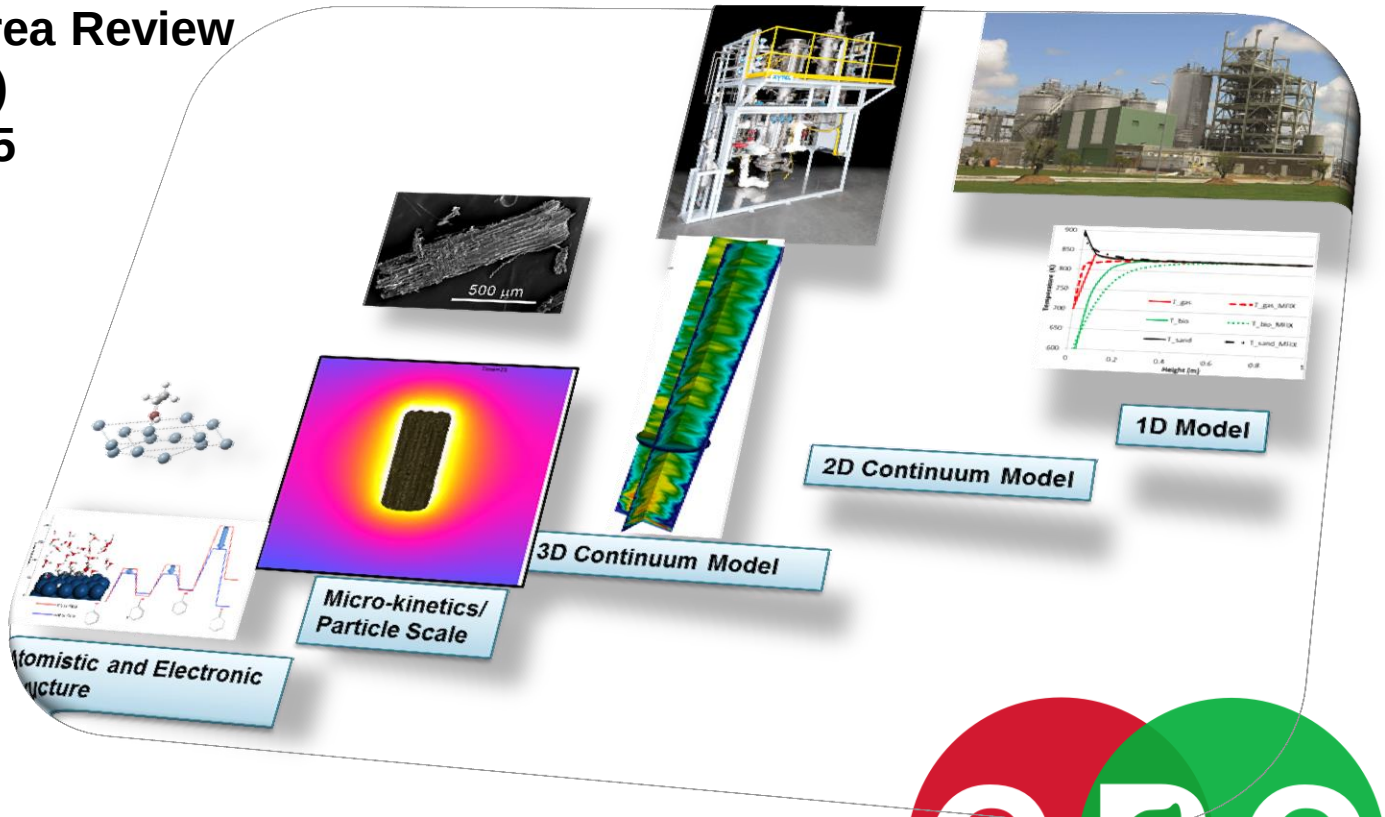
Computational Pyrolysis Consortium

DOE Bioenergy Technologies Office (BETO)
2015 Project Peer Review

Biotechnology Area Review
C. Stuart Daw (PI)
March 23-27, 2015



OAK RIDGE National Laboratory
NREL National Renewable Energy Laboratory
Pacific Northwest NATIONAL LABORATORY
INL Idaho National Laboratory
Argonne NATIONAL LABORATORY

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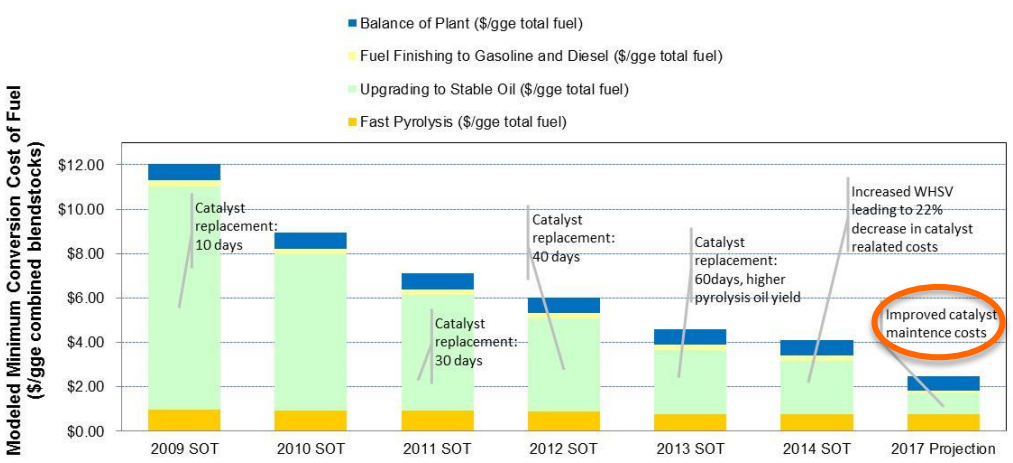
Goal Statement

- **Through computational modeling, enable BETO experimental groups to attain 2017/2022 technical targets faster and more efficiently**
  - FY2017: Accelerate 2017 vapor-phase upgrading demonstration; Guide development of 50% longer life liquid-phase hydrotreating catalyst.
  - FY2022: Guide development of new vapor- and liquid-phase upgrading catalysts to achieve 6% O, 44% C yield.

Fast Pyrolysis with Upgrading Waterfall



Sue Jones (PNNL), Thermochemical Platform Analysis, WBS 2.1.0.301

Ex – situ catalytic fast pyrolysis targets

Process Parameter	2014 SOT	2015 Target	2016 Target	2017 Target	2022 Target / Design Case
Hydrogen Addition during Vapor Upgrading	Initial focus on use of hydrogen to reduce coke and non-condensable gases; after 2017 incorporate hydrogen to improve product quality by increasing H/C ratio				
Molecular Combination (Coupling)	Initial work using model compounds; after 2017 demonstrate using pyrolysis vapors				
Additional Process Options	Base cases assume fluidized catalysts (modified zeolites); consider the option to use catalysts that are feasible in fixed bed reactors (preceded by a hot gas filter)				
Vapor Products	Wt. % of dry biomass unless noted. Values rounded off except for smaller improvements.				
Non-Condensable Gases	35	34	32	30	23
Aqueous Phase (% C Loss)	25 (2.9)	25 (2.9)	25 (2.4)	26 (2.3)	30 (1.3)
Solids (Char + Coke)	12 + 11	12 + 10.8	12 + 10.5	12 + 10.2	12 + 8.0
Organic Phase	17.5	18.5	20.2	22.0	27.2
H/C Molar Ratio	1.1	1.1	1.2	1.3	1.6
Carbon Efficiency (%)	27	28	31	34	44
Oxygen Content (% of organic)	15.0	14.8	14.0	12.5	6.4
Hydroprocessing C Eff. (% of org.liq.)	88	88	89	90	94
Carbon Eff. to Fuel Blendstocks (%)	23.5	25.0	27.6	30.6	41.5
Energy Efficiency to Fuels (LHV basis)	30.4	32.3	36.0	40.2	56.6
Diesel-Range Product (% GGE basis)	15	15	14	14	55
Minimum Fuel Selling Price ($ / GGE)	$6.47	$5.92	$5.24	$4.58	$3.31

Abhijit Dutta (NREL), Thermochemical Platform Analysis, WBS 2.1.0.302

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Goal Statement (cont.)

- **Relevance and tangible outcomes for United States:**
  - Help experimental partners reduce time to demonstrate technical goals and economic viability for biomass thermochemical conversion
    - Reduce experimental operational space and improve information yield
    - Identify and suggest new experimental approaches and materials
  - Expand scientific underpinnings of technology
    - Identify new opportunities and physical limits
    - Utilize unique DOE experimental and computational facilities
  - Provide link between laboratory results and commercial scale up
    - Separate transport effects from kinetics and chemistry
    - Develop process condition targets for industry (e.g., temperature gradients, RTDs)
    - Provide more accurate estimates for impact of non-ideal process conditions
    - Reduce commercial risk
  - Enable more accurate/chemistry and physics-based TEA to predict trends (e.g., realistic trends in reaction conversion vs. temperature, feed preparation)

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Quad Chart Overview

Timeline

- Project start date: May 1, 2013
- Project end date: September 30, 2017
- Percent complete: 40%

Barriers

- **Tt-E** Improve bio-oil quality, carbon efficiency
- **Tt-G** Improve upgrading catalysts
- **Tt-K** Improve process integration & scale up

Budget

	Total Costs FY 10 – FY 12	FY 13 Costs	FY 14 Costs	Total Planned Funding (FY 15-Project End Date)
DOE Funded	$0	$2.2MM (6 month effort)	$3.5MM	$10.6MM

Partners

- NREL(42%), ORNL(27%), PNNL(18%), ANL(8%), INL(4%)
- Subcontracts: U Delaware
- Partner TU Munich (in kind data), BP, MIT, LANL, Oxford, Northwestern, ISU
- Computational resources
  - Peregrine (EERE)
  - OLCF, ALCF, EMSL (Office of Science)
  - Olympus, Cascade, PIC, NERSC
- Leveraged EFRC: CCEI and C3Bio

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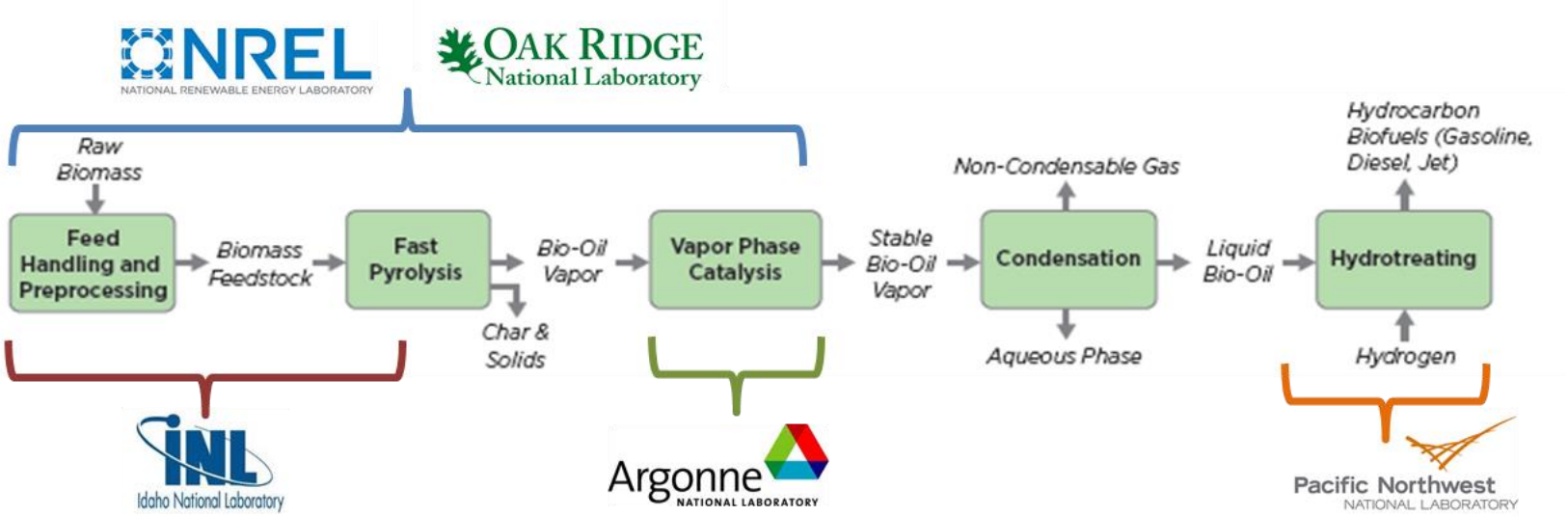
1 - Project Overview - Lab Roles



