U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Consortium for Computational Physics and Chemistry (CCPC)

WBS: 2.5.1.301/302/303/304/306

U.S. Department of Energy (DOE)
Bioenergy Technologies Office (BETO)
2017 Project Peer Review

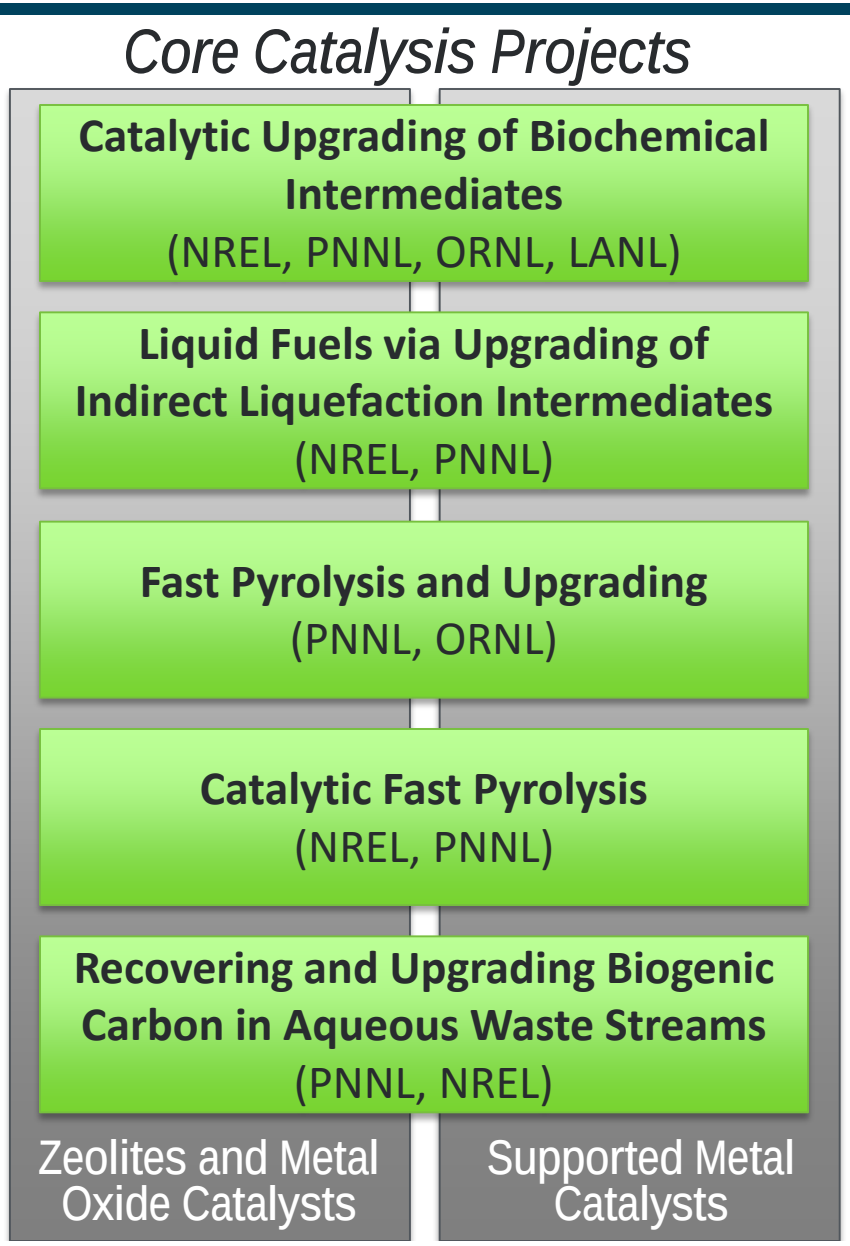
Thermochemical Conversion

March 7th, 2017

Project Leads:

Jim Parks – ORNL
David Robichaud – NREL
Peter Ciesielski – NREL
Roger Rousseau – PNNL
Asanga Padmaperuma – PNNL
Bill Rogers – NETL
Madhava Syamlal – NETL
Rajeev Assary – ANL
Larry Curtiss - ANL

ChemCatBio Structure



Enabling Projects

Advanced Catalyst Synthesis and Characterization
(NREL, ANL, ORNL)

Catalyst Cost Model Development
(NREL, PNNL)

Consortium for Computational Physics and Chemistry
(ORNL, NREL, PNNL, ANL, NETL)

Consortium Integration

- Core catalysis projects focused on specific *applications*
- *Collaborative* projects leveraging core capabilities across DOE laboratories
- *Cross-fertilization* through discussion groups

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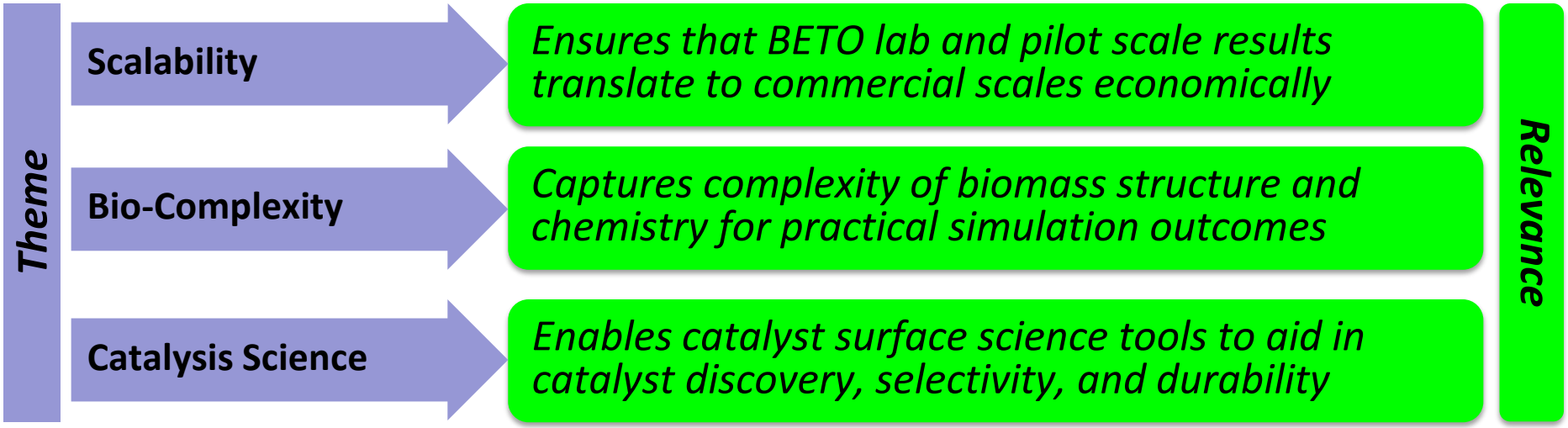
Goal Statement

Accelerate progress on experimental BETO projects toward critical program verification goals and successful technoeconomic analysis (TEA) outcomes that result in economic sustainability of bioenergy by applying:

(1) **process and reactor models** that incorporate feedstock and catalyst properties, to guide reactor design and operation and inform and understand reactor scale up from lab, to pilot, to commercial scales; and

(2) **catalyst models** that provide active site energetics and entropics to guide the experimental design and discovery of next generation catalysts and improve durability and cost-effectiveness.



Quad Chart Overview

Timeline

- Project start date: 10/1/2015
- Project end date: 9/30/2018
- Percent complete: 50%

Budget

	FY15 Costs	FY16 Costs	Total Planned Funding (FY17-Project End Date)
DOE Funded	$3.3M	$3.2M	$6.3M

*FY17 operating budget reduced to $3.0M

Barriers addressed & Actions

- Ct-A. Feedstock Variability and Ct-F. Efficient High-Temp Deconstruction to Intermediates
  - ***Feedstock dependent models coupled with reactor simulations to predict yield variations***
- Ct-H. Efficient Catalytic Upgrading
  - ***Atomistic models of catalytic chemistry to accelerate the design of new materials; reactor modeling to determine optimal residence times***
- Ct-J. Process Integration
  - ***Scalable reactor/process models that can be coupled to define integrated operations***

Partners

- NREL (53%), ORNL (24%), ANL (10%), NETL (8%), PNNL (5%)
- ChemCatBio
- Feedstock Conversion Interface Consortium
- Integration and Scale Up Project (NREL)
- 9-member Industry Advisory Panel
- 5 Universities (list in Additional Slides)

Project Overview

- The CCPC is a **consortium of BETO's modeling expertise** representing a hub for the computational needs for the biofuels program
- **The CCPC is a team with diverse applied computational expertise** where ideas, approaches, and findings can be discussed and advanced via cross-talk
- With modeling collaborations beginning in 2013, the CCPC is now mature with best practices being honed and shared across BETO

Objectives:

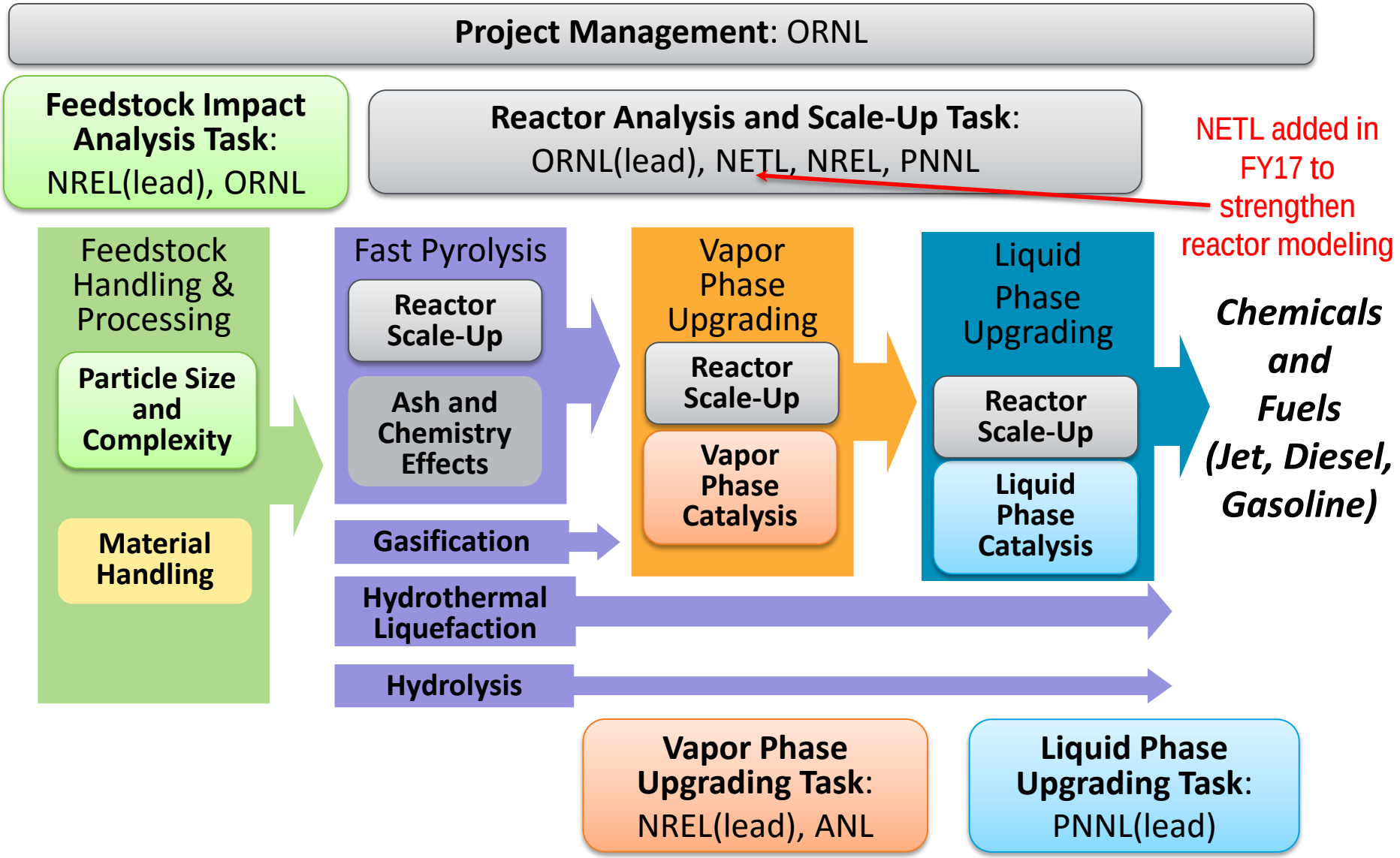
(1) Provide predictive simulation tools to enable BETO experimental teams to maximize yield and fuel chemistry based on reactor design, operational parameters, feedstock type, and feedstock particle size distributions during pilot scale verification

(2) Simulations of reactor scale up effects and predictive impact on linkage of BETO bench and pilot scale results to full plant TEA

(3) In conjunction with ChemCatBio, more rapid advancements in catalyst formulation and design that result in experimentally observed improvements (yield, selectivity, durability, lifetime, cost)

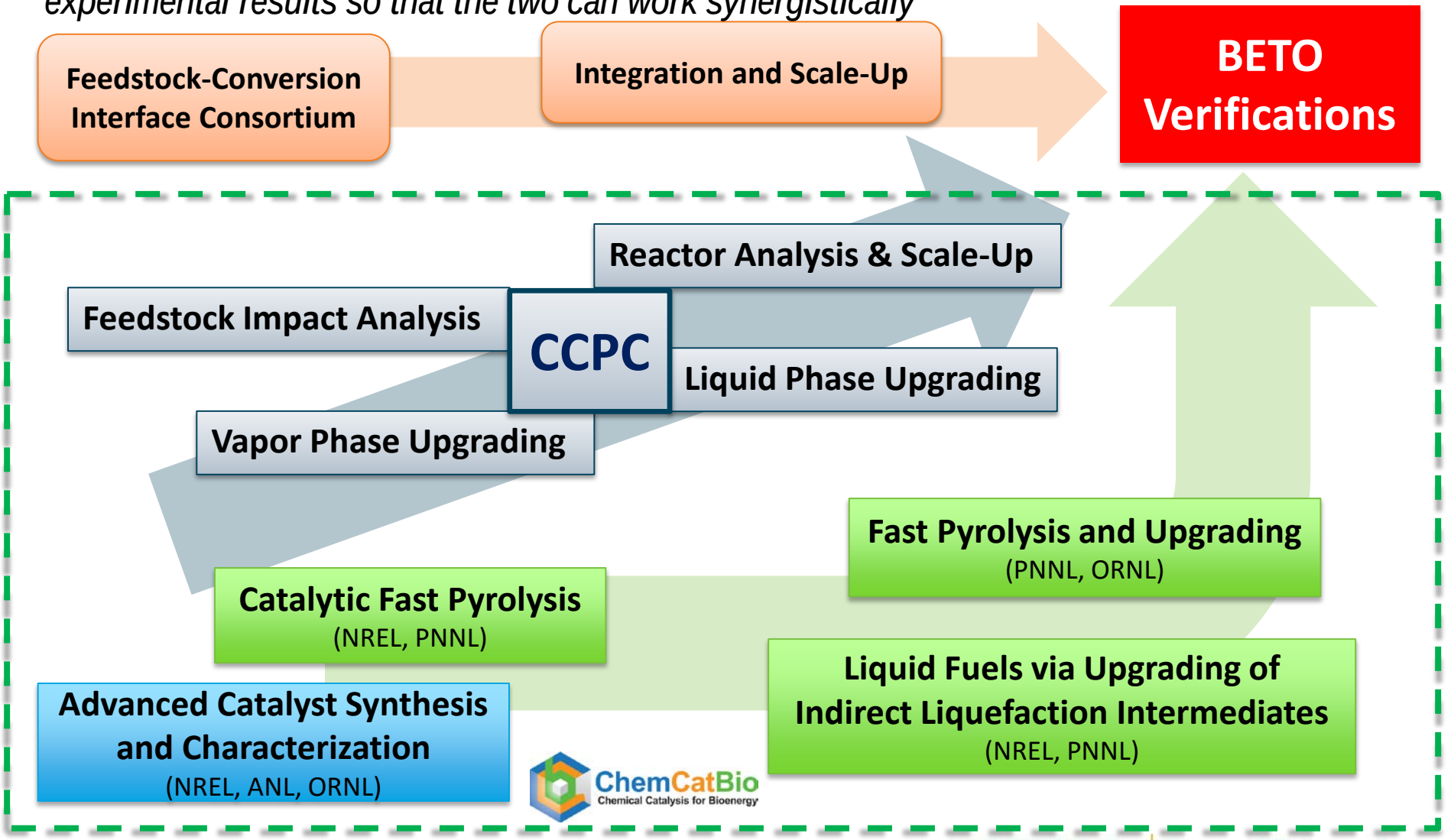
Note: more detailed timeline in additional slides

Approach (Management): Technical tasks organized around conversion processes



Approach: 8 joint/linked FY17 milestones* with experimental teams highlight collaborations

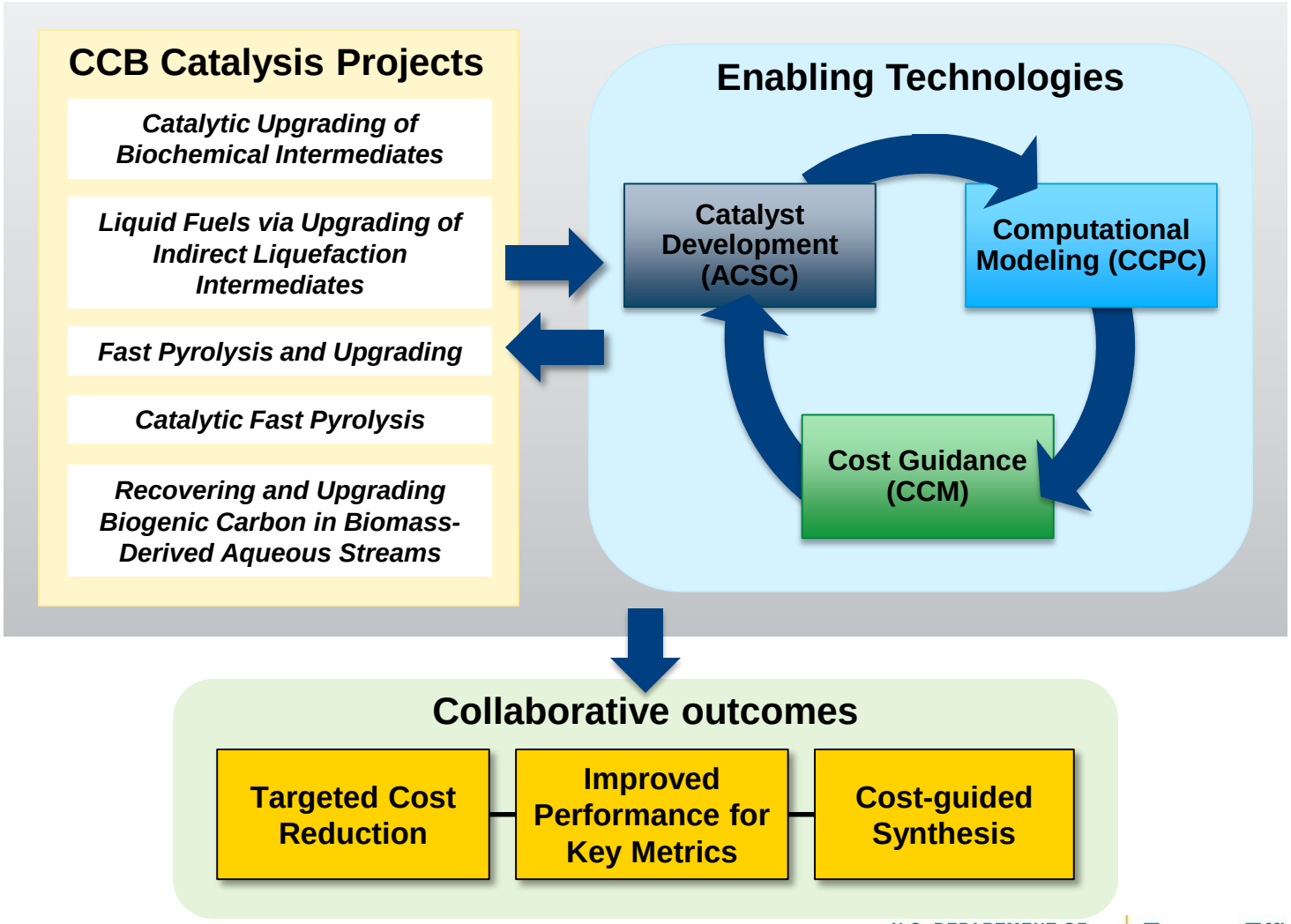
8 joint/linked milestones address 2015 reviewer comment *"…tied directly to projects on experimental results so that the two can work synergistically"*



