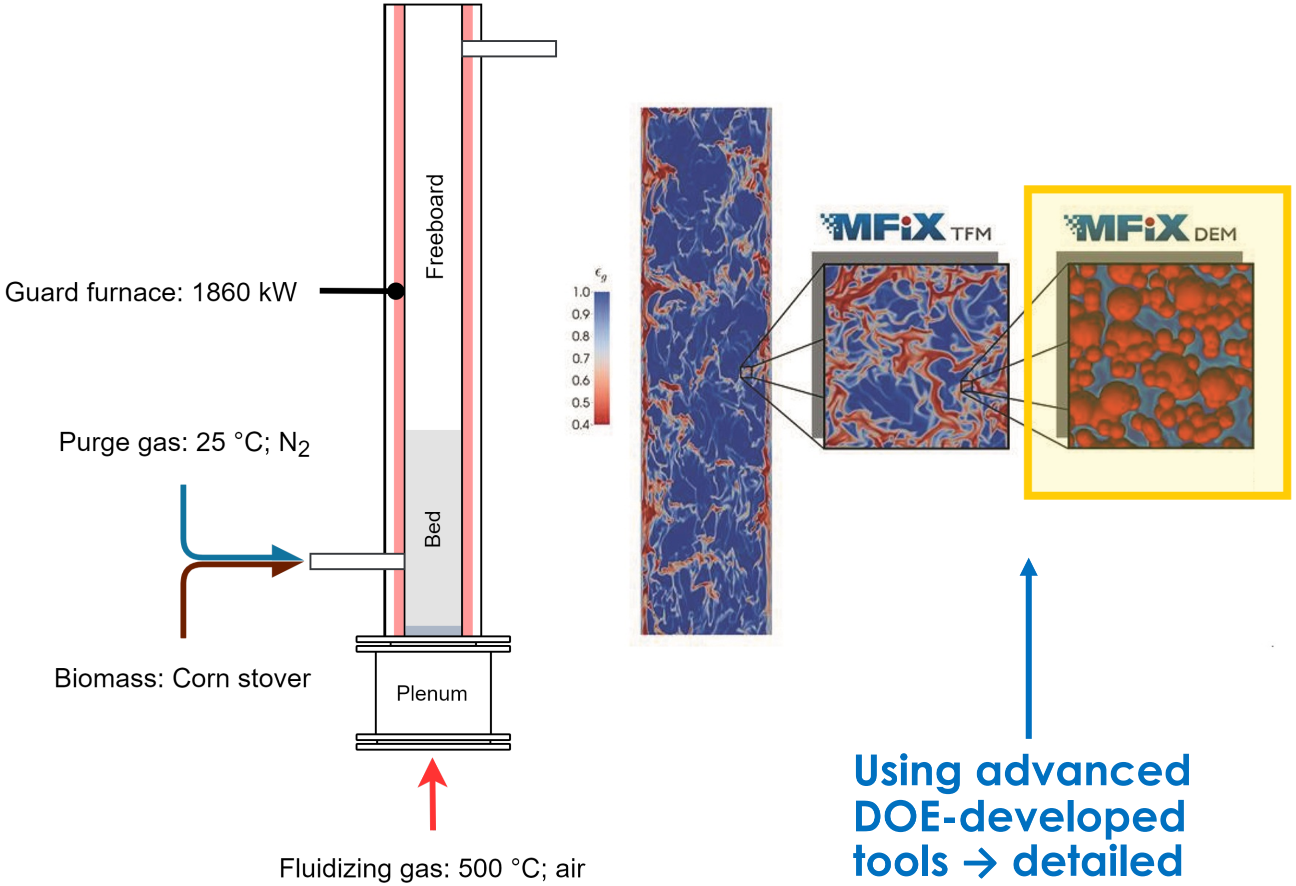
time resolved model vs experimental relative particle density



Reactor-scale model of ISU autothermal pyrolysis reactor

- Develop reactor-scale model for ISU autothermal pyrolyzer to explore detailed physical processes and predict product yields.
- Currently, integrating biomass particle-scale into reactor-scale model to improve simulation physics.
    - This step is critical to get full physics captured.
- Evaluate impact of reactor design (e.g., biomass inlet position) and other process variables on pyrolysis performance.