ORNL
- Team coordination & public interface
- Feedstock impacts
- VP & LP reactor scale up
- Reduced order modeling

NREL
- Feedstock impacts
- VP catalysis mechanisms, kinetics
- VP reactor scale up
- VP experimental interface

INL
- Feedstock characterization
- Data & reference case archival

ANL
- VP catalysis mechanisms

PNNL
- LP catalytic mechanisms & kinetics
- LP reactor scale up
- LP experimental interface

CPC Technical Focus areas: 1) Feedstock impacts; 2) Reactor analysis/scale up; 3) Vapor-phase (VP) catalysis; 4) Liquid-phase (LP) catalysis

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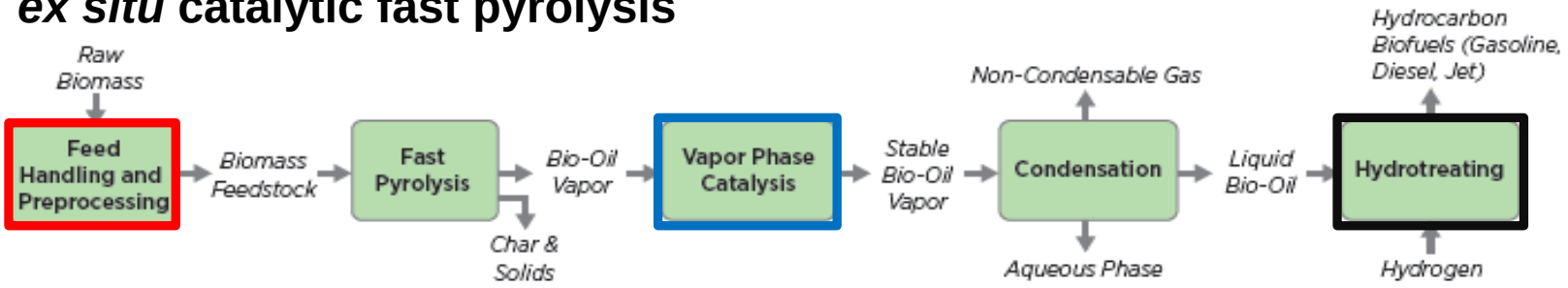
1 - Project Overview - Objectives

***ex situ* catalytic fast pyrolysis**



Process Bottlenecks identified by TEA

Feedstocks

- Structural effects*
- Composition & moisture effects*
- Ash effects*
- Biomass blends*
- Transport vs. chemistry*

Pyrolysis/Vapor-Phase Upgrading (VPU)

- Yield of fuel range molecules (44% C yield, 6% O)*
- Hydrogen utilization/Low pressure hydrogen activation**
  - Aromatic/coke/light gas reduction
- Stoichiometry and rate of de-oxygenation**
- Catalyst cost and stability**
- Fouling/catalyst deactivation**
- Transport vs. chemistry*

Hydrotreating/Liquid-Phase Upgrading (LPU)

- Catalysts cost and longevity*
- Yield of fuel range molecules*
- Reaction severity*
- Hydrogen utilization*
- Transport vs. chemistry*

*Important for all three paths
**Important for ex situ and in situ VPU

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2 - Approach (Technical)

- **Modeling of reactors and catalyst chemistry**
  - Use existing CFD code to model reactors (e.g. raw oil C yield/MW/%O, vapor and liquid catalytic upgrading as functions of feedstock and operating conditions, production scale)
  - Model catalytic chemistry to expand scientific underpinning and encourage development of new catalyst and process options to accelerate progress toward 2017/2022 technical targets
  - Develop validated low-order models for use in TEA, assistance to industry
- **Critical success factors**
  - Assist experimental partners in planning VPU reactor operation (e.g. MW, cat:biomass, biomass feed rate) with less set up time, more demonstration time at target yields and composition (34%C yield, 12% O in 2017).
  - Identify new catalysts, conditions that increase hydrotreating catalyst lifetime 3X for 2017, 5X for 2022
  - Identify new catalysts with increased C-C coupling and hydrogenation, increasing C yield from 34 to 44%, decreasing O from 12 to 6%, and boosting diesel range from 15 to 55% by 2022
  - Kinetics and transport-based TEA models that accurately predict trends for industry relevant scales

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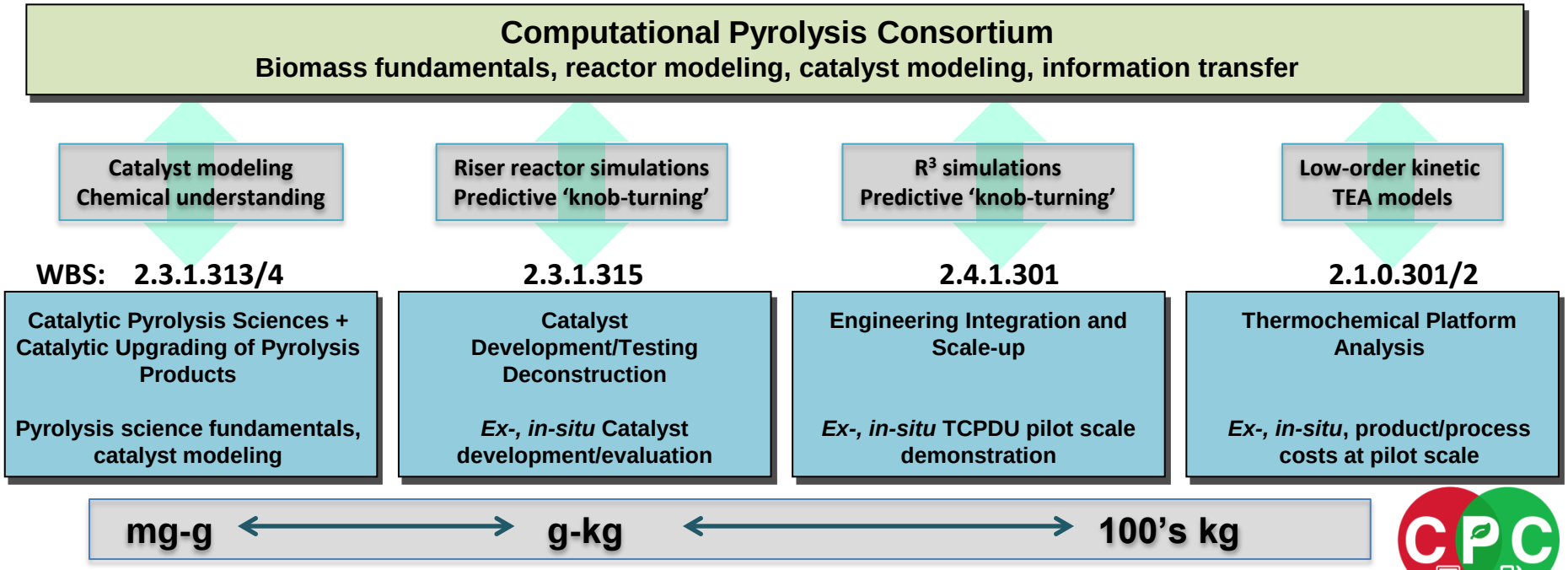
2-Approach (Technical)

- **Challenges**
  - Effective transfer of chemistry and physics knowledge to experiments
  - Extrapolation of lab and pilot-scale knowledge to industrial context
  - Modeling complex pyrolysis product chemistry with tractable number of species and kinetic rate parameters
  - Identifying rate/selectivity controlling factors in each process step
  - Translation of above information to compact, user-friendly format



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2 - Approach: CPC breakdown – 5 tasks

Task	Lab leads	Objective
Coordination/integration	ORNL	Provide leadership and strategic vision for the consortium, facilitate communications outside of the CPC (BETO, industry advisors), and ensure projects are integrating with one another
Feedstock impact modeling*	NREL/ORNL/ INL	Determine heat and mass transport of structurally-accurate biomass particles to quantify impact of feedstocks species and particle size on bio-oil yield
Multi-phase reactor analysis, scale-up*	ORNL/NREL/ PNNL	Show how operating conditions impact residence time distributions and transport in vapor and liquid phase upgrading and thereby impact bio-oil content.
Vapor phase upgrading catalyst chemistry and optimization*	NREL/ANL	Determine rate-determining steps for C-C coupling and deoxygenation to help meet 2022 technical targets.
Liquid phase upgrading catalyst chemistry and optimization*	PNNL	Model the activity, selectivity and longevity of catalysts that permit hydrotreating of condensed phase to interpolate experimental results and inspire the development of novel, effective catalysts.

*** Technical focus areas**

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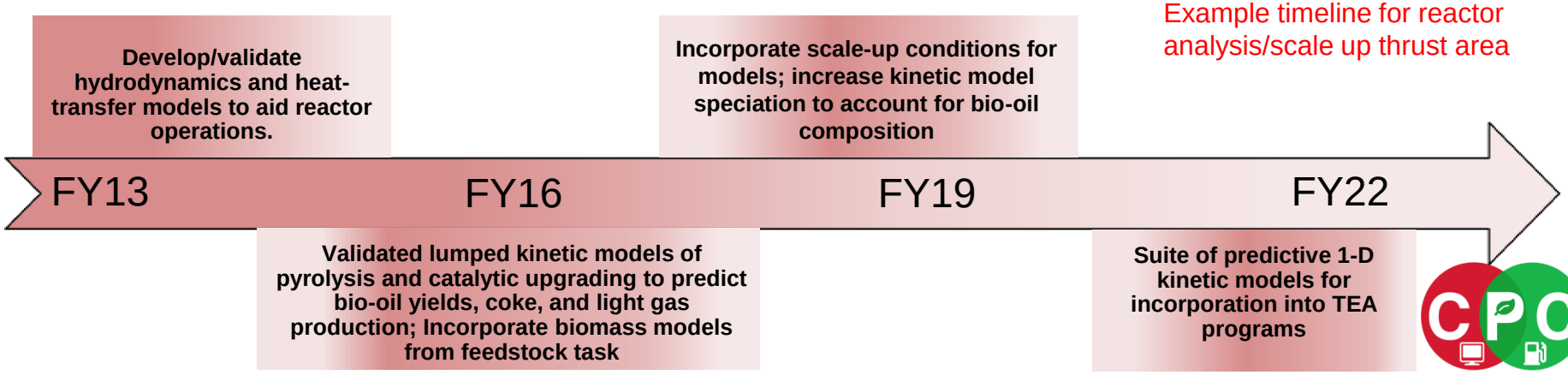
2-Approach (Technical)