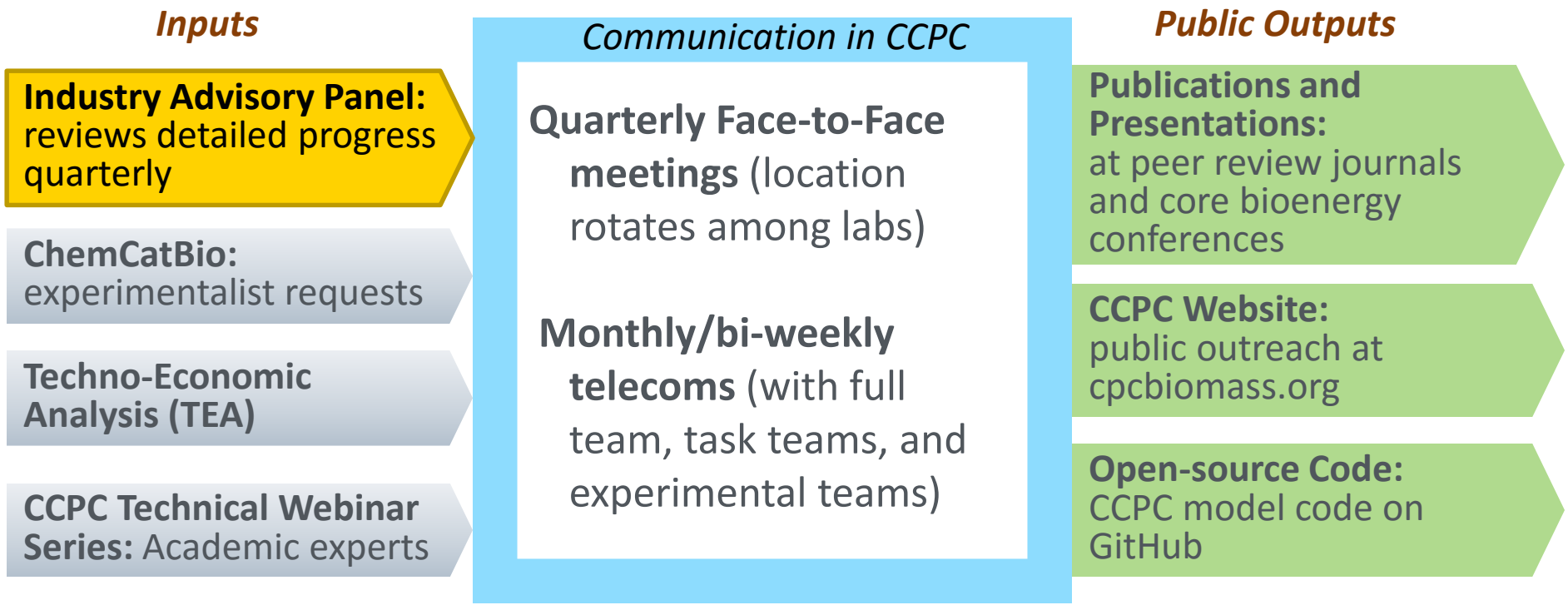
*see additional slides for full list of milestones

Project overview – Integrated approach

Establish an integrated and collaborative portfolio of catalytic and enabling technologies



Approach: Exchange across technical community provides guidance, relevance, and direction



Industry Advisory Panel [*representing >100 years of combined experience*]

David Dayton (**RTI**), George Huff (**MIT, retired BP**), Jack Halow (**Separation Design Group**), Mike Watson (**Johnson Matthey**), Randy Cortright (formerly **Virent Energy Systems**), Richard Quann (**ExxonMobil**), Steve Schmidt (**WR Grace**), Tom Flynn (**Babcock & Wilcox**), Rick Wessel (**Babcock & Wilcox**)

Approach: Focus on physics and chemistry that gives impactful tools to accelerate bioenergy processes

CCPC Focused Outcomes

- **Biomass Particle Models**
- **Residence Time Distributions**
- **Surface Chemistry Energetics**
- **Reaction Kinetic Rates**
- **Coking and Fouling Rates**

Critical Success Factors:

Our tools used by community to accelerate experiments and improve Techno-Economic Analyses

Python™ - www.python.org

GitHub - github.com

GitLab - about.gitlab.com

Git - git-scm.com

MATLAB® - www.mathworks.com

COMSOL Multiphysics® www.comsol.com

C3M - mfix.netl.doe.gov/c3m

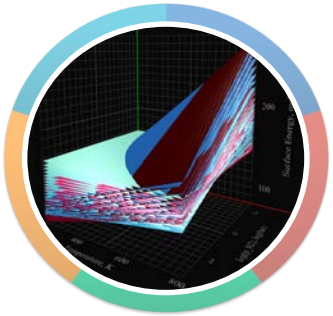
MFiX - mfix.netl.doe.gov/mfix

C3M Carbonaceous Chemistry for Computational Modeling

MFiX DEM

MFiX TFM

Notable Tech Transfer



Surface Phase Explorer

spe.nrel.gov (public)

CSFMB©/CeSFaMB™

CCPC assisted Prof. de Souza-Santos in including biomass pyrolysis chemistry into new version of CSFMB© commercial software (Brazil)

www.csfmb.com

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Technical Approach: Challenges and Success Factors

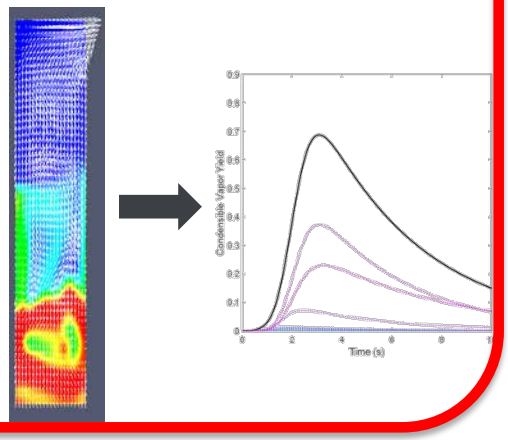
Process Modeling

Challenge

Enable vastly diverse biomass feedstock to be modeled ***efficiently*** across scales of processes to maintain yield and selectivity from bench to commercial scale

Critical Success Factors

Models that capture feedstock ***complexity*** and accurately predict reactor performance ***at multiple scales***



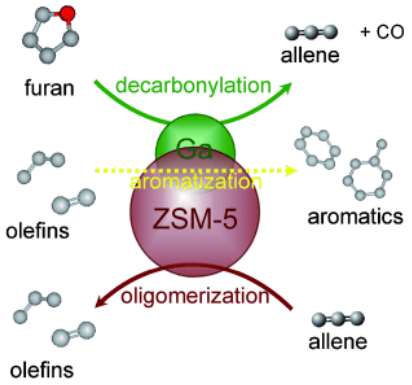
Catalysis Modeling

Challenge

Develop tools to ***quickly*** determine catalyst structure and surface chemistry reactions to enable synthesis of improved catalysts

Critical Success Factors

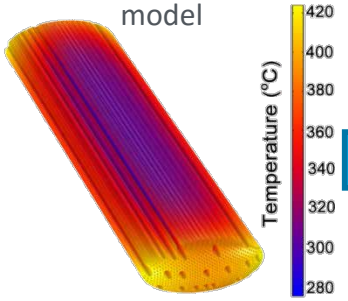
Predictions and testable hypotheses that ***accelerate*** ChemCatBio's synthesis of new catalysts with improved lifetime, activity, & selectivity



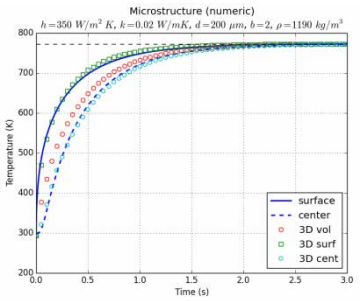
Technical Approach: Complex realism to effective simplicity

Complex effects of biomass particles captured in low-order particle models for use in reactor scale models

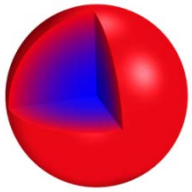
Complex, 3D particle model



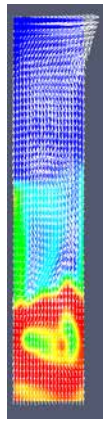
Results fit to low-order model



Low order particle model that capture complex behavior



Reactor-scale model



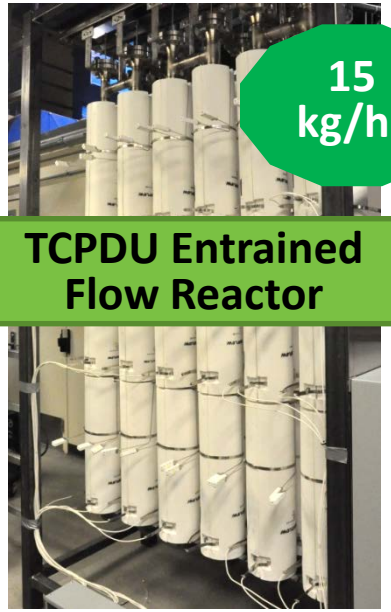
Resulting reactor models enable scalable prediction of pyrolysis yield

2" Fluidized Bed Reactor

0.5 kg/hr

DCR Fluidized Bed Reactor

2 kg/hr



15 kg/hr

TCPDU Entrained Flow Reactor

All Three Reactors at NREL

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Accomplishments: Reduced order particle models capture biomass complexity in practical form for reactor models

Objective: Develop reduced order biomass particle models to facilitate integration with reactor-scale simulations.

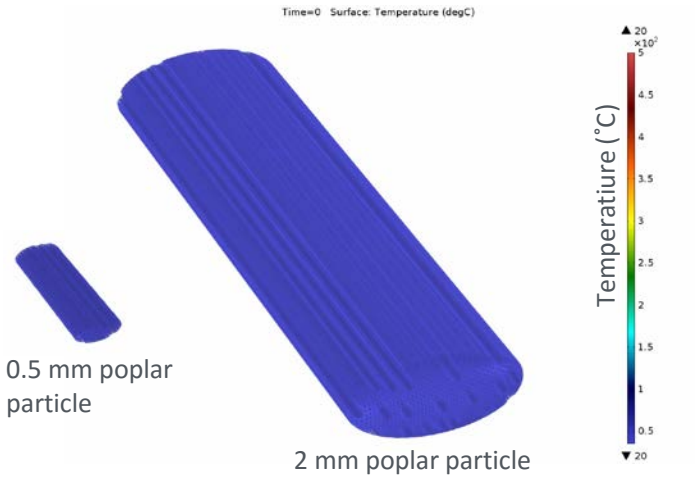
Accomplishments:

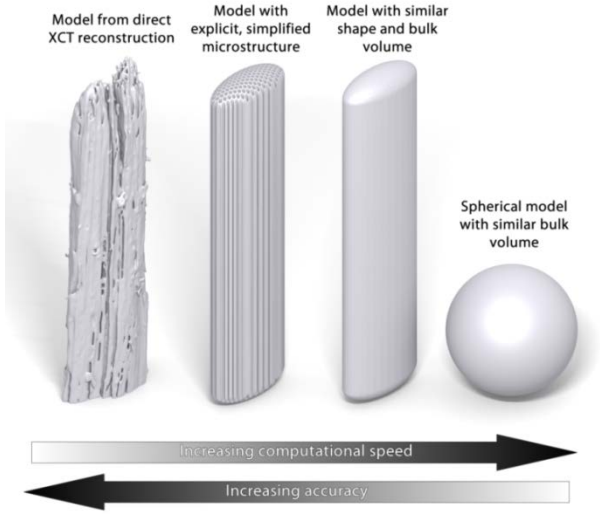
- Performed sensitivity analysis using fully-resolved 3D models to determine which complexities are most impactful
- Developed fast, 1D model that replicates behavior of 3D models using effective particle dimensions and properties

Relevance:

The reduced order particle models enable reactor-scale simulations over 100x faster while still capturing effects from biomass complexity

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





Top: Heating transfer simulation for poplar particles of 2 different sizes. **Bottom:** visualization of order-reduction in biomass particle modeling

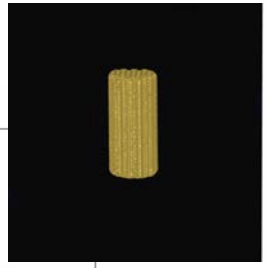
Biomass Feedstock → Pyrolysis → Vapor Phase Upgrading → Liquid Phase Upgrading

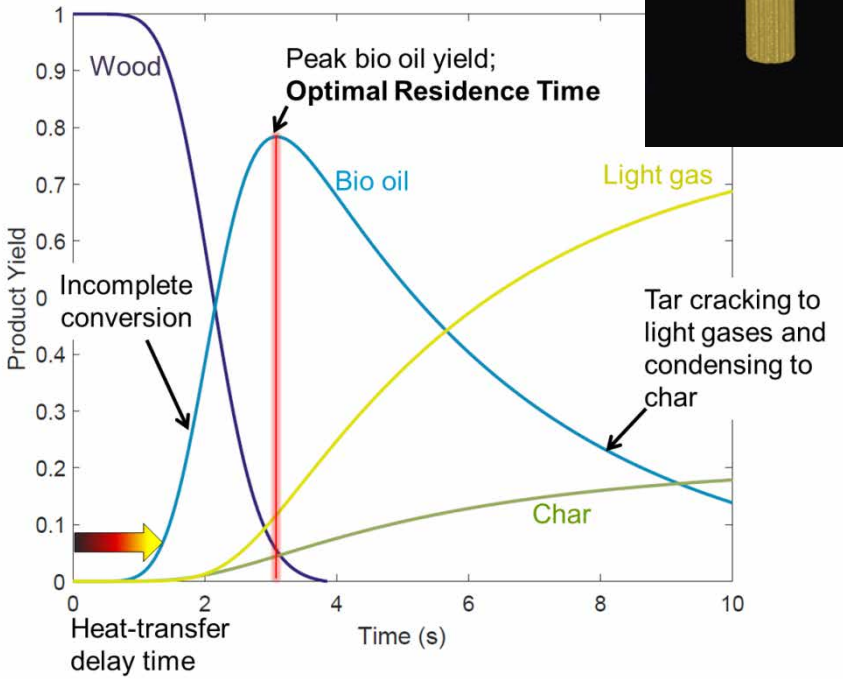
Accomplishments: Optimal residence time predicted based on feedstock-specific parameters

Objective: Predict optimal residence time (i.e., time of peak tar yield) as a function of feedstock-specific parameters

Accomplishments:

- Coupled heat transfer, mass transfer, fluid dynamics, and chemical reaction for particle scale models of fast pyrolysis
- Simulations account for important process variables such as **particle size, shape, biomass species, moisture content, and reactor temperature**
- Provides estimates of time-resolved product evolution





Above: Simulation of product evolution during pyrolysis of a ~3 mm pine particle at 500 °C.

Relevance: Simulations provide estimates of optimal operating conditions, including reactor temperature and residence time, for pyrolysis experiments.

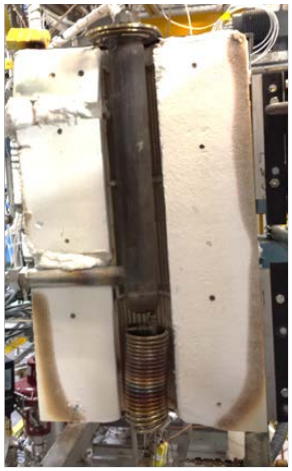
CCPC Publication: Wiggins, Ciesielski, & Daw, Low-Order Modeling of Internal Heat Transfer in Biomass Particle Pyrolysis. *Energy&Fuel* ***2016***

Biomass Feedstock | Pyrolysis | Vapor Phase Upgrading | Liquid Phase Upgrading

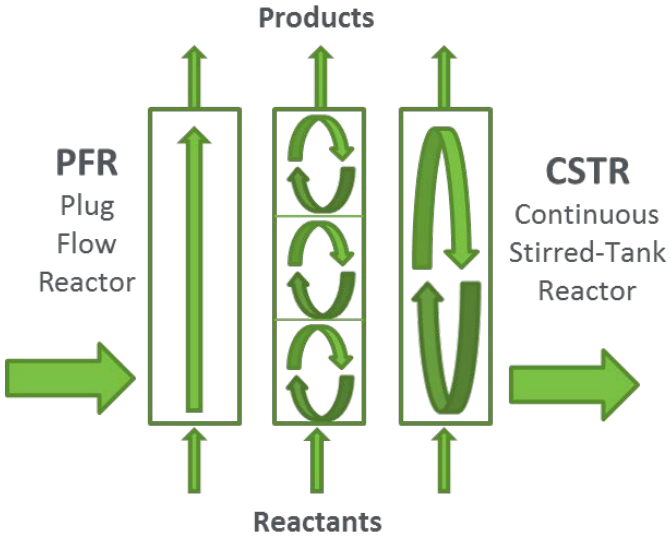
Accomplishments: Low-order reactor model captures multiphase residence time distributions

Objective: Predict product yields (gas, tar, char) from fast pyrolysis of biomass particles in a bubbling fluidized bed reactor.

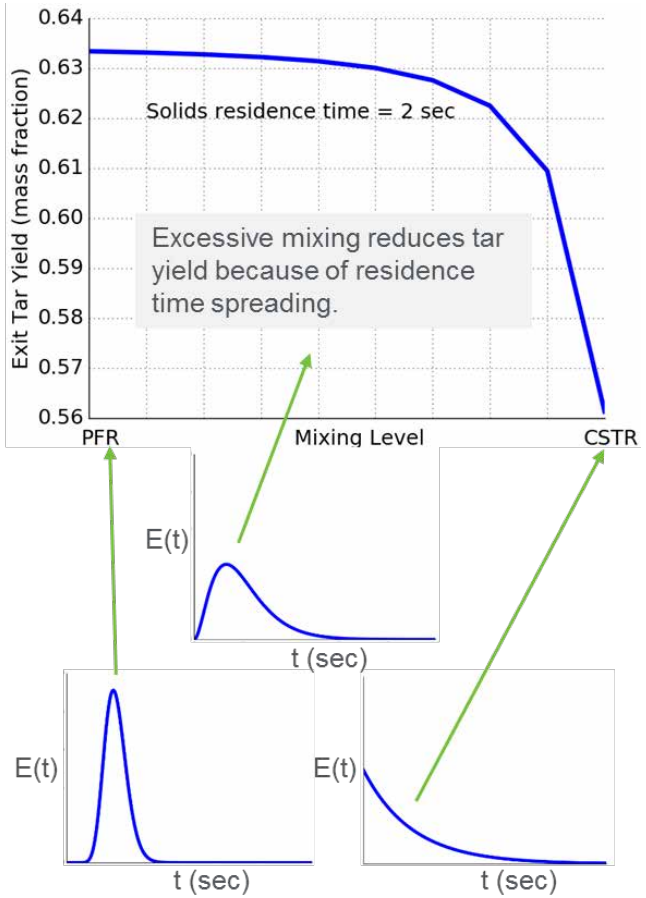
Accomplishment: Constructed low-order reactor mixing models to estimate residence times of biomass particles and the resulting oil yield.