NOTE: reactor model results shown on following slides are preliminary results for purpose of showing model utility. Final integration of particle-scale model effects of char oxidation and overall validation of reactor model ongoing.



Using advanced DOE-developed tools → detailed physics down to the particle level

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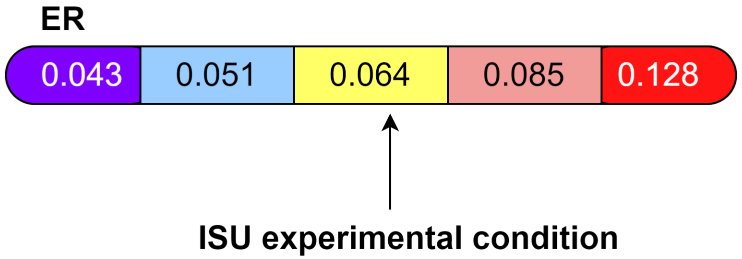
Equivalence ratio study overview

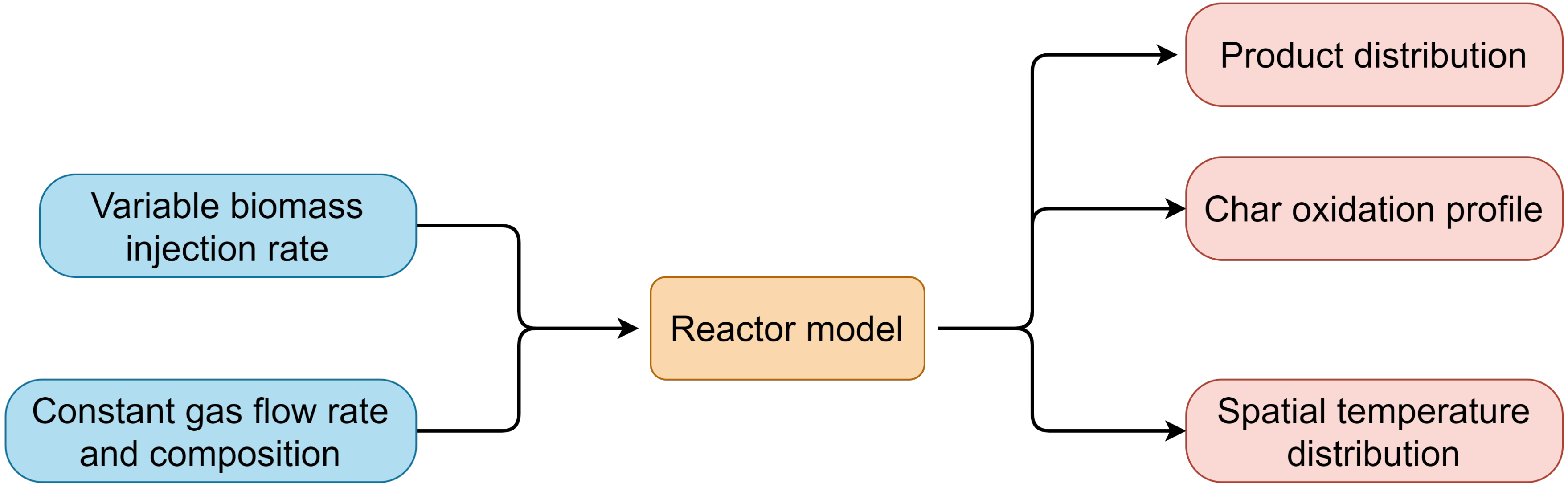
$$Equivalence\ ratio\ (ER) = \frac{Actual\ mass\ flow\ rate\ of\ O_2}{Mass\ flow\ rate\ of\ O_2\ needed\ at\ stoichiometric\ combustion}$$



