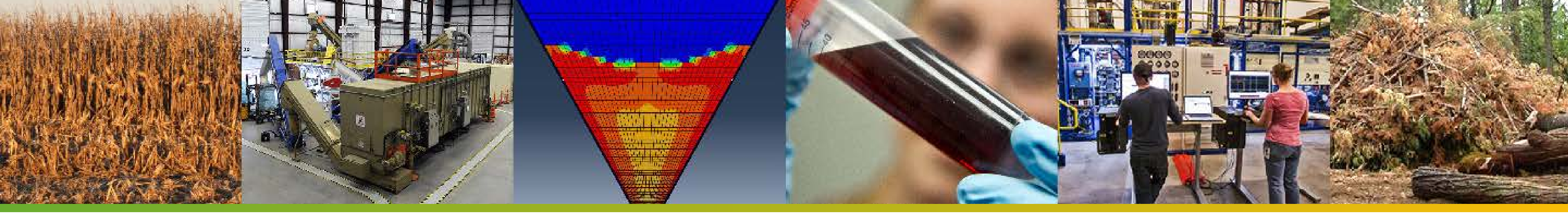


DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

FCIC Task 6: High Temperature Conversion

March 15th, 2021
Feedstock Conversion Interface Consortium

Daniel Carpenter (NREL)
Jim Parks (ORNL)

FEEDSTOCK-CONVERSION
INTERFACE CONSORTIUM

FCIC – High Temperature Conversion Team

NATIONAL RENEWABLE ENERGY LABORATORY

Daniel Carpenter (Lead)
Peter Ciesielski
Meagan Crowley
Tim Dunning
Brennan Pecha
Steven Rowland
Anne Starace

Oak Ridge National Laboratory

Jim Parks (co-Lead)
Gavin Wiggins
Zach Mills
Jun Qu
Charles Finney
Femi Oyedeji

NATIONAL ENERGY TECHNOLOGY LABORATORY

Bill Rogers
Xi Gao
Liqiang Lu

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

Matt Flake
Suh-Jane Lee
Ruoshui Ma
Miki Santosa
Mike Thorson
Huamin Wang

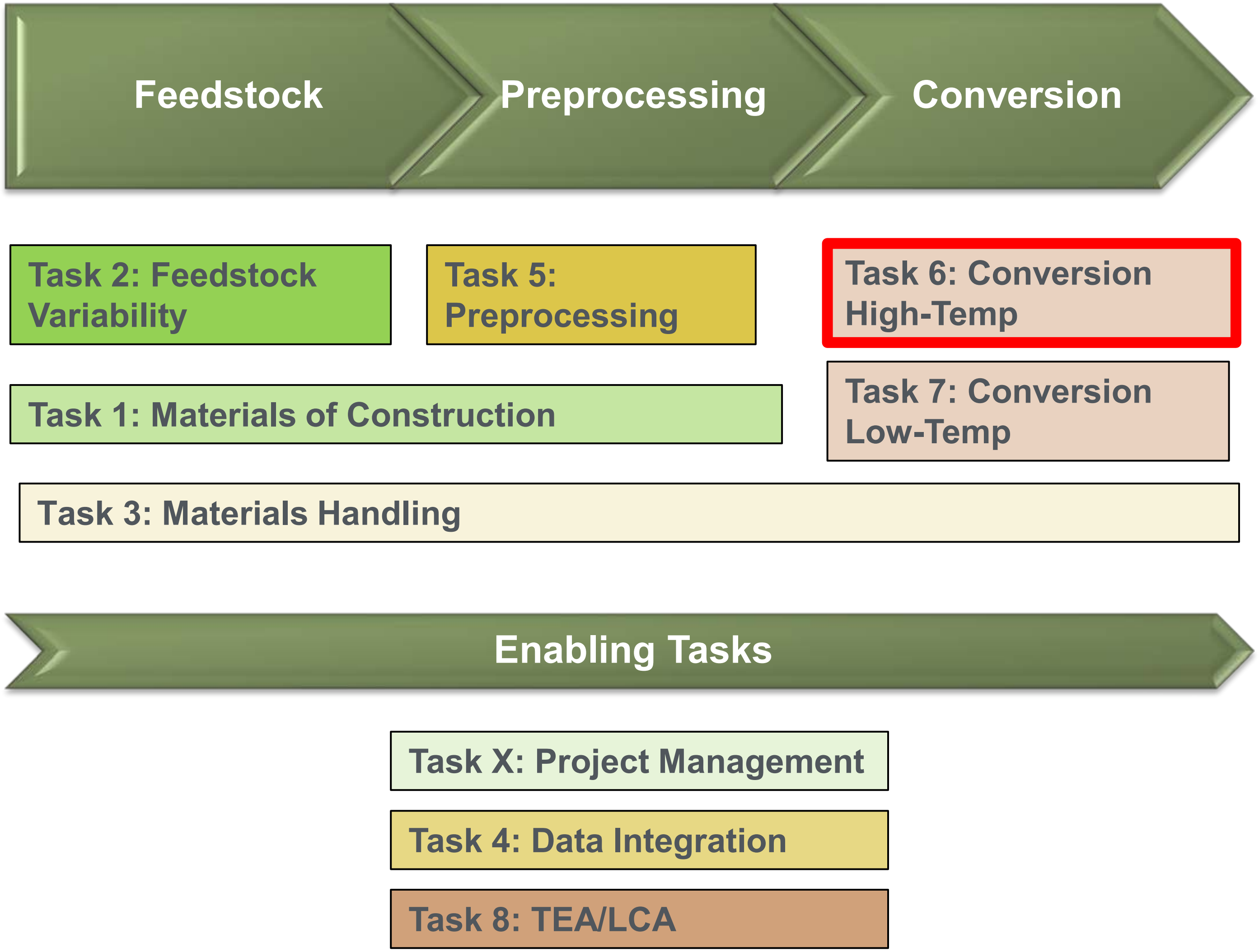
Argonne NATIONAL LABORATORY

George Fenske

Idaho National Laboratory

Jordan Klinger
Neal Yancey

FCIC Task Organization



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

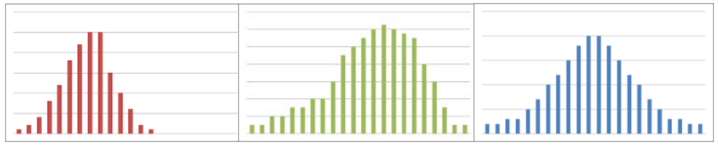
Task 6 & 7: Conversion (High- & Low-Temp Pathways): Produce homogeneous intermediates to convert into market-ready products

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

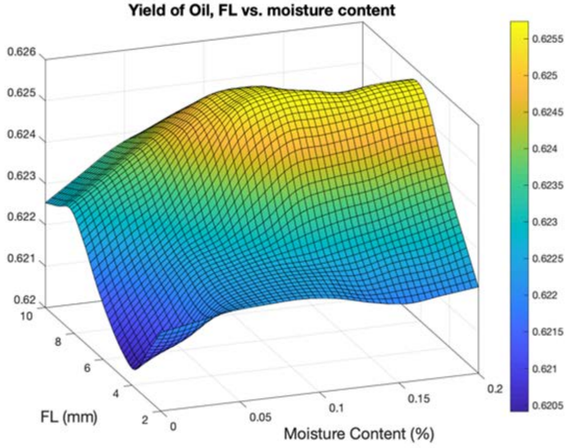
Project Overview

- **Objective:** (1) Develop science-based understanding to predict the effects of variable feedstock attributes and process parameters on pyrolysis product quality; (2) build a validated, multiscale experimental and computational framework to predict product yields and quality
- **Current limitations:** Feedstock impacts on high-temperature unit operations are either not known or are poorly-defined; Current design principles are based on empirically-derived guidelines, useful only over a very narrow range of feedstock properties
- **Relevance:** This work will de-risk high temperature biorefinery design, integration, and operation to enable flexible processes that are robust and responsive to natural and market feedstock variability, while maximizing productivity
- **Risks:** (1) Biomass is complex and feedstock attributes are cross-correlated; (2) Detailed pyrolysis product characterization is limited; (3) Difficult/expensive to assess downstream processability of intermediate products

Feedstock Attributes – “CMAs”
(physical, chemical, mechanical)



Temperature
Residence time
Reactor design



Project Overview: Task 6 Scope in Process

From: Preprocessing Operations (Task 5)
(drying, milling, densification, separations, etc.)

CMAs

TASK 6

Feed Auger

Pyrolysis Reactor

Primary Unit Ops

CPPs

Note: ALL unit op research includes both experiments and modeling

CQAs

Separation

Vapor Phase Upgrading

CMAs

Condenser

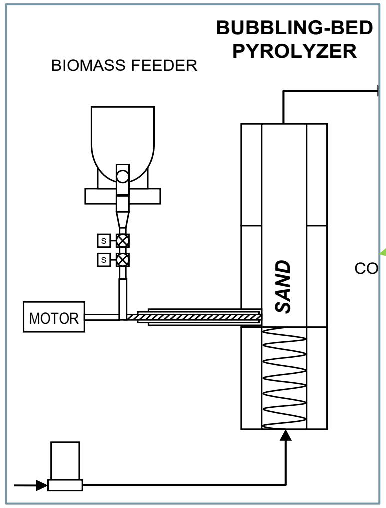
CMAs

Hydrotreating

Distillation

Downstream operations that FCIC outputs affect

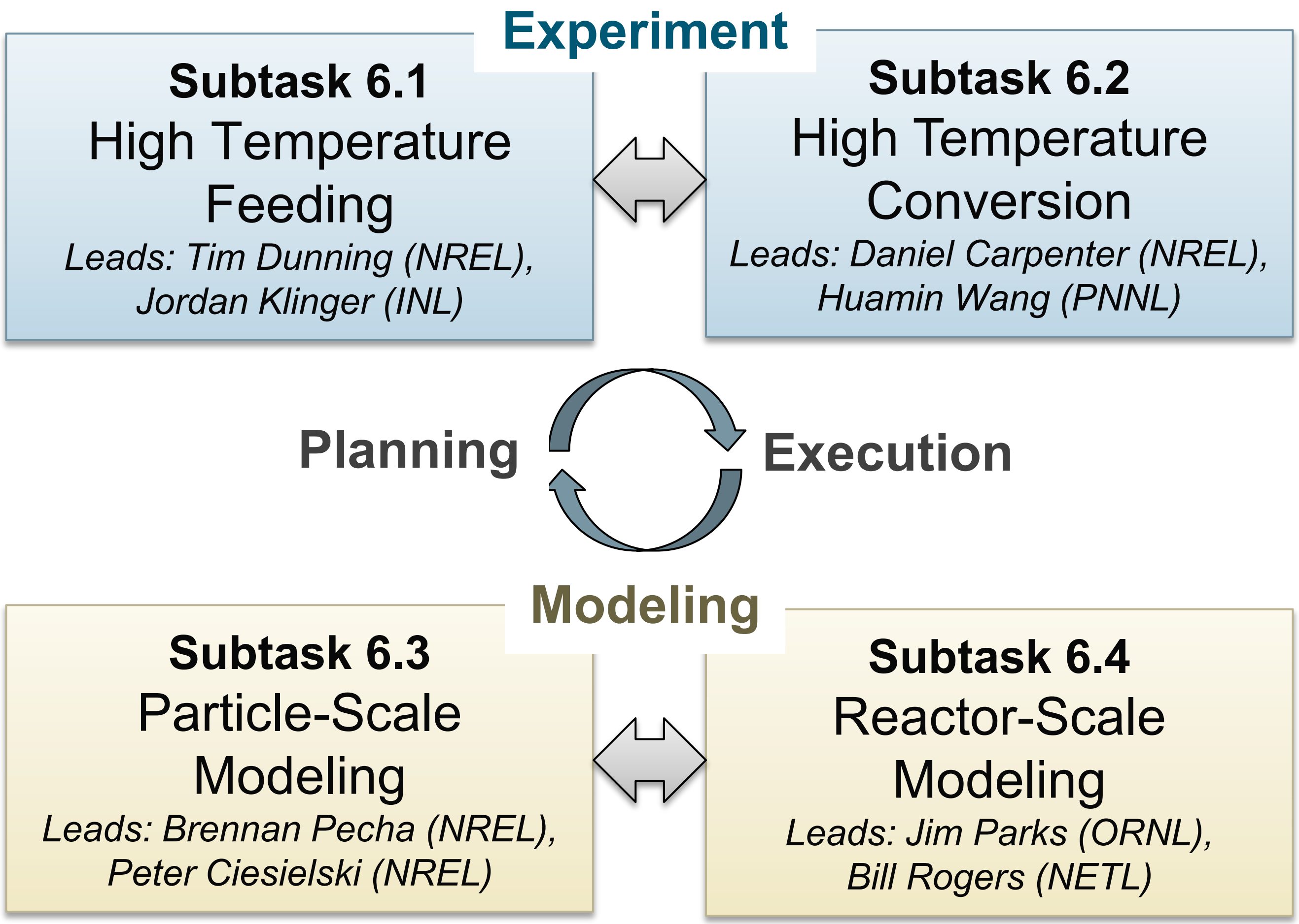
Fuel Product Specifications Chemistry



Experiments On Bubbling-Bed Pyrolyzer

Modeling with the Consortium for Computational Physics and Chemistry

1 – Management and Communication



Experiment

Subtask 6.1
High Temperature Feeding
Leads: Tim Dunning (NREL), Jordan Klinger (INL)

Subtask 6.2
High Temperature Conversion
Leads: Daniel Carpenter (NREL), Huamin Wang (PNNL)

Planning

Execution

Modeling

Subtask 6.3
Particle-Scale Modeling
Leads: Brennan Pecha (NREL), Peter Ciesielski (NREL)

Subtask 6.4
Reactor-Scale Modeling
Leads: Jim Parks (ORNL), Bill Rogers (NETL)

Multidisciplinary project team to address industry-relevant problems

Risks: Annual operating plan identifies risks and mitigation strategies; connections with core Program work and computational tool development are maintained with ChemCatBio and CCPC to ensure relevance

Communication strategy:

- **Task 6:** Close coordination via frequent meetings between experimental and modeling subtasks
- **FCIC:** Biweekly cross-task coordination for FY21 case study and engagement with Industry Advisory Board
- **Beyond FCIC:** connections to industry on related projects and to other BETO Consortia

1 – Management (Cont.)