FY 2015 CPC Milestones

	ORNL	NREL	ANL	INL	PNNL
Q1	Provide simulation results and guidance for the NREL DCR VPU tests.	Model hydrogenation over 1 metal surface and examine catalytic support effects for ability to increase hydrogen uptake by >10% over base case. Provide results to 2.3.1.314 for experimental validation.	Model large pore zeolite catalytic reactions for three reactions of furan with C2-C3 model compounds, investigate activation/deactivation mechanisms and provide results to database.	Measure size and shape distributions for a wood feed material at two grind sizes relevant for fast pyrolysis (e.g., hammer mill grinding using 6 mm and 4 mm screens).	Analyze fiducial reaction data; Attend Int. Workshop on Bioenergy and Environment (RSW, Tianjin, China)
Q2	Establish computational framework linking pyrolysis to other stages of bio-oil upgrading.	Inform TEA models with improved particle heat transfer for hard and soft wood. Use riser reactor CFD investigate particle size, flow rates, and reactor dimensions. Provide results to 2.1.0.302 for use and validation of a 1D TEA models.	Model H-ZSM-5 Zeolite modifications on one catalytic reaction. Explains the effect of three types of Lewis acid sites for catalytic carbon-carbon bond formation.	Complete set up of cylindrical fixture and gas measurement apparatus and perform initial gas diffusion measurements at room temperature for H_20, CO, and CO_2.	Analyze gunking kinetics; Review, with NREL, of reactions that are best done in liquid or gas phase
Q3	Archive raw bio-oil conversion/quality tables for non-catalytic bubbling bed fast pyrolysis in INL and website database.	Model furan formation from cellulose fragments over modified zeolite catalysts. Identify 3 promising candidates for increasing furan concentration by 10% over the base case. Provide results to 2.3.1.313 for validation.	Model three catalytic carbon-carbon bond formation reactions on aluminosilicate surfaces with Lewis and Bronsted acid sites. Document results and implications for catalyst design in database.	Update library database with fixes for bugs found in beta version deployed in FY14. Upload data from INL's thermal property measurements into the library and link to NREL/ORNL fast pyrolysis particle model.	Refine recommendations for catalysts & process conditions; Forward reduced models to ORNL
Q4	Validate CFD and low-order model predictions against DCR vapor-phase upgrading measurements , predict upscaling to commercial implications.	Incorporate lumped kinetic models developed in 2.3.1.313 into CFD models. Identify key parameters that influence residence time and product distributions.	Develop microkinetic models for carbon-carbon bond formation between furan and acetaldehyde/glyoxal/glyceraldehyde in zeolite catalysts. Document in database..	Complete gas diffusion measurements for $H_2$0, CO, and CO_2 using heating rates as fast as 20 °C/min.	Start extended modeling incorporating rule-based networks and cybotactic effects. Joint presentation with NREL presentation at the ACS meeting in Denver.

Example timeline for reactor analysis/scale up thrust area



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2 - Approach (Management) - Coordination

- **Quarterly all-lab team meetings rotated between national lab partners and monthly telecoms**
  - Strategic planning, decision-making, and problem solving
  - Direct interaction with experimental partners to discuss validation and feedback from models
  - Recommendations from industry advisory panel on scope and approach toward eventual commercialization

Examples:

- *Plug-and-play al-a-carte models*
- *Experimental model validation*
- *Component speciation*
- *Scale-up*

Advisory Panel Members

Richard Quann (Exxon Mobil)
David Dayton (RTI)
Randy Cortright (Virent)
Mike Watson (Johnson Matthey)
Jack Halow (Sepn. Design Group)
George Huff (BP)
Stephen Schmidt (WR Grace)
Tom Flynn and Shengteng Hu (B&W)
Zia Abdullah (Battelle)- New!

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2 - Approach (Management) – Public Outreach

- **Monthly team webinars**
  - Invited technical web presentations
    - Facilitate academic involvement
      - Prof. Robert Brown – Iowa State University
      - Michael Antal – Hawaii Natural Energy Institute
      - Dion Vlachos- Delaware Catalysis Center for Energy Innovation
      - Daniel Resasco and Steven Crossley- University of Oklahoma
- **Public website (www.cpcbiomass.org)**
  - R&D results highlights
- **CPC organized ACS Computational Pyrolysis and Upgrading of Bio-Oils Symposium (March 25, 2015)**
  - Invited talks aimed at computational/experimental interface, opportunities and challenges

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3 – Technical Accomplishments/Progress/Results

Examples (more details in back-up slides):

- **Feedstock impacts**
  - Improved ability to link biomass properties (including grinding/drying) and pyrolysis conditions to raw-oil C yield and O level
  - Validating reaction & transport models with NREL & PNNL lab studies
- **Multi-phase reactor analysis/scale up**
  - Identified DCR operating parameters for optimal catalyst contacting
  - Developed basis for low-order vapor-phase upgrading riser modeling
  - Identified how to separate liquid-phase transport effects and improve scalability
- **Vapor-phase catalysis**
  - Developed catalytic mechanisms for C-C coupling and HDO
- **Liquid-phase catalysis**
  - Identified reactor fouling mechanisms and mitigation paths
  - Identified promising approach for reduced-order kinetics

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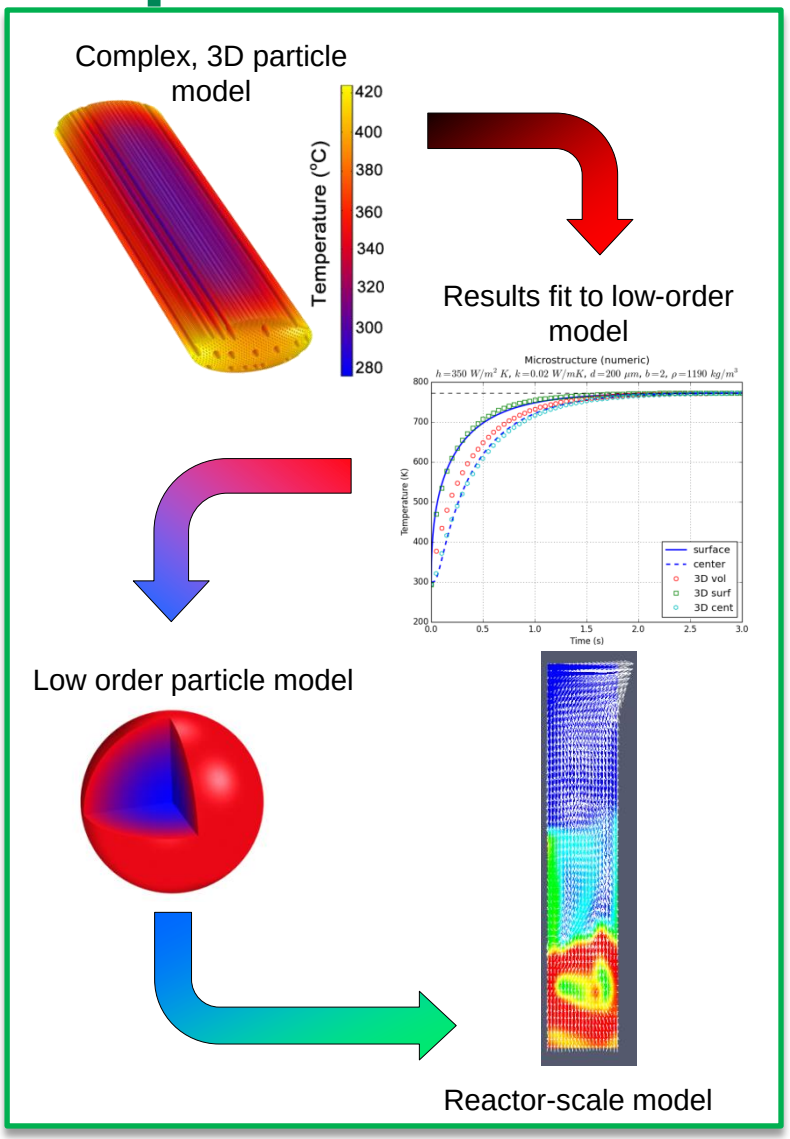
Technical Progress: Feedstock Impacts

Objective: Account for variations in biomass feedstock species (including blends), particle size, and moisture on raw oil yield, composition, and process scale-up.

Accomplishments:

- Constructed structurally-accurate, size appropriate models of hard and soft wood particles.
- Related particle microstructure to heat transfer and pyrolysis yield and composition and defined new experiments to validate correlations.
- Translated particle models to low-order form for process scale modeling.

Significance: Rates of heat and mass transport to biomass particles during pyrolysis can shift raw oil yields from levels as low as 30% to as high as 75%*. The levels of O present in the raw oil can be similarly affected. These factors are especially important in process scale up. CPC models are used to identify where improved assumptions and experimental data are needed to more accurately predict cost and yield trends.



* Bridgewater, Biomass & Bioenergy, (38), 2012, 68-94

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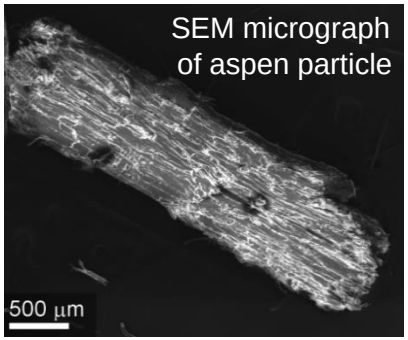
Technical Progress: Feedstock Impacts-Particle-Scale Modeling

- Detailed microscopy (experimental collaborators: Catalytic Pyrolysis Sciences Project, C3Bio EFRC) providing highly resolved species-specific microstructure.
- Allows assessment of microstructure on heat/mass transfer during pyrolysis.
- This is enabling simulations of oil yield and composition at the particle scale (sans detrimental external reactor effects) as functions of feedstock species, particle size distribution, and moisture.



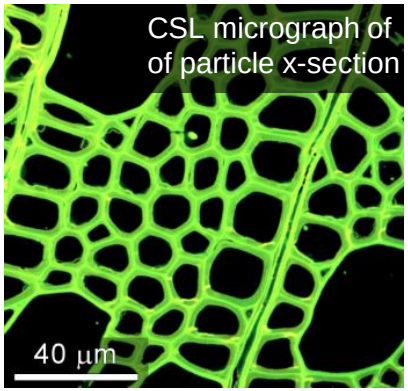
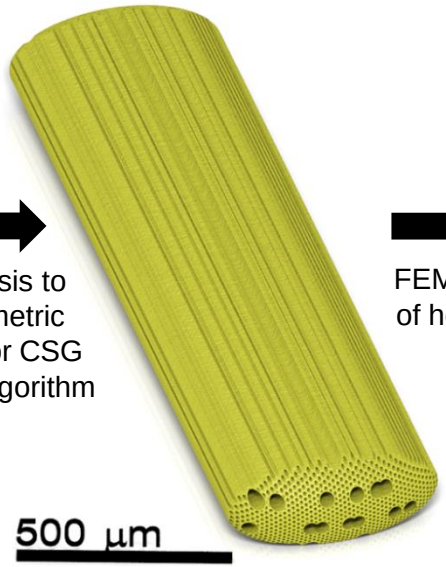


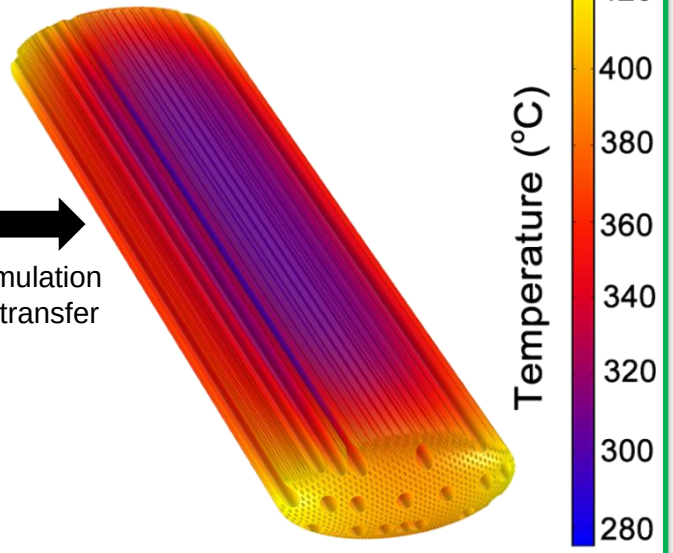
Image analysis to extract geometric parameters for CSG construction algorithm

3D biomass particle model with realistic geometry



FEM simulation of heat transfer

Simulation snapshot showing temperature profile at t = 0.5s.



[1] 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 Morphology and Resolved Microstructure for Simulations of Intraparticle Transport Phenomena. *Energy & Fuels* **2015,** *29* (1), 242-254..