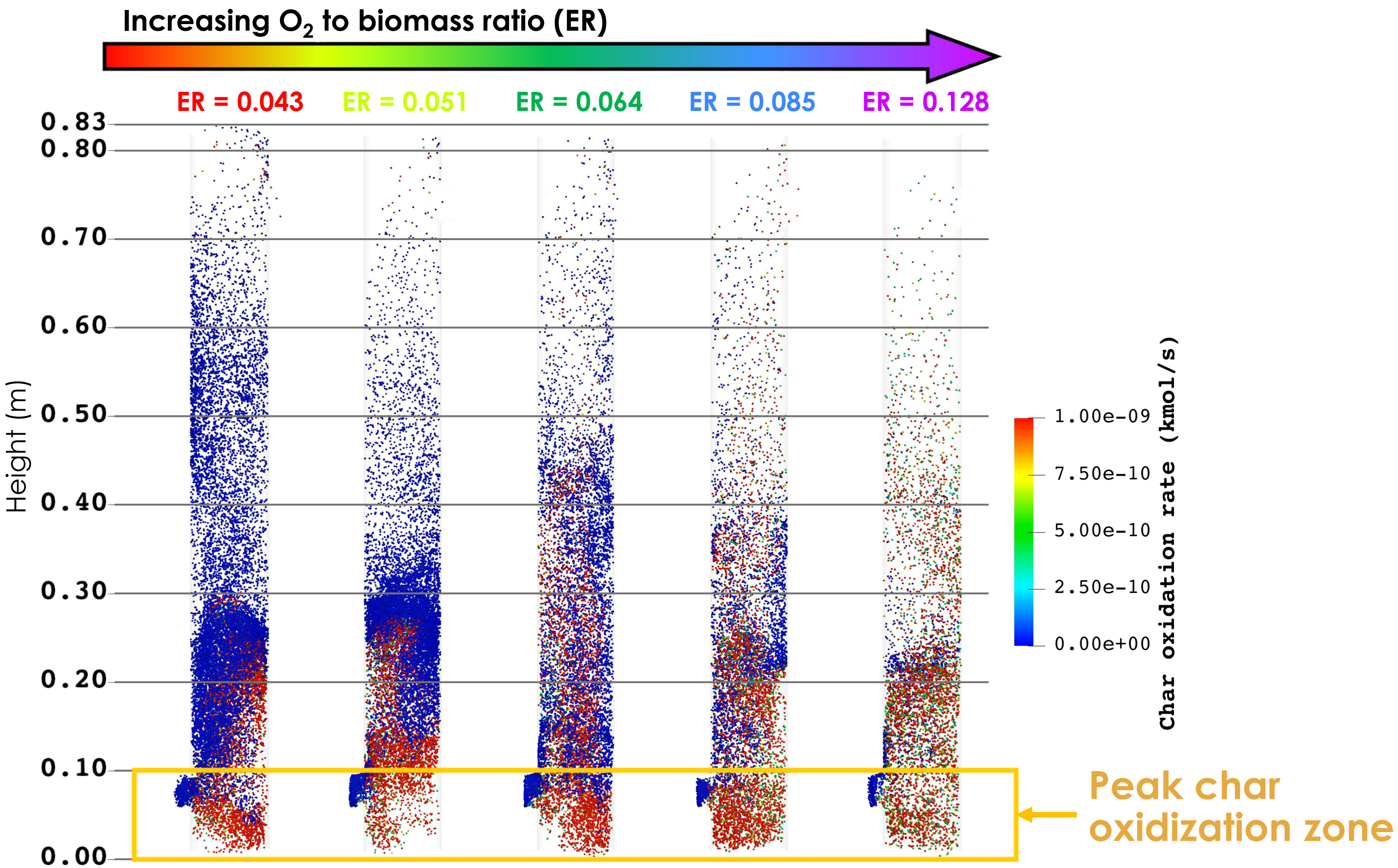
ER

0.043	0.051	0.064	0.085	0.128

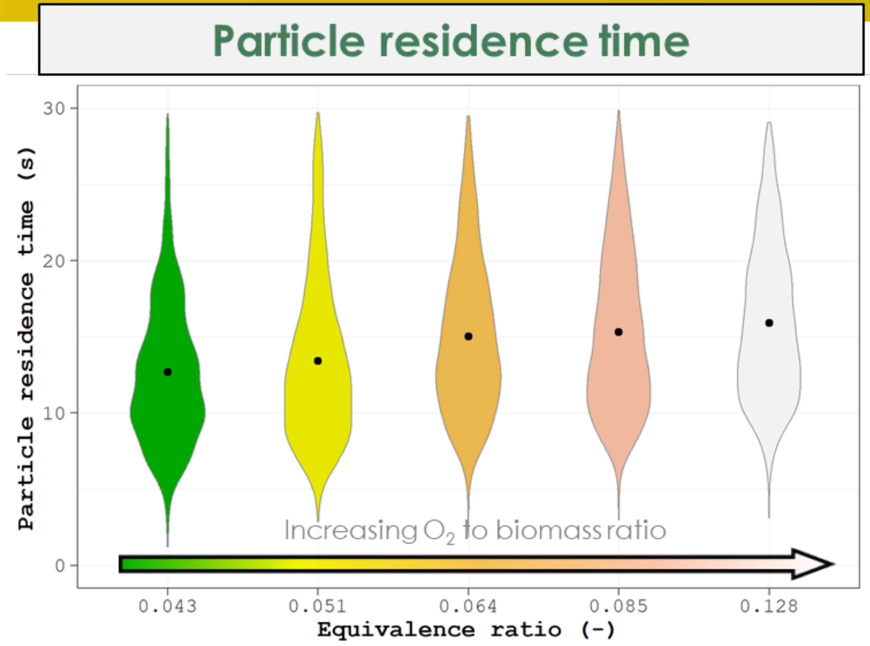
ISU experimental condition

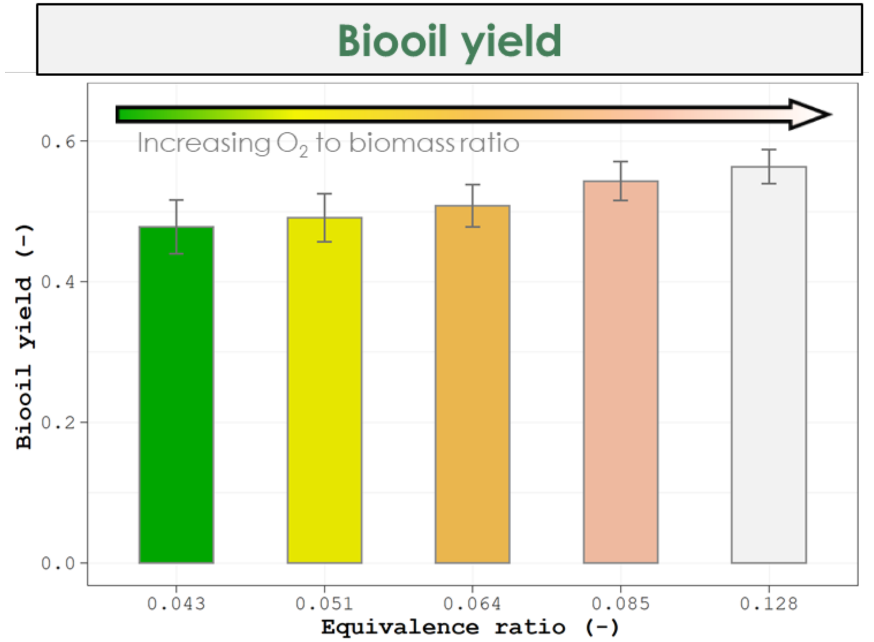


Model provides particle residence time and impacts on biooil yield as a function of equivalence ratio



Peak char oxidization zone





Higher equivalence ratio → higher average char oxidation rate & longer particle residence time → in higher biooil yield