Bubbling fluidized bed reactor at NREL for biomass fast pyrolysis experiments.



Reactor simulated with different levels of mixing.



Residence time distributions as a function of time for different mixing regimes.

Relevance: Computationally efficient and scalable approach provides accurate residence time distribution for predicting pyrolysis yield.

Biomass Feedstock → Pyrolysis → Vapor Phase Upgrading → Liquid Phase Upgrading

Major Accomplishments: Combined particle and reactor models to predict accurate yields for two different feedstock size distributions

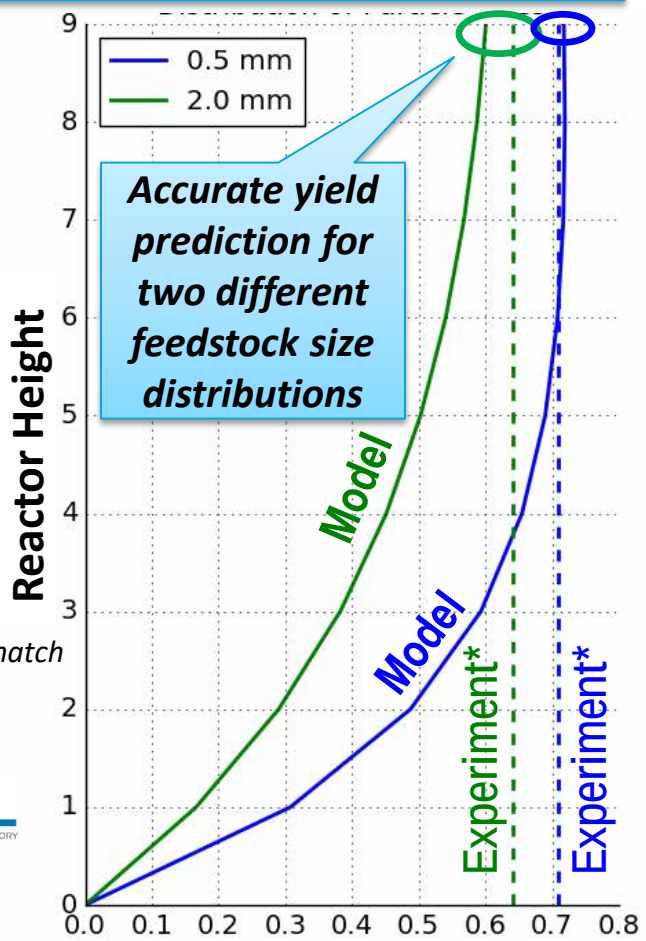
Accomplishments:

- Combined particle and reactor simulations
- Validated pyrolysis model for 2” fluidized bed reactor against two different particle size distributions and moisture contents of pine with FCIC experimental team

Relevance: Coupled multiscale simulations predicted bio-oil yields within 2% of experimental error.

- drive out-year experimental design and process optimization in FCIC
- inform scale up between 0.5 kg/hr bench and 15 kg/hr pilot systems.

Yield Predictions for 0.5 mm and 2.0 mm Particle Size Distribution (PSD) Ensembles



*data from NREL 2”FBR reactor

Cross-cutting NL-NL and modeling-experimental collaboration and workflow

INL sends feedstock characterization to NREL

NREL models feedstock; translates to ORNL

ORNL models reactor with low-order particle model

ORNL model results match NREL experimental results!

CCPC Publication: Ciesielski, Wiggins, & Daw in Fast Pyrolysis of Biomass, eds. Robert Brown & Kaige Wange. In press

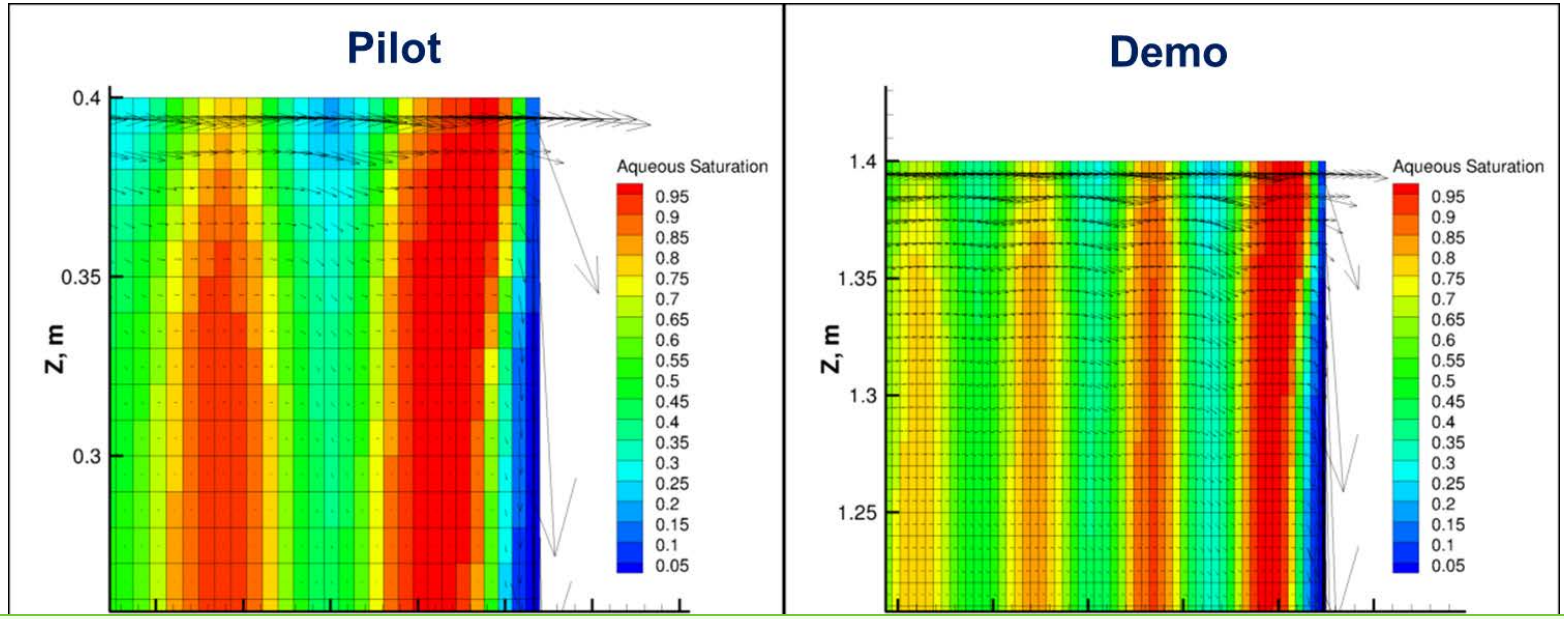
Biomass Feedstock → Pyrolysis → Vapor Phase Upgrading → Liquid Phase Upgrading

Accomplishments: Catalyst packing geometry can be used to optimize flow path and minimize fouling

Objective: Reduce fouling of hydrotreating reactor

Accomplishments:

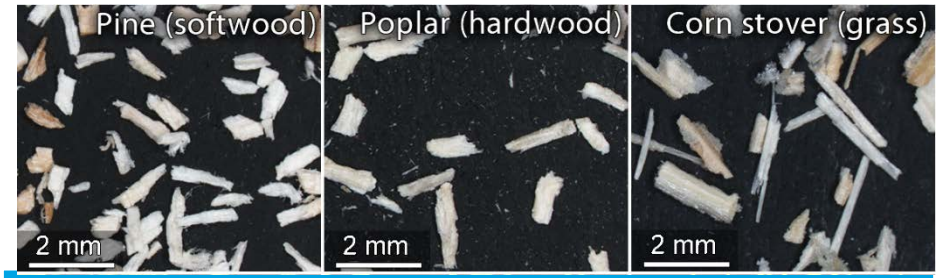
- Porosity and permeability in a tubular down-flow reactor have been shown to affect multi-phase flow in wall region
- Channeling from the high porosity of the bed at the wall creates hydrogen-rich and hydrogen-starved zones → gunking occurs in the latter



Relevance: Reactor engineering shows pathways to minimize maldistribution which can reduce hydrogen consumption and minimize fouling processes

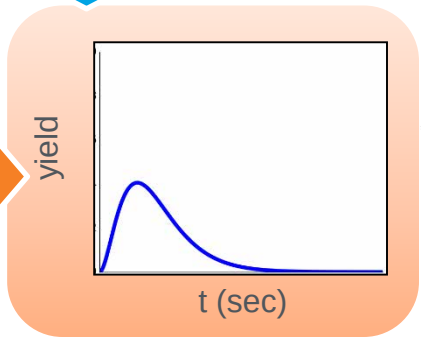
Biomass Feedstock → Pyrolysis → Vapor Phase Upgrading → Liquid Phase Upgrading

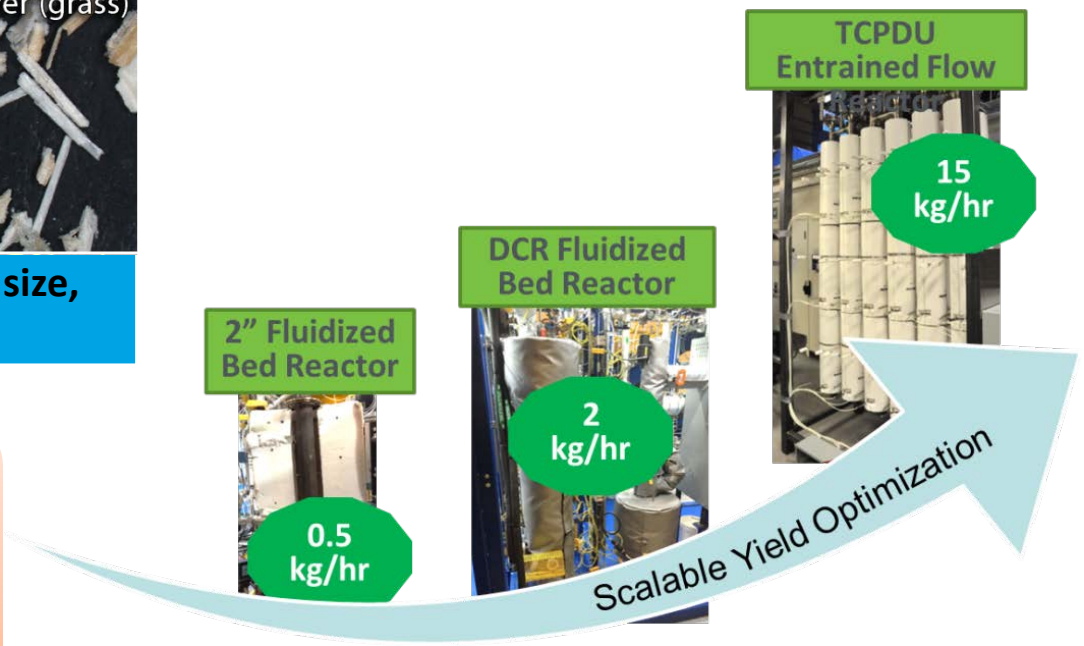
Relevance: Process Modeling: Bio-Complexity & Scalability



Models capturing complexities of particle size, shape, speciation, and chemistry

Reactor models capturing multiphase flows and residence times





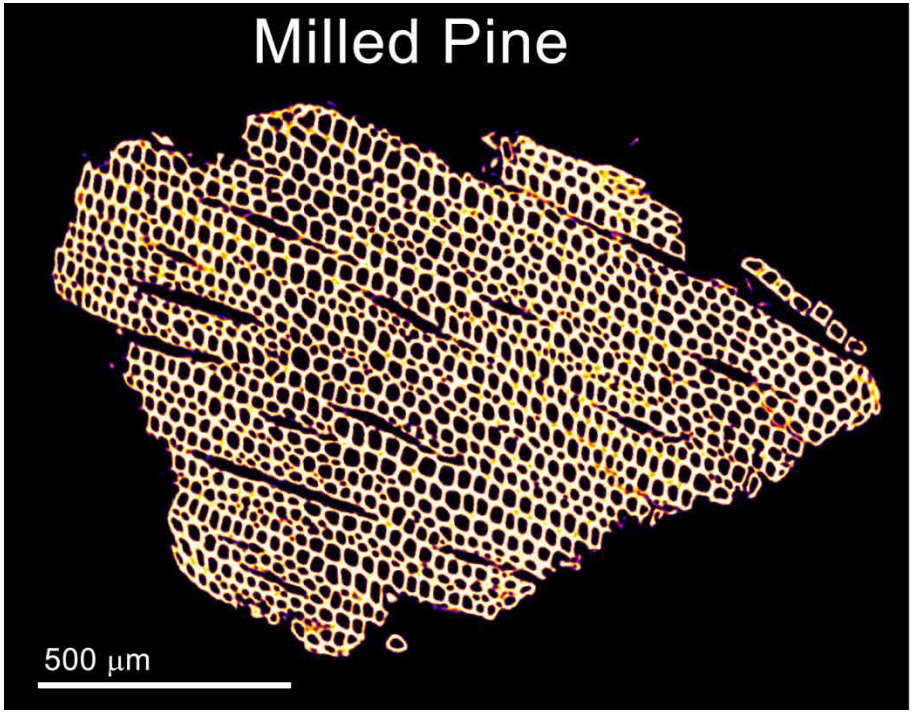
Relevance to BETO and Industry:

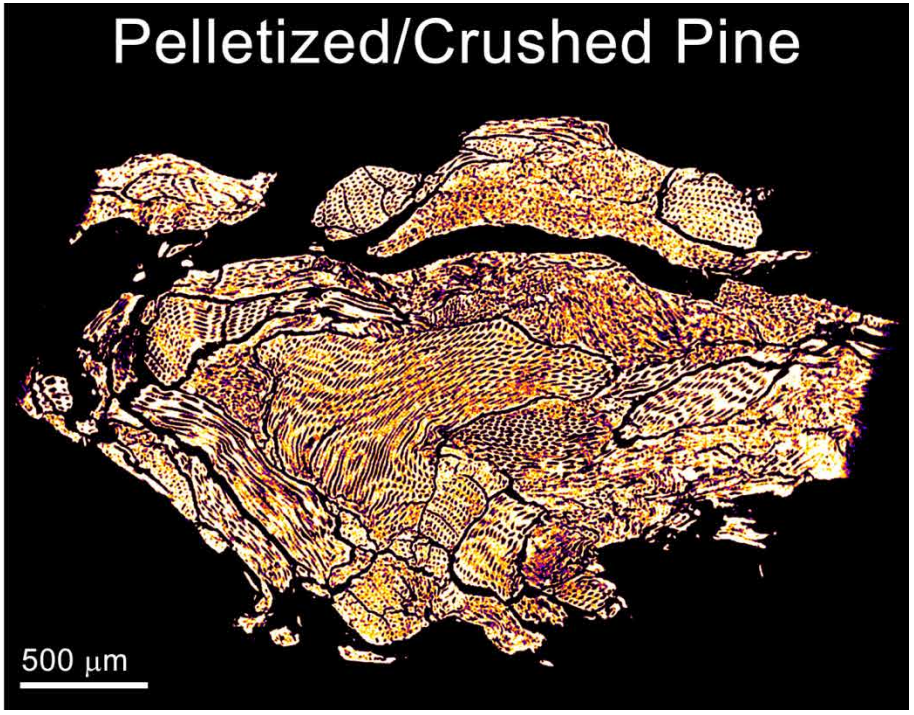
The models developed in the CCPC provide a 'window into the reactor'. This enables the BETO platform and industry to:

- Troubleshoot issues with reactors as they arise, reducing system downtime
- Conduct commissioning of new systems more efficiently
- Facilitate scale-up of processes and new catalyst formulations from the bench to pilot scale
- Methodology is being used to extend modeling success to *in situ* and *ex situ* CFP

Future Work: Biomass particle models advancing for pelletized/crushed and blended feedstocks

- Pelletization alters microstructure and intra-particle transport behavior
  - We are developing particle models for pelletized feedstocks based on micro X-ray computed tomography data (with Colorado School of Mines)
- Particle models also advancing for blended feedstocks for verification

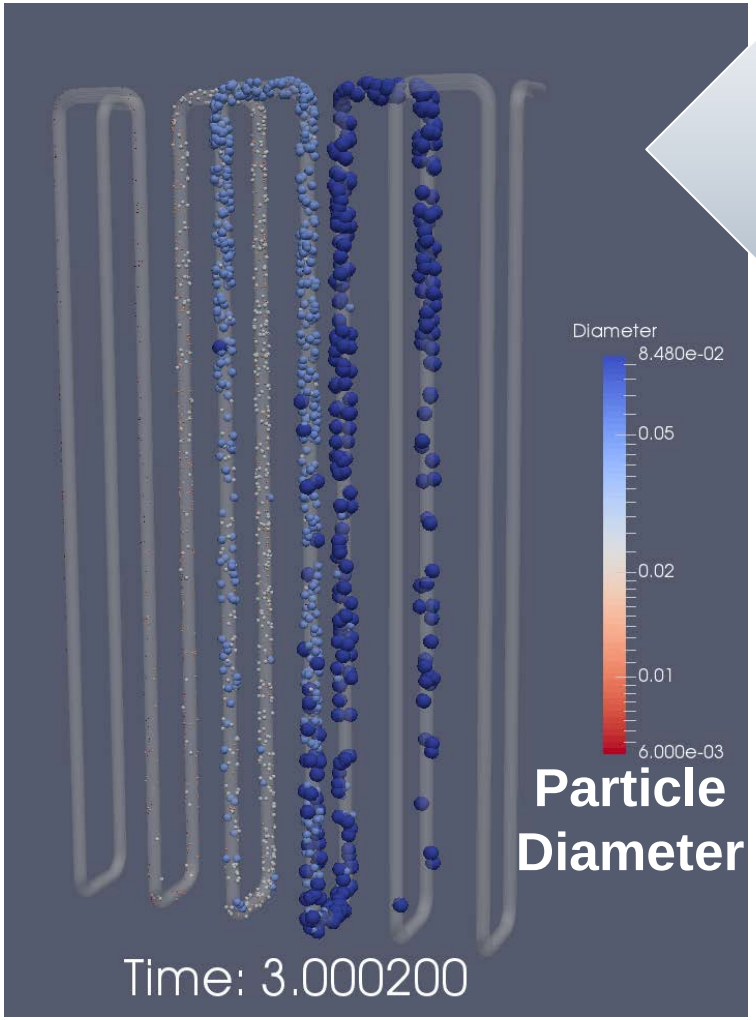




Images: B. Kappes (CSM), P. Ciesielski (NREL)