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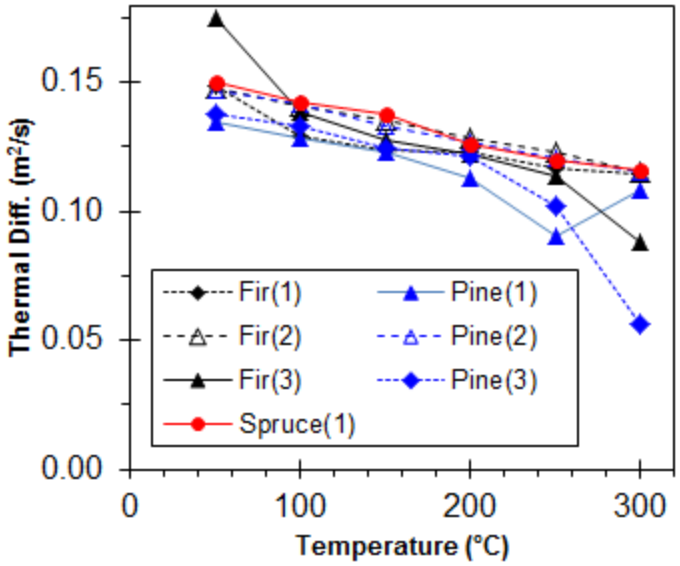
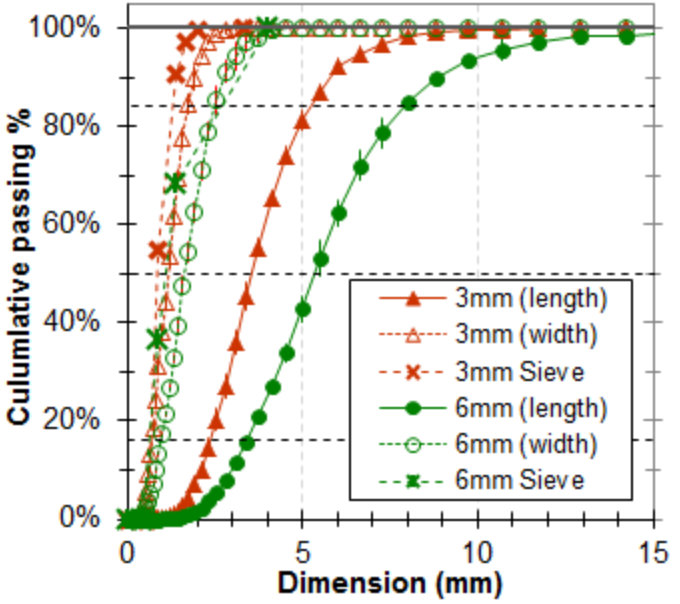
Technical Progress: Feedstock Impacts- Biomass Properties





Objective: Determine effective thermal properties that impact kinetics and are needed for accurate bio-oil yield predictions

Accomplishments:

- Developing correlations accessible to broader community with biomass data
  - INL library and CPC website
- Examples of publicly made measurements
  - Standard sieve analyses of ground feedstocks
  - Optical size and aspect measurements

Significance:

Variations in feedstock sieve distributions and thermal properties can have a large impact on reactor operations (residence times, flow properties). Understanding these variations can enable end-users to better optimize reactor systems and predict bio-oil yield and composition.

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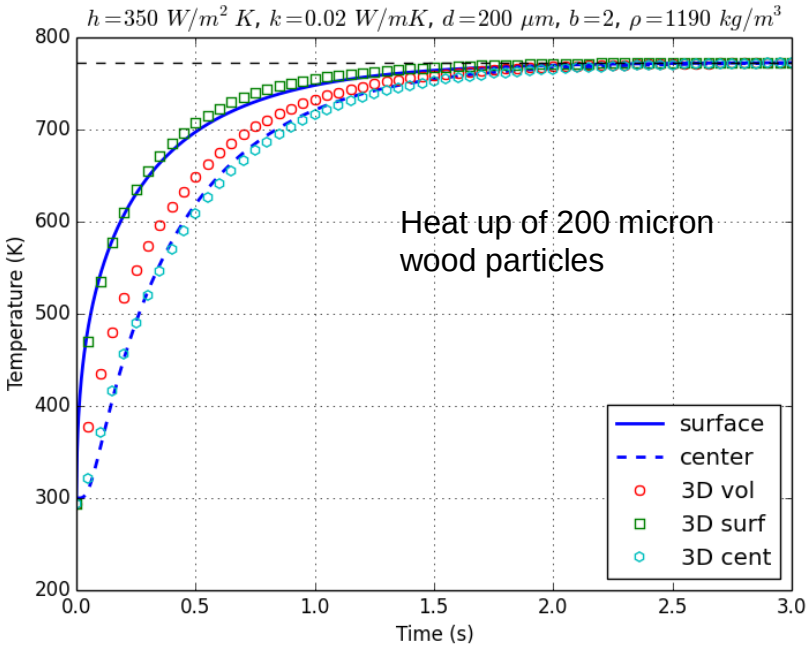
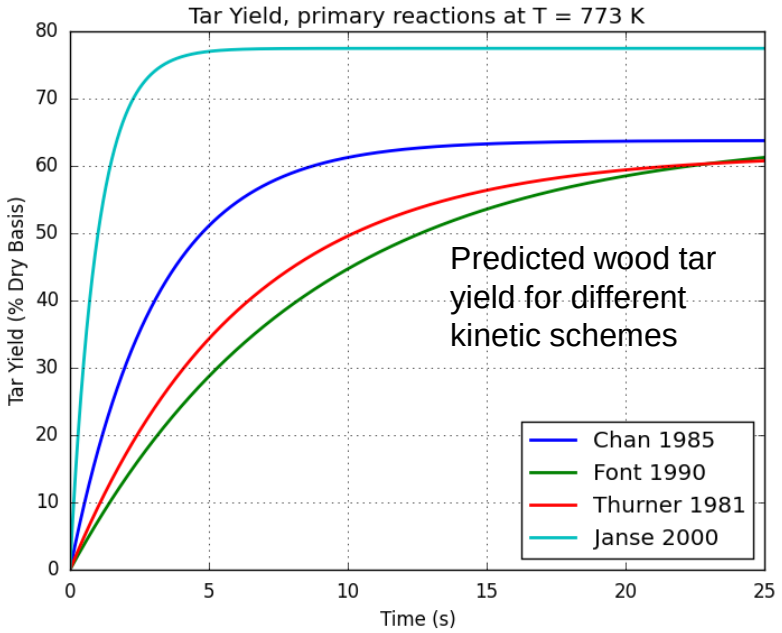
Technical Progress: Feedstock Impacts- Pyrolysis Reactions

- Developed 1D approximations of particle heat up and reaction
- Approximations give good agreement with 3D using minimum particle width and shape factor
- Coupled with reaction kinetics, predicts ideal limits for raw oil C yields and %O
- Reveals that existing kinetics data are inadequate and motivates the need for additional experiments (not currently included in lab AOPs)



1D approximations compare well with detailed 3D simulations



Tar generation kinetics in the literature are widely inconsistent

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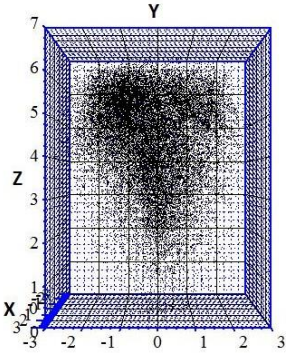
Technical Progress: Feedstock Impacts- Pyrolysis Scale-up

Objective: Understand controlling physics of particle mixing during pyrolysis to meet bio-oil targets for in situ CFP.

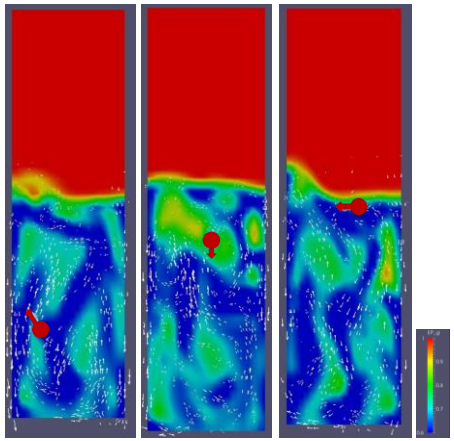


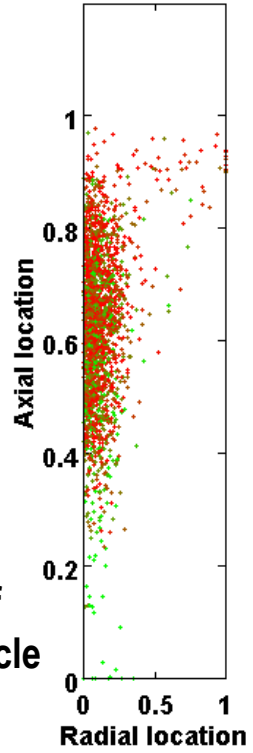
Magnetic particle tracking experiment at Separation Design Group

Accomplishment:

- Models were validated using magnetic tracer experiments
- Low-order statistical mixing models provides rapid simulation of particle residence time distributions
- Able to link particle heat-up and reaction sub-models to feedstock properties and pyrolysis conditions

Biomass particle mixing profiles from CFD





Steady-state distribution of biomass particle conversion in the pyrolysis reactor

Significance: Better understanding of the controlling physics in pyrolysis reactors is needed to optimize reactor conditions. This will be particularly critical for in situ catalytic fast pyrolysis where catalyst/vapor contact time and catalyst deactivation/regeneration are crucial considerations in order to optimize bio-oil yields, reduce light gas formation (cracking), and maintain low oxygen content in bio-oil.

*Daw and Halow, *Ind. Eng. Chem. Res.*, 2014, *53* (41), pp 15836–15844

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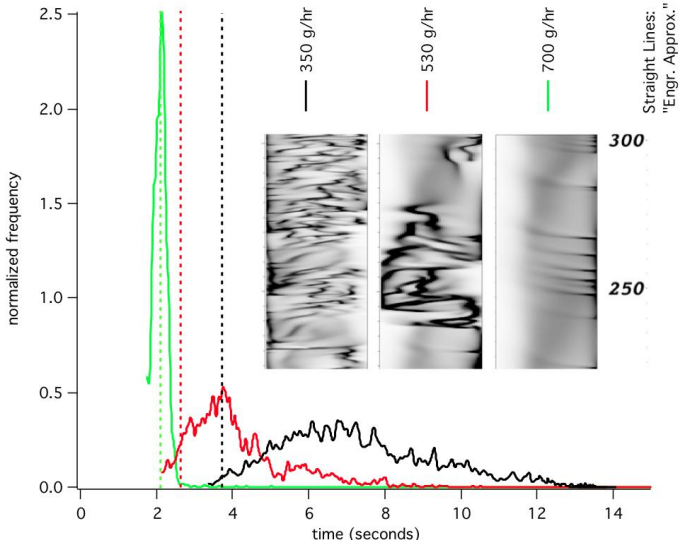
Technical Progress: Vapor-Phase Reactor Modeling

Objective: Identify critical parameters expected to control catalyst performance in DCR vapor phase upgrading demonstration.

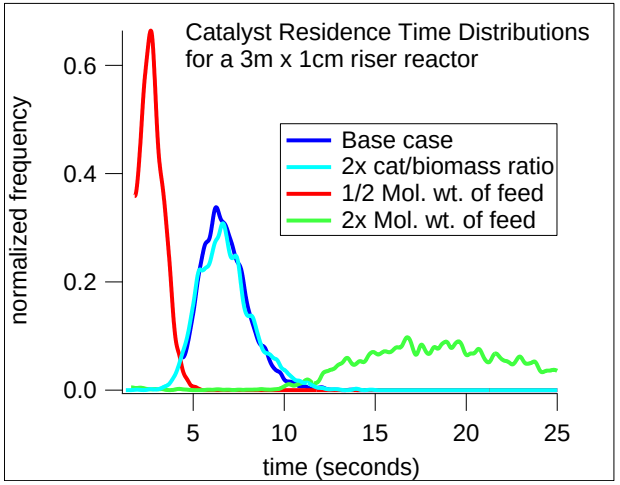
Accomplishment:

- Lab experiments with HZSM-5 reveal optimal vapor/catalyst contact time*
  - –Too short ➔ catalyst not fully utilized
  - –Too long ➔ catalyst cokes, deactivates
- CFD simulations identified DCR conditions needed to achieve target performance
- Simulations reveal catalyst clustering generates broad catalyst residence time distributions that can extend beyond the optimal performance window

Significance: Residence time distribution (RTD) control appears to be critical for optimizing catalyst performance. CFD simulations are providing guidance regarding which reactor operating parameters are needed to reach the 34% C yield and 12.5% O-content targets by 2017. This predictive ability should allow DCR team to spend less time optimization reactor conditions, more time on demonstration experiments.