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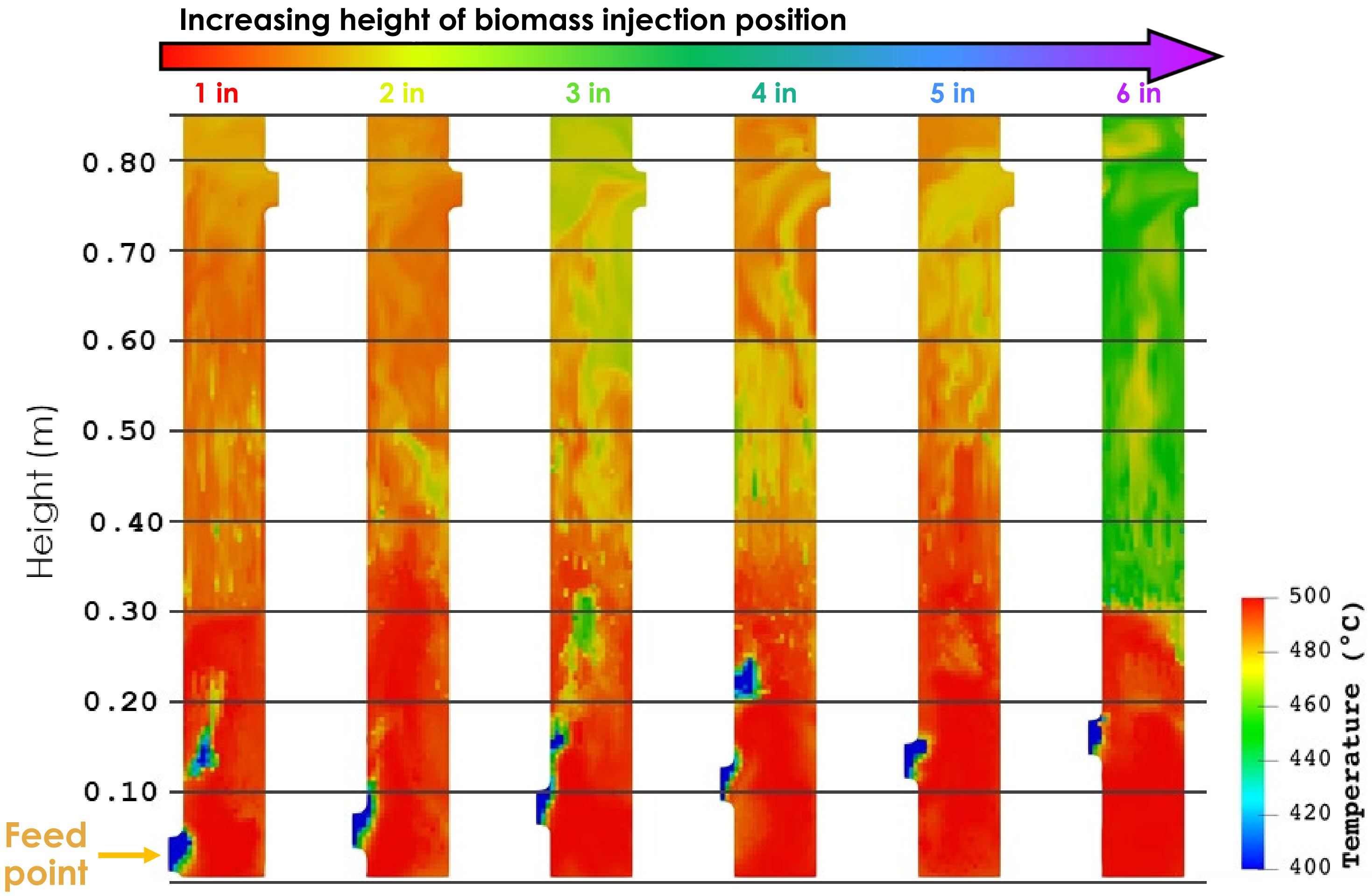
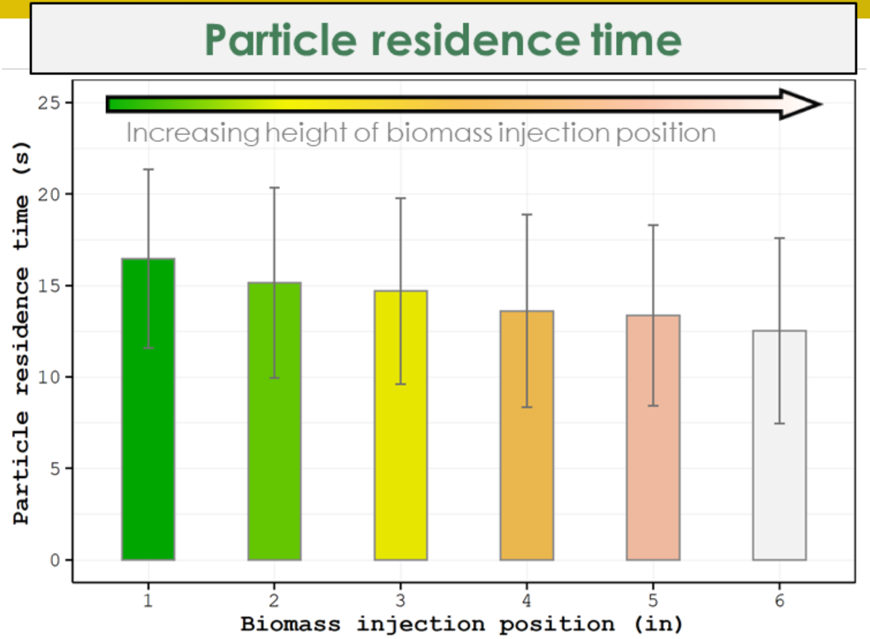
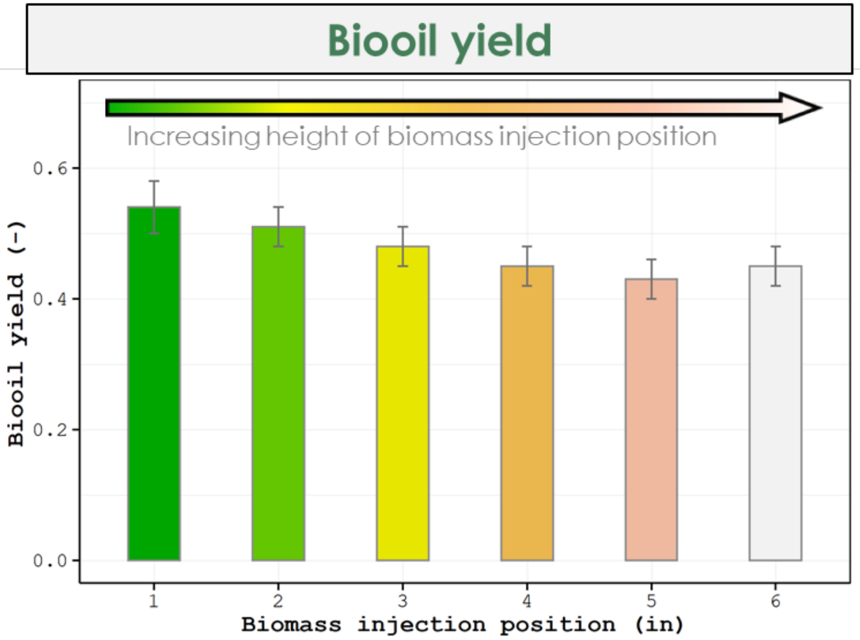
Model captures effect of biomass injection point on biooil yield