Subtask	Lead(s)	Major Responsibilities
6.1 Biomass Thermal Transformations During High-Temperature Feeding	Tim Dunning (NREL), Jordan Klinger (INL)	Collect experimental and material characterization data (coordinate efforts at INL, NREL, ANL, ORNL) and with Subtask 3.2 (modeling); develop design heuristics
6.2 Impacts of Forest Residue Variability on Critical Pyrolysis Product Attributes	Daniel Carpenter (NREL), Huamin Wang (PNNL)	Collect experimental and material characterization data (coordinate efforts at NREL and PNNL); coordinate with and provide validation data to modeling Subtasks 6.3/6.4
6.3 Mesoscale Simulation of High-Temperature Conversion	Brennan Pecha (NREL, Peter Ciesielski (NREL)	Develop particle models for high temperature conversion and validate using experimental results; coordinate transfer of results to reactor modeling team
6.4 High-Temperature Reactor Scale Modeling	Jim Parks (ORNL), Bill Rogers (NETL)	Develop CFD and reduced-order reactor models for high temperature conversion and validate using experimental results; implement in MFiX open-source suite

A multiscale approach for biomass pyrolysis

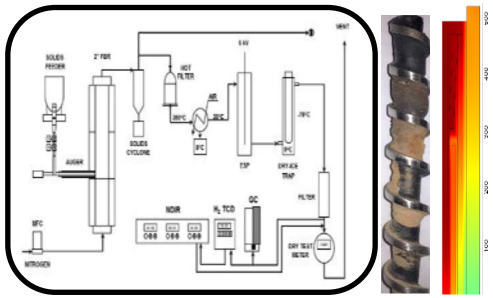
Technical Approach: **Coupled multi-scale experimentation, modeling, and advanced product characterization**

Sample collection and fractionation

Characterize Inputs (MAs)

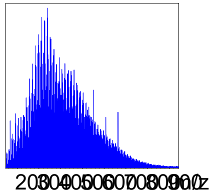
- **Physical Characteristics**
- **Chemical Speciation**
- **Aerodynamic Properties**
- **Other Properties**

Model validation experiments

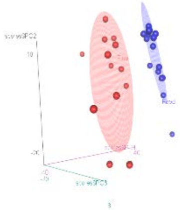


Characterize Outputs (QAs)

Bio-oil



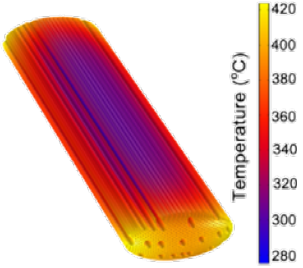
Conversion screening



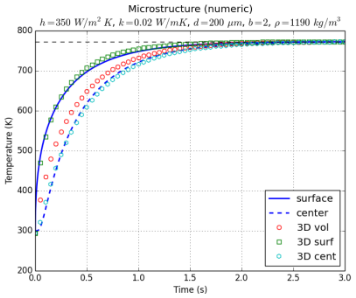
Fuel Blendstock

Real biomass particle (XCT reconstruction)

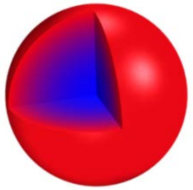
3D particle model (Finite Element Model)



Results fit to reduced-order model



Reduced-order particle model that captures complex behavior



Reactor-scale models incorporating particle effects (Computational Fluid Dynamics)

MFiX

Critical Feedstock/Particle Characterization

Objective: Capture feedstock Critical Material Attributes (CMAs) and effect on conversion process

Anatomical Fractions of Forest Residues

Feedstock Particle

Characteristics (CMAs)	*Critical Model Input Needed For…*
Physical Characteristics Particle shape/size, density, structure, porosity	Meso-scale modeling of feedstock variability
Chemical Speciation Lignin, hemicellulose, cellulose, moisture, ash, etc.	Kinetic rates for predicting conversion in meso- and process-scale models
Aerodynamic Properties Density and aerodynamic properties (fluidization)	Computational Fluid Dynamic (CFD) process-scale models to estimate feedstock residence times, enabling industry-scale reduced order models
Other Properties Surface properties (stickiness), attrition susceptibility	Feed auger modeling and tracking particle conglomeration or breakage/wear

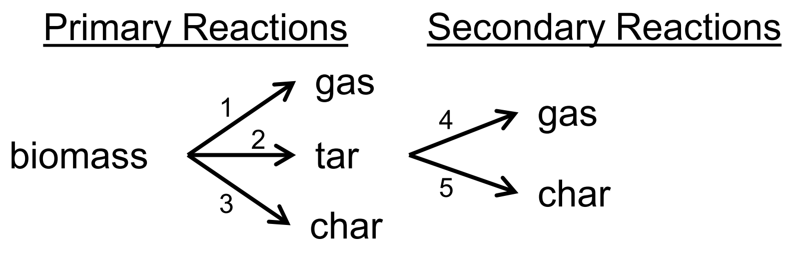
Updated Comprehensive Kinetics to Capture Complex Biochemistry of Feedstocks (progress since last review)

DiBlasi* Kinetics

Before *Now*

- Very simplified and not sufficient for FCIC objectives
- Primary and secondary reactions produce gas, tar (condensable liquid or bio-oil), and char
- Density is primary way to differentiate feedstocks

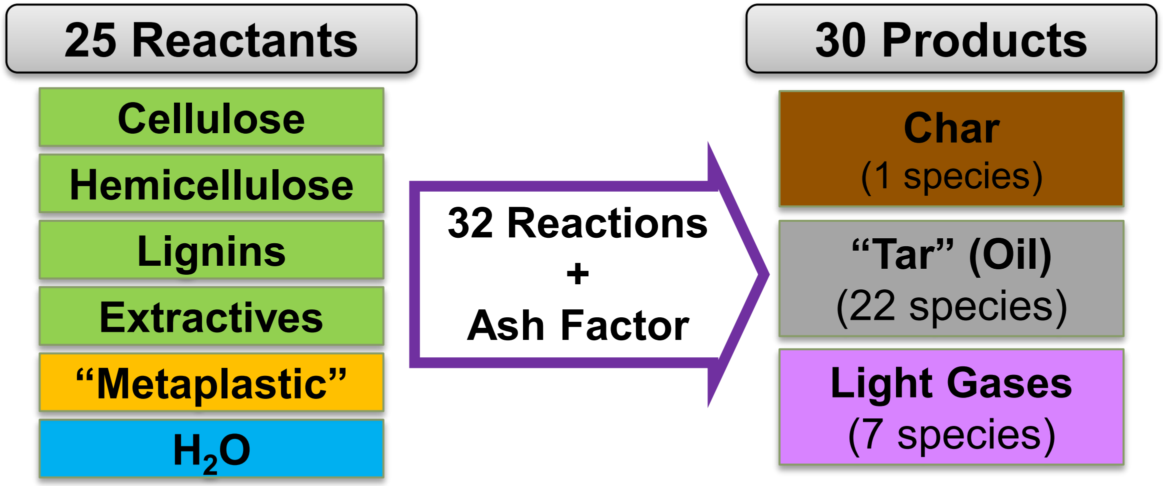
5 Reactions
3 Products
No Ash Effect



Debiagi**/CRECK*** Kinetics

- Feedstocks and products differentiated by chemical composition
- Common set of kinetics being used in models of varying complexity (reduced order to computational fluid dynamics)
- Includes Ash Factor to account for effects from ash

32 Reactions
30 Products
Includes Ash Effect



25 Reactants

Cellulose
Hemicellulose
Lignins
Extractives
"Metaplastic"
H_2O

32 Reactions
+
Ash Factor

30 Products

Char
(1 species)
"Tar" (Oil)
(22 species)
Light Gases
(7 species)

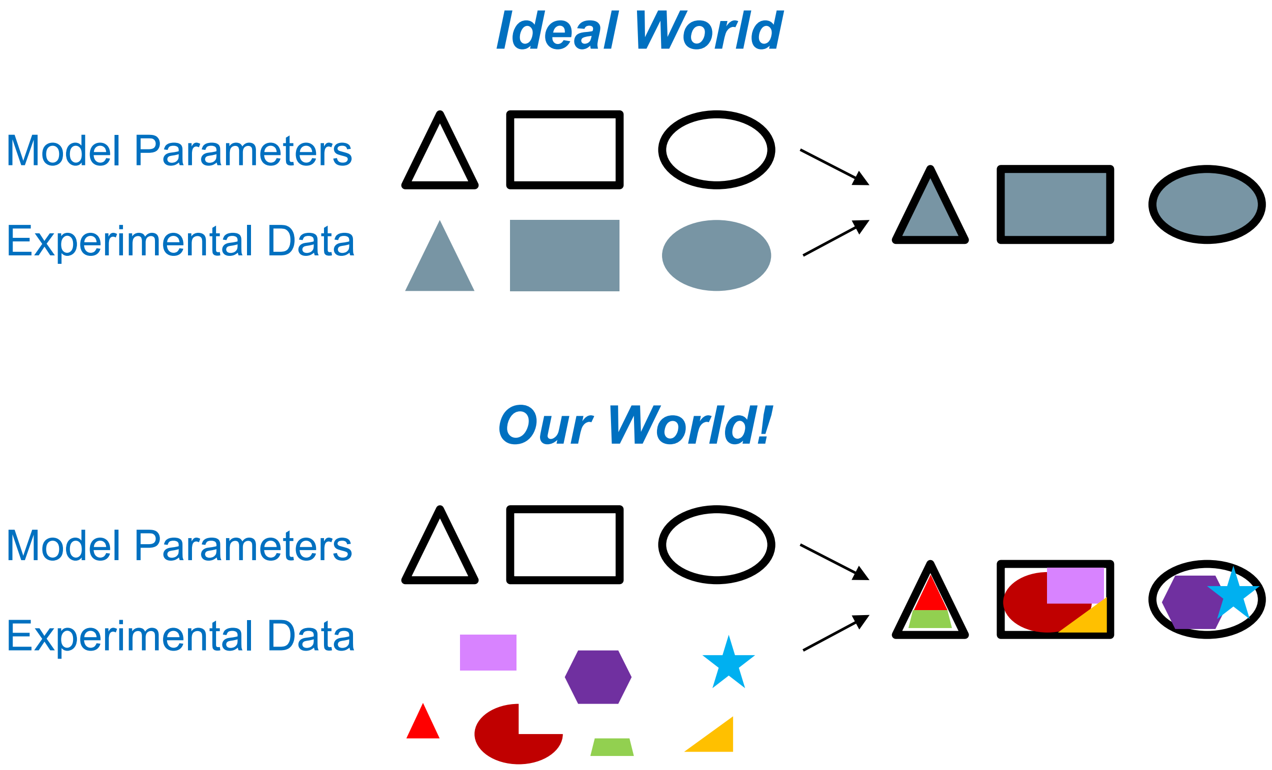
*DiBlasi, *Combustion Science and Technology*, **90**, pp 315–340 (1993).

P. Debiagi, G. Gentile, A. Cuoci, A. Frassoldati, E. Ranzi, and T. Faravelli, *Journal of Analytical and Applied Pyrolysis* **134 (2018) 326-335.

***CRECK Modeling Group at Politecnico di Milano (http://creckmodeling.chem.polimi.it/)

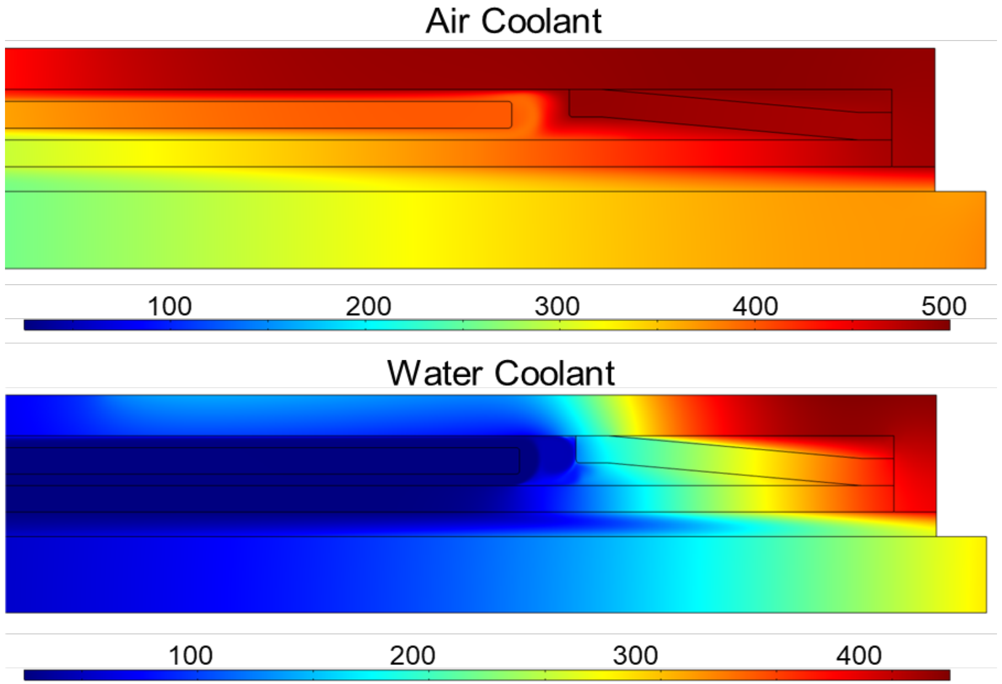
Coupling of Analytical Data to Kinetics is Critical

Challenge/Risk	Mitigation Approach
Difficult to couple model kinetics input/output chemistry to experimental chemistry results (especially product side)	(1) Lots of discussion between modelers and experimentalists (2) In-depth discussions with Debiagi (who has been superbly supportive) (3) Large number of samples analyzed (4) Working with BETO analytical projects to improve analytical capabilities
Experimental validation challenging due to: (1) high number of CMAs/properties (2) limited amount of experiments and (3) rarity of completely pure feedstocks for experiments	(1) Lots of discussion between modelers and experimentalists (2) Careful design of experiments for validation runs (3) Extensive analysis of feedstocks for validation runs (4) Knowledge/selection of purity levels resulting from classification techniques
Difficult to fully integrate high fidelity particle-scale model into high fidelity CFD reactor model	(1) Now: convert particle-scale model to reduced-order variant for incorporation into CFD model (2) Future: utilize high performance computing resources to retain more particle-scale details



Biomass Changes During Feeding are Part of Broader FCIC Studies of Feed Process

- Task 6 R&D scope:
  - Characterize early volatile emissions and tendency to recondense
  - Long duration feeding tests for temperature profile, torque, and deposition data
  - Heated auger tests to characterize feedstock changes under auger conditions (moisture, agglomeration, etc.)
- Feeding process studies in collaboration with other tasks:
  - Task 1 (Materials of Construction): metallurgy, integrity, deposition
  - Task 3 (Material Handling): modeling flowability and consistency of feed



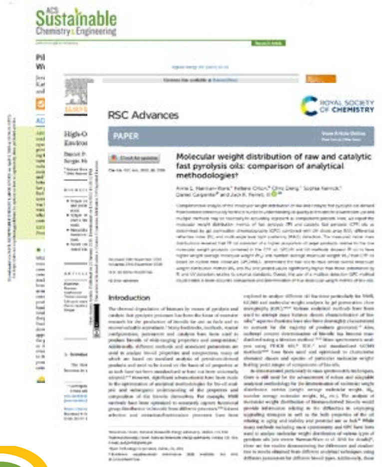
Temperature distributions in biomass inlet with air (top) and water (bottom) as cooling fluid.