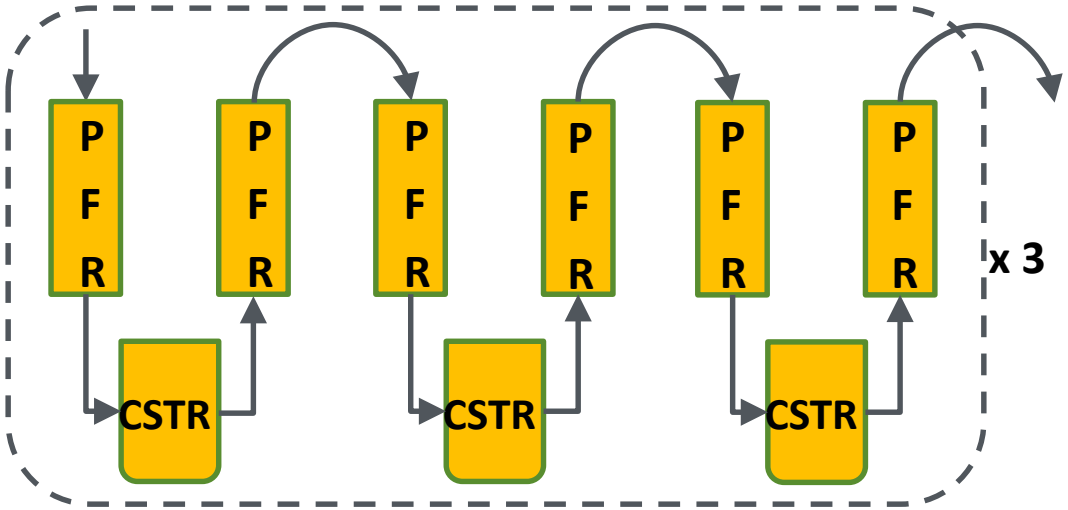
Annual Milestone LINKED with Integration and Scale-Up project (WBS 2.4.1.301)

Future Work: Scalability - extend low-order pyrolysis model to TCPDU Entrained Flow Reactor



Larger size biomass particles have higher residence times due to reactor geometry
Note: for visualization, particles shown at 50x diameter (relative to reactor scale)

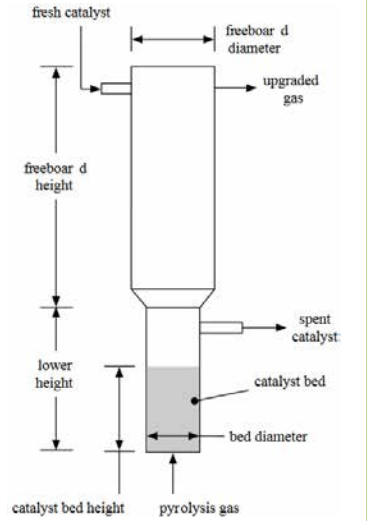
Progress to-date: MFiX-DEM model (left) of Entrained Flow Reactor to determine residence time distributions for low-order model (below)



Annual Milestone LINKED with Integration and Scale-Up project (WBS 2.4.1.301)

Future Work: Developing scalable upgrading reactor models to support verification success

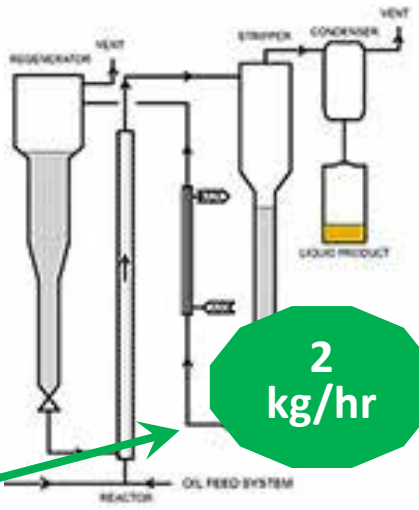
2” Fluidized Bed Reactor Upgrader*



0.5 kg/hr

Relevant to new BETO catalysts

Davison Circulating Riser (DCR) Reactor*

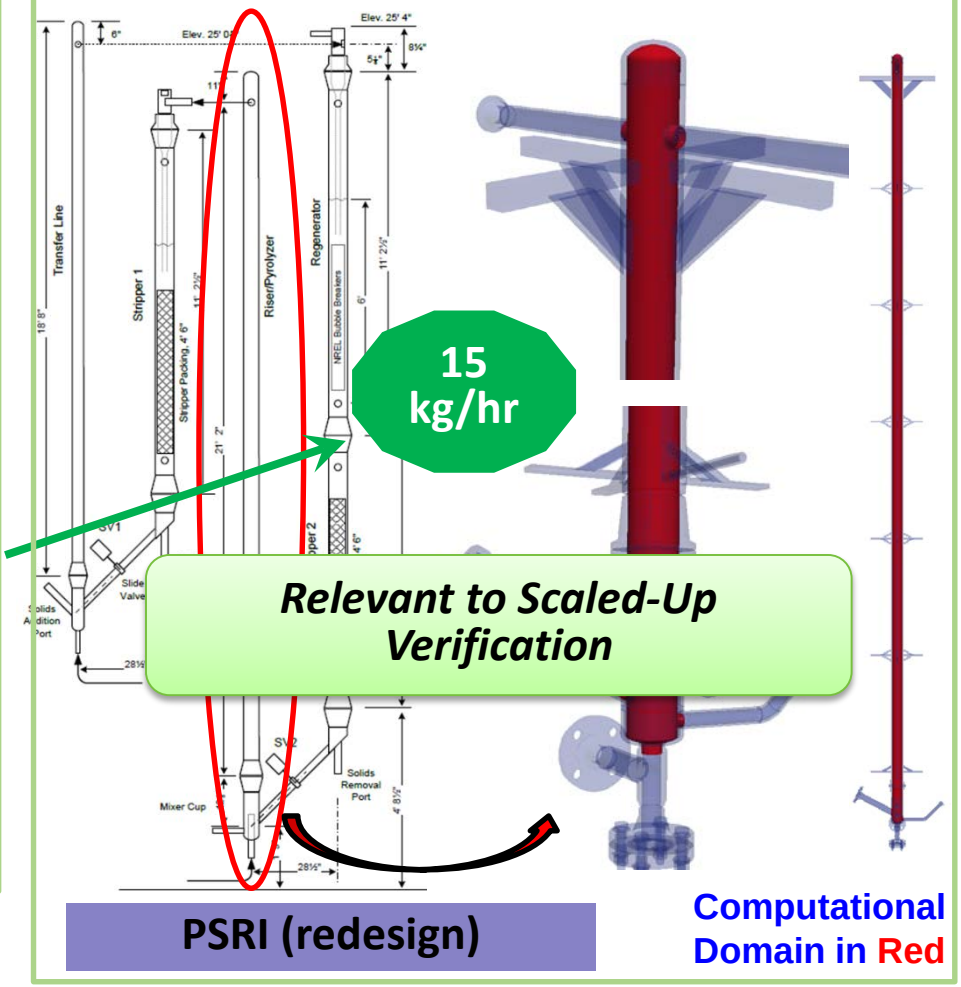


2 kg/hr

WR Grace

Relevant to Industry

TCPDU R-Cubed Upgrader*



15 kg/hr

Relevant to Scaled-Up Verification

PSRI (redesign)

Computational Domain in Red

***All (3) Reactors at NREL**

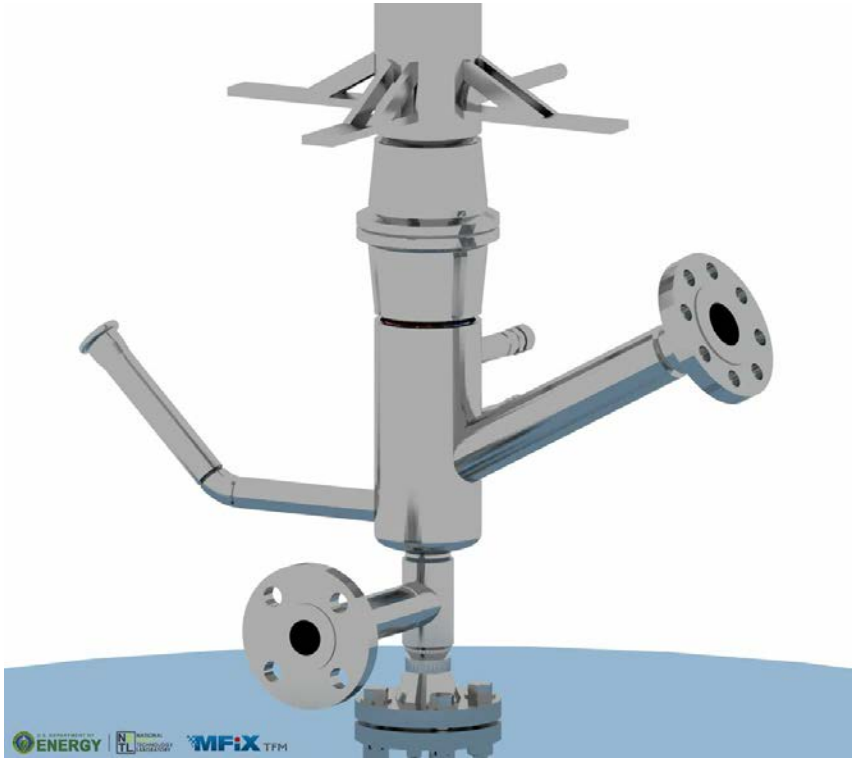
Stretch Annual Milestone LINKED with Integration and Scale-Up (WBS 2.4.1.301)

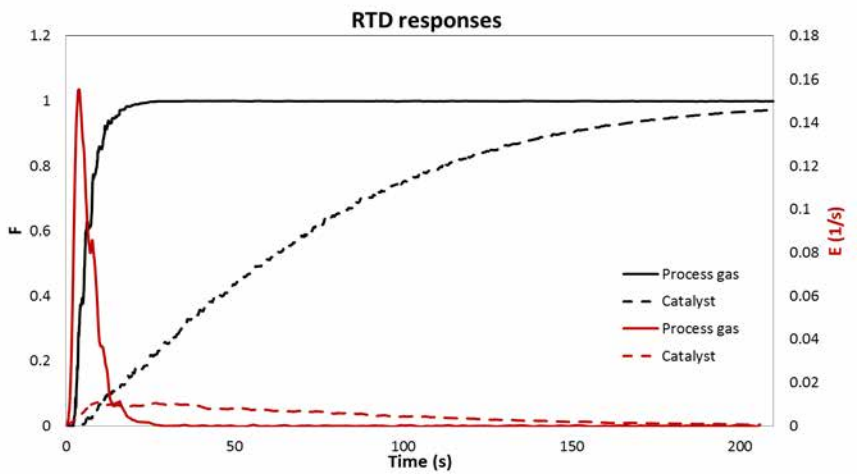
Progress To-Date: Physics of catalyst flow in R-Cubed riser captured via MFiX model

Objective: Accelerate commissioning of R-cubed riser reactor.

Accomplishments:

- Constructed initial R-cubed model in MFiX based on collaboration with Integration and Scale Up
- Currently using model to investigate impact of process conditions on residence time distributions of pyrolysis gases and catalyst solids





Predicted residence time response for solids and gases

Relevance: Simulations provide expectations on reactor performance ***prior*** to commissioning. Will enable faster commissioning and optimization.

Stretch Annual Milestone LINKED with Integration and Scale-Up (WBS 2.4.1.301)

Technical Approach: Challenges and Success Factors

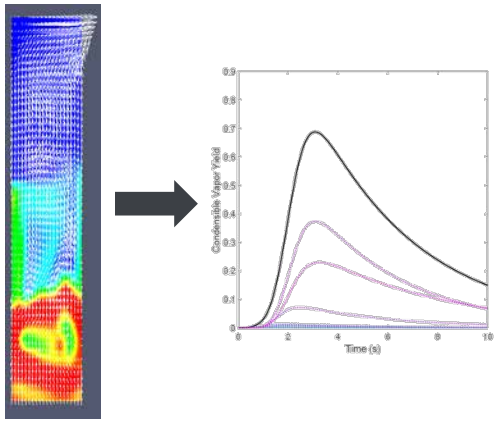
Process Modeling

Challenge

Enable vastly diverse biomass feedstock to be modeled ***efficiently*** across scales of processes to maintain yield and selectivity from bench to commercial scale

Critical Success Factors

Models that capture feedstock ***complexity*** and accurately predict reactor performance ***at multiple scales***



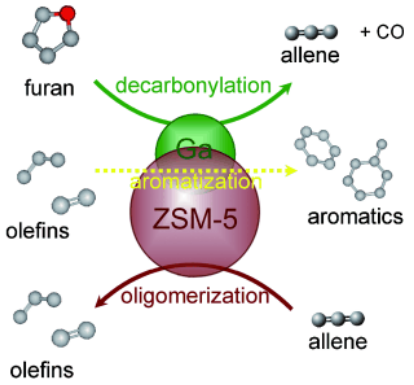
Catalysis Modeling

Challenge

Develop tools to ***quickly*** determine catalyst structure and surface chemistry reactions to enable synthesis of improved catalysts

Critical Success Factors

Predictions and testable hypotheses that ***accelerate*** ChemCatBio's synthesis of new catalysts with improved lifetime, activity, & selectivity



Technical Approach: Catalyst Models Cover Range of Materials

Mixed metal phosphides characterization

- Catalytic upgrading of pyrolysis products
- Correlate H and CO absorption energies with experimental observations to guide new catalyst discovery

RuSn active phase identification

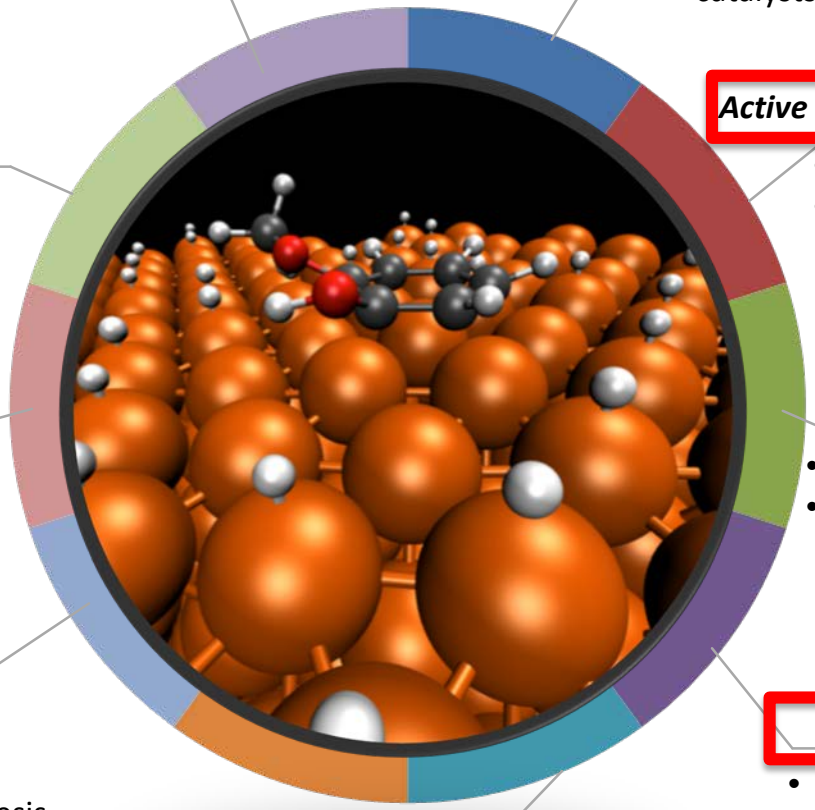
- Catalytic Upgrading of Sugars
- Identify opportunities to avoid poisoning of catalysts by Ni

Structural design of zeolites

- ChemCatBio
- Determine impact of explicit mesopores on mass transport in zeolites

Active phase for Cu-Beta hydrogenation

- ACSC & IDL
- Enhance alkane activation and increase yields of diesel/jet fuels from IDL



Supported metal catalyst design

- ACSC & IDL
- Design structure function relations to enhance HDO over metal catalysts

Understanding Mo_2C coke from batch to continuous feed

- ChemCatBio (CFP) & ACSC
- Comparing H and aromatic absorption to answer experimental observation of coke formation under different reaction conditions

Tailoring dopants in zeolites

- CFP and Aqueous Reforming
- Design catalysts with improved activities and test these hypothesis

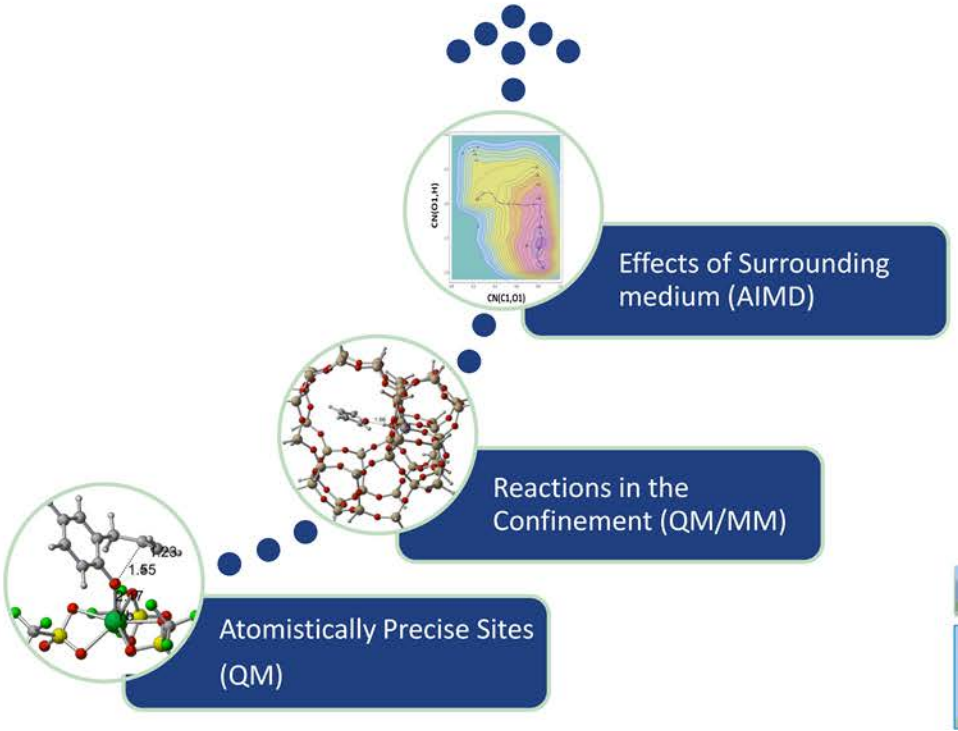
Optimize catalytic activity of Mo_2C

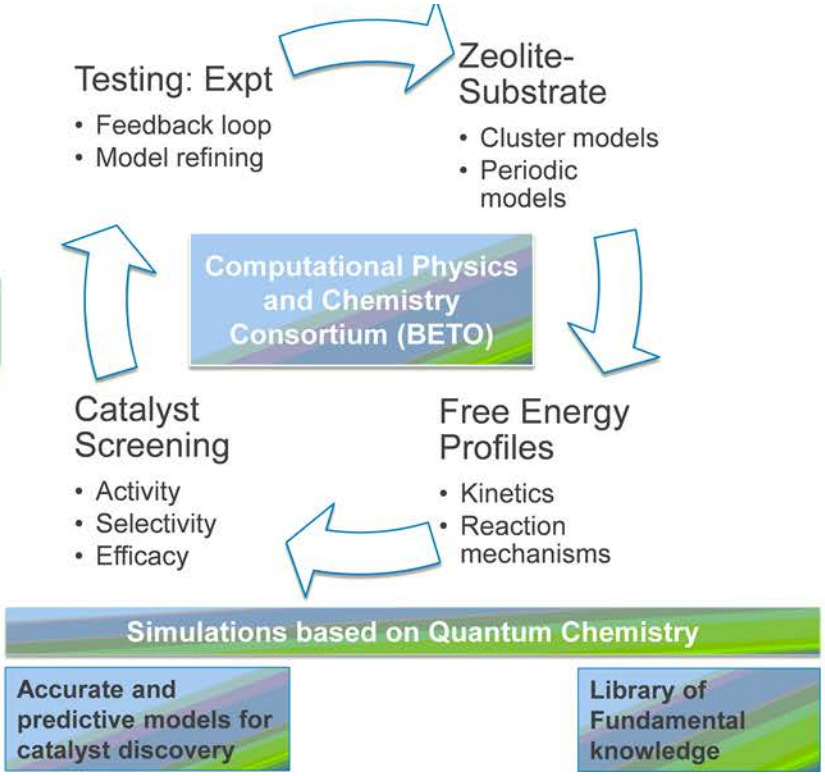
- ChemCatBio (CFP)
- Reactivity of Ni* or /Ca* doped Mo_2C surfaces towards hydrogenation - 'Carbon-Carbon' coupling balance in the vapor phase