Higher biomass injection →

Lower particle residence time →

Lower exothermic char oxidation & lower biooil yield

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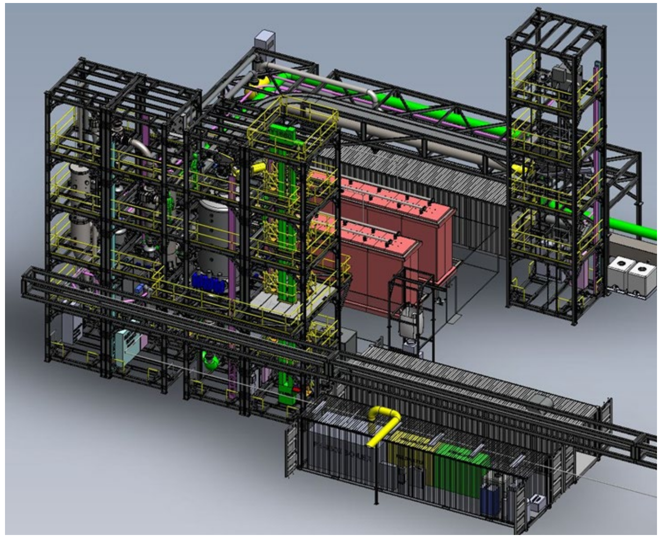
Demonstrating autothermal pyrolysis in a 50 TPD modular biorefinery