3 – Impact

Impact:

- Feedstock variability effects almost every unit operation; we are providing a **science-based understanding** of how CMAs, CPPs, and CQAs are related for high temperature biomass conversion
- Biorefinery design engineers and operators will be able to develop unit operations and integrated processes that are more **robust, flexible, and market-responsive** with respect to feedstock variability
- This project provides direct, quantitative feedback to **inform the value of preprocessing** approaches as related to conversion performance and overall biorefinery production costs

Dissemination: Peer reviewed publications & reports; open-source code; modules for process model software (ASPEN); LabKey interface; webinars; handbook of engineering design principles



ACS Sustainable Chemistry & Engineering

RSC Advances

ROYAL SOCIETY OF CHEMISTRY

PAPER

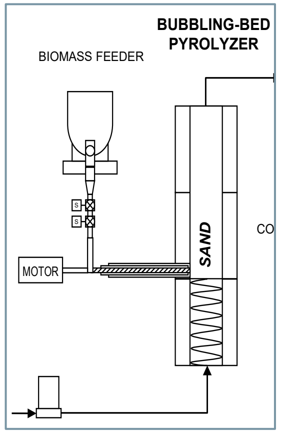
Molecular weight distribution of raw and catalytic fast pyrolysis oils: comparison of analytical methodologies†

Introduction

MFiX

WebTools

LabKey



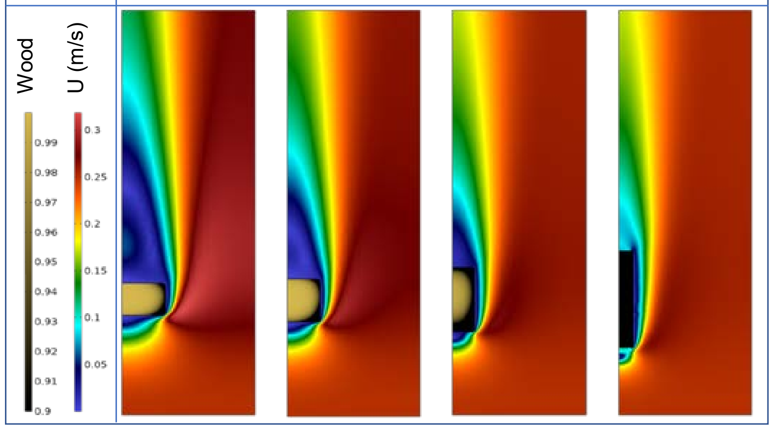
Modeling Toolset Providing Impact Beyond FCIC

Particle-scale model aids **Forest Concepts** in understanding feedstock shape (aspect ratio) effects

"The modeling data developed by NREL gave our company an understanding of how our production engineers can co-optimize reactors and feedstock properties to improve functional performance. This conversion data will also help our customers select the optimal feedstock for their specific conversion process."
- James H. Dooley, CTO at Forest Concepts

forestconcepts

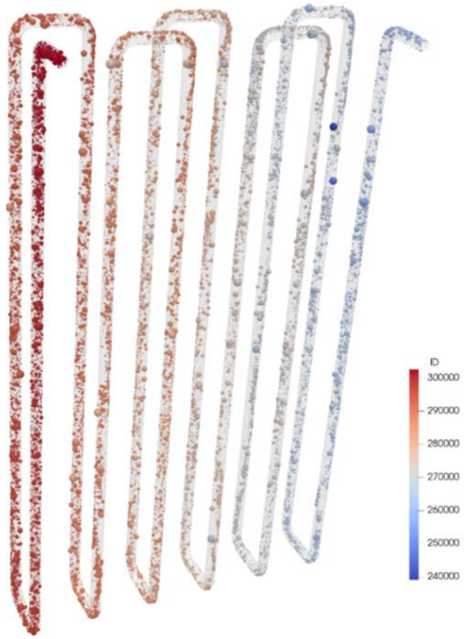
Length	2.8 mm	3.7 mm	5.6 mm	8.4 mm
Radius	3.3 mm	2.5 mm	1.7 mm	1.1 mm



Reactor-scale model (MFiX) utilized to inform **BETO Catalytic Fast Pyrolysis Verification** decisions

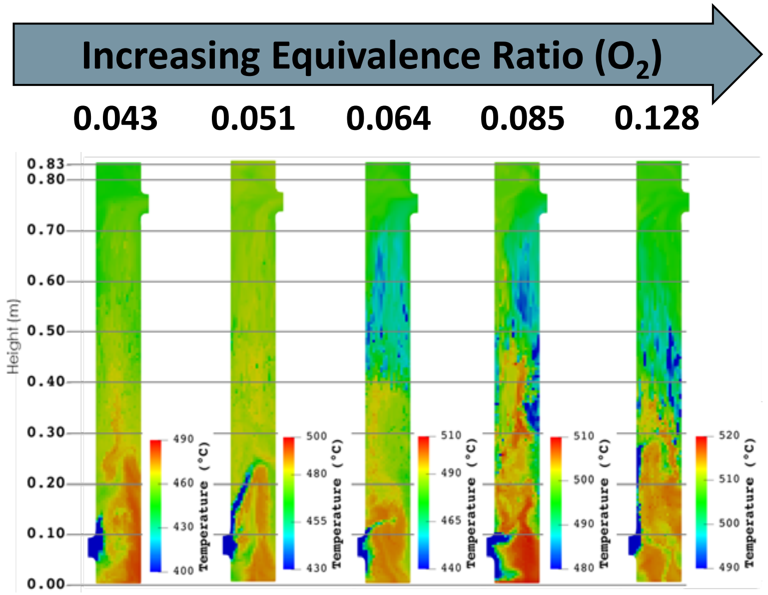
NETL model of Entrained Flow Reactor in NREL Thermo-Chemical Process Development Unit captured different residence times to calculate impact of size distribution on yield

Feedstock: 60% air-classified Forest Residues (pine)/30% Clean Pine/10% Hybrid Poplar



Reactor-scale model (MFiX) providing insight into Auto-Thermal Pyrolysis with **Iowa State University**

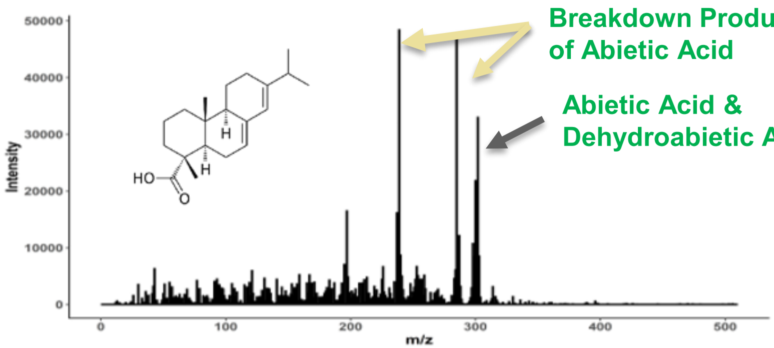
Spatial distribution of reactor temperature during auto-thermal pyrolysis for varying equivalence ratio (O_2 content) provides critical information for optimizing exothermic heat release and product chemistry


Increasing Equivalence Ratio (O_2)

0.043 0.051 0.064 0.085 0.128

Understanding pyrolysis fundamentals

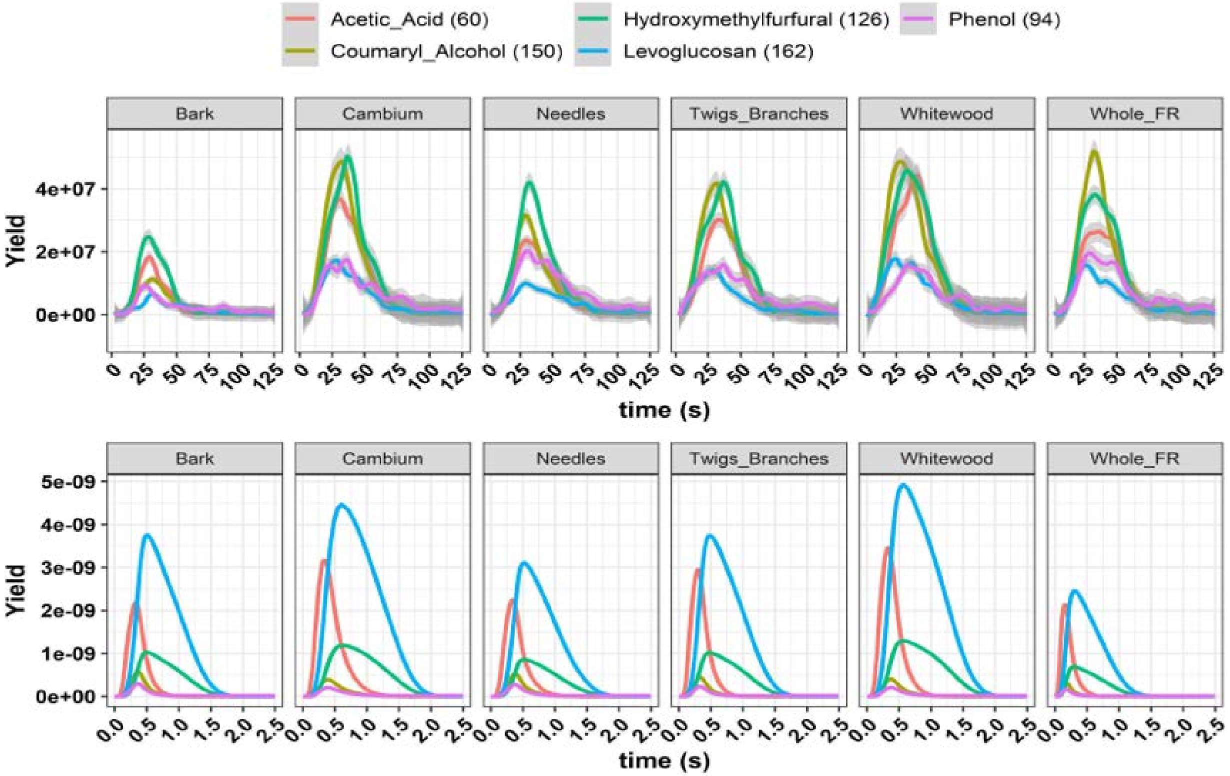
Whole Tree Pine 200°C



Breakdown Products of Abietic Acid

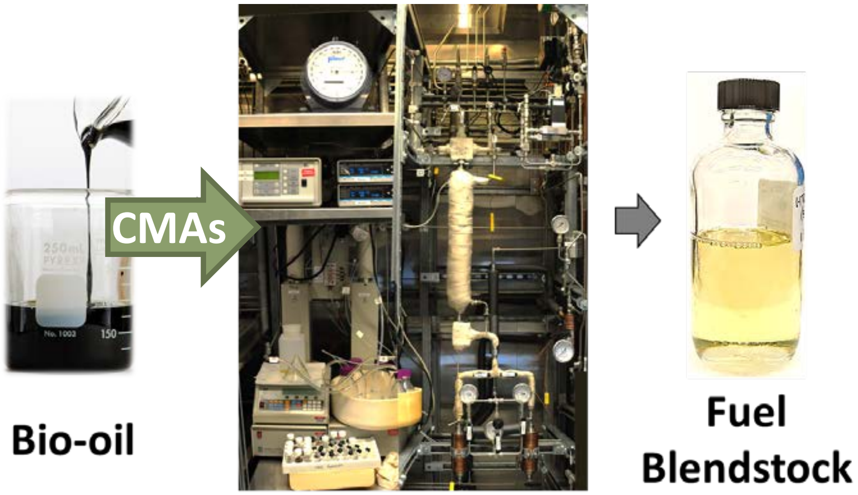
Abietic Acid & Dehydroabietic Acid

- Early volatiles are distinct for pine anatomical fractions; 12-15% *non-water* mass loss at 300 ºC
- Characterization of auger and deposits reveal metallurgy, adhesion, and cohesion insights



- Measured vs. predicted real-time release of pyrolysis vapor molecular species from pine residue fractions
- Method development and model refinement are ongoing

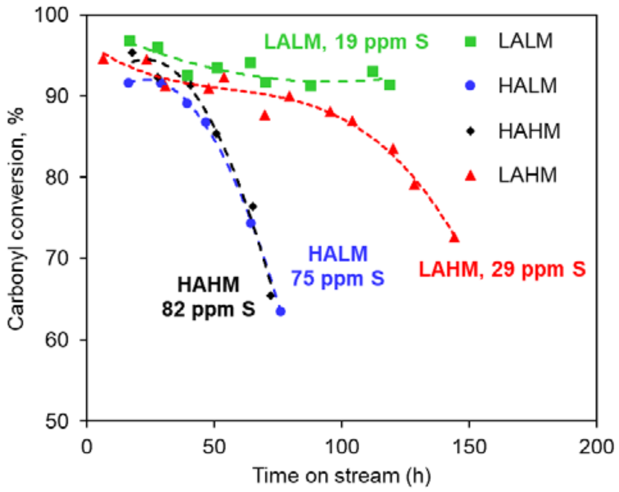
Determining CMAs for Hydrotreating



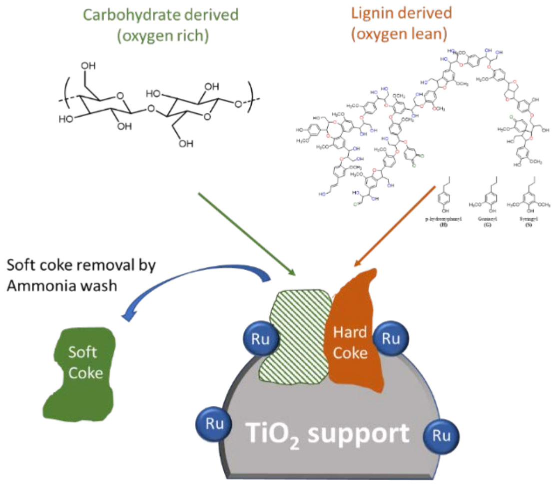
Example CMAs

- Viscosity
- Homogeneity
- Foulant precursor content (carbonyls and others TBD)
- Inorganic content & speciation
- Sulfur and nitrogen content
- Oxygen and water content
- Particulate content
- Acidity

- Sulfur content and type in biomass determine the sulfur content in bio-oil and catalyst stability of bio-oil stabilizer
- Lignin and carbohydrate derived components in bio-oil are hypothesized to cause "hard" and "soft" coke deposits on bio-oil stabilizer catalyst, respectively