Impact of vapor/catalyst ratio on catalyst residence time distribution



RTD impact of bio-oil MW

*Mukarakate et al. *Green Chemistry* 2014, *16* (3), 1444

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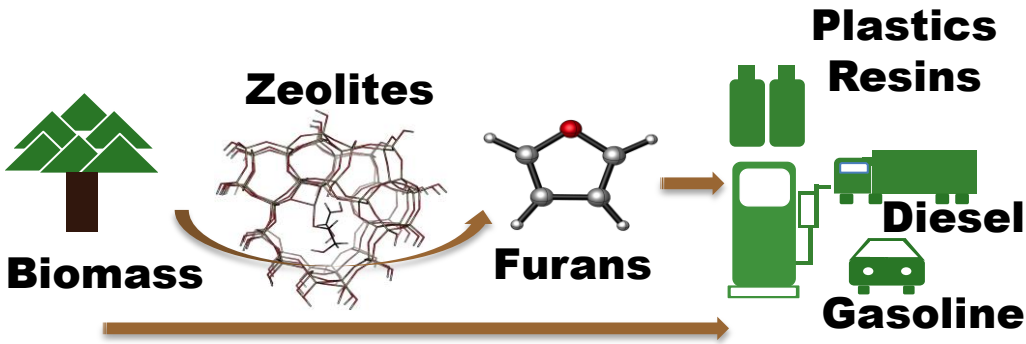
Technical Progress: Catalytic Fast Pyrolysis – Furan generation from light oxygenates

Accomplishment:

- Identified the minima on the cellulose potential energy surface are furans, however actual pyrolysis products tend to be small C2-3 oxygenates suggesting kinetic limitations.
- Calculated the rate-determining steps for the coupling reactions between small oxygenations (e.g. glycoaldehyde) found in cellulose pyrolysis toward the formation of furan-like molecules
- Validated hypothesis with microscale experiments – low yields
- Using knowledge of the rate-determining steps, we are working with experimental partners to design and test modified zeolites that significantly increase furan yields



Objective: Identify new pathways toward furans as an alternative to BTX-heavy bio-oil.

Significance: Furans as a product offers a variety of possible advantages over current BTX product streams. There is active work in the scientific community to convert furans to diesel or higher value chemicals.

S. Kim et al. J. Phys. Chem. A. accepted (2015)
S. Kim et al. ACS Catalysis to be submitted (2015)

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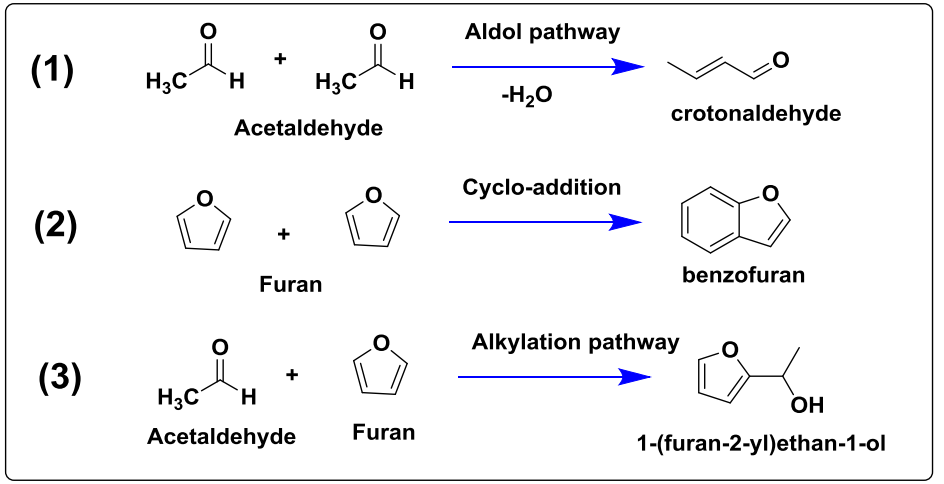
Technical Progress: Vapor-phase catalysis- Furan-acetaldehyde coupling

Objective: Reduce coke formation (increase bio-oil yield) and remove undesired components of bio-oil by coupling aldehydes with furans.

Accomplishment:

- Aldol pathway is kinetically preferred to alkyl pathways in HZSM5
- Computed intermediate/products are verified with experimental partners (Catalytic Pyrolysis Sciences Project).



Detailed computations on three model reactions are performed to investigate various reaction mechanisms occur during the catalytic pyrolysis

Significance: Aldehydes are known to coke excessively over zeolite catalysts through C-C coupling reactions quickly followed by cyclization via the double bond (the Aldol path). Coupling with furans (alkylation pathway) will result in less coke and improved bio-oil yields. Need to identify catalysts that enable alkylation to dominate aldol chemistry.

C. Liu et al. J. Phys. Chem. A. 111, 4392-4404 (2014)
C. Liu et al. ACS Catalysis to be submitted (2015)

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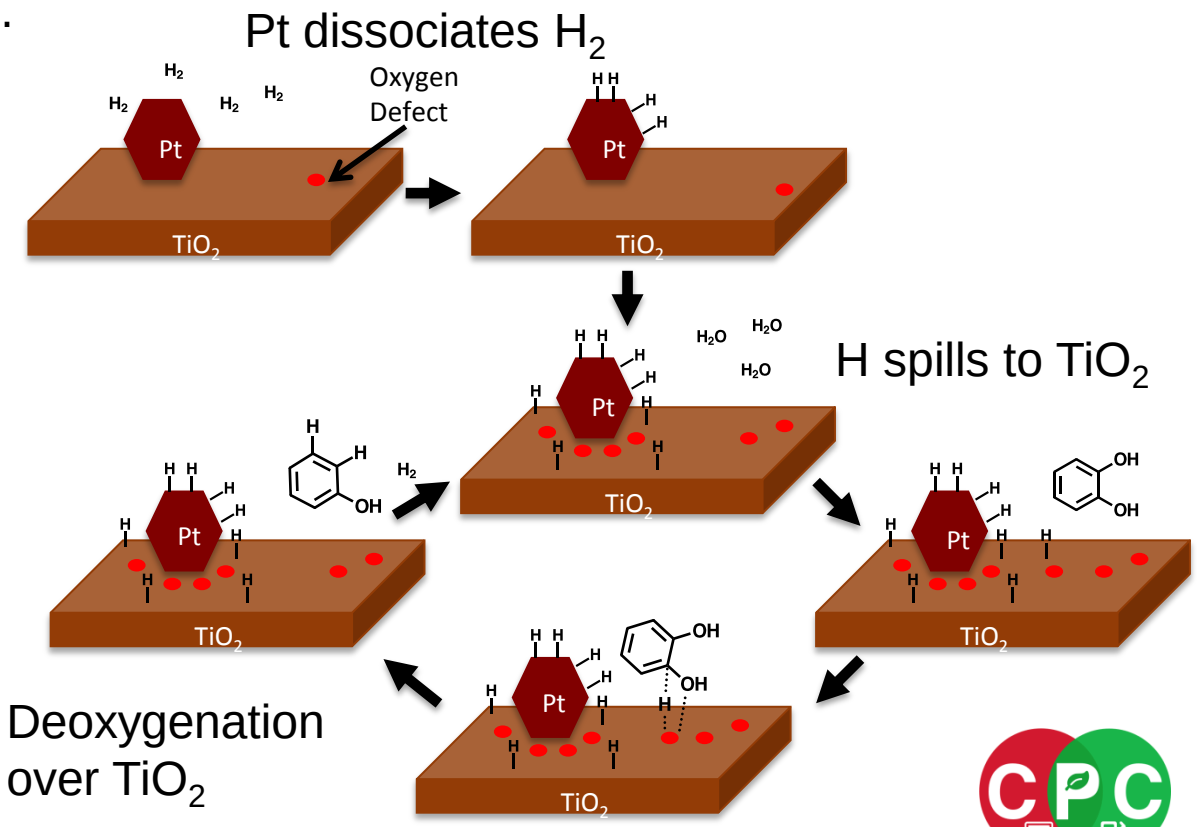
Technical Progress: Vapor-phase catalysis- Spillover of hydrogen in lignin deoxygenation

Objectives: Provide mechanistic understanding of hydrodeoxygenation of lignins over nanoparticle supports to help create low-pressure hydrogen utilization. Increase H/C ratio in bio-oil and reduce coking (carbon loss).

Accomplishments: Working with the Catalytic Upgrading of Pyrolysis Products Project, identified reaction pathway over the active phase and the support under low pressure.

Significance:

This understanding allows us to optimize the catalyst through modification of the active phase and the support and should ultimately lead to increased low-pressure hydrogenation efficiency.



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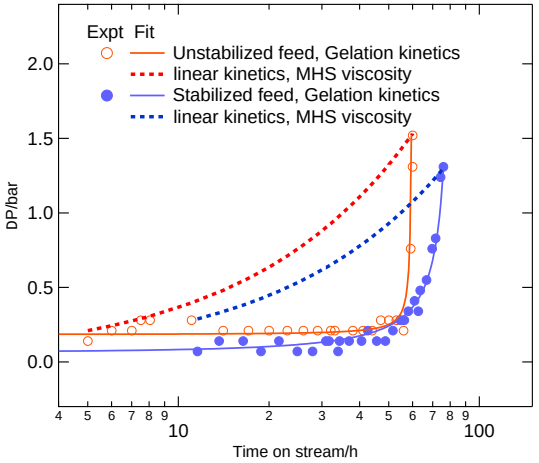
Technical Progress: Liquid-phase catalysis and reactor modeling

Objectives: Increase catalyst life, increase C yield, and mitigate process severity.

Accomplishments:

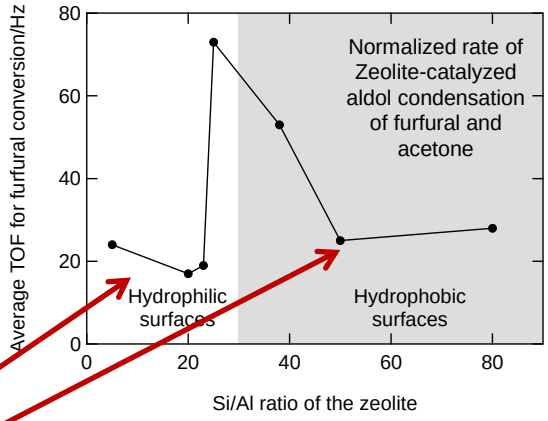
- Improved understanding of fouling is leading to potential solutions for extending catalyst life and C yield.
- Promising approaches for evaluating experimental results with global lower-order kinetics has been identified.
- **Experimental path** has been identified to separate transport effects from kinetic limits.



Reactor fouling via gelation follows different path vs. step polymerization

Significance:

- Ways to extend catalyst life and C yield now being **experimentally validated** at PNNL.
- Reveals options for real-time **experimental** process diagnostics and control.
- Inclusion of fiducial reactions and stochastic modeling enhances usefulness, scalability of **experimental** data.
- Directly supports bio-oil target cost trajectory (Impacts critical TEA factors: catalyst lifetime, C yield, and process severity).