Controlling solvophilicity

- FP + upgrading
- Reduce gunking in HT reactors

Technical Approach: Models for Catalysis Design





Atomistic simulations using static to dynamic models to support CCB:

- ***Understand*** catalyst activity and yield selectivity
- ***Guide*** new catalyst syntheses (ACSC)
- ***Optimize*** reactor conditions

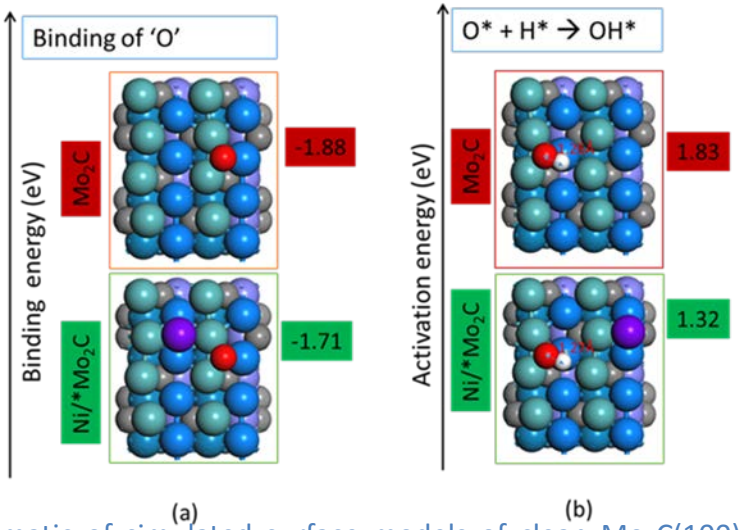
Accomplishments: Designing more effective Mo_2C catalysts

Objective: Provide guidelines to improve the Mo_2C catalysts for the upgrading of bio-oil

Accomplishment:

- Developed DFT models of Mo_2C and Ni/Mo_2C catalytic sites
- Investigated thermodynamics and kinetics of sorption and desorption of intermediates (O, OH, H_2O) on various sites
  - crucial step in the deactivation of catalysts

Presence of Ni improves stability of Mo_2C via decreasing catalytic deactivation



Schematic of simulated surface models of clean Mo_2C(100) and Nickel doped Mo_2C catalysts for (a) binding energies of 'O' and (b) activation energy required to form OH species in the gas phase

Relevance: Screening a wider parameter space of dopants to improve catalysts by promoting desired reactions (deoxygenation, C-C coupling) will reduce catalyst discovery time and cost.

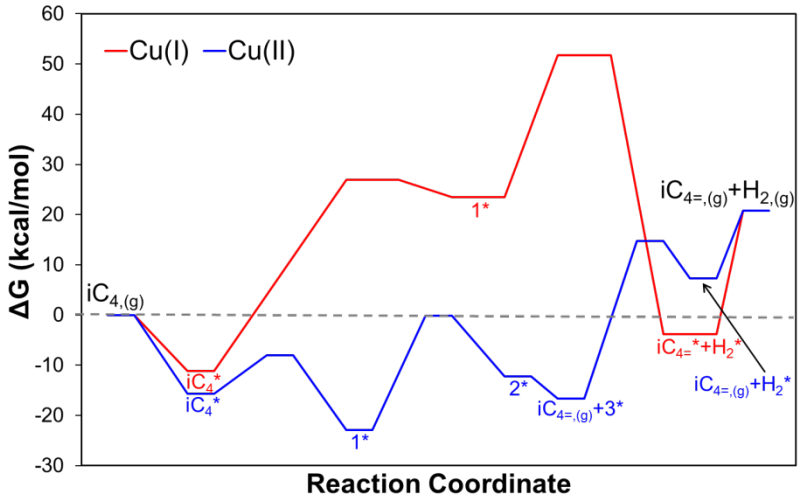
Biomass Feedstock → Pyrolysis → Vapor Phase Upgrading → Liquid Phase Upgrading

Accomplishments: Identified active site and mechanism for C4 product upgrading with beta zeolite

Objective: With IDL and ACSC identify the active site structure responsible for low-temperature alkane activation in Cu-Beta.

Accomplishment:

- Using DFT, identified the location, oxidation state, and reactivity of isobutane dehydrogenation over Cu-Beta
- In isolated Al-acid sites, copper is located in the wall of the straight channels of Beta zeolite in the +1 oxidation state – consistent with experimental results.
- Model predicts if framework aluminums are located in pairs, Cu(II) would be the preferred active site with all barriers below the exit channel (ideal situation).



Comparison of Cu(I) – 1 Al, and Cu(II) – 2 Al sites for dehydrogenation of isobutane in Cu-Beta

Relevance: Consistency between modeling and experiment has set the groundwork for computationally guided catalyst design. Recent work[1] suggests that Al-pairing can be tuned over a wide range and opens this up as a potential new knob in the synthesis toolbox going forward.

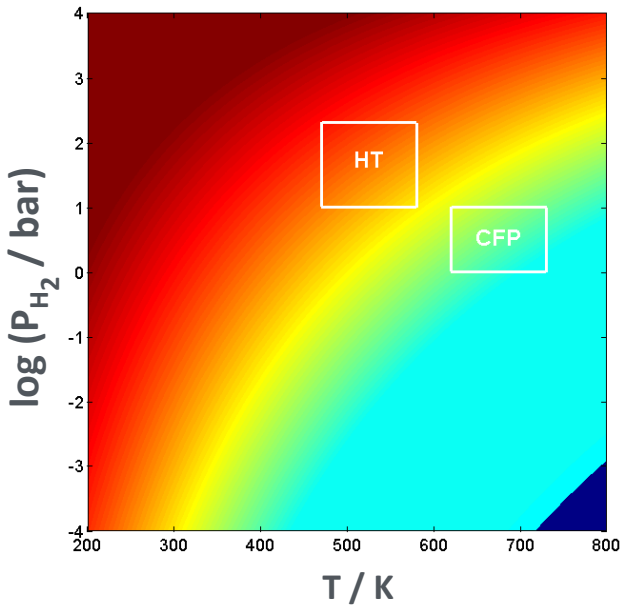
[1]Pashkova, J. *Chemistry - A European Journal* **2016,** 3937.

Accomplishments: Developed a tool for identifying catalytic surfaces under reaction conditions

Objective: Develop a quick-turnaround tool that can show the thermodynamic state of a catalyst surface under experimental reaction conditions.

Accomplishment:

- Developed a web-based tool (Surface Phase Explorer,* www.spe.nrel.gov) that can provide phase diagrams and absorption profiles under reaction conditions
- Focus on thermochemistry reduces computational costs, resulting in quick turnaround for experimental teams (weeks, not months).
- SPE is being used (or has been used) on 6 different projects to date – both biochem and thermochem applications.



Hydrogen coverage on Rh_2P. Boxes highlight experimentally relevant regimes.

Relevance: Reduced computational costs and fast turnaround allows the CCPC to impact multiple catalyst design projects without worry of resource dilution. This capability brings computational modeling one step closer to being a standard tool in the catalyst designers toolbox akin to NH_3 TPD or X-ray characterization techniques.

CCPC Publication: Ferguson et al., *J. Phys. Chem. C*, Vol. 120, 2016, pp. 26249-26258

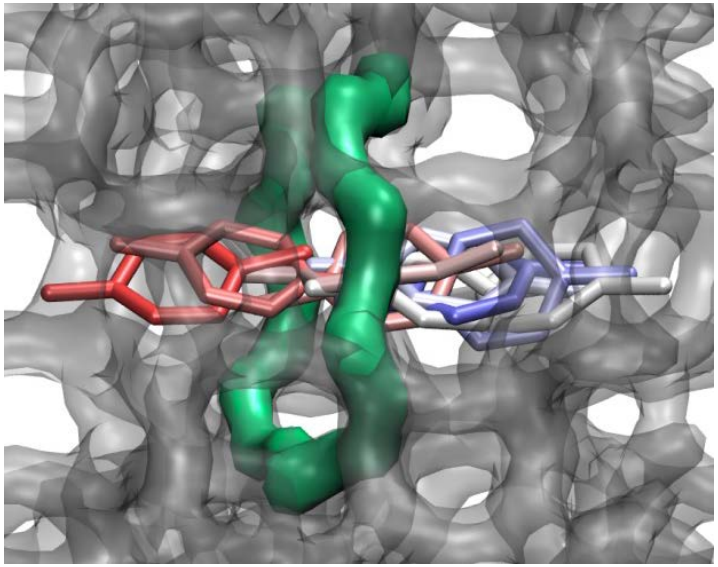
Biomass Feedstock → Pyrolysis → Vapor Phase Upgrading → Liquid Phase Upgrading

Accomplishments: Providing in-silico diffusivity measurements for porous materials

Objective: Develop a rapid use model of zeolite mass transport for use by experimental partners

Accomplishment:

- Developed an effective method for computationally measuring diffusivity in micro and mesopores of zeolites
- Method has been used to determine diffusivity of multiple pyrolysis-relevant species
  - Cannot be experimentally determined
- Constructed catalyst particle models (similar to biomass particle models) that can be used for screening of conditions and inclusion of coking/pore blocking



Frame depicting the transport of xylene through a pore in HZSM-5.

Relevance: Zeolites are ubiquitous in catalysis, yet mass transport in these systems is poorly explored. The combination of the modeling scales will provide an efficient means of investigating mass transport, including guiding synthesis to include mesopores to maximize access to catalytic sites and reduce mass loss to coking.

CCPC Publication: Bu et al., *J. Phys. Chem. C*, DOI 10.1021/acs.jpcc/6b10871

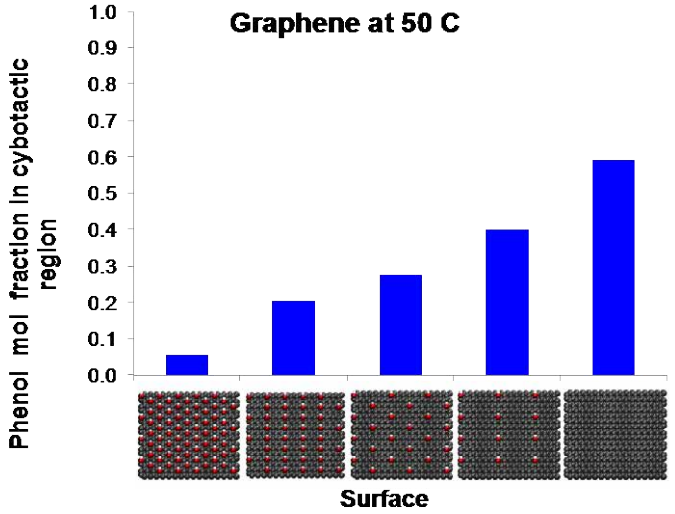
Biomass Feedstock → Pyrolysis → Vapor Phase Upgrading → Liquid Phase Upgrading

Accomplishments: Control of catalyst solvophilicity can improve conversion

Objective: Optimize catalyst conversion by controlling solvophilicity of catalyst surface

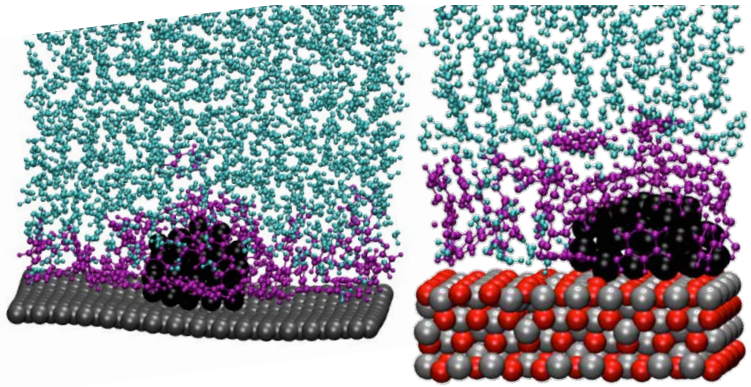
Accomplishment:

- Simulated the kinetics and thermodynamics of catalysts in multicomponent solvents with sufficient detail to capture conversion dependence on
  - Temperature and composition of fluid phase
  - Composition of the support (hydro or lipophilic)
  - Size of metal particles



lipophilic hydrophilic

Relevance: Project has motivated and guided a cross-laboratory effort to synthesize (ACSC/NREL) new catalysts with controlled solvophilicity which will be tested in hydrotreating reactors (CCB/PNNL) to gauge impact on fouling



CCPC Publication: Cantu et al., *Catal. Today*, **2016**, http://dx.doi.org/10.1016/j.cattod.2016.08.025

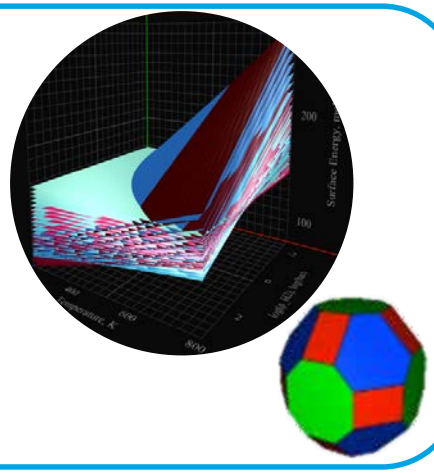
Biomass Feedstock → Pyrolysis → Vapor Phase Upgrading → Liquid Phase Upgrading

Relevance: Catalyst modeling accelerates discovery

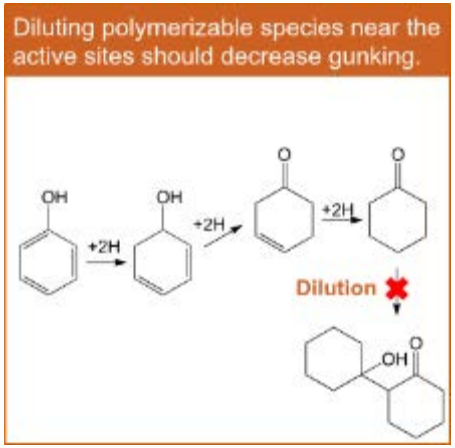
Collaborative projects with ChemCatBio result in:

Understanding of catalyst active sites (structure-function relations) and deactivation/fouling mechanisms

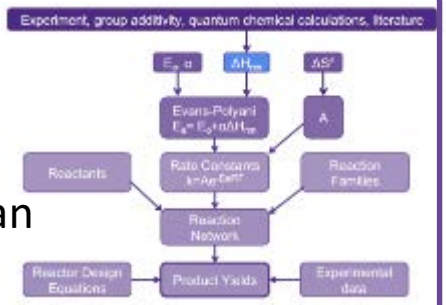
Tool development that has led to faster turnaround and higher impact on experimental projects



Guiding catalyst discovery through testable hypotheses



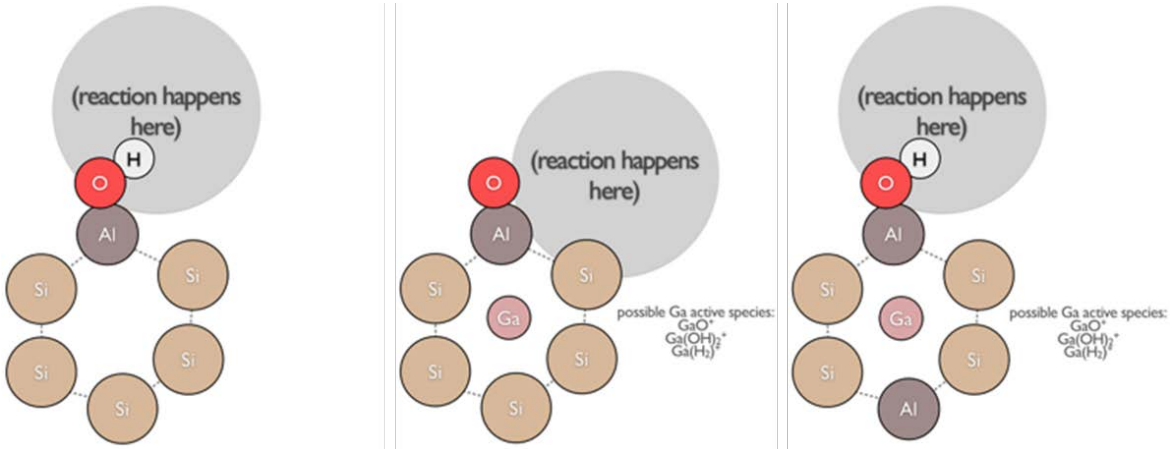
Process optimization based on computationally derived kinetics and mass transport that can link catalyst design to reactor models



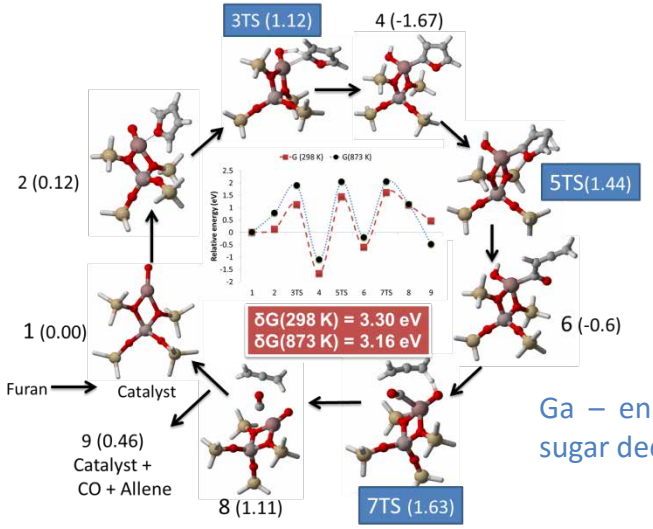
Modeling accelerates catalyst discovery for lower cost, more durable catalysts

Future Work: Enhancement of zeolites with Lewis metals to tailor reactivity

- Investigate influence of extra-framework Lewis metals on catalyst reactivity on both Brønsted and Lewis reactivity
- Develop database of model reactions to increase responsiveness to new experimental requests



Possible interactions between Lewis and Brønsted reactive centers.