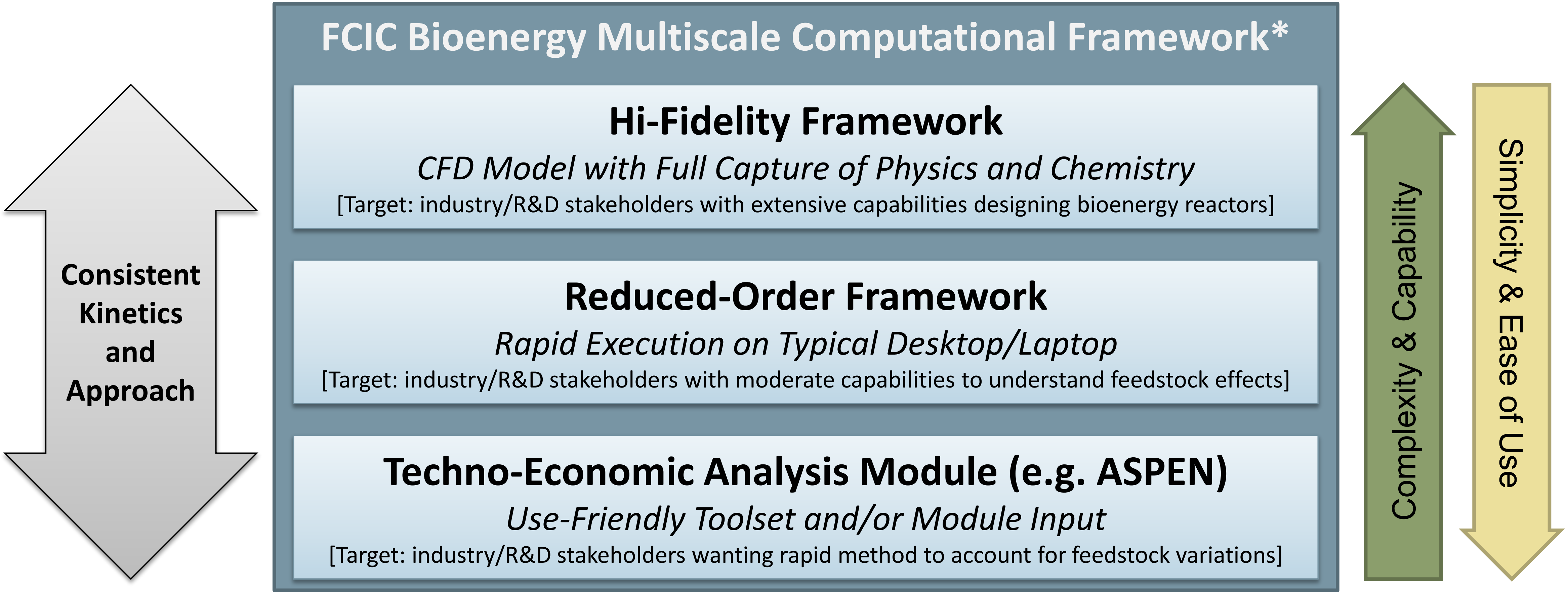
Impact of S in bio-oil on catalyst stability of bio-oil stabilizer



Impact of bio-oil composition on coke formation on bio-oil stabilizer catalyst

Computational Framework Outcome Includes Three Levels of Complexity & Capability for Range of Users

End-of-Project Outcome: A validated, multiscale experimental and computational framework that allows biorefinery design engineers and operators to optimize productivity and control critical product quality attributes with variable incoming feedstock attributes.



Consistent Kinetics and Approach

FCIC Bioenergy Multiscale Computational Framework*

Hi-Fidelity Framework

CFD Model with Full Capture of Physics and Chemistry

[Target: industry/R&D stakeholders with extensive capabilities designing bioenergy reactors]

Reduced-Order Framework

Rapid Execution on Typical Desktop/Laptop

[Target: industry/R&D stakeholders with moderate capabilities to understand feedstock effects]

Techno-Economic Analysis Module (e.g. ASPEN)

Use-Friendly Toolset and/or Module Input

[Target: industry/R&D stakeholders wanting rapid method to account for feedstock variations]

Complexity & Capability

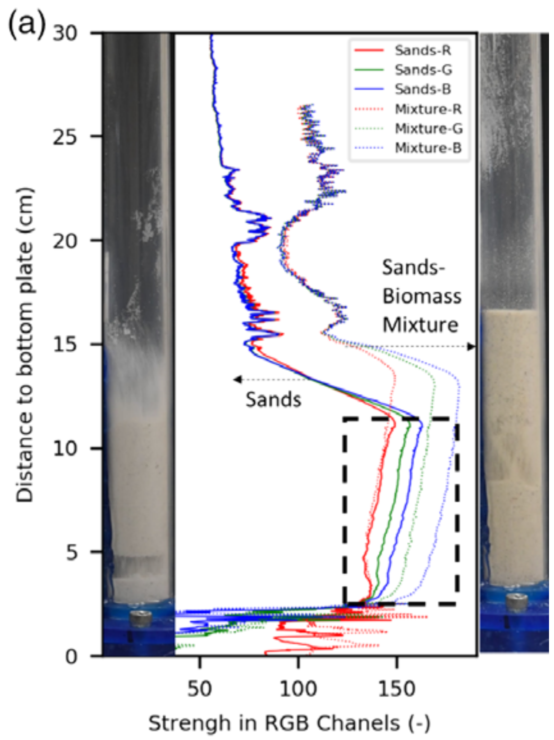
Simplicity & Ease of Use

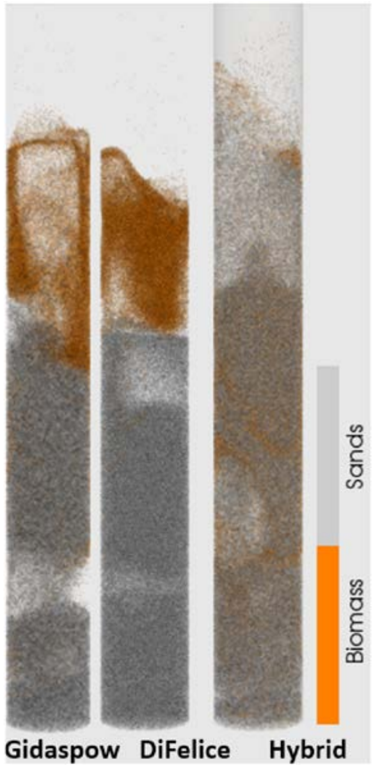
***Tech Transfer via Publications, WebTools, and Open-Source Code**

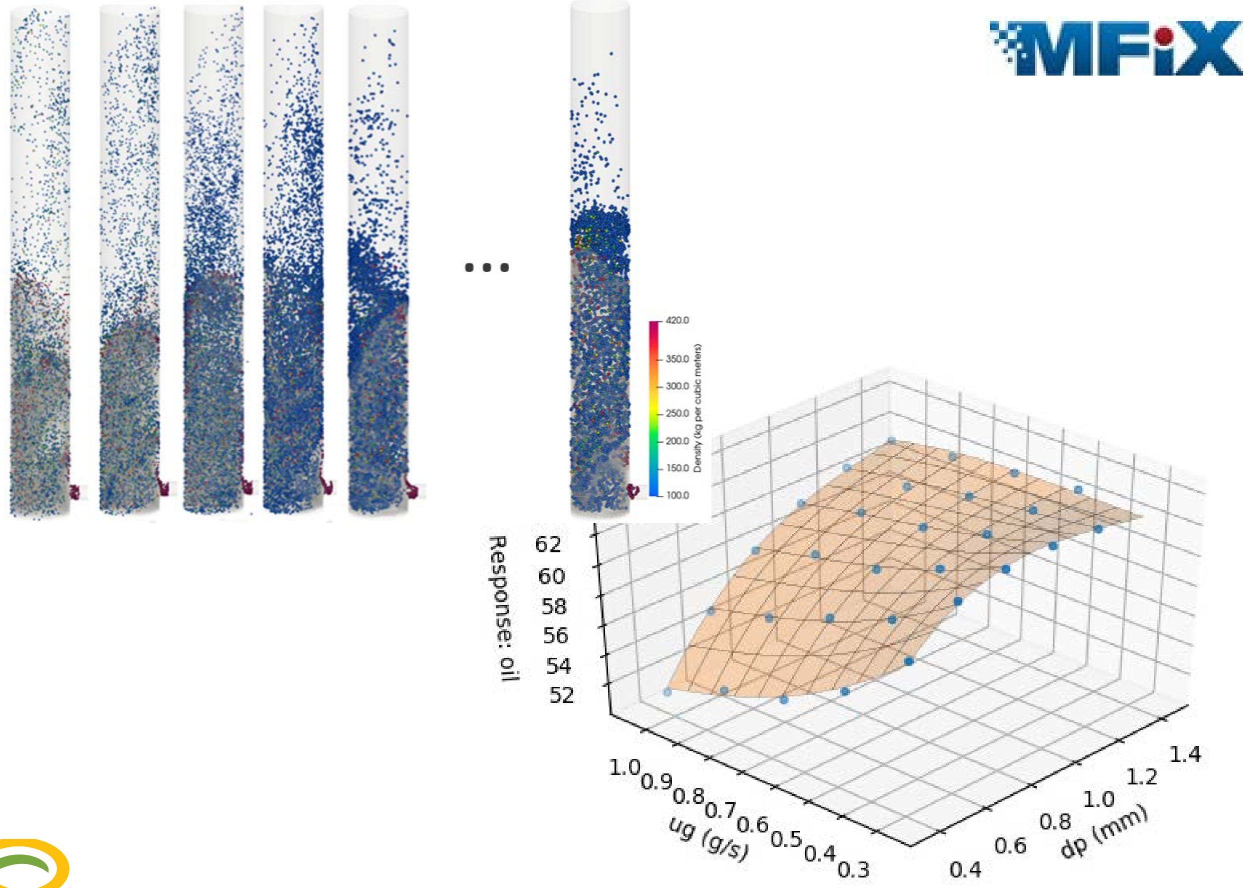
Hi-Fidelity CFD Framework Captures Fluidization and Chemistry for Reactor Design and Operation Guidance

Full fluidization of sand and biomass coupled with Debiagi kinetics enables comprehensive CFD (MFiX) prediction of pyrolysis oil yield and chemistry

Matrix of Computational Framework simulations provides reactor design guidance and operational maps for different feedstocks and operating conditions



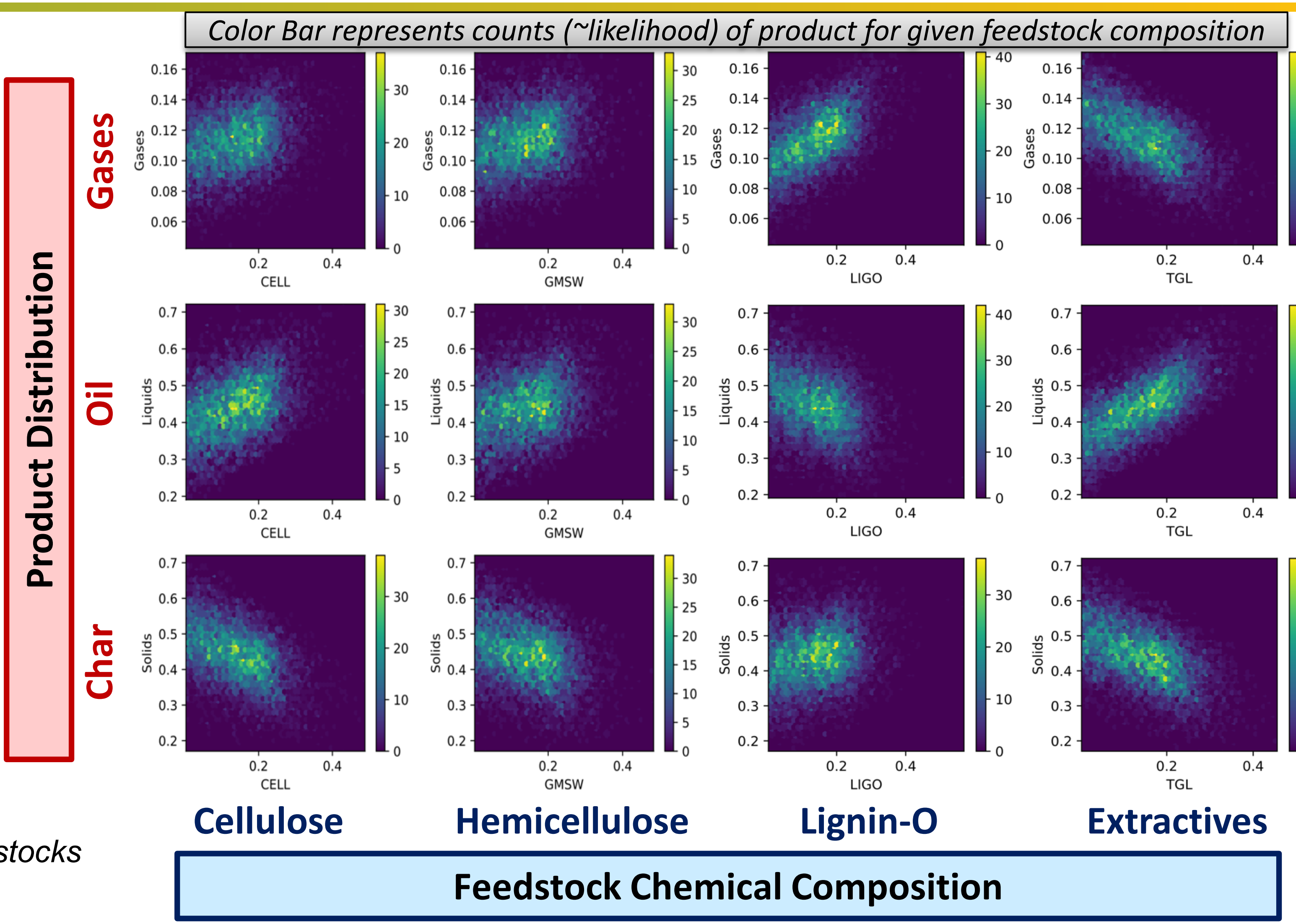




CFD=computational fluid dynamics

Reduced-Order Framework Efficiently Calculates Impact of Feedstock Properties on Product Distributions

- The reduced-order simulation framework is:
  - **Efficient:** can calculate product yields for ***a large set*** of feedstock compositions and properties ***suitable for advanced data analytics (AI/ML)***
  - **Flexible:** can be applied to different reactors, feedstocks, systems, etc.
- Code execution in Python on common laptop computer
- Sobol* sensitivity analysis feedstock chemical composition impact on product distribution performed using 9,000 randomly generated samples spanning range of biomass compositions in **Phyllis2**** feedstock database
  - Reactor Conditions:
    - Residence Time=10 sec.
    - Temperature =500ºC
    - Pressure=101.3 kPa



Color Bar represents counts (~likelihood) of product for given feedstock composition

***Phyllis2, database for (treated) biomass, algae, feedstocks for biogas production and biochar, https://phyllis.nl/ ECN.TNO*

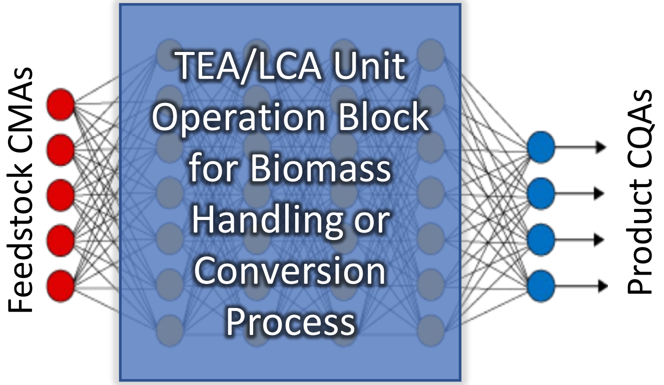
*I.M. Sobol, *Mathematics and Computers in Simulation* **55**, pp. 271-280 (2001).
Herman et al., *Journal of Open Source Software*, **2**(9), 97 (2017).