- Iowa project
  - Redfield, IA
  - Privately funded by Stine Seed Company
  - Conversion of herbaceous biomass into bio-asphalt and biochar (with net carbon removal)
  - Commissioning Spring 2021
- California project
  - El Dorado Hills, CA
  - Funded by CA Energy Commission
  - Feasibility of converting wood waste into drop-in biofuels
  - Commissioning Fall 2022



3-D model of modular plant

Completed pyrolysis reactor module

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Summary

- **Management**
  - Collaboration across project teams focused on two thrusts: **biomass-to-electricity** and **biomass-to-fuel**
- **Approach**
  - Multi-scale modeling approach with expansion of modeling toolset developed by CCPC and Feedstock Conversion Interface Consortium applied to experimental reactors at CanmetENERGY and Iowa State University with validation data
- **Impact**
  - Model results for **CanmetENERGY Fluidized Bed BioPower Combustor** enable visualization and quantification of spatial locations of pyrolysis, volatile oxidation, and char oxidation processes for biomass-to-electrons [important for understanding process and reactor design and control]
  - Model results for **Iowa Status University Autothermal Pyrolysis Fluidized Bed Reactor** provide capability to capture char oxidation effects at both particle and reactor scales thereby enabling capture of feedstock effects on autothermal biomass-to-fuel processes
- **Progress and Accomplishments**
  - NETL computational fluid dynamics (CFD) model has been validated with data from CanmetENERGY reactor
  - NREL particle scale model advanced to account for char oxidation that is critical to autothermal pyrolysis; validation with ISU experimentalists
  - ORNL computational fluid dynamics (CFD) model of reactor for understanding effects of equivalence ratio and spatial location of exotherm

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A multi-scale problem
… A multi-lab solution

OAK RIDGE National Laboratory

NREL NATIONAL RENEWABLE ENERGY LABORATORY

NETL NATIONAL ENERGY TECHNOLOGY LABORATORY

Quad Chart

Timeline

- Project start date: October 31, 2018
- Project end date: September 30, 2021

	FY2019-FY2021
DOE Funding	$1.5M ORNL: $450k NETL: $450k NREL: $450k Iowa State Univ.: $150k (via subcontract thru NREL)
Cost Share	15%

Project Partners

- ORNL, NETL, NREL, Iowa State University
- Industry Partners: CPFD (Computational Particle Fluid Dynamics), Babcock and Wilcox, Sacramento Municipal Utility District (SMUD), McMinnville Electric System, POET, CanmetENERGY (Natural Resources Canada)

Barriers Addressed (from MYPP)

Ct-N. Multi-scale computational framework towards accelerating technology development

ADO-D. Technical Risk of Scaling

Note: MYPP=BETO Multi-Year Program Plan

Project Goal

Develop models and determine critical parameters to enable improved reactor design and optimal controls for more efficient and cost-effective biopower generation

End of Project Milestone

(1) develop particle-scale model of biomass combustion at air-to-fuel ratios consistent with efficient combustion processes and autothermal pyrolysis, (2) develop combustion model for NOx emission prediction, (3) develop and verify detailed multiphase computational fluid dynamics-based models of fluidized bed combustors to provide the capability to determine residence time distributions and reactor temperature distributions for design and optimization, (4) combine particle-scale sub-model and/or results into combustion reactor model for comprehensive model to predict biomass conversion efficiency and resulting emissions and compare with coal baseline, and (5) verify models with experimental data including full reactor verification.

Funding Mechanism

Funding Opportunity Announcement (FOA)

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Thank You

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A multi-scale problem … A multi-lab solution

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NATIONAL ENERGY TECHNOLOGY LABORATORY
NREL NATIONAL RENEWABLE ENERGY LABORATORY
Pacific Northwest NATIONAL LABORATORY
INL Idaho National Laboratory