Support properties greatly impact catalyzed aldol condensation rate

Potentially optimal surfaces

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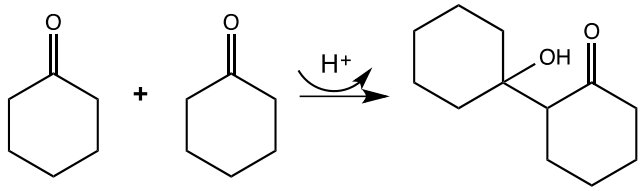
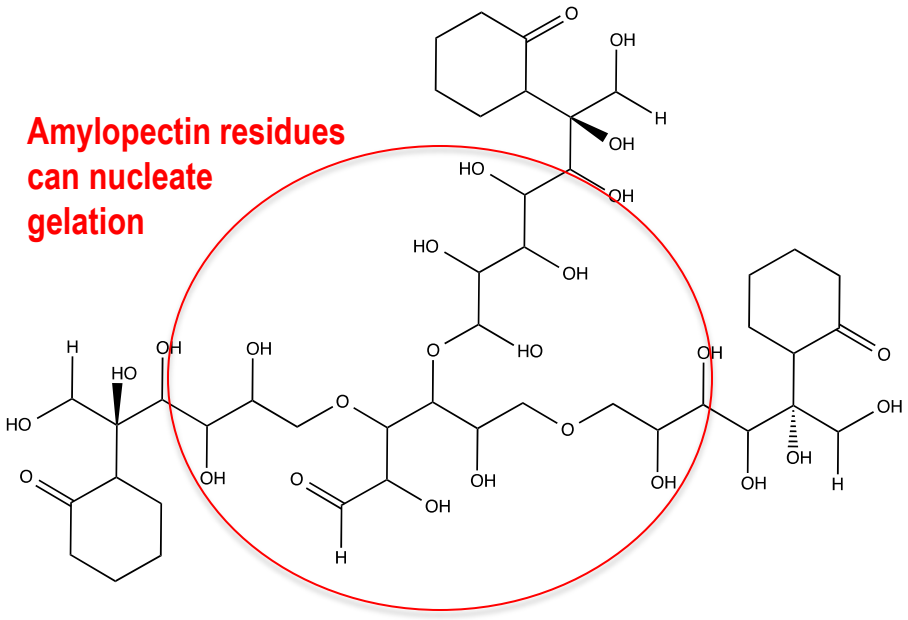
Technical Progress: Liquid-phase catalysis/ reactor modeling- Aldol condensation to gels



Prototypic Aldol condensation



Gel formation vs. linear polymerization

- Aldol condensation of 3 phenols with aldehydes in a fragment of amylopectin to form star polymers.
- Viscosity changes with gel 'networks' are very nonlinear vs. linear polymerization
- Supported by reactor DP data from 2 separate PNNL experiments.
- Selection of right catalyst support and/or surfactant addition might inhibit aldol condensation.

Gel formation leads to abrupt 'criticality' events that are hard to anticipate. This makes liquid phase upgrading process control more challenging and careful support selection critical.

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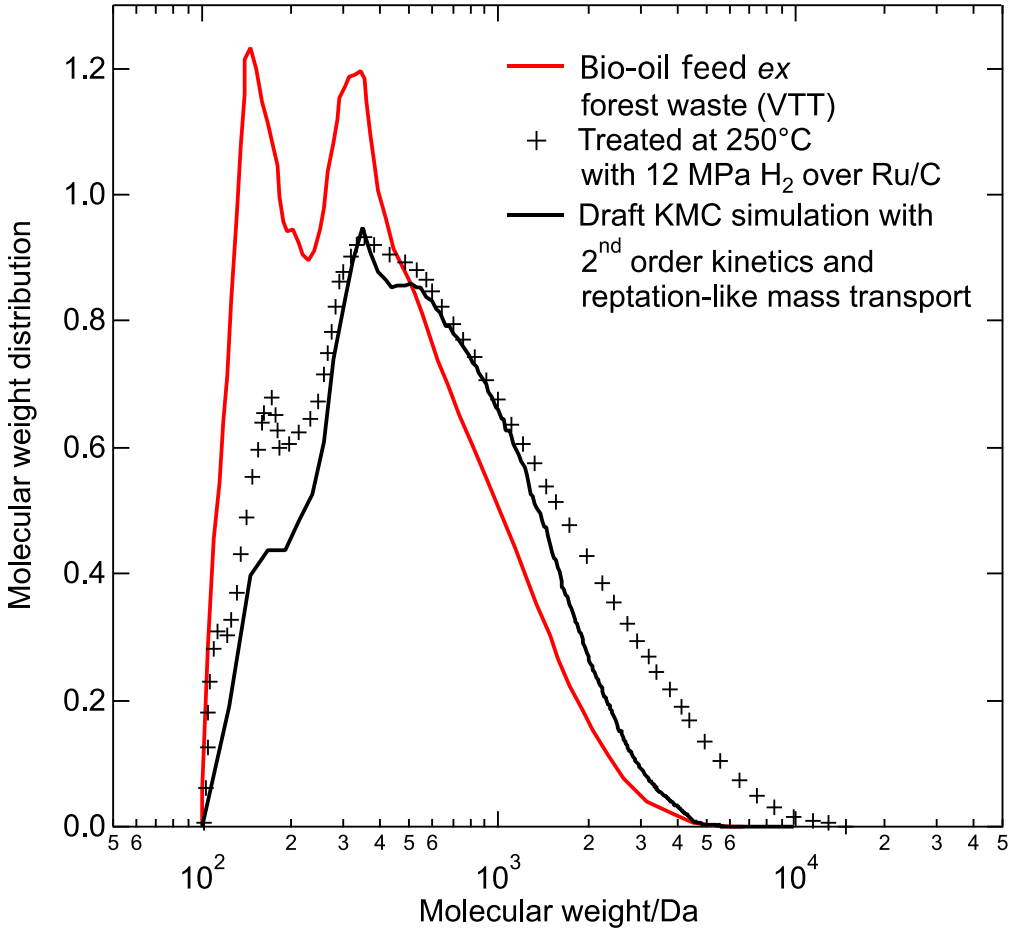
Technical Progress: LPU catalyst/reactor modeling- Monte Carlo kinetics can approximate the upgrading manifold



Kinetic Monte-Carlo offers a path forward to deal with major trends in MW yields without fully resolving the component micro-kinetics.

Data

- Mercader, at al., AIChE J, **2011**

Model

- 2nd order kinetics
- All species assumed reactive
- Simple Gillespie KMC
- 600K time steps
- MW dependent mass transport

Next steps

- More efficient solver (tau-leaping)
- 1st order HDO reactions
- Add speciated reactants and products
- Add multifunctional species
- Add thermal cracking

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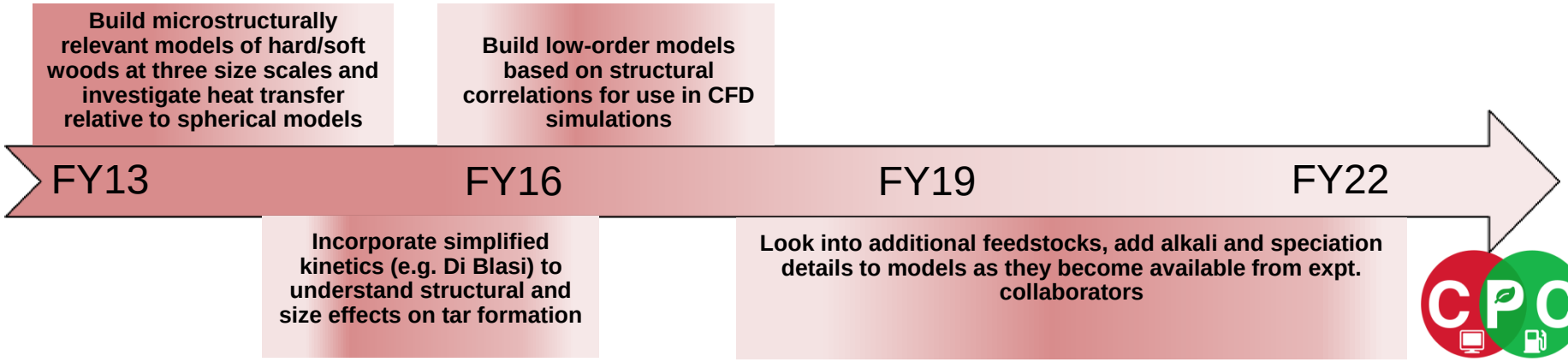
Future Work (1) – coordination and feedstock modeling

- CPC Coordination
  - Expand information and data sharing on CPC website
  - Complete component model interface framework for overall integration
  - Work with experimental teams to coordinate AOPs
  - Promote external and industry collaborations
- Feedstock effects
  - Devise chemically sensible models of the effects to replace the current, black box models
  - Develop correlations linking standard industry-accessible biomass measures with critical transport and kinetics parameters
  - Implement low-order (physically-based) versions of pyrolysis models that can be used to rapidly and accurately assess the impact of biomass type and pre-processing (e.g., for TEA)



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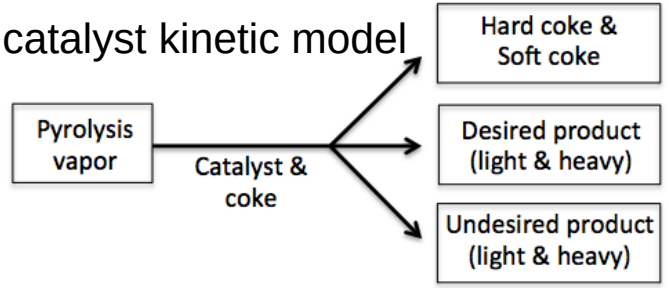
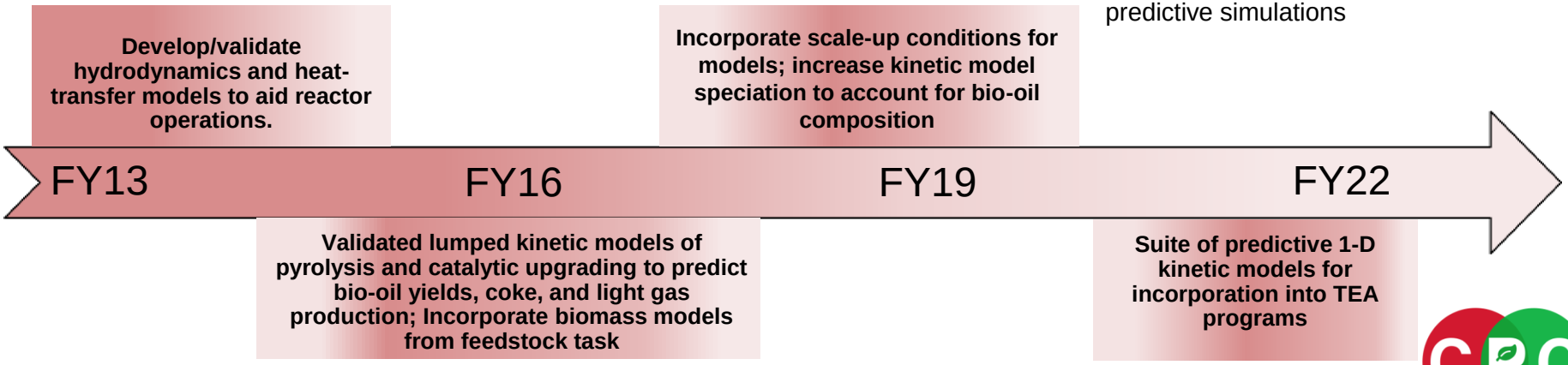
Future Work (2) – reactor analysis/scale up

- Continue assisting 2017 DCR catalytic VPU demonstration planning based on CFD with hydrodynamics and heat transfer.
- Identify partner to produce kinetic models needed for simulations
- Guide oil speciation analytics.
- Interpret results of fiducial experiments, assess implications for scale-up.
- Develop global kinetics needed for fully coupled transport-reaction simulations of DCR and hydrotreating reactors.
- Assist in DCR and LPU experimental data analysis and catalyst kinetic model validations.
- Begin simulations of R-cubed reactor for 2022.