Utilizing Framework as Techno-Economic Analysis (TEA) Module for Prediction of Cost Impacts of Feedstock Material Attributes

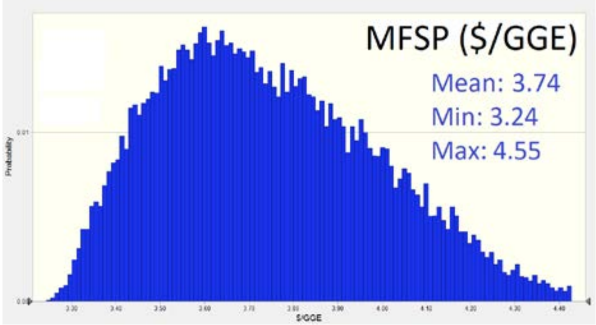
Varied Parameters	
Feedstock Material Attributes (CMAs)	• mineral matter content • moisture content • particle size • extractives content
Process Parameters (PPs)	• reactor temperature

Feedstock Properties

Input Parameters

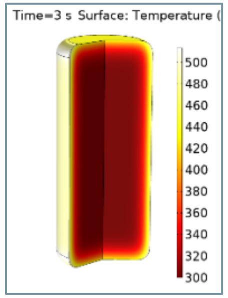


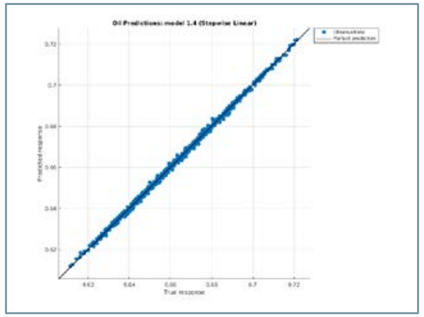
Output MFSP

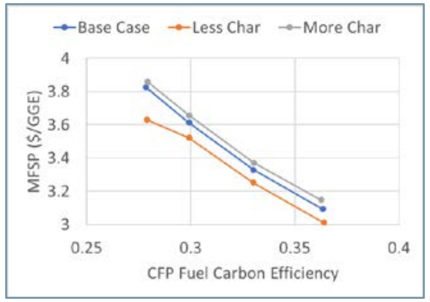


MFSP Distribution

Machine learning (ML) style regression analysis to develop correlations that can be evaluated in integrated process modelling software (e.g. Aspen Plus)







Validated Particle-Scale Model (Task 6.3)

Multiple Linear Regression Models (Task 6.3)

Link with MFSP from CFP TEA models (Task 8.3)

Monte-Carlo Simulation

Brennan Pecha, Matt Wiatrowski, Meagan Crowley, Abhijit Dutta, Peter Ciesielski

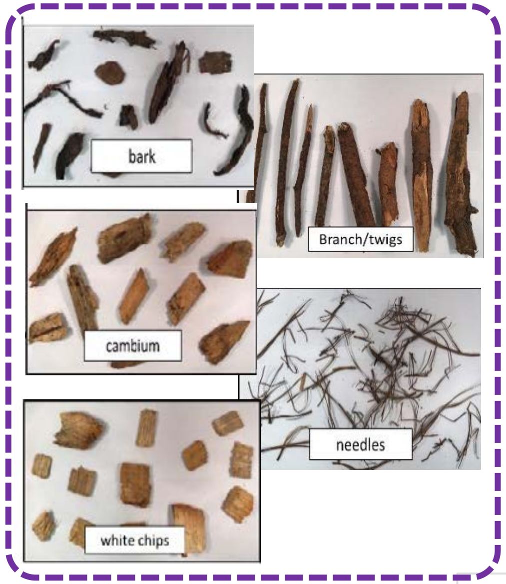
MFSP: Minimum Fuel Selling Price; **FP**: Fast Pyrolysis; **CFP**: Catalytic Fast Pyrolysis;
TEA: Techno-Economic Analysis

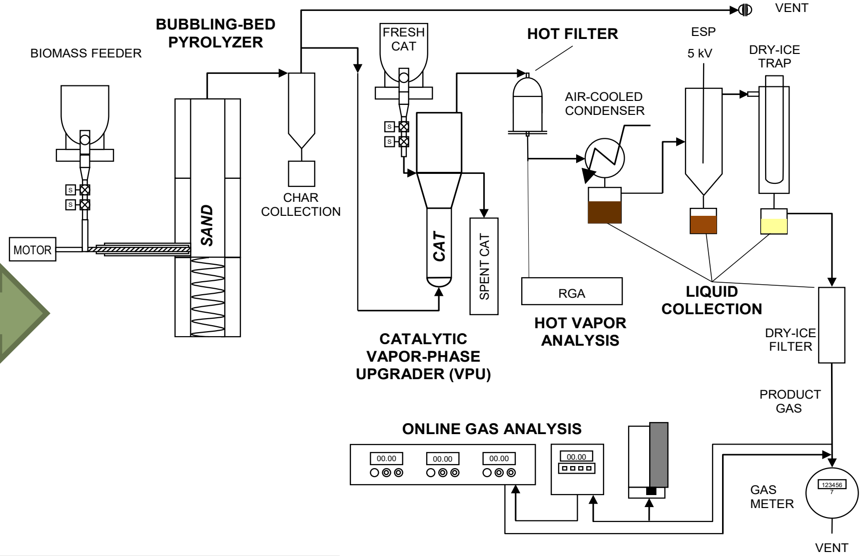
Experimental Validation In Progress (FY21 Q2)

Feedstocks:
- Residues (13-yr & 23-yr trees)
- Anatomical fractions
- Densified
- Air classified

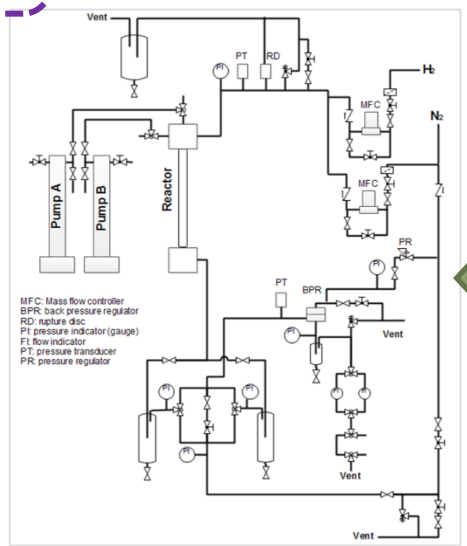
Data outputs:
- Process data; mass balances
- On-line vapor/gas analysis
- Detailed feedstock, catalyst, char, and oil product analysis

Outcomes:
- Conversion **performance** and product **quality** (CQAs) as a function of **feedstock** CMAs (composition, preprocessing, format)
- Model validation
- Inorganics and sulfur distribution





Bio-oil

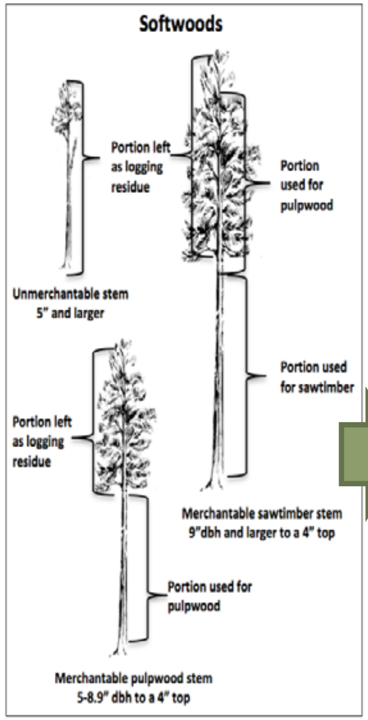


Fuel Blendstock

☐ **= Detailed Characterization**

Case Study to Demonstrate Utility

FY21 Case Study of Interest and Associated Connections



(Bardon and Hazel, 2014)

Task 2: Feedstock Variability
Feedstock data on 13-yr vs 23-yr tree

Task 5: Pre-Processing
Data on distribution of feedstock CMAs

Task 6: High Temp Conversion
Translation of CMAs to CQAs in unit op

Pre-Processing

Physical Characteristics

Chemical Speciation

Aerodynamic Properties

Other Properties

Fast Pyrolysis

Downstream Upgrading

ChemCatBio
Chemical Catalysis for Bioenergy

Task 8: Crosscutting Analysis
TEA and LCA (with data input along process)

Summary

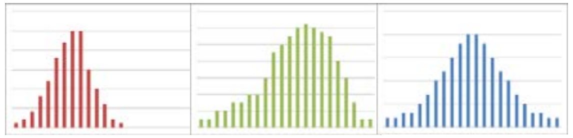
Management: **Multidisciplinary**, multi-lab team with computational and experimental expertise; **annual operating plan** defines work breakdown, milestones, risks, and mitigation strategies; **close connections** with core Program work (ChemCatBio) and computational tool development (CCPC) to ensure relevance

Technical Approach: Coupled multi-scale experimentation, modeling, and advanced product characterization to accurately capture the fundamental physics and chemistry of high-temperature biomass **feeding** and **pyrolysis reactor** unit operations.

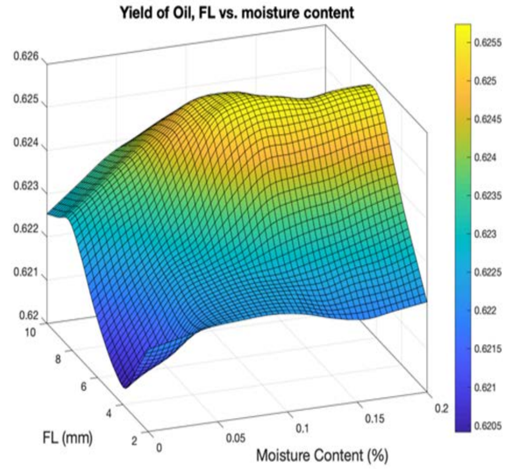
Impact: **Science-based** understanding of feedstock variability effects enables more **robust** and **flexible** integrated processes with respect to feedstock variability and quantitative feedback to inform the value of preprocessing approaches

Progress: Characterized pine residue **volatiles**, feed auger **deposits** and **deformation**; completed multi-scale, high-fidelity **computational model framework**, hybrid gas/biomass/sand **drag model**, and sensitivity analysis w.r.t feedstock attributes; sulfur, lignin, sugars impact on **hydrotreating**

Feedstock Attributes – "CMAs"
(physical, chemical, mechanical)



Temperature
Residence time
Reactor design



Quad Chart Overview- FCIC, Task #6 High Temperature Conversion

Timeline

- 10/1/2018 - 9/30/2021

	FY20	Active Project
DOE Funding	$1,732 K	FY19- $2,010 K FY20- $1,732 K FY21- $1,732 K Total- $5,474 K

Project Partners (N/A)

Barriers addressed

19Ft-E FSL Feedstock Quality: Monitoring and Impact on Preprocessing and Conversion Performance

19Ct-A CONV Defining Metrics around Feedstock Quality

Project Goal

Develop the science-based understanding required to accurately predict the effects of variable feedstock attributes and process parameters on pyrolysis product quality attributes. Develop a validated, multiscale experimental and computational framework that allows biorefinery design engineers and operators to optimize productivity and control critical product quality attributes with variable incoming feedstock attributes.

End of Project Milestone

All results and models validated and integrated into final experimental and computational framework that captures the fundamental physics and chemistry of biomass feeding and pyrolysis unit operations as a function of feedstock particle size, anatomical fraction, and inorganic speciation, achieving 95% agreement between experiment and simulation, and providing actionable information for biorefinery design engineers and operators to optimize productivity and control critical product quality attributes with variable incoming feedstock attributes. Analyze carbon cycle and production practices for the case study of 13-yr, 23-yr pine trees in a catalytic fast pyrolysis process.

Funding Mechanism (N/A)

Thank you!
Questions?