Ga – enhanced reactivity for sugar decarbonylation.

Quarterly Milestone Linked to FY18 ChemCatBio Milestones

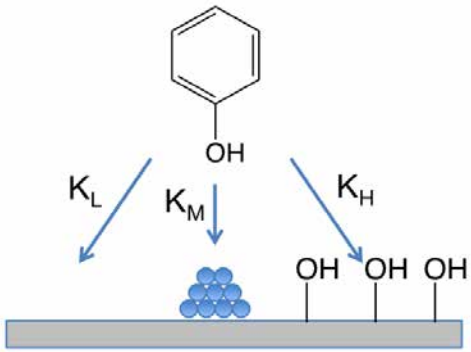
Future Work: Catalysis modeling of complex liquid phase upgrading

- Construction of **ab-initio** microkinetic models for LPU including
  - Particle size and support effects
  - Temperature effects
  - Species concentration

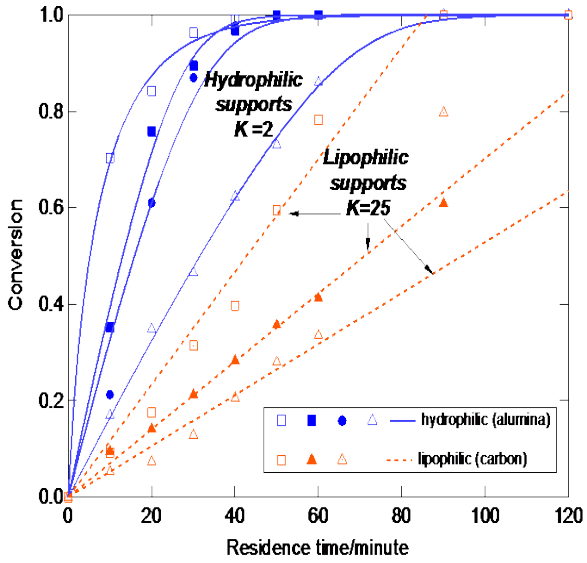
- Positions us for reactive CFD on bench and demo scale with higher fidelity than can be achieved with macrokinetics

- Direct comparison of theory predictions with experiment, 2nd generation model for enhanced performance and refined hypotheses

- The data can be used to avoid Edisonian serial research



$$\frac{K_M}{K_L} \simeq 3 \ll \frac{K_M}{K_H} = 70$$



Quarterly Milestone supporting Liquid Phase Upgrading experiments

Future work: Multiscale modeling of zeolite transport and deactivation to enhance access to active sites

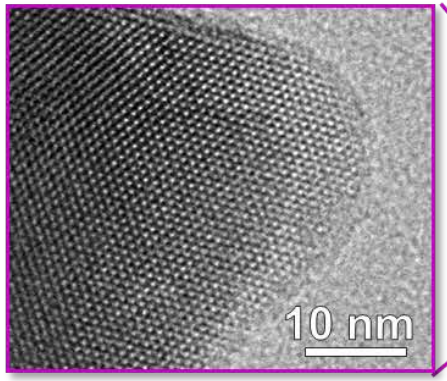
Molecular Scale

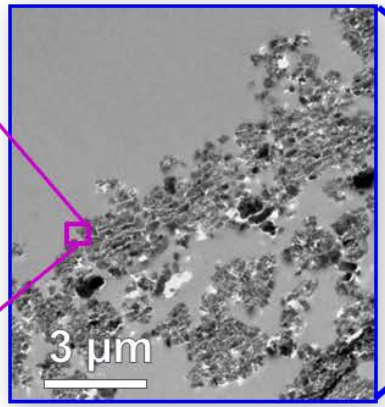
Micro/Meso Scale

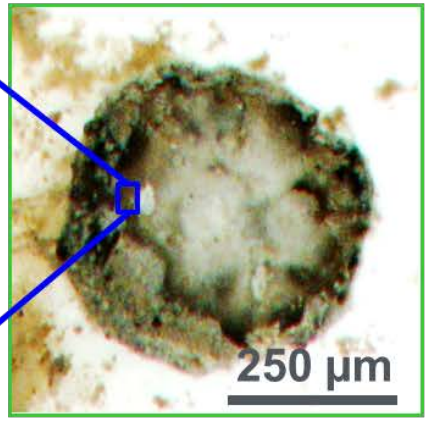
Whole-Particle Scale

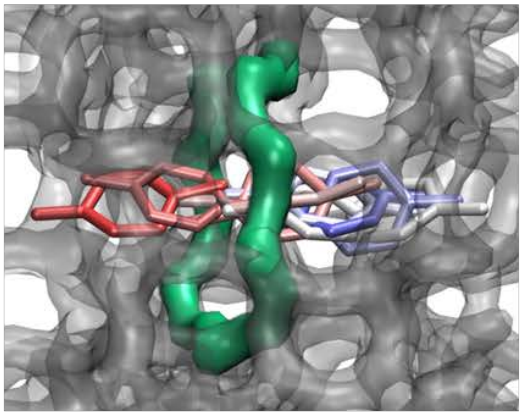
ACSC

CCPC

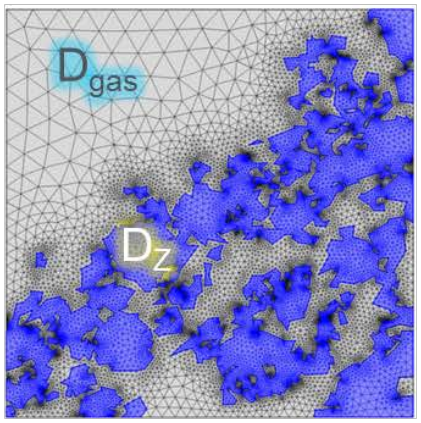




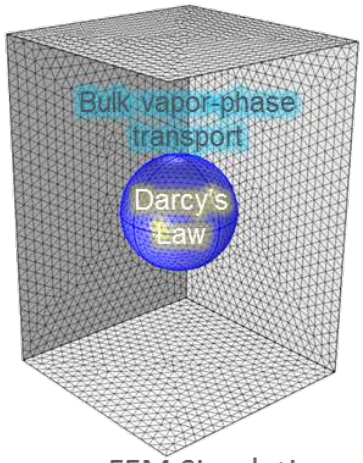




Molecular dynamics to estimate D_Z



FEM simulations reaction/diffusion to estimate permeability

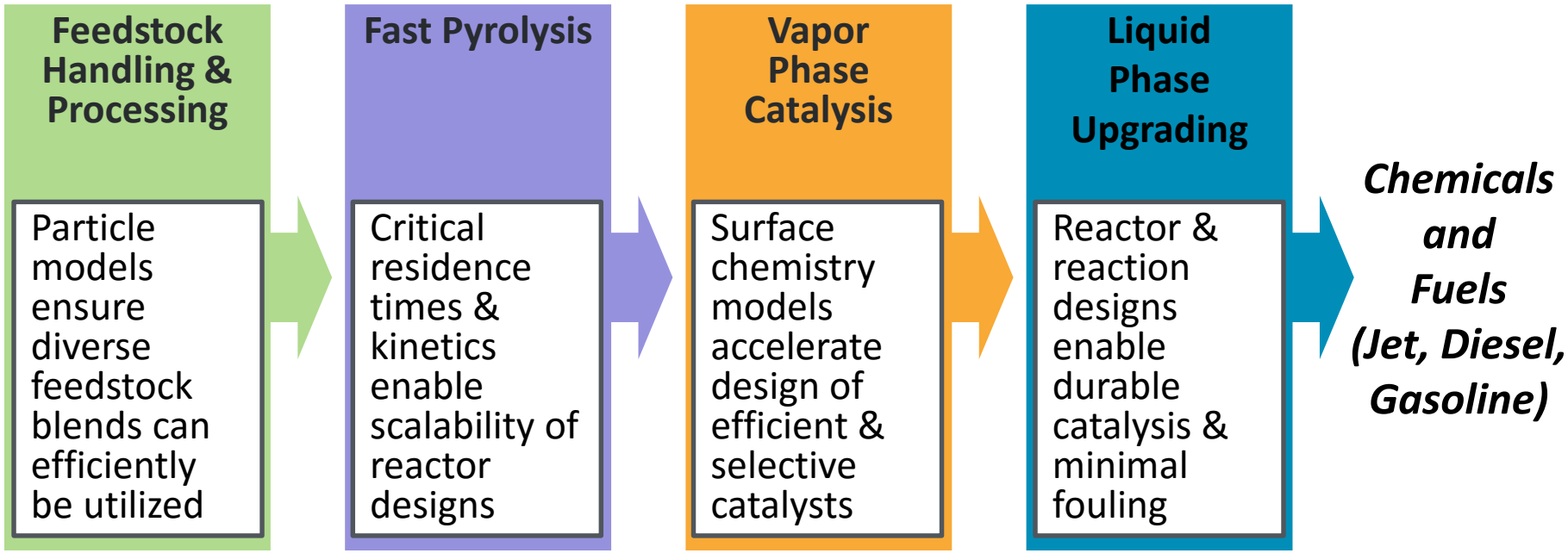


FEM Simulations reaction/convection/diffusion with Darcy's Law

Quarterly Milestone LINKED to Milestone on Advanced Catalyst Synthesis and Characterization

Summary: Models span scale and complexity to accelerate cost-effective biomass-to-fuel processes

Approach: key inputs from Industry Advisor Panel and technical community plus close-coupling to experimentalists enables success



Relevance: accelerating deployment of biomass conversion technologies through process and catalysis modeling

- **30 publications and 29 presentations (since last Peer Review)***
- Tech transfer via web tools and key parameter input to modeling codes

*Publication/presentation lists in additional slides

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Brandon Knott

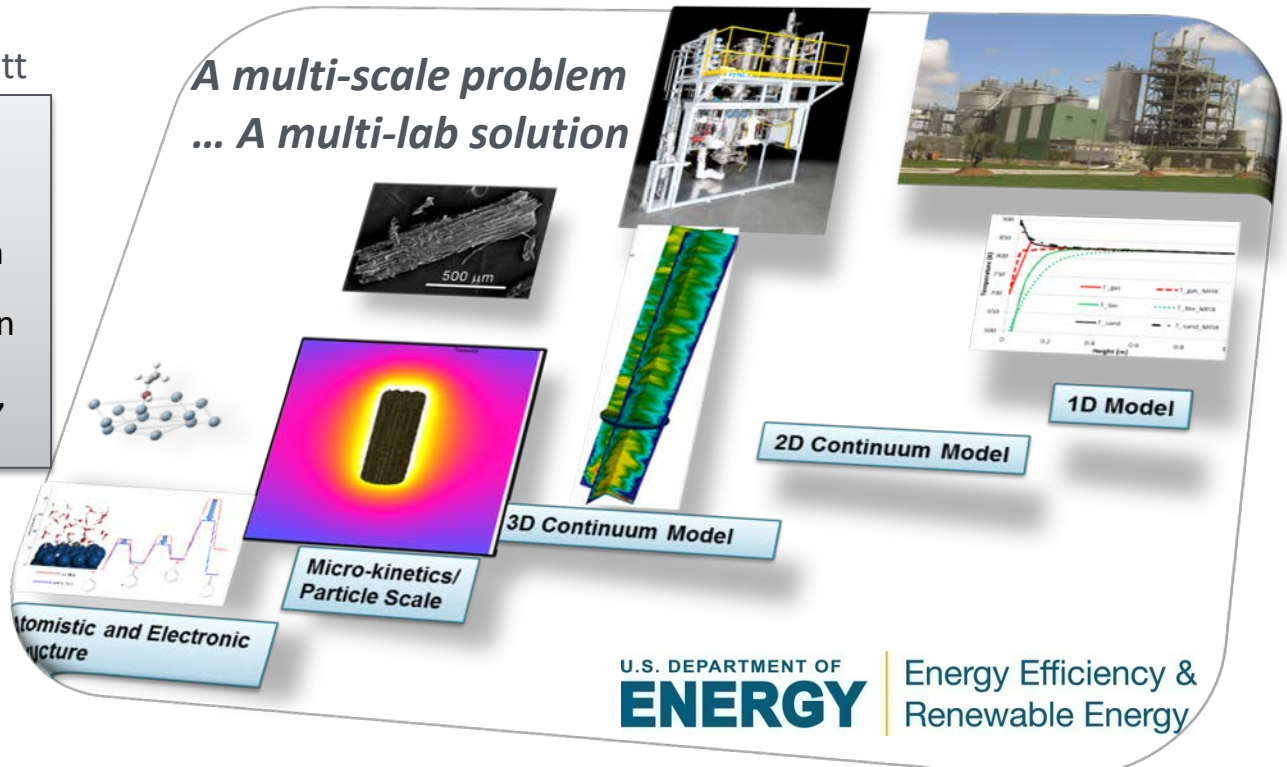
Roger Rousseau
Bob Weber
Vanda Glezakou
David Cantu
Asanga Padmaperuma

Bill Rogers
Madhava Syamlal
Tingwen Li
Dirk VanEssendelft
Balaji Gopalan

Larry Curtiss
Rajeev Assary
Lei Cheng
Cong Liu
Dale Pahls

Industry Advisory Panel

David Dayton (RTI), George Huff (MIT, retired BP), Jack Halow (Separation Design Group), Mike Watson (Johnson Matthey), Randy Cortright (formerly Virent Energy Systems), Richard Quann (ExxonMobil), Steve Schmidt (WR Grace), Tom Flynn (Babcock & Wilcox), Rick Wessel (Babcock & Wilcox)



ChemCatBio
Chemical Catalysis for Bioenergy

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

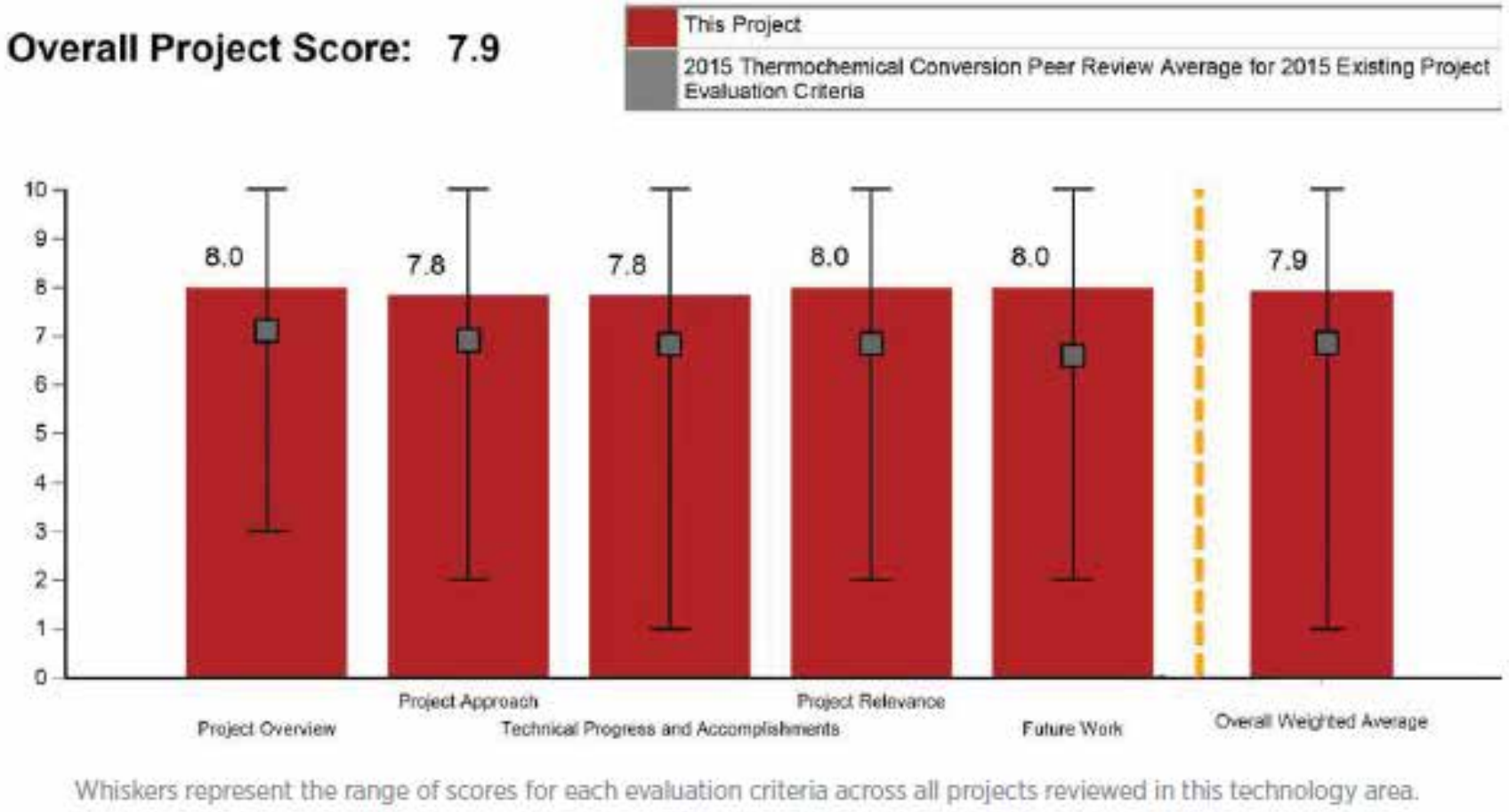
Additional Slides

Contents of Additional Slides

- Responses to 2015 Reviewers' Comment
- Project Timeline: CCPC History and Path to Success
- Go/No-Go Review [August 2016]
- Publications (since 2015 Peer Review)
- Presentations (since 2015 Peer Review)
- Commercialization & Technology Transfer
- Milestones
- List of Collaborating BETO Projects
- List of Collaborators and Partners
- Industry Advisory Panel Expertise Matrix

Responses to 2015 Reviewers' Comments (1/6)

- Overall, project scored well during 2015 Peer Review



Note: The 2015 Peer Review Report is publicly available at https://energy.gov/eere/bioenergy/2015-project-peer-review (the CCPC project is on pages 352-353)

Responses to 2015 Reviewers' Comments (2/6)

Generally Positive Comments (from 2015 Peer Review):

- *"Clearly, a well-planned and coordinated effort that will help establish technical fundamentals, which can be leveraged by others."*
- *"The consortium provides a very useful way to focus the computational capabilities of the laboratories on biomass problems."*
- *"The inclusion of an external advisory committee with significant industry representation is a very useful way to keep this group focused."*
- *"Excellent program that brings modeling/computing technical expertise to this field to identify critical science, engineering, and economic critical issues and directions. Very critical to have modeling aid in the scale-up of a new process technology. Brings together a larger organization and communication across the laboratories."*

CCPC Response/Actions:

- Keep our collaborative approach and coordination
- Keep utilizing the valuable external industry advisory committee

Responses to 2015 Reviewers' Comments (3/6)

Comments on Scope (from 2015 Peer Review):

- *"It seems scope of the project is way too large; might be better to concentrate on two or three areas."*
- *"The consortium should determine sooner rather than later which approaches have the most promise and focus on them."*
- Regarding *"broad-scoped approach"…"It [the project] now needs to work toward a focused outcome, otherwise its value to subsequent projects is diluted."*

CCPC Response/Action:

- The project has continued to be broad in scope, and we agree that poses a challenge with regard to maintaining focus on a concentrated set of deliverables. However, funding resources have been able to support our broad scope, and active program management by DOE has enabled the most promising results to be moved forward. Adjustments have been made to resource distribution (see Go/No-Go slides) in this regard. Also, the Industry Advisory Panel has been quite helpful in maintaining focus on the critical outcomes from the project tasks.