Lumped kinetic mechanisms needed for predictive simulations



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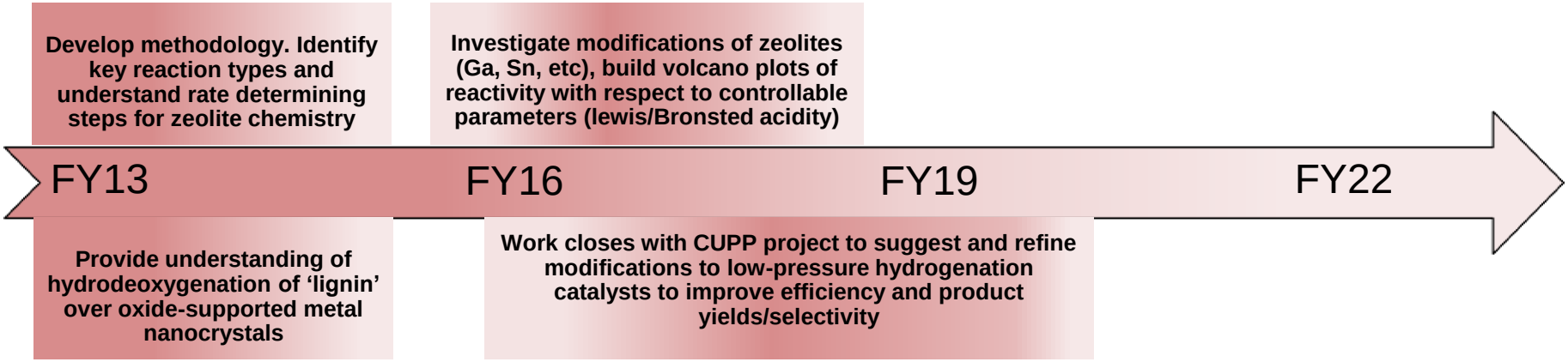
Future Work (3) – vapor phase catalysis

- Continue to validate zeolite chemistry results. Investigate modifications (other metals, channel sizes, etc) that can enhance desired chemistry (oil) over undesired (coking/light gases)
- Develop global kinetics needed for fully coupled transport-reaction simulations of DCR.
- Assist in DCR experimental data analysis and validate models for ZSM-5 performance.
- Begin simulations of R-cubed reactor and nano-catalyst VPU demonstration for 2022.



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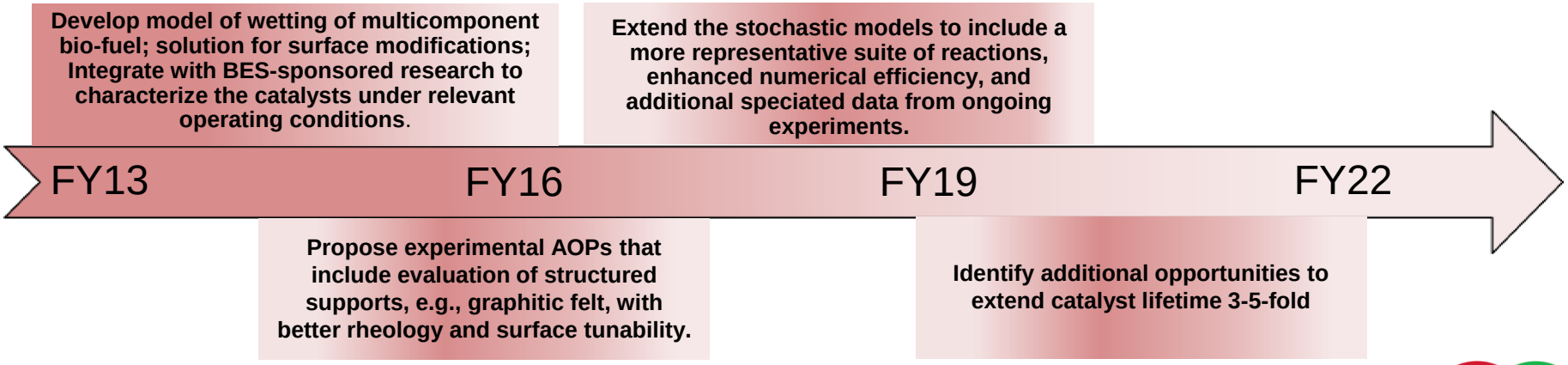
Future Work (4) – liquid phase catalysis

- Collaborate with experiments to validate potential of process controls and surfactants to improve catalyst life and C yield.
- Guide oil speciation analytics.
- Propose experimental AOPs for structured catalytic supports (e.g., graphitic felt, with better rheology and surface tunabilty).
- Extend stochastic models to include a more representative suite of reactions, enhanced numerical efficiency, and additional speciated experimental data.
- Integrate with BES-sponsored research to characterize the catalysts under relevant operating conditions.



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Summary

CPC progress has been considerable:

- Linked biomass feedstock to vapor- and liquid-phase upgrading feeds with particle-scale and pyrolysis modeling
- Identified DCR reactor vapor/catalyst rate parameters critical to 2017 vapor phase upgrading demonstration
- Identified features of ZSM-5 catalyst chemistry that can enhance C-C coupling in vapor phase to achieve 34%C yield, 12%O
- Identified new nano-catalyst-based chemistry for low-pressure hydrodeoxygenation. Working on modifications to improve effectiveness.
- Identified promising routes to extending liquid phase upgrading catalyst life by 1.5 (2017) and 3X (2022) and MW selectivity
- Identified low-order approach for approximating LPU kinetics
- Aligned inter-lab collaborations with BETO bio-oil targets
- Set up direct contacts with experimental and TEA teams

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Acknowledgements

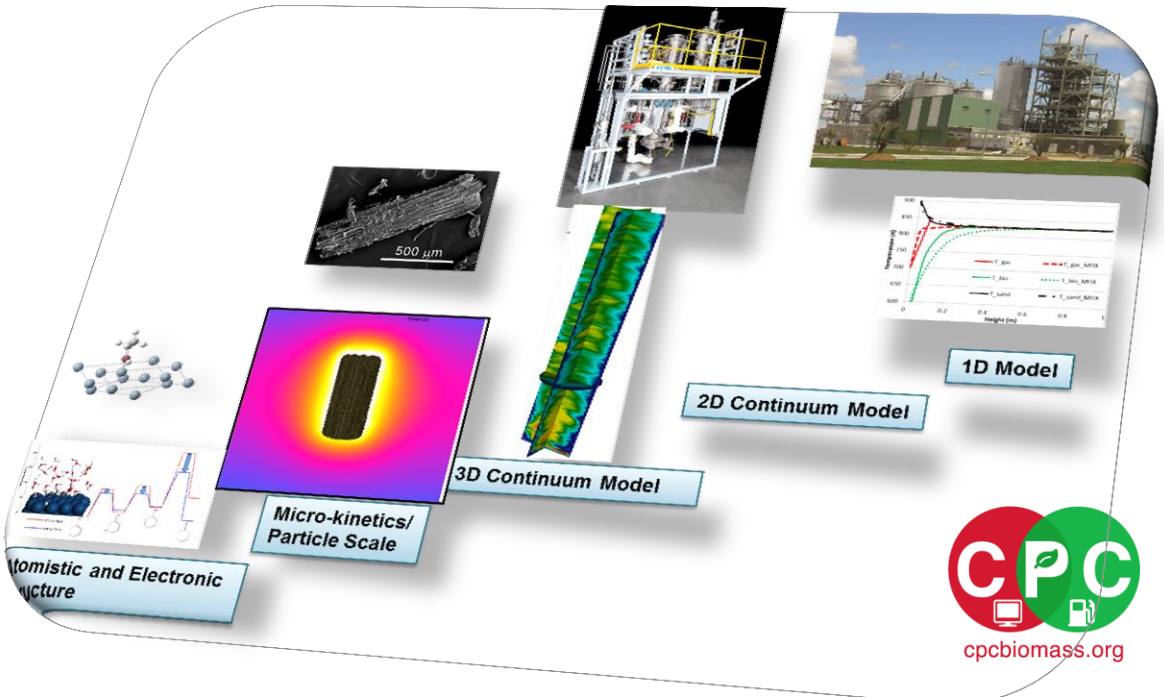
Computational Resources

Peregrine (EERE)

OLCF, ALCF, EMSL (Office of Science)

A multi-scale problem

A multi-lab solution



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Backup Slides

Publications

1. 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, J. Phys. Chem. A, accepted
2. Weber, Robert S., Olarte, Mariefel, V. and Wang, Huamin, "Modeling the Kinetics of Deactivation of Catalysts during the Upgrading of Bio-oil", 2015, Energy & Fuels, 29, 273-277.
3. 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 Morphology and Resolved Microstructure for Simulations of Intraparticle Transport Phenomena. Energy & Fuels 2015, 29 (1), 242-254.
4. J.M. Clark, M.R. Nimlos, D.J. Robichaud, "*Bimolecular decomposition pathways for carboxylic acids of relevance to biofuels*." J. Phys. Chem. A, 2015, 510-516.
5. A. Trendewicz, R, Braun, A. Dutta, J.L. Ziegler. One dimensional steady-state circulating fluidized-bed reactor model for biomass fast pyrolysis. Fuel 133: 253-262, 2014.
6. Yeohoon Yoon, Roger Rousseau, Robert S. Weber, Donghai Mei, and Johannes A. Lercher. First-principles Study of Phenol Hydrogenation on Pt and Ni Catalysts in Aqueous Phase. J. Am. Chem. Soc., 2014.
7. C.S. Daw, J.S. Halow, and S. Pannala. Random Walk Model for Biomass Particle Mixing in Bubbling Fluidized Beds. Ind. Eng. Chem. Res., 2014, 53 (41), pp 15836–15844.
8. C. Liu, R.S. Assary, L.A. Curtiss. Investigation of Thermochemistry Associated with the Carbon-Carbon Coupling reactions of Furan and Furfural using Ab Initio Methods. J. Phys. Chem. A, 2014.
9. Ferguson, Cheng, L., Bu, L, Kim, S., Robichaud, D. J., Nimlos, M. R., Curtiss, L. "The stability of carbocations in H-ZSM5 at high temperature: Are carbocations present as intermediates of dehydration reactions in vapor phase upgrading of pyrolysis oil?" Chem. Phys. Lett. submitted.
10. Clark, J., Pilath, H.M., Mittal, A., Moens, L., Robichaud, D. J., Johnson, D. K., "Direct production of propene from the thermolysis of PHB. An Experimental and DFT Investigation", J. Phys. Chem. A, submitted

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Publications in preparation

1. *Weber, R.S., Nimlos, M.R. Strike a Happy Medium: Upgrading of biogenic fuel feedstocks gas or condensed phase.*
2. Ziegler, J.L.; Pannala S.; Grout, R.W.; Robichaud, D.J .; and Nimlos, M.R. “Residence Time Distributions in Riser Reactors for Upgrading Biomass Pyrolysis Vapors: Part 1 validation and numerics”
3. Ziegler, J.L.; Pannala S.; Grout, R.W.; Robichaud, D.J .; and Nimlos, M.R. “Residence Time Distributions in Riser Reactors for Upgrading Biomass Pyrolysis Vapors: Part 2 Pilot scale simulations and operational parameter study”
4. A. Trendewicz, R, Braun, A. Dutta, J.L. Ziegler. ”Kinetic TEA model development.”
5. G.A. Ferguson, G.T. Beckham, M.J. Biddy, “*The mechanism of selective-ring opening of cycloalkanes on metal surfaces studied by periodic density functional theory calculations*.”
6. G.A. Ferguson, J. Clark, D. Robichaud, K. Gurchalla, G.T. Beckham, “*ab initio phase diagrams of coabsorption of hydrogen and guaiacol over Pt*.”
7. Clark, J., Ferguson, G. A., Beckham, G., Robichaud, D.,”Effects of van der Waals on linear scaling relations”, in preparation.
8. G.A. Ferguson, M. Griffin, J. Clark, D. Robichaud, G.T. Beckham, J. Schaidle, D. Ruddy, S. Habas “Deoxygenation reactions of lignins over oxide supported metals”
9. S. Kim, D. Robichaud, L. Bu, M.R. Nimlos, G.T. Beckham, “*Density functional theory and experimental study of furan formation mechanisms in H-ZSM5 zeolites from oxygenated pyrolysis-derived species*.” J. Phys. Chem. A.
10. Trendewitz, A., Ziegler, J., Robichaud, D. J., Dutta, A., “Investigation of fluid dynamics and heat transfer in circulating fluidized bed reactors for entrained flow pyrolysis: Steady-state and transient 1D, 2D, and 3D non-reactive simulations.