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NREL/PR-5100-79467

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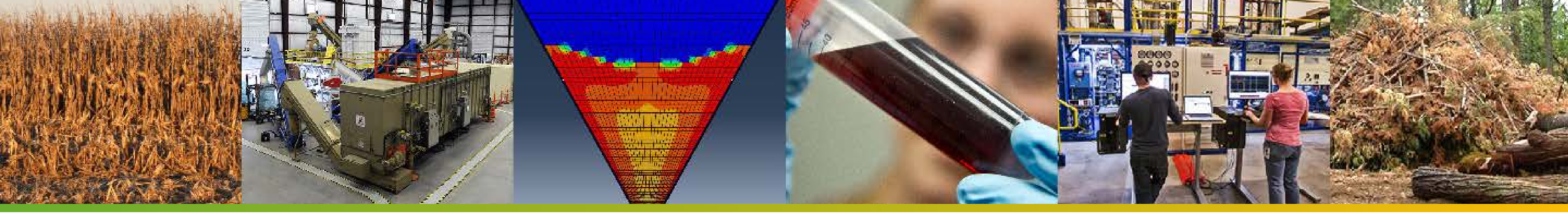
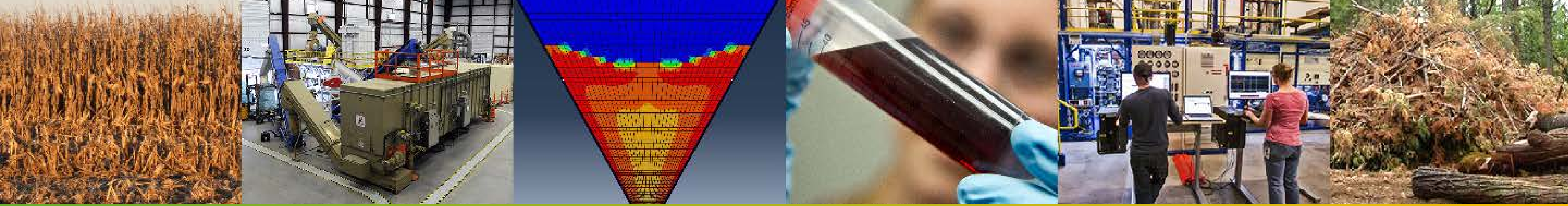


Thank you

energy.gov/fcic

fcic
FEEDSTOCK-CONVERSION
INTERFACE CONSORTIUM



Additional Slides

fcic
FEEDSTOCK-CONVERSION
INTERFACE CONSORTIUM

Publications

Publications

1. M.A. Ardila-Barragán, C.F. Valdés-Rentería, M.B. Pecha, A. López-Díaz, E. Gil-Lancheros, M.C. Vanegas-Chamorro, J.E. Camporredondo-Saucedo, L.F. Lozano-Gómez, "Gasification of coal, Chenopodium Album biomass, and co-gasification of a coal-biomass mixture by thermogravimetric-gas analysis," Revista Facultad de Ingeniería (2019) 28, 53-77 https://doi.org/10.19053/01211129.v28.n53.2019.10147.
2. P.N. Ciesielski, M.B. Pecha, A. Lattanzi, V.S. Bharadwaj, M.F. Crowley, L. Bu, J.V. Vermaas, K.X. Steirer. "Advances in multiscale modeling of lignocellulosic biomass," ACS Sustainable Chemistry and Engineering (2020) 8(9), 3512-3531 https://doi.org/10.1021/acssuschemeng.9b07415.
3. J. Klinger, D. Carpenter, V. Thompson, N. Yancey, R. Emerson, K. Gaston, K. Smith, M. Thorson, H. Wang, D. Santosa, I. Kutnyakov. "Pilot Plant Reliability Metrics for Grinding and Fast Pyrolysis of Woody Residues Pilot plant reliability metrics" ACS Sus Chem Eng (2020), 8, 2793-2805, DOI: 10.1021/acssuschemeng.9b06718.
4. L. Lu, X. Gao, M. Shahnam, W.A. Rogers, "Open Source Implementation of Glued Sphere Discrete Element Method and Non-spherical Biomass Fast Pyrolysis Simulation," AIChE J. n/a (n.d.) e17211. https://doi.org/10.1002/aic.17211.
5. L. Lu, X. Gao, A. Gel, G. Wiggins, M. Crowley, B. Pecha, M. Shahnam, W.A. Rogers, J. Parks, P.N. Ciesielski. "Investigating Biomass Composition and Size Effects on Fast Pyrolysis using Global Sensitivity Analysis and CFD Simulations," Chem. Eng. J. (2020) 127789. https://doi.org/10.1016/j.cej.2020.127789.
6. L. Lu, X. Gao, M. Shahnam, W.A. Rogers. "Bridging particle and reactor scales in the simulation of biomass fast pyrolysis by coupling particle resolved simulation and coarse grained CFD-DEM," Chem. Eng. Sci. 216 (2020) 115471. https://doi.org/10.1016/j.ces.2020.115471.
7. L. Lu, X. Gao, M. Shahnam, W.A. Rogers. "Coarse grained computational fluid dynamic simulation of sands and biomass fluidization with a hybrid drag," AIChE J. 66 (2020) e16867. https://doi.org/10.1002/aic.16867.
8. L. Lu, J. Yu, X. Gao, Y. Xu, M. Shahnam, W.A. Rogers. "Experimental and numerical investigation of sands and Geldart A biomass co-fluidization," AIChE J. 66 (2020) e16969. https://doi.org/10.1002/aic.16969.
9. J. Montoya, C. Valdes, H. Chaquea, M.B. Pecha, F. Chejne, "Surplus electricity production and LCOE estimation in Colombian palm oil mill using empty fresh bunches (EFB) as fuel," Energy (2020) 202, 117713 https://doi.org/10.1016/j.energy.2020.117713.
10. A. Harman-Ware, K. Orton, C. Deng, S. Kenrick, D. Carpenter, J. Ferrell. "Molecular weight distribution of raw and catalytic fast pyrolysis oils: comparison of analytical methodologies" RSC Advances (2020), 10 (7), 3789-3795, DOI: 10.1039/C9RA09726K.

Presentations

Presentations

1. D. Carpenter, V. Thompson, K. Gaston, N. Yancey. “Pilot plant reliability metrics for grinding and fast pyrolysis of woody residues,” tcbiomass+, Rosemont, IL, October 2019 (oral).
2. T. Dunning. “Determining Design Criteria for Feeding Biomass into a Fluidized Bed using a Feed Screw.” tcbiomass+, Rosemont, IL, October 2019 (oral).
3. R. Emerson, S. Rowland, J. Klinger, D. Carpenter, C. Pilgram, L. Ware, E. Fillerup, A. Starace. “Impacts of biopolymer structural and chemical attributes on the product distribution of fast pyrolysis and catalytic fast pyrolysis of loblolly pine,” Thermal & Catalytic Sciences Symposium, Richland, WA (Virtual), October 2020 (oral).
4. L. Lu, X. Gao, A. Gel, M. Shahnam, W. Rogers. “Influences of Biomass Compositions, Particle Sizes, and Fluidization Gases on Fast Pyrolysis.” 2020 Virtual AIChE Annual Meeting.
5. L. Lu, Xi Gao, M. Shahnam, W. Rogers. “Hybrid drag model for the simulation of biomass fast pyrolysis.” AIChE 2019 Annual Meeting, Orlando, Nov 2019.
6. M.B. Pecha. “High temperature conversion of wood and waste to fuels at the National Renewable Energy Laboratory,” Scaling Biochar Forum, Sonoma, CA (Virtual), Oct. 13, 2020 (oral).
7. M.B. Pecha, X. Gao, Z. Mills, G. Wiggins, C. Finney, W. Rogers, J. Parks, P. Ciesielski, D. Carpenter, K. Gaston, K. Smith. “High fidelity multiscale modeling of fast pyrolysis of woody feedstock blends in a fluidized bed reactor and entrained flow reactor” Thermal & Catalytic Sciences Symposium (Virtual), Richland, WA, October 2020 (oral).
8. M.B. Pecha. “How biomass burns and char is produced, particle size optimum, resulting biochar outcomes.” Biomass to Biochar Workshop (Virtual), Pullman, WA, April 27, 2020 (oral).
9. S. Rowland, A. Starace, K. Hietala, D. Carpenter. “Insight into Biomass Pyrolysis from Molecular Beam Mass Spectrometry,” ASMS June 3, 2019 (poster).

High-Temperature Conversion

Unit Operations
- High-Temp Feeding*
- Catalytic Fast Pyrolysis
- Hydrotreating

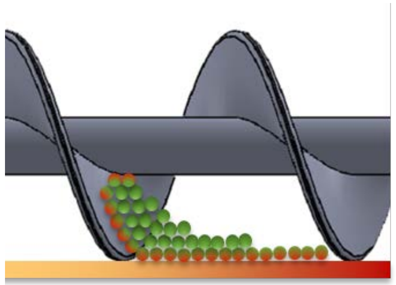
CPPs

- Auger geometry
- **Auger speed***
- **Temperature gradient**
- **Metallurgy**
- **Surface finish***

(CQAs from Preprocessing-Task 5)

CMAs → **Feed Auger** → **CQAs (Pyrolyzer CMAs)**

- Particle size distribution*
- Ash content & speciation
- **Extractives content***
- **Compressibility**
- **Particle stress-strain response**



- **Apparent particle size distribution**
- **Feed rate consistency**
- Moisture content
- Ash content & speciation
- **Particle morphology**

**Critical coordination with FCIC 3.2 and CCPC*

High-Temperature Conversion

Unit Operations

- High-Temp Feeding
- Pyrolysis Reactor
- Hydrotreating

CPPs

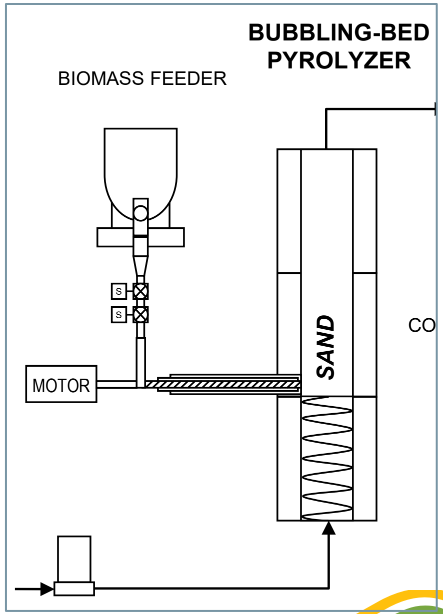
- **Reactor geometry**
- **Carrier gas flow rate**
- Biomass Feed Rate
- **Temperature/heat transfer**

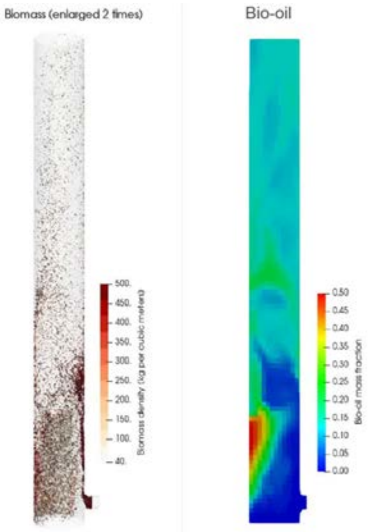
(CQAs from feed auger)

CMAs

- **Particle size/shape distribution**
- **Particle density**
- Moisture content
- **Biopolymer composition***
- **Inorganic content & speciation**

Pyrolysis Reactor





(Catalytic upgrader CMAs)

CQAs

- **Organic oil/carbon yield**
- **Particulate/alkali carryover***
- **Pyrolysis vapor/oil molecular weight distribution***
- **Pyrolysis vapor/oil composition (aldehydes, phenols, etc.)**
- Viscosity*

High-Temperature Conversion

Key Unit Operations

- High-Temp Feeding
- Catalytic Fast Pyrolysis
- **Hydrotreating**

CPPs

- Temperature
- Pressure
- Bio-oil Space Velocity
- Hydrogen to Bio-oil Ratio
- Catalyst

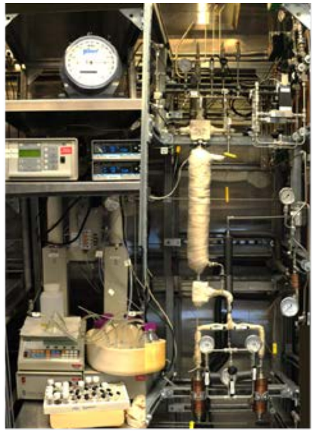
(CQAs from Pyrolyzer or Vapor Upgrader)

CMAs

- Viscosity
- Homogeneity
- **Foulant precursor content (e.g. carbonyls and other TBD species)**
- **Inorganic content & speciation**
- Sulfur and nitrogen content
- Oxygen and water content
- **Particulate content**
- Acidity

Hydrotreater

Bio-oil



Fuel Blendstock

CQAs

Product Yields

Hydrogen Usage

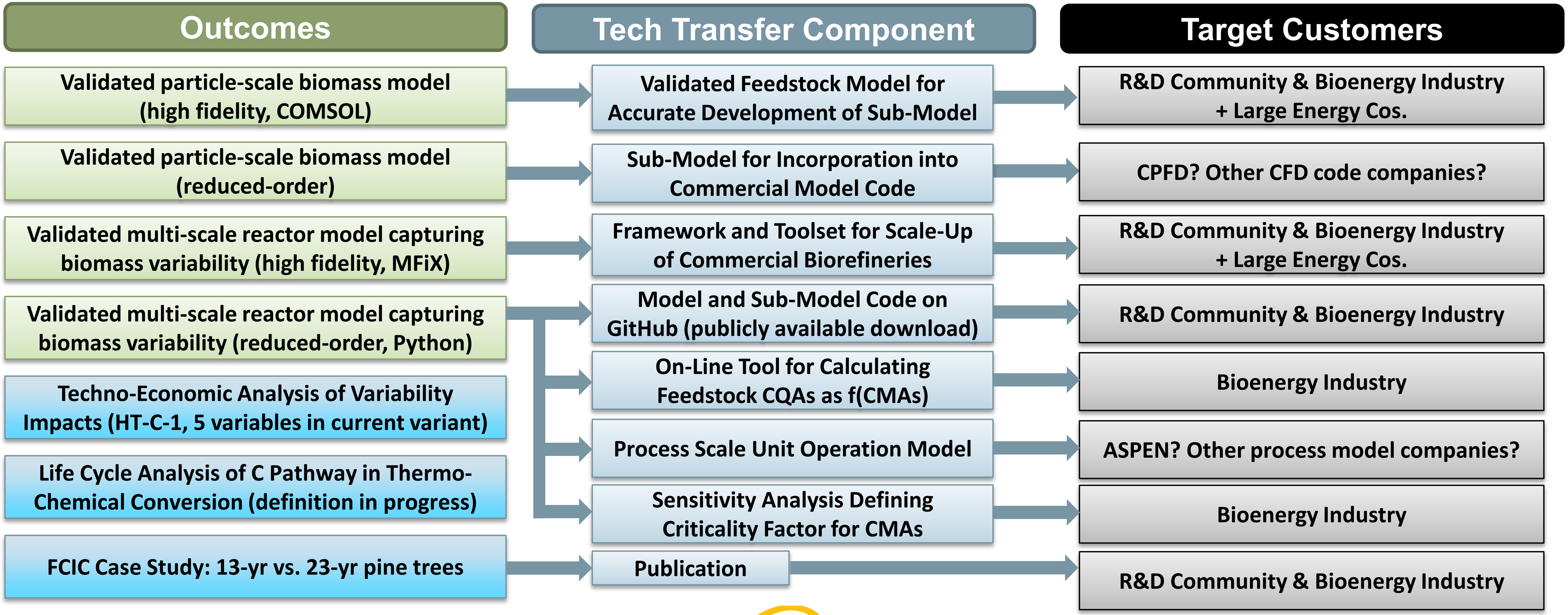
Product Quality

- Composition
- Fuel quality

Catalyst lifetime

Task 6 – Modeling Tech Transfer

Outcome: A validated, multiscale experimental and computational framework that allows biorefinery design engineers and operators to optimize productivity and control critical product quality attributes with variable incoming feedstock attributes.