Note: Response/Action continued on next slide

Responses to 2015 Reviewers' Comments (4/6)

Comments on Scope (from 2015 Peer Review):

CCPC Response/Action (continued from previous slide):

- For process modeling tasks, we focused a significant portion of our efforts in the last two years pyrolysis step (i.e. significant reduction in VPU reactor modeling) resulting in a win for modeling pine pyrolysis. Going forward we are rebalancing resources to again make VPU a priority and are leveraging lessons learned from the pyrolysis modeling effort.
- For the catalyst design tasks, we have been setting up those tasks to become a standard tool (similar to DRIFTS or TPD) that experimental teams can use for their catalyst design work. As such, many of our catalyst design projects are short, focused efforts to answer well defined questions and our aim is fast turnaround and impact (months). We only maintain a few (1-2) long term projects on catalyst design that extend past a single fiscal year.

Responses to 2015 Reviewers' Comments (5/6)

Comment on Experimental Ties (from 2015 Peer Review):

- *"Modeling work also needs to be tied directly to projects on experimental results so that the two can work synergistically together."*

CCPC Response/Actions:

- Excellent comment. We have increased our engagement with experimental projects, and each CCPC task is now collaborating closely with multiple projects. In addition, "joint" and "linked" milestones between CCPC and experimental projects further combine efforts between modeling and experimental activities in BETO.

Responses to 2015 Reviewers' Comments (6/6)

Comment on Catalytic Pyrolysis (from 2015 Peer Review):

- *"One of the issues facing catalytic pyrolysis is determining which reactions are catalytic and which are not. Will the modeling work address this?"*

CCPC Response/Actions:

- Yes. While most of our activities are focused on separate pyrolysis and catalytic upgrading processes, defining which pyrolysis reactions are catalytic is part of our approach. Furthermore, the catalytic effects of ash can affect pyrolysis yields and needs further study/definition (literature sparse related to ash effects); our project is addressing this issue which is critical for enabling effective utilization of herbaceous feedstocks.

Project Timeline: CCPC History and Path to Success

Collaborations Began

Initiated multi-NL collaboration on modeling

2015 Peer Review

- Demonstrated 3D biomass particle models for heat transfer
- Validated hydrodynamics of pyrolysis reactor
- Constructed preliminary model of DCR riser VPU

Project Start

CCPC 3-year project started building off of initial collaboration

Peer Review Feedback

Focused efforts on pyrolysis in response to reviewer 'dilution' comment

End of 3-year project cycle

- Demonstrate pyrolysis predictions across multiple reactors and feedstocks
- Validate VPU models
- Address 'kinetics' risk

Aug. 2016 (mid-cycle Go-NoG review passed → "Go")

- Validated 1D particle models that capture 3D heat transport effects
- Combined 1D particle, kinetic, and reactor models to predict moisture and particle size distribution effects on bio-oil yield.
- Kinetic models are major source of uncertainty

FY17

- Brought in NETL to work on VPU reactors
- Follow success of pyrolysis approach to VPU (combine particle, kinetic, and reactor modeling with validation against multiple systems at NREL).

Goal for 2022

- Al a carte modeling tools that are publicly available to predict performance of pyrolysis, ex situ and in situ CFP
- Address kinetics issue for CFP
- Link to LPU/Hydrotreating for unified modeling toolset
- Explore advanced issues with modeling (aerosols, reactor coking/plugging, etc) as motivated by IAB

Go/No-Go Review [August 2016] (1/3)

On August 2, 2016, a Go/No-Go review of the CCPC was conducted.

The Criteria for the Go/No-Go review were:

1) Using particle scale modeling and reactor simulations, demonstrate ability to predict pyrolysis oil yields from a fast pyrolysis reactor;

2) Show two examples (one VPU, one LPU) in which modeling has been used to inform an experimental BETO project.

The results from the Go/No-Go review were:

"Conditional Go"; rescope (Criterion 2B) and redistribution of funds required for FY17.

Go/No-Go Review [August 2016] (2/3)

Specific directions from the Go/No-Go review included:

Moving forward, criterion 1 and 2A should continue, and also consider expansion of scope in lieu of large LPU modeling efforts; significant redistributions of funding within CPC and rescope must be considered prior to the start of FY17's AOP, as this is necessary to support more value-add and relevant tasks. LPU modeling should be decreased to CPC's "minimum planning level" until experimentation can validate preliminary models, such that the feedback "cyclic-interconnected development continuum" loop closure can be demonstrated in a useful, transformative manner.

CCPC Actions in Response to Go/No-Go Review Feedback:

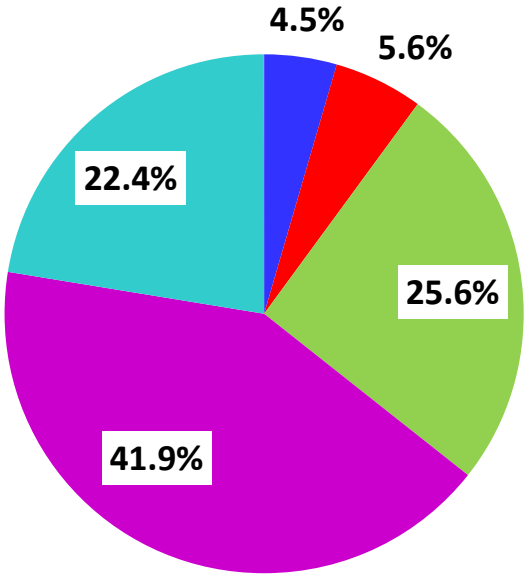
- The CCPC redistributed resources across the tasks and made significant funding additions to the Feedstock Impact Analysis task. Modest funding additions were also made for the Reactor Analysis and Scale-Up and Vapor Phase Upgrading (VPU) tasks.
- The Liquid Phase Upgrading (LPU) task was scaled back significantly. Recommendations from the LPU task were made to experimental teams, and the project is awaiting results from those experiments before next steps.

Graphs summarizing the resource redistribution are shown on the next slide

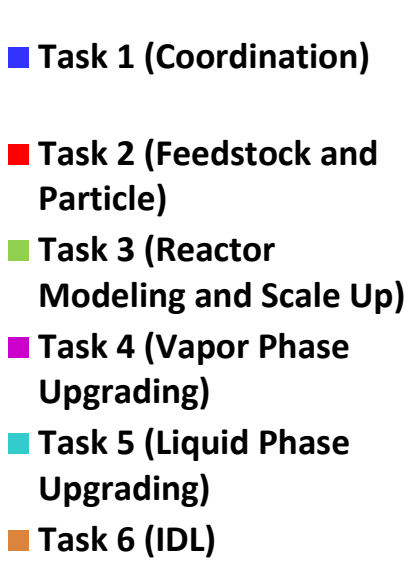
Go/No-Go Review [August 2016] (3/3)

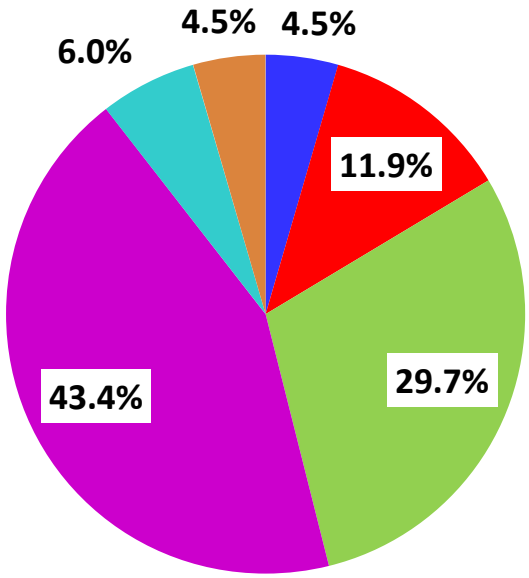
CCPC Actions in Response to Go/No-Go Review Feedback:

- Revised funding resource allocation for FY17 based on feedback



Original FY17 Task Resource Allocation





Revised FY17 Task Resource Allocation

Publications (since 2015 Peer Review) (1/3)

1. Clark, J. M.; Nimlos, M. R.; Robichaud, D. J, "Biomolecular Decomposition Pathways for Carboxylic Acids or Relevance to Biofuels", published *in Journal of Physical Chemistry A* 2015, **119**, 501. DOI: 10.1021/jp509285n
2. Ciesielski, P. N.; Crowley, M. F.; Nimlos, M. R.; Sanders, A. W.; Wiggins, G. M.; Robichaud, D.; Donohoe, B. S.; Foust, T. D, "Biomass Particle Models with Realistic and Resolved Microstructure for Simulations of Intrapartcile Transport Phenomena", 2015, **29**, 242-254, Published in *Energy and Fuels*. DOI: 10.1021/ef502204v.
3. Ferguson, G. A.; Cheng, L.; Bu, L.; Kim, S.; Robichaud, D. J.; Nimlos, M. R.; Curtiss, L. A.; Beckham, G. T., "Carbocation Stability in H-ZSM5 at High Temperature", Published in *Journal of Physical Chemistry A* 2015, **119**, 11397 -11405. DOI: 10.1021/acs.jpca.5b07025.
4. Kim, S.; Robichaud, D. J.; Beckham, G. T.; Paton, R. S.; Nimlos, M. R., "Ethanol Dehydration in HZSM-5 Studied by Density Functional Theory: Evidence for a Concerted Process", published in *Journal of Physical Chemistry A* 2015, **119**, 3604 - 3614. DOI: 10.1021/jp513024z.
5. Liu, C.; Evans, T. J.; Cheng, L.; Nimlos, M. R.; Mukarakate, C.; Robichaud, D. J.; Assary, R. S.; Curtiss, L. A., "Catalytic Upgrading of Biomass-Derived Compounds via C-C Coupling Reactions: Computational and Experimental Studies of Acetaldehyde and Furan Reactions in HZSM-5", published in *Journal of Physical Chemistry C* 2015, **119**, 24025 - 24035. DOI: 10.1021/acs.jpcc.5b08141.
6. Liu Yang, George Tsilomelekis, Stavros Caratzoulas, and Dionisios G. Vlachos, “Mechanism of Brønsted acid Catalyzed Glucose Dehydrogenation”, 2015, **8**, 1334-1341, published in *ChemSusChem* dx.DOI.org: 10.1002/cssc.201403264.
7. Robert Weber, Mariefel V. Olarte, Huamin Wang, “Modeling the Kinetics of Deactivation of Catalysts during the Upgrading of Bio-Oil”, published in *Energy&Fuels* 2015, **29**, 273-277. dx.doi.org/10.1021/ef502483t.
8. Buckingham, G. T.; Porterfield, J. P.; Kostko, O.; Troy, T. P.; Ahmed, M.; Robichaud, D. J.; Nimlos, M. R.; Daily, J. W.; Ellison, G. B., "The thermal decomposition of the benzyl radical in a heated micro-reactor. II. Pyrolysis of the tropyl radical", published in *Journal of Chemical Physics* 2016, 145. DOI: http://dx.doi.org/10.1063/1.4954895.
9. Clark, J. M.; Pilath, H. M.; Mittal, A.; Michener, W. E.; Robichaud, D. J.; Johnson, D. K., "Direct Production of Propene from the Thermolysis of Poly(β-hydroxybutyrate) (PHB). An Experimental and DFT Investigation", published in *The Journal of Physical Chemistry A* 2016, **120**, 332 - 345. DOI: 10.1021/acs.jpca.5b09246.
10. Stuart Daw, Gavin Wiggins, Qingang Xiong, and Emilio Ramirez. "Development of a Low-Order Computational Model for Biomass Fast Pyrolysis: Accounting for Particle Residence Time." ORNL/TM-2016/69 (2016).

Publications (since 2015 Peer Review) (2/3)

11. David C. Cantu, Yang-Gang Wang, Yeohoon Yoon, Vassiliki-Alexandra Glezakou, Roger Rousseau, Robert S. Weber, "Heterogeneous catalysis in complex, condensed reaction media", Published in *Catalysis Today*, 2016, http://dx.doi.org/10.1016/j.cattod.2016.08.025.
12. Ferguson, G. A.; Vorotnikov, V.; Wunder, N.; Clark, J.; Gruchalla, K.; Bartholomew, T.; Robichaud, D. J.; Beckham, G. T., "Ab Initio Surface Phase Diagrams for Coadsorption of Aromatics and Hydrogen on the Pt(111) Surface", published in *J. Phys. Chem. C* 2016, **120**, 26249-26258. DOI: 10.1021/acs.jpcc.6b07057.
13. Gavin M. Wiggins, Peter N. Ciesielski, and C. Stuart Daw. "Low-Order Modeling of Internal Heat Transfer in Biomass Particle Pyrolysis." published in *Energy & Fuels*, 2016, **30**, 4960-4969. DOI: 10.1021/acs.energyfuels.6b00554.
14. Griffin, MB; Ferguson GA; Ruddy, DA; Biddy, MJ; Beckham, GT; Schaidle, JA, "Role of the Support and Reaction Conditions on the Vapor-Phase Deoxygenation of m-Cresol over Pt/C and Pt/TiO2 Catalysts," published in *ACS Catalysis* 2016, **6**, 2715-2727. doi:10.1021/acscatal.5b02868.
15. Kim, S.; Evans, T. J.; Mukarakate, C.; Bu, L.; Beckham, G. T.; Nimlos, M. R.; Paton, R. S.; Robichaud, D., "Furan Production from Glycoaldehyde over HZSM-5", Published in *ACS Sustainable Chemistry and Engineering* 2016, **4**, 2615 - 2623. DOI: 10.1021/acssuschemeng.6b00101.
16. Kumbhani, S. R.; Cline, T. S.; Killian, M. C.; Clark, J. M.; Keeton, W. J.; Hansen, L. D.; Shirts, R. B.; Robichaud, D. J.; Hansen, J. C., "Erratum to "Water Vapor Enhancement of Rates of Peroxy Radical Reactions", Published in *International Journal of Chemical Kinetics* 2016, **47**, 395-409. DOI: 10.1002/kin.21002.
17. "Kumbhani, S. R.; Cline, T. S.; Killian, M. C.; Clark, J.; Keeton, W.; Hansen, L. D.; Shirts, R. B.; Robichaud, D. J.; Hansen, J. C., ""Response to the Commenton Paper "Water vapor Enhancement of Rates of Peroxy Radical Reactions", published in *International Journal of Chemical Kinetics* 2016, **48**, 395. DOI 10.1002/kin.21001."
18. Schaidle, J. A.; Blackburn, J.; Farberow, C. A.; Nash, C.; Steirer, K. X.; Clark, J.; Robichaud, D. J.; Ruddy, D. A., "Experimental and Computational Investigation of Acetic Acid Deoxygenation over Oxophilic Molybdenum Carbide: Surface Chemistry and Active Site Identity", Published in *ACS Catalysis* 2016, **6**, 1181 - 1197. DOI: 10.1021/acscatal.5b01930.
19. Qingang Xiong, Jingchao Zhang, Fei Xu, Gavin Wiggins, and C. Stuart Daw. "Coupling DAEM and CFD for simulating biomass fast pyrolysis in fluidized beds." *Journal of Analytical and Applied Pyrolysis*, 2016, **117**, 176-181. http://dx.doi.org/10.1016/j.jaap.2015.11.015.

Publications (since 2015 Peer Review) (3/3)

20. Q .Xiong, F. Xu, E. Ramirez, S. Pannala, C.S. Daw, "Modeling the impact of bubbling bed hydrodynamics on tar yield and its fluctuations during biomass fast pyrolysis", published in *Fuel*, 2016, **164**, 11-17. http://dx.doi.org/10.1016/j.fuel.2015.09.074
21. Robinson, A; Ferguson, GA; Gallagher, JR; Cheah, S; Beckham, GT; Schaidle, JA; Hensley, JE, Medlin, JW, "Enhanced Hydrodeoxygenation of m-Cresol over Bimetallic Pt–Mo Catalysts through an Oxophilic Metal-Induced Tautomerization Pathway," published in *ACS Catalysis* 2016, **6**, 4356-4368. doi: 10.1021/acscatal.6b01131.
22. Xu, M.; Mukarakate, C.; Robichaud, D. J.; Nimlos, M. R.; Richards, R. M.; Trewyn, B. G., "Elucidating Zeolite Deactivation Mechanisms During Biomass Catalytic Fast Pyrolysis from Model Reactions and Zeolite Syntheses", Published in *Topics in Catalysis* 2016, **59**, 73-85. DOI: 10.1007/s11244-015-0507-5.
23. Drouin, B. J.; Benner, D. C.; Brown, L. R.; Cich, M. J.; Crawford, T. J.; Devi, V. M.; Guillaume, A.; Hodges, J. T.; Mlawer, E. J.; Robichaud, D. J.; Oyafuso, F.; Payne, V. H.; Sung, K.; Wishnow, E. H.; Yu, S., "Multispectrum analysis of the oxygen A-band", published in *Journal of Quantitative Spectroscopy and Radiative Transfer* 2017, **186**, 118-138. http://dx.doi.org/10.1016/j.jqsrt.2016.03.037.
24. E. Ramirez, C.E.A. Finney, S. Pannala, C.S. Daw, J. Halow, Q. Xiong, "Computational study of the bubbling-to-slugging transition in a laboratory-scale fluidized bed", published in *Chem. Eng. J.* (Amsterdam, Neth.), 2017, **308**, 544-556. http://dx.doi.org/10.1016/j.cej.2016.08.113
25. Foust, T.; Ziegler, J.; Pannala, S.; Ciesielski, P.; Nimlos, M.; Robichaud, D., "Predictive Model for Particle Residence Time Distributions in Riser Reactors, Part 1.: Model Development and Validation", published in *ACS Sustainable Chemistry & Engineering* 2017. doi: 10.1021/acssuschemeng.6b02384.
26. Lintao Bu, Mark R. Nimlos, David J. Robichaud, Seonah Kim, "Diffusion of biomass pyrolysis products in H-ZSM-5 by molecular dynamics simulations", published in *J. Phys. Chem. C*, 2017, **121**, 500-510. DOI: 10.1021/acs.jpcc.6b10871.
27. Mingxia Shou, Lei Cheng, Bin Lu, Larry A. Curtiss, R. S. Assary, "Role of Ga sites on furan decarbonylation over Ga/ZSM-5 – A first-principle investigation, submitted to *ACS Sustainable Chemistry and Engineering* Jan 2017.
28. Pecha, M. B.; Garcia-Perez, M.; Foust, T. D.; Ciesielski, P. N., "Estimation of Heat Transfer Coefficients for Biomass Particles by Direct Numerical Simulation Using Microstructured Particle Models in the Laminar Regime", published in *ACS Sustainable Chemistry & Engineering* 2017, **5**, 1046-1053. DOI: 10.1021/acssuschemeng.6b02341.
29. Larissa Kunz, Ryan McDonough, Lintao Bu, Robin Cywar , Matthew Y. Yung, Gina Chupk, Cong Liu, Ryan Patalano, Kristiina Iisa, Mark R. Nimlos, Rajeev S. Assary, Larry A. Curtiss, Seonah Kim , David J. Robichaud, "Kinetic Determination of Alcohol Dehydration to Olefins over Zeolites", 2017 submitted to *Journal of Physical Chemistry*
30. Farberow, C. A.; Cheah, S.; Kim, S.; Miller, J. T.; Gallagher, J. R.; Hensley, J. E.; Schaidle, J. A.; Ruddy, D. Exploring low-temperature dehydrogenation at ionic Cu sites in beta zeolite to enable alkane recycle in dimethyl ether homologation. 2017 *ACS Catalysis* (submitted)