Outcomes

- Validated particle-scale biomass model (high fidelity, COMSOL)
- Validated particle-scale biomass model (reduced-order)
- Validated multi-scale reactor model capturing biomass variability (high fidelity, MFiX)
- Validated multi-scale reactor model capturing biomass variability (reduced-order, Python)
- Techno-Economic Analysis of Variability Impacts (HT-C-1, 5 variables in current variant)
- Life Cycle Analysis of C Pathway in Thermo-Chemical Conversion (definition in progress)
- FCIC Case Study: 13-yr vs. 23-yr pine trees

Tech Transfer Component

- Validated Feedstock Model for Accurate Development of Sub-Model
- Sub-Model for Incorporation into Commercial Model Code
- Framework and Toolset for Scale-Up of Commercial Biorefineries
- Model and Sub-Model Code on GitHub (publicly available download)
- On-Line Tool for Calculating Feedstock CQAs as f(CMAs)
- Process Scale Unit Operation Model
- Sensitivity Analysis Defining Criticality Factor for CMAs
- Publication

Target Customers

- R&D Community & Bioenergy Industry + Large Energy Cos.
- CPFD? Other CFD code companies?
- R&D Community & Bioenergy Industry + Large Energy Cos.
- R&D Community & Bioenergy Industry
- Bioenergy Industry
- ASPEN? Other process model companies?
- Bioenergy Industry
- R&D Community & Bioenergy Industry

Experiments planned for 2” Fluidized Bed Reactor

Cycle 1	**Residues**	Benchmark material (23 y.o. tops/branches)	Cycle 12	**Air classified 1**	To verify ash reduction impacts (fan speed 1?)
Cycle 2	**Stem wood**	Anatomical fraction – model validation; 23 y.o.	Cycle 13	**Air classified 2**	To verify ash reduction impacts (fan speed 2?)
Cycle 3	**Bark**	Anatomical fraction – model validation; 23 y.o.	Cycle 14	**Residues (rep 2)**	Benchmark material – QC (23 y.o. tops/branches)
Cycle 4	**Needles**	Anatomical fraction – model validation	Cycle 15	**Whole tree (13-year-old thinnings)**	Impact of tree age and performance of whole young tree vs. older residues
Cycle 5	**Bark + Needles**	2-component blend	Cycle 16	**TBD (from 13-year-old thinnings)**	Select anatomical fraction or whole residue for age comparison (based on microscale test results)
Cycle 6	**Pine pellets, ρ1**	To understand particle density effects (pelletized + crushed/crumbled)	Cycle 17	**CFP – Residues**	Benchmark material (23 y.o. tops/branches)
Cycle 7	**Pine pellets, ρ2**	To understand particle density effects (pelletized + crushed/crumbled)	Cycle 18	**CFP – Stem wood**	Anatomical fraction – explicit in conversion models
Cycle 8	**Residues (rep 1)**	Benchmark material – QC (23 y.o. tops/branches)	Cycle 19	**CFP – Bark**	Anatomical fraction – explicit in conversion models
Cycle 9	**Pine crumbles**	Using Forest Concepts rotary sheer operation (~2mm smallest crumble)	Cycle 20	**CFP – Needles**	Anatomical fraction – explicit in conversion models
Cycle 10	**Residues:bark:needles 1:1:1**	Represents “dirtier” residue, lower feedstock quality	Cycle 21	**CFP - Air classified, 1 or 2**	To verify ash reduction impacts (fan speed x?)
Cycle 11	**Residues:bark:needles 1:2:2**	Represents “dirtier” residue, lower feedstock quality	Cycle 22	**CFP – Residues (rep)**	Benchmark material – QC (23 y.o. tops/branches)

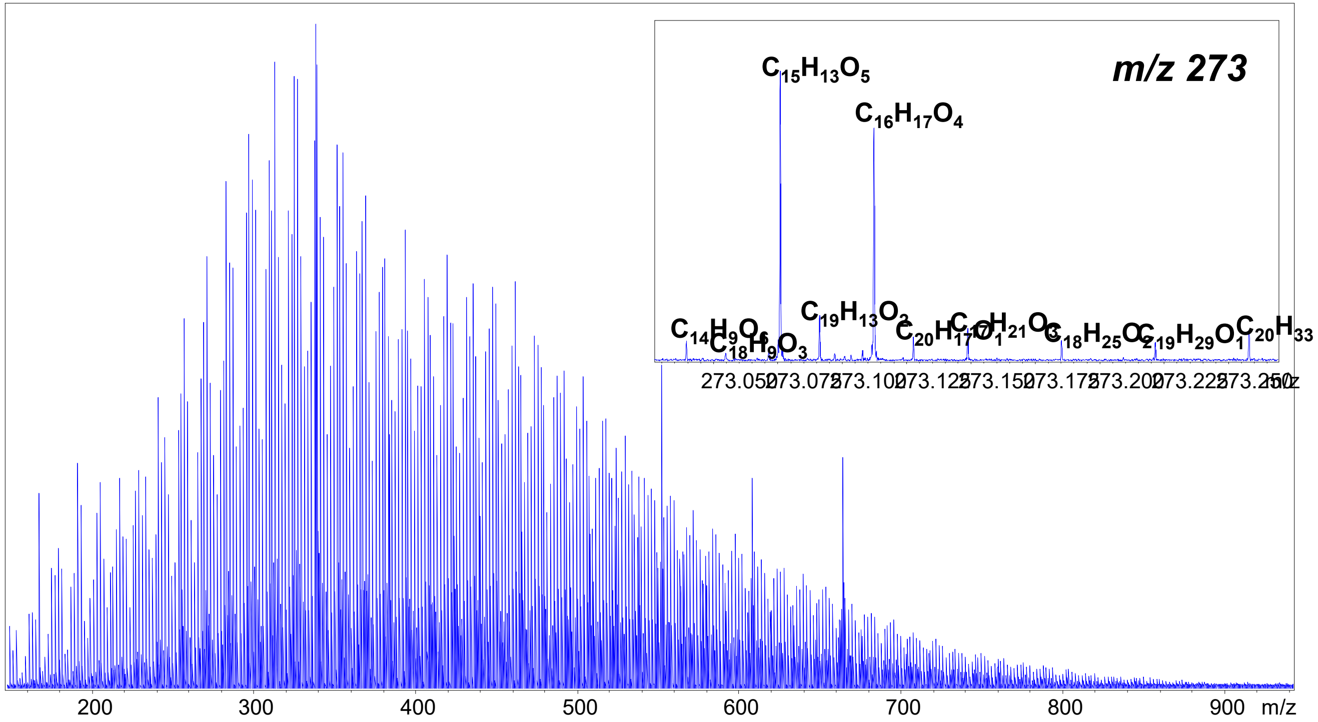
13/23 Case Study Material Characterization

Feedstock/bed material (model CMAs)
Particle size/shape distribution (Qicpic)
Particle structure/energy (bulk density, skeletal density, particle envelope density, mercury intrusion porosity, surface energy, surface area, DRIFTS)
Particle density (PTA)
Surface roughness, topology, surface chemistry (Raman)
Aerodynamic properties (cold flow testing)
Proximate analysis (volatile matter, ash, moisture, fixed carbon)
Ultimate analysis (C, H, O, N, S)
Ash analysis (Al, Ca, Fe, Mg, Mn, P, K, Si, Na, S, Ti)
Structural organic composition (cellulose, hemicellulose, lignin)

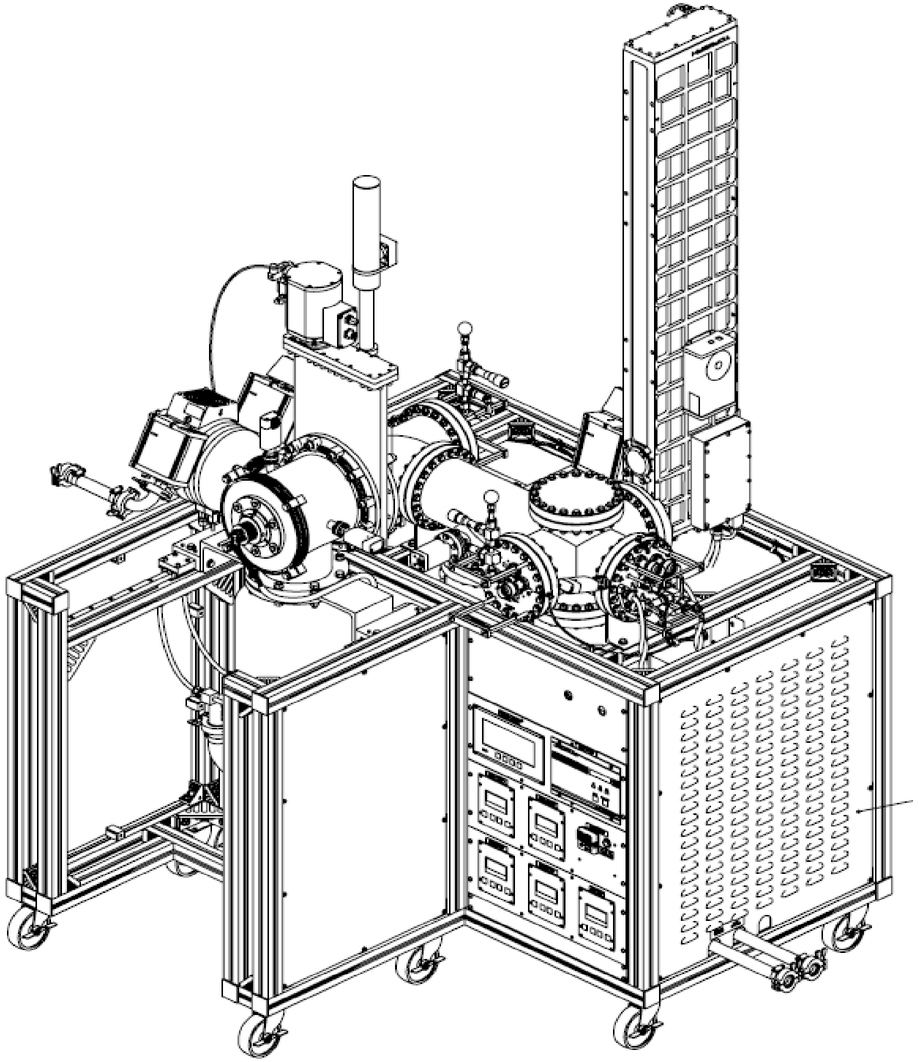
Oil/Char
Proximate analysis (volatile matter, ash, moisture, fixed carbon)
Ultimate analysis (C, H, O, N, S)
Ash species (Al, Ca, Fe, Mg, Mn, P, K, Si, Na, S, Ti)
Water content (KF)
GC-MS
TAN
Carbonyl content
^{13}C NMR
^{31}P NMR
GPC
Char structure, porosity, surface area, residual HC analysis

New Analytical Tools Coming Online

- Standard assay for pyrolysis oil analysis
- New analytical capabilities



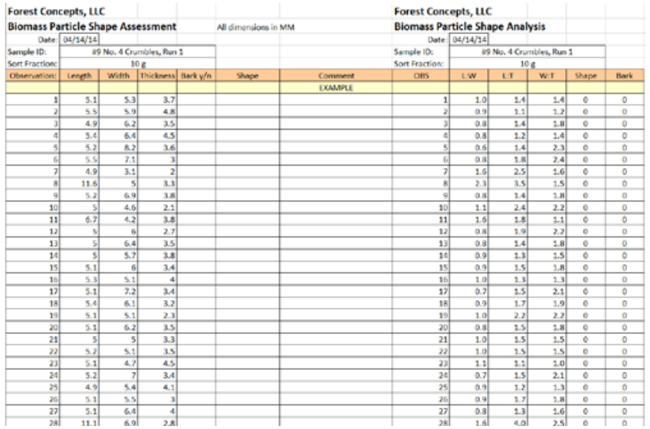
High-resolution py-oil analysis (FT-ICR)



High-resolution py-vapor analysis (MBMS)

Particle Scale Model Aids Industry in Understanding Feedstock Shape Effects on Pyrolysis Performance

Particle analysis of “Crumbles”



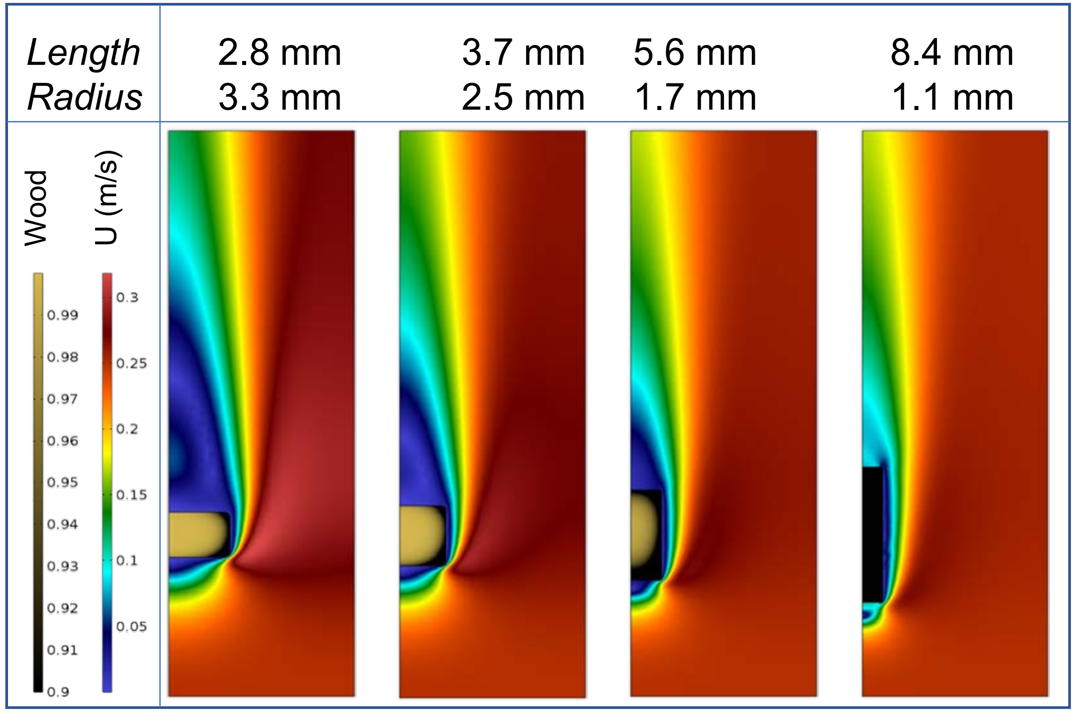
Forest Concepts, LLC
Biomass Particle Shape Assessment All dimensions in MM
Date: 04/14/14
Sample ID: #9 No. 4 Crumbles, Run 1
Sort Fraction: 10 g

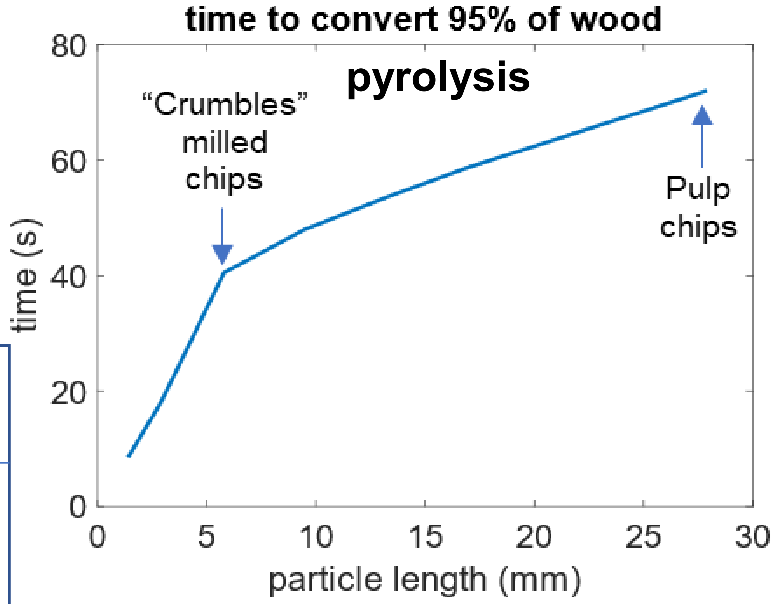
Observation:	Length	Width	Thickness	Bark y/n	Shape	Comment
						EXAMPLE
1	5.1	5.3	3.7			
2	5.5	5.9	4.8			
3	4.9	6.2	3.5			
4	5.4	6.4	4.5			
5	5.2	8.2	3.6			
6	5.5	7.1	3			
7	4.9	3.1	2			
8	11.6	5	3.3			
9	5.2	6.9	3.8			
10	5	4.6	2.1			
11	6.7	4.2	3.8			
12	5	6	2.7			
13	5	6.4	3.5			
14	5	5.7	3.8			
15	5.1	6	3.4			
16	5.3	5.1	4			
17	5.1	7.2	3.4			
18	5.4	6.1	3.2			
19	5.1	5.1	2.3			
20	5.1	6.2	3.5			
21	5	5	3.3			
22	5.2	5.1	3.5			
23	5.1	4.7	4.5			
24	5.2	7	3.4			
25	4.9	5.4	4.1			
26	5.1	5.5	3			
27	5.1	6.4	4			
28	11.1	6.9	2.8			

Forest Concepts, LLC
Biomass Particle Shape Analysis
Date: 04/14/14
Sample ID: #9 No. 4 Crumbles, Run 1
Sort Fraction: 10 g

OBS	L:W	L:T	W:T	Shape	Bark
1	1.0	1.4	1.4	0	0
2	0.9	1.1	1.2	0	0
3	0.8	1.4	1.8	0	0
4	0.8	1.2	1.4	0	0
5	0.6	1.4	2.3	0	0
6	0.8	1.8	2.4	0	0
7	1.6	2.5	1.6	0	0
8	2.3	3.5	1.5	0	0
9	0.8	1.4	1.8	0	0
10	1.1	2.4	2.2	0	0
11	1.6	1.8	1.1	0	0
12	0.8	1.9	2.2	0	0
13	0.8	1.4	1.8	0	0
14	0.9	1.3	1.5	0	0
15	0.9	1.5	1.8	0	0
16	1.0	1.3	1.3	0	0
17	0.7	1.5	2.1	0	0
18	0.9	1.7	1.9	0	0
19	1.0	2.2	2.2	0	0
20	0.8	1.5	1.8	0	0
21	1.0	1.5	1.5	0	0
22	1.0	1.5	1.5	0	0
23	1.1	1.1	1.0	0	0
24	0.7	1.5	2.1	0	0
25	0.9	1.2	1.3	0	0
26	0.9	1.7	1.8	0	0
27	0.8	1.3	1.6	0	0
28	1.6	4.0	2.5	0	0

Pyrolysis particle model parameterized to un-milled and “crumbled” wood chips illustrates value proposition of Forest Concepts to bioenergy producers

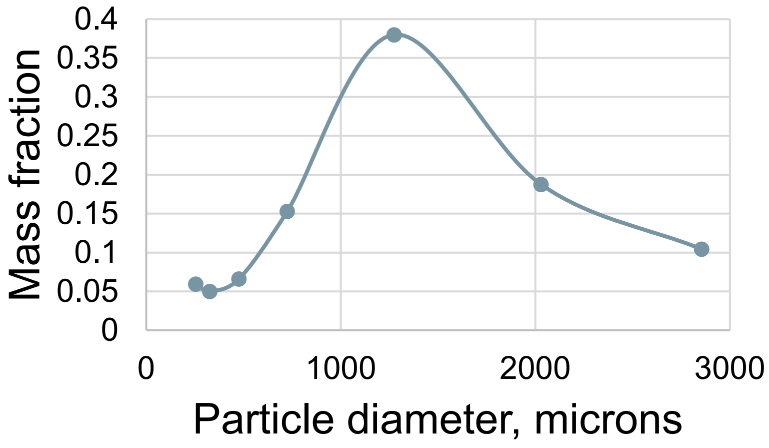


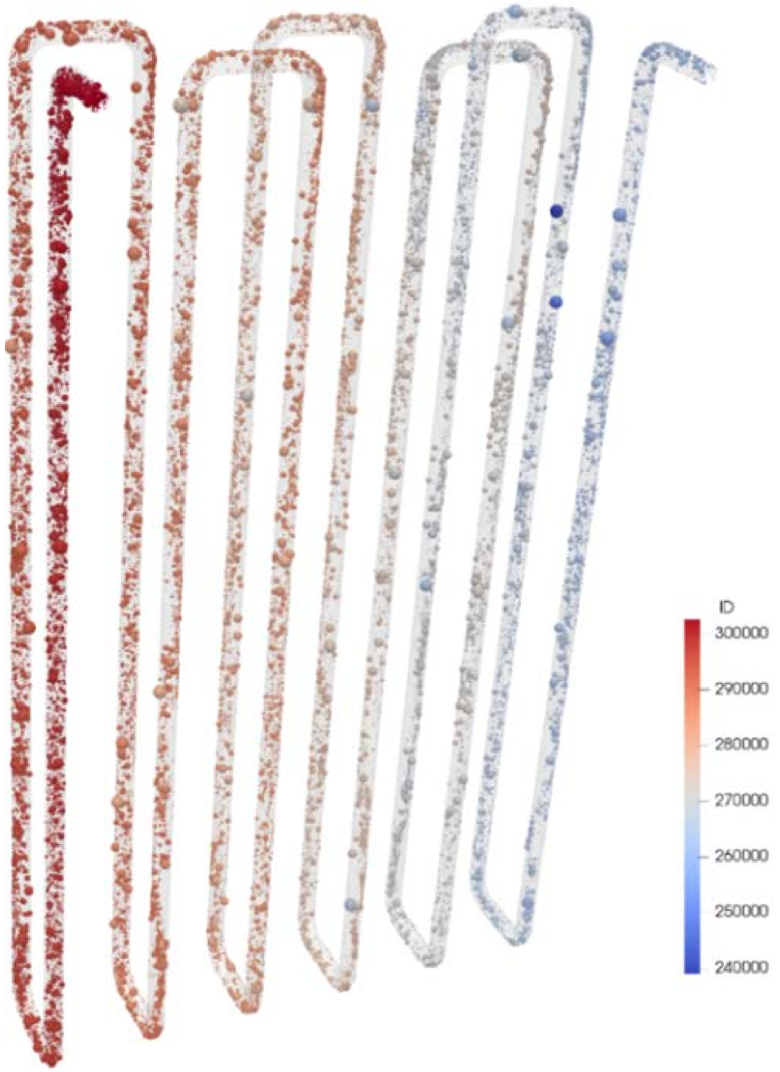


"The modeling data developed by NREL gave our company an understanding of how our production engineers can co-optimize reactors and feedstock properties to improve functional performance. This conversion data will also help our customers select the optimal feedstock for their specific conversion process." - James H. Dooley, CTO at Forest Concepts

CFD (MFiX) Model Utilized to Inform BETO Catalytic Fast Pyrolysis Verification Decisions

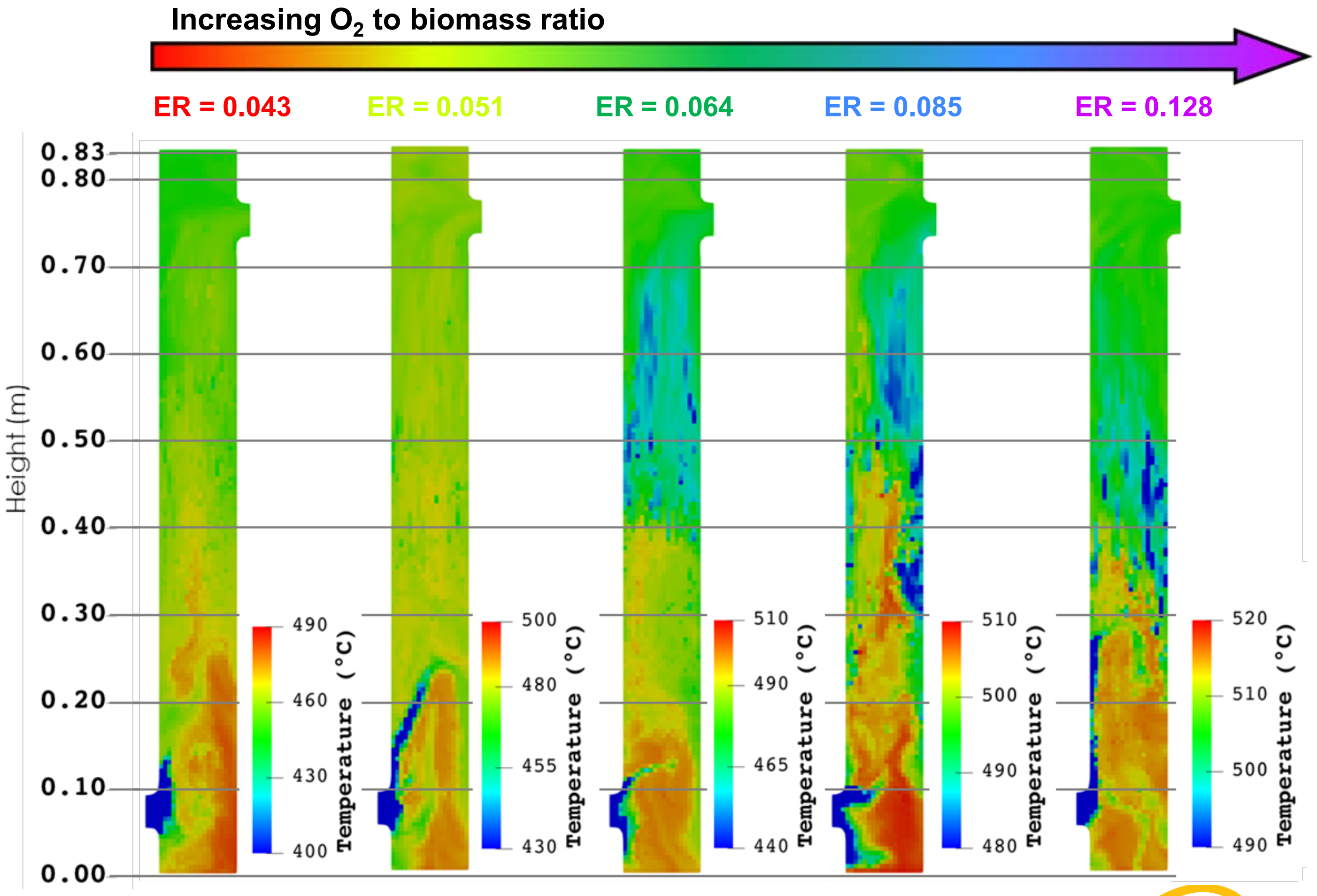
- NETL CFD (MFiX) model of Entrained Flow Reactor in NREL Thermo-Chemical Process Development Unit (TCPDU)
- Feedstock: 60% air-classified Forest Residues (pine)/30% Clean Pine/10% Hybrid Poplar
- Model captured different residence times for distribution of particle sizes to calculate impact of size distribution on yield
- Model also utilized to understand fluidization impacts on yield for adding H_2 content to process gas (for downstream catalytic deoxygenation)

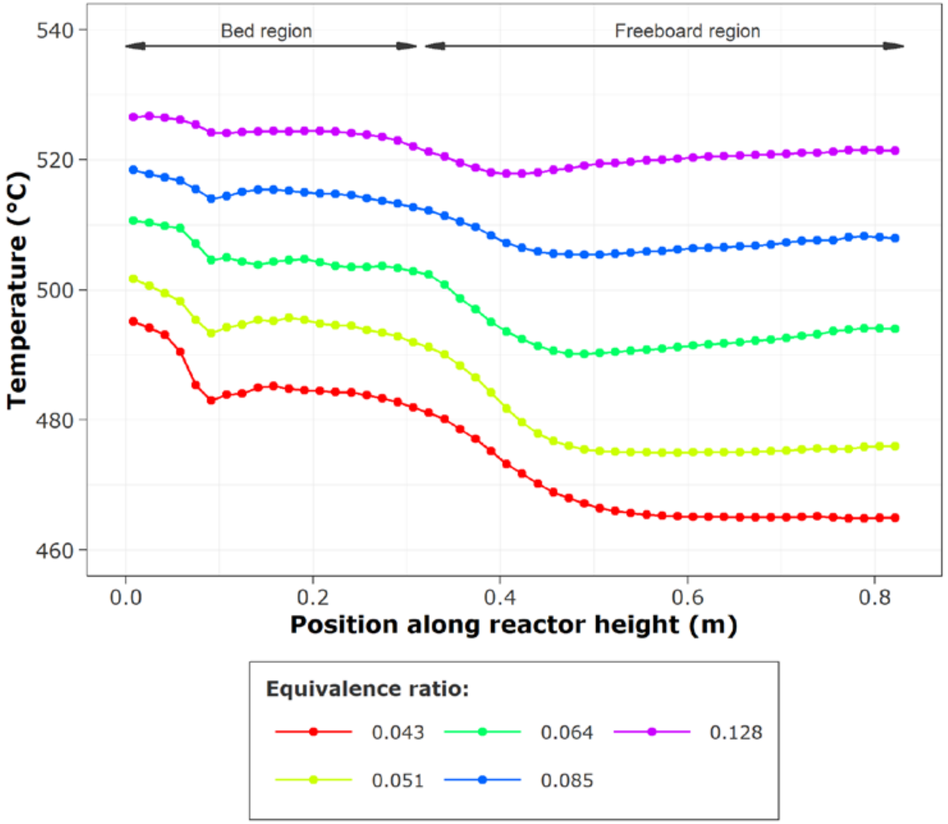




CFD (MFiX) Model Calculates Reactor Temperatures in Auto-Thermal Pyrolysis with Iowa State University

ORNL, NREL, NETL, & Iowa State University utilizing previous version of FCIC toolset to calculate spatial distribution of reactor temperature during auto-thermal pyrolysis for varying O_2 [equivalence ratio (ER) shown]





Note: R&D part of BETO BioPower project being reviewed at…