Presentations (since 2015 Peer Review) (1/3)

1. Robert Weber, “Modeling the Kinetics of Deactivation of Catalysts during the Upgrading of Bio-Oil” presented at the 4th International Workshop on Bioenergy and Biofuels.
2. Mark Nimlos and Robert Weber, “Strike a happy medium: Identifying appropriate reaction conditions for upgrading bio-oil”, 249th ACS National Meeting, Denver, CO, COMP division.
3. Yoon Y, RJ Rousseau, RS Weber, D Mei, and JA Lercher, “First-principles Study of Phenol Hydrogenation on Pt and Ni Catalysts in Aqueous Phase”, 249th ACS National Meeting, Denver, CO, COMP division.
4. Donghai Mei, Yeohoon Yoon, Roger Rousseau, Robert Weber, and Johannes Lercher. "Aqueous phase phenol hydrogenation over metal catalysts," Abstract submitted to College of Chemical Engineering, Zhejiang University of Technology, Hangzhou, China, 2015.
5. Yeohoon Yoon, Roger Rousseau, Robert Weber, Donghai Mei, and Johannes Lercher, "Effects of Aqueous Phase Environment on Phenol Hydrogenation over Pt and Ni Catalysts," NAM24, Pittsburgh, PA, June 2015.
6. Robert Weber and Roger Rousseau, “Reactions in Complex Media”, 250th ACS National Meeting, Boston, August 2015
7. Robert Weber, “Reactions in Complex Media", Keynote Lecture to 18th Brazilian Congress on Catalysis. Porto Seguro, Brazil, September, 2015
8. Yang-Gang Wang, David Cantu, Vanda Glezakou, Roger Rousseau, “Classical, molecular-dynamic simulations on water/phenol speciation at the surface-liquid interface”, 251st ACS National Meeting, San Diego, CA, 12-16 March 2016. COMP 58.
9. David Cantu, Yang Gang Wang, Yeohoon Yoon, Asanga Padmaperuma, Michael Lilga, Vanda Glezakou, Roger Rousseau, “Computational modeling of electrochemical bio-oil upgrading”, 251st ACS National Meeting, San Diego, CA, 12-16 March 2016. COMP 138.
10. David C. Cantu, Yang-Gang Wang, Yeohoon Yoon, Vassiliki-Alexandra Glezakou, Roger Rousseau, Robert S. Weber, “Speciation at Liquid-Solid Interfaces in the Processing of Renewable Fuels” 251st ACS National Meeting, San Diego, CA, 12-16 March 2016. ENFL 373.
11. Cantu D, Y Wang, Y Yoon, VA Glezakou, RJ Rousseau, and RS Weber. "Modifying liquid-solid interfaces for the processing of renewable fuels." Presented by Robert S Weber at 252nd ACS National Meeting, PHILADELPHIA, Pennsylvania, on August 22, 2016.

Presentations (since 2015 Peer Review) (2/3)

12. G. Wiggins, C. S. Daw, P. Ciesielski. “Modeling the Impact of Biomass Particle Size Distribution and Shape on Heating Behavior During Fast Pyrolysis”, Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products, Chapel Hill, NC, November 2, 2016.
13. E. Ramirez, C. S. Daw, C. E. A. Finney, S. Pannala, J. Parks, “Computational study on biomass fast pyrolysis oil yield: effects of the bubbling-to-slugging transition in a laboratory-scale fluidized bed,” Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products, Chapel Hill, NC, November 2, 2016.
14. E. Ramirez, C. S. Daw, C. E. A. Finney, S. Pannala, J. Halow, Q. Xiong, “Computational study of the bubbling-to-slugging transition in a laboratory-scale fluidized bed,” AIChE National Meeting, San Francisco, CA, November 16, 2016.
15. G. Wiggins, C. S. Daw, E. Ramirez, “Modeling the Impact of Biomass Particle Residence Time on Fast Pyrolysis Yield and Composition,” AIChE National Meeting, San Francisco, CA, November 15, 2016.
16. E. Ramirez, C. E.A. Finney, S. Pannala, C. S. Daw, J. Halow, Q. Xiong, “Computational study of the bubbling-to-slugging transition in a laboratory-scale fluidized bed”, NETL 2016 Workshop on Multiphase Flow Science, Morgantown, WV, August 9, 2016.
17. E. Ramirez, C.E.A. Finney, C. S. Daw, J. Halow, “Optimizing fluidized bed hydrodynamics for biomass fast pyrolysis oil yield”, East Tennessee Collegiate Division Meeting of the Tennessee Academy of Science, Knoxville, TN, April 22, 2016.
18. E. Ramirez, C.E.A. Finney, C. S. Daw, J. Halow, “Resolving hydrodynamic transitions in bubbling bed biomass pyrolysis reactors”, ORAU Annual Meeting on Application of Big Data Analytics, Oak Ridge, TN, March 9, 2016.
19. Q. Xiong, C.S. Daw, and S. Pannala, “Coupling CFD and DAEM for simulating biomass fast pyrolysis in fluidized beds,” presentation, AIChE 2015 National Meeting, Salt Lake City, NV, November 9-13, 2015.
20. E. Ramirez, C. S. Daw, S. Pannala, Q. Xiong, C.E.A. Finney, “Resolving hydrodynamic transitions in bubbling bed biomass pyrolysis reactors”, NETL 2015 Workshop on Multiphase Flow Science, Morgantown, WV, August 12, 2015.
21. E. Ramirez, C. S. Daw, S. Pannala, Q. Xiong, C.E.A. Finney, “Resolving hydrodynamic transitions in bubbling bed biomass pyrolysis reactors”, ORAU 3rd Annual Faculty and Postgraduate Poster, Oak Ridge, TN, August 4, 2015.
22. Cong Lu, Cheng Lei, Rajeev Assary, Larry Curtiss, In silico zeolite catalyzed carbon-carbon coupling reactions for furan upgrading, American Society Meeting, March 25, 205, Denver, CO.
23. Cheng Lei, Larry A. Curtiss, Rajeev Assary, First-principles studies of furan upgrading by Ga/ZSM-5" American Chemical Society Meeting, Aug16-20, 2015, Boston, MA

Presentations (since 2015 Peer Review) (3/3)

24. Rajeev S. Assary, Larry A. Curtiss, Lei Cheng, Cong Liu, Modeling catalytic vapor phase upgrading using first principles", American Chemical Society Meeting, Aug 21, 2016, Philadelphia
25. Ferguson, GA; Vorotnikov, V; Wunder, N; Clark, J; Gruchalla, K; Bartholomew, T; Robichaud, D; Beckham, GT, "Multi-dimensional phase diagrams for the coadsorption of aromatic oxygenates and hydrogen on metallic surfaces," ACS National Meeting, Philadelphia, PA; August 2016.
26. Vorotnikov, V; Baddour, F; Griffin, MB; Habas, S; Ruddy, DA; Beckham, GT; Schaidle, JA, "Computational and experimental insights into the shape and faceting of Rh2P nanoparticles for biomass upgrading," ACS National Meeting, Philadelphia, PA; August 2016.
27. L. Bu, M.R. Nimlos, D.J. Robichaud, S. Kim. Diffusion of pyrolysis oxygenates in H-ZSM-5. The 252nd ACS National Meeting, August 23rd, 2016, Philadelphia, PA.
28. Lintao Bu, Mark R. Nimlos, David J. Robichaud, and Seonah Kim. Diffusion of Biomass Pyrolysis Products in H-ZSM-5 by Molecular Dynamics Simulations. J. Phys. Chem. C, 2017, 121, 500-510.
29. Peter Ciesielski. Improving Biomass Conversion Processes through Advanced Imaging, Modeling, and Simulation. Workshop on Second Generation Bioethanol 2016, Brazilian Bioethanol Science and Technology Laboratory (CTBE), Campinas, Brazil. Dec 1st, 2016.

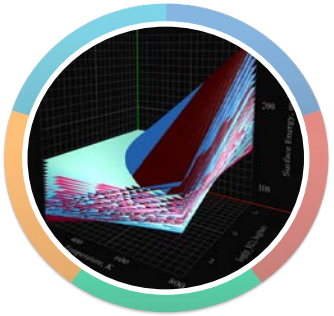
In addition, CCPC has been active in organizing the following conferences/meetings:

- Symposium organizer, "Advances in Computational Catalysis" (CATL division), American Chemical Society Meeting 2016, August, Philadelphia
- Symposium organizer, "Advances in Computational Catalysis-II" (CATL division), American Chemical Society Meeting 2017, August, Washington DC

Commercialization & Technology Transfer

(1) Public release of "Surface Phase Explorer"

- Surface Phase Explorer is a web-based tool for exploring phase diagrams (based on ab initio data) associated with the coadsorption of two species on a surface.
- Available to the public at spe.nrel.gov



(2) Assist Including Biomass Parameters in *CSFMB©/CeSFaMB™*

- CCPC assisted Prof. de Souza-Santos in including biomass pyrolysis chemistry into new version of CSFMB© commercial software (Brazil)
- See www.csfmb.com

(3) Public release of CCPC code on GitHub

- CCPC code and bioenergy specific modeling parameters (kinetics, thermal properties, etc.) have been loaded to GitHub
- Available to the public at github.com/pyrolysis

Milestones: Feedstock Impact Analysis (Task 2)

Due	Annual Milestone
Q3 (June 30, 2017)	**Task 2&3. Predict pyrolysis yields on feedstocks between 2FBR and TCPDU.** Use feedstock characterization data provided by INL (WBS 2.2.1.501) for 2 pelletized feedstocks, namely Clean Pine and TCPDU Blend 2 (45% clean pine, 25% forest residues, 30% construction and demolition waste) to construct representative biomass particle models. Develop reactor-flow conversion simulations coupled to ensemble calculations to predict pyrolysis yields of these feedstocks blends in the TCPDU entrained flow reactor and the 2" fluidized bed reactor. Validate the entrained flow reactor model with experimental results reported by 2.4.1.301 to achieve particle-scale pyrolysis simulations that are sufficiently predictive (i.e., can predict yields within measured experimental error). Provide physics-based understanding of any differences observed in the Q2 milestone on 2.4.1.301/2.2.1.304 between the two reactor scales as well as recommendations on how to align residence times and heat transfer between the two reactors to 2.4.1.301/2.2.1.304. [NREL lead with ORNL] NOTE: This Annual Milestone is linked to the FY17 Q1 milestone in the Integrated and Scale-Up project at NREL (WBS 2.4.1.301)
Linked Milestone	**LINKED MILESTONE in Integrated and Scale-Up project at NREL (WBS 2.4.1.301):** Provide the CPC task (WBS 2.5.1.301-5) with mechanical drawings of the TCPDU entrained flow and ex-situ CFP reactors, temperature profiles and other process data from recent operations, crushed feed samples taken from the feed-train and other information as requested to achieve the CPC milestones of developing particle-scale simulations and scaled reactor modeling. (FY17 Q1 milestone)

Milestones: Reactor Analysis and Scale-Up (Task 3)

Due	Quarterly Progress Milestone
Q1	Define validation experiments to run during R3 Upgrader reactor commissioning process and provide to 2.4.1.301 at NREL [ORNL lead, NETL and NREL assist] Note: feeds into Annual Milestone for R3 Upgrader. Linked to Q1 milestone on 2.4.1.301.

Due	Stretch Annual Milestone
Q4 (September 30, 2017)	Develop initial R3 Upgrader model in MFiX and provide predictions of residence time and heat transfer and compare to 2" bubbling bed upgrading reactor for scale-up comparison. Enables rapid optimization of R3 Upgrader operation to achieve BETO goals and provides analysis of scale-up feasibility for a 2" bubbling bed upgrading reactor ("Baldwin reactor") to R3 Upgrader reactors which is critical to attaining value from ChemCatBio catalyst development activities. [ORNL lead, NETL assist] NOTE: This Annual Milestone is linked to the FY17 Q1 milestone in the Integrated and Scale-Up project at NREL (WBS 2.4.1.301)
Linked Milestone	**LINKED MILESTONE in Integrated and Scale-Up project at NREL (WBS 2.4.1.301):** Provide the CPC task (WBS 2.5.1.301-5) with mechanical drawings of the TCPDU entrained flow and ex-situ CFP reactors, temperature profiles and other process data from recent operations, crushed feed samples taken from the feed-train and other information as requested to achieve the CPC milestones of developing particle-scale simulations and scaled reactor modeling. (FY17 Q1 milestone)

Also links to Qtly

Milestones: Vapor Phase Upgrading (Task 4)

Due	Quarterly Progress Milestone
Q1 *Joint Milestone*	**Identify the active-site structure(s) responsible for low-temperature alkane activation and reincorporation into the chain-growth cycle on modified beta zeolite catalysts.** Understand C4 activation over the Cu/BEA catalyst to inform catalyst design to maximize/control C4 reincorporation, and thereby, increase carbon yield from DME to C5+ gasoline products and consequently decrease the MFSP. This is a joint milestone with the ACSC (WBS#2.5.4.304) and the CCPC (WBS#2.5.1.302), where in-situ/operando XAS analysis of the ionic Cu site structure(s) and computational modeling of the energetics of C4 activation at the ionic Cu sites will be coupled with experimental C4 activation studies. These combined results will inform an iterative computational effort to identify and explore additional ionic metal sites (non-Cu-based) that will enable catalyst design to maximize C4 reactivation and reincorporation into the chain growth pathway. These new, predicted catalyst formulations will be identified as synthetic targets for the next generation of catalysts within this project. [NREL lead] NOTE: This milestone is a Joint Milestone with Advanced Catalyst Synthesis and Characterization (2.5.4.304) and Liquid Fuels via Upgrading of Syngas Intermediates (2.3.1.305). Subcontract with UCLA. Feeds into Q2 milestone on CCPC.
Q3 *Linked Milestone*	**Evaluate the changes in reaction energetics of a Ni-doped Mo2C for furan coupling in the condensed phase.** Investigate the vapor phase carbon-carbon coupling of furan molecules in Ni/Mo2C (longer term catalysts) to understand the reaction mechanisms and the catalyst deactivation. Reaction energetics, including rate determining steps, will be provided to ChemCatBio (WBS # 2.3.1.301), along with a more detailed understanding of the role of nickel in the Mo2C catalyst and a prediction of the optimum weight percentage of nickel to guide future synthesis and catalyst optimization. [ANL lead] NOTE: This Quarterly Milestone support activities on ChemCatBio (2.3.1.301).
Q3 *Linked Milestone*	**Computationally screen Lewis-acidic zeolites across 4 reaction classes to guide compositional synthesis for improved activity and selectivity.** Model the kinetics of dehydration, dehydrogenation, cyclization, and decarbonylation in zeolite catalyst modified with 5 different Lewis metals. Metals are chosen based on candidates proposed by 2.3.1.314 and will include at least Cu and Ga (remaining 3 TBD) as well as oxidation states and different terminations (oxide vs hydroxide). Using this kinetic analysis, make recommendations that can be experimentally tested that will prove the hypothesis that zeolites can be designed to enhance dehydration/dehydrogenation (good reactions) and reduce cyclization/decarbonylation (bad reaction, coke former). [NREL lead, ANL assist] NOTE: This Quarterly Milestone is linked to planned milestones in FY18 on ChemCatBio (2.3.1.315 and 2.3.1.305).
Q4 *Linked Milestone*	**Identify optimal macroporousity in zeolites for CFP to guide catalyst structural synthesis.** Using 3D structural models of a ZSM-5 catalyst particle, investigate the relationship between mesoporous volume fraction and coking/product yields. Models will include mesoporous/microporous diffusion of species, and utilize kinetics from Adajay et al. kinetic scheme (or best available). Models will be informed by and compared to image data produced by the ACSC (ORNL). Recommend optimal range of mesoporous volume fraction based on catalyst reactor residence times to ACSC for targeted synthesis and benchmark results against standard zeolite (e.g. Nexceris) via CCB. [NREL lead] NOTE: This Quarterly Milestone is linked to milestones on the Advanced Catalyst Synthesis and Characterization (2.5.4.303-5).

Milestones: Vapor Phase Upgrading (Task 4)

Due	Annual Milestone (Regular)
Q2 March 31, 2017 ***Linked Milestone***	**Evaluate effect of subsurface oxygen on reaction energetics over Mo2C catalysts.** Model the effect of surface and subsurface oxygen coverage in Mo2C catalysts on surface oxygen binding energies and reaction energetics of ethanol dehydration. Compare modeling results against experimental ethanol dehydration work on CCB (2.3.1.314). Based on modeling/experimental results determine if oxygen binding is an appropriate descriptor of catalyst activity and make recommendations for improved catalyst design (e.g. dopants to reduce oxygen binding strength). [NREL lead] NOTE: This Annual Milestone is linked to FY18 milestone on ChemCatBio (2.3.1.314).

Milestones: Liquid Phase Upgrading (Task 5)

Due	Quarterly Progress Milestone
Q1	Homologation with NETL and ORNL to devise a path towards use of CFD to model the complex flow in LPU. Determine whether the NETL software, MFIX, is suitable for modeling the 4-phase flow in an LPU reactor to help determine how to avoid flow mal-distributions that can lead to localized fouling, poor utilization of hydrogen and ineffective utilization of the catalyst. [PNNL lead with NETL and ORNL]
Q3	Task 5. Full LPU catalyst model relating optimal particle size and support effects. Subsequent suggested catalyst targets to experimental team. [PNNL lead]

Collaborating BETO Projects

- All ChemCatBio Projects
- Integration and Scale Up – NREL (WBS 2.4.1.301)
- Thermochemical Feedstock Interface – NREL (WBS 2.2.1.304)
- Feedstock-Conversion Interface Consortium
- Multi-scale Physical and Structural Particle Mechanics - INL (Feedstock Program - WBS 1.2.1.3)
- Bio-oil quality improvement and catalytic hydrotreating of bio-oils – PNNL and ORNL (WBS 2.3.1.301,302)
- Thermochemical Platform Analysis Update – NREL and PNNL

Collaborators and Partners (outside of National Labs)

Universities

- UCLA (Ken Houk)
- Colorado School of Mines (Cristian Ciobano, Brandon Knapps)
- Northwestern Univ. (Linda Broadbelt)
- Washington State Univ. (Brennan Pecha, Manuel Garcia-Perez)
- University of Tennessee (Nour Abdoulmoumine)

Industry

- Industry Advisory Panel Entities:
  - RTI
  - Johnson Matthey
  - WR Grace
  - Babcock & Wilcox
  - Separation Design Group
  - ExxonMobil
  - BP (via George Huff, retired)
  - Virent Energy Systems
- PSRI (Particulate Solid Research, Inc)

Industry Advisor Panel Expertise Matrix

The table below provides a matrix of the experience areas for the CCPC Industry Advisor Panel. The panel represents a diverse range of expertise covering all activity areas of the CCPC.

	David Dayton (RTI)	Tom Flynn (B&W)	Richard Quann (Exxon Mobil)	Randy Cortright (formerly Virent)	Mike Watson (Johnson Matthey)	Jack Halow (Separation Design)	George Huff (formerly BP)	Steve Schmidt (WR Grace)	Rick Wessel (B&W)
Feedstock	X	X							X
Reactor analysis		X	X			X	X		X
VPU catalysis	X		X		X	X		X	
LPU catalysis	X		X	X	X			X	