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Presentations (1)

1. Emilio Ramirez, C. Stuart Daw, Sreekanth Pannala, Jack Halow, Charles E.A. Finney and Janine Galvin. Computational Analysis of Biomass Particles in a Bubbling Bed. 2014 AIChE Annual Meeting, Atlanta, GA, November 16-21.
2. Gavin Wiggins, C. Stuart Daw, Jack Halow. Low-Order Modeling of Biomass Particle Mixing and Reaction in a Bubbling-Bed Fast Pyrolysis Reactor. 2014 AIChE Annual Meeting, Atlanta, GA, November 16-21.
3. E. Ramirez, C.S. Daw, J. Galvin, J. Halow, S. Pannala, and C. Finney. Computational analysis of biomass particles in a bubbling bed. TCS 2014 Conference, Denver CO, September 2-5, 2014.
4. G. Wiggins, C.S. Daw, and P. Ciesielski. Particle-scale computational modeling of woody biomass pyrolysis. TCS 2014 Conference, Denver CO, September 2-5, 2014.
5. Ziegler, J.L.; Pannala S.; Grout, R.W.; Robichaud, D.J .; and Nimlos, M.R. Effects on FCC Catalyst Residence Time Distributions Through Simulations of Circulating Reactors. AIChE Spring Meeting and Global Congress on Process Safety, New Orleans April 2014: Enabling Process Innovation Through Computation-EPIC session.
6. Ziegler, J.L.; Pannala S.; Grout, R.W.; Robichaud, D.J .; and Nimlos, M.R. 2014 NETL Workshop on Multiphase Flow Science, Morgantown, August 6-7, 2014: “A Study of Resident Time Distributions in Riser Reactors for Upgrading Biomass Pyrolysis Vapors”
7. Ziegler, J.L.; Pannala S.; Robichaud, D.J .; and Nimlos, M.R. Using 3D Simulation to Calculate FCC Catalyst Residence Time Distributions in a Pilot-Scale, Circulating Riser Reactor for Pyrolysis Vapor Upgrading. TCS: Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products. Denver CO, September 2-5, 2014.
8. Ciesielski, P. N.; Grout, R; Donohoe, B. S.; Nimlos, M. R.; Foust, T. D., Construction of biomass particle models from microscopy data for simulation of transport phenomena with realistic system geometry. AIChE Fall Meeting, San Francisco, CA, November 2013
9. Ciesielski, P. N.; Crowley, M. F.; Robichaud, D.; Donohoe, B. S.; Nimlos, M. R.; Foust, T. D., Simulations of Heat and Mass Transport during Biomass Conversion Processes using 3D Biomass Particle Models with Resolved Microstructure. Comsol Conference, Boston, MA, October 2014.
10. Ciesielski, P. N.; Crowley, M. F.; Robichaud, D.; Sanders, A.; Donohoe, B. S.; Nimlos, M. R.; Foust, T. D.. Frontiers in Biorefining, Prince Edward Island, GA, October 2014. 3D Biomass Particle Models with Realistic Morphology and Resolved Microstructure for Finite Element Simulations of Intra-Particle Transport Phenomena.
11. Ciesielski, P. N.; Crowley, M. F.; Robichaud, D.; Sanders, A.; Donohoe, B. S.; Nimlos, M. R.; Foust, T. D., Biomass Feedstock Modeling: Simulations of Intra-Particle Transport Phenomena during Biomass Conversion Processes using 3D Particle Models with Resolved Microstructure. Biomass 2014, Washington DC, July 2014.
12. Ciesielski, P. N.; Foust, T. D.; Crowley, Donohoe, B. S.; Robichaud, D.; Nimlos, M. R., Simulations of Microscale, Intra-Particle Heat and Mass Transport during Fast Pyrolysis using Biomass Particle Models with Resolved Microstructure. TCS Biomass 2014, Denver, CO, September 2014.

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Presentations (2)

13. Lintao Bu, Seonah Kim, Tabitha Evans, Calvin Mukarakate, David Robichaud, Mark Nimlos, Gregg Beckham, TCSBiomass, Theoretical and experimental study on furan formation over H-ZSM-5 using model compounds in pyrolysis oil
14. Jared Clark, Mark Nimlos, David Robichaud, TCSBiomass, Pyrolytic decomposition of organic acids for the upgrading of pyrolysis oil and the production of fuel intermediates
15. David Robichaud, Calvin Mukarakate, Rhodri Jenkins, Jared Clark, Mark Nimlos, TCSBiomass, Selective hydrogenation of carbonyls
16. Jared Clark, Mark Nimlos, David Robichaud, 247th ACS, Comparison of uni-molecular and bi-molecular thermal decomposition pathways for carboxylic acids of relevance to biofuels
17. Haoxi Ben, David Robichaud, Mark Nimlos, Calvin Mukarakate, Gregg Beckham, Glen Ferguson, Seonah Kim, 248th ACS, Dehydration of ethanol on zeolite – a mechanistic study by isotopic tracing and in-situ NMR monitoring
18. Mark R Nimlos, Calvin Mukarakate, David Robichaud, Rhodri Jenkins, 248th ACS, Selective hydrogenation of biomass pyrolysis vapors
19. Seonah Kim, Lintao Bu, David Robichaud, Mark R Nimlos, Gregg T Beckham, 248th ACS, Density functional theory study of furan formation in H-ZSM-5
20. Robichaud, D. J., University of Bath Summer showcase, Interface between computation and experiments: where we can go from here.
21. Rousseau, R., Mei, D., Yoon, Y., Weber, R., Lercher, J., 249th ACS, First principles study of phenol hydrogenation on Pt and Ni catalysts in aqueous phase
22. Mayes, H., Zhou, X., Beckham, G., Broadbelt, L., 249th ACS, Charting elementary steps in the cellulose pyrolysis reaction network.
23. Liu, Cong, Assary, R., Curtiss, L., 249th ACS, In silico zeolite catalyzed carbon-carbon coupling reactions for furan upgrading
24. Kim, S., Robichaud, D., Bu, L, Mukarakate, C., Evans, T., Beckham, G., Paton, R., Nimlos, M., 249th ACS, Mechanistic Study of fran formation in HZSM-5 using quantum mechanical modeling.

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2013 Peer Review Comments and Responses (1)

- **Appears to be valuable work, but the large scope also appears to base-load the NL's and justify their existence as much as feeding pre-commercial development.**

Response: Our primary objective is to increase the value of non-proprietary bio-oil technology information generated by national labs. Other DOE programs have made major investments at national labs to create unprecedented computational modeling and simulation capabilities. Coordinated use of these additional research tools by BETO will accelerate progress and reduce costs. By working closely with lab and pilot-scale experiments, computational modeling can make more effective use of experimental results and improve planning of future experiments and process demonstrations. Results from this project will be publicly available and provide more accurate and objective technical information on which DOE and other public agencies can base strategic decisions.

- **Looks promising, but too early to tell for sure. Involve industry, and focus on tools more than individual process technologies.**

Response: Industry relevance is maintained by a panel of industry-connected advisors who provide oversight. The panel helps us identify priorities and minimize activities that may be of academic interest but do not address key technology barriers. Several of the labs in this project are already collaborating with industry partners via CRADAs, Work-for-Others, and as members of teams funded by successful proposals to DOE-issued FOAs. Many of the R&D capabilities at the labs stemming from these pre-existing activities will be leveraged by the computational modeling activity, as long as there are no conflicts with confidentiality agreements. Likewise, we expect that the additional data, insights, and computational tools generated by this activity can lead to further lab-industry CRADAs, Work-for-Others, or other types of joint lab-industry partnerships.

- **Organization seems to be in place to make this project a success**

Response: We acknowledge that the current national lab management structure can make close collaboration among multiple labs a challenging effort. However, we believe that our previous experience with the CLEERS activity provides a useful precedent to work from. We firmly believe that the team members involved in the CPC provide an unprecedented range of technical biomass conversion and process modeling experience and expertise.

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2013 Peer Review Comments and Responses (2)

- **The use of a consortium to provide fundamental information that will educate and guide applied efforts is important. In future years, DOE will want to ensure that the consortium continues to fine-tune its efforts to maintain focus on the highest priority issues relevant to BETO and avoid wandering into academically interesting, but secondary topics.**

Response: We believe computational modeling is most productive when it is directed at testing fundamental hypotheses about the chemistry or physics governing energy transformation processes. Because we are emphasizing models that test hypotheses concerning the inherent physical limits of biomass to bio-oil conversion rather than designing specific equipment, we expect that our results will be useful for a broad range of specific commercial bio-oil technologies.

- **This is important/required work that will add value to the BETO effort. This is a good use of our national lab assets. It leverages existing knowledge and should remain grounded by the inclusion of a panel of industry advisors.**

Response: We are working diligently to leverage our activities in this project with facilities and capabilities partially or wholly supported by other parts of DOE, especially the Office of Science. We believe the CPC is providing a unique opportunity for bridging the gap that often exists between the fundamental and applied research parts of the DOE.

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Selected Advisor feedback (Oct. 2014)

- Make sure all the boxes connect (between labs, and also process areas, feedstock/pyrolysis/vapor phase upgrading/liquid phase upgrading).
  - New CPC structure (task oriented, not lab oriented)
  - CPC/sub-team/experimental/TEA meetings
  - More direct links to BETO project structure
  - Plan for model component interface
- Do a risk analysis of activities on the projects.
  - Setting priorities based on TEA
  - All projects have an experimental collaborator to ensure relevance and tie-in to technical targets
- The biggest issue is the need for experimental validation in the near term.
  - All projects have an experimental collaborator to provide validation
  - Simulating ongoing experiments at NREL & PNNL
  - Including data from Separation Design & literature
- Make results a la carte. i.e. allow potential users of the information generated by the CPC to pick and choose what they need.
  - GitHub distribution of some code components (sub-models)
  - Website and INL library distribution of reference cases
  - Direct links between widely used software packages

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Selected Advisor feedback (Feb. 2015)

- How are we eliminating redundancy among the labs
  - Each of the labs is participating on one or more sub-teams that are focused on 4 main R&D activity areas that have been corporately identified by the CPC team. In addition to these R&D areas, ORNL is acting as the overall team coordinator to help identify potential overlap issues. Through monthly all-lab telecoms, sub-team meetings, and quarterly face-to-face team meetings, we continually update each other on our progress and make strategic decisions to prevent redundancy and maximize synergy.
- Why do we need CFD as there a lot of correlations in the literature? (specifically in regards to slugging, but relevant to other areas)
  - Our detailed reviews of the literature on slugging correlations (and other issues) have revealed inconsistencies in the available information, so we have initiated CFD simulations that will be validated with ambient experiments using a companion reactor of the same dimensions and the same bed material. We expect to use the information thus obtained to make more accurate predictions of the slugging transition conditions and providing reactor operators a tool that can be used for real time monitoring to anticipate when they are near slugging and how to adjust accordingly.
- How to account for catalytic effects of ash/inorganic impurities in biomass within the pyrolysis reactor.
  - We recognize that catalytic effects from ash during pyrolysis can be especially important. In the case of our models, this will be accounted for in the reaction kinetics both inside and external to the biomass particles. It should be noted that currently, no such kinetic mechanism exists in the literature. The CPC is actively trying to identify a suitable experimental partner to generate those kinetic mechanisms for inclusion with our reactor simulations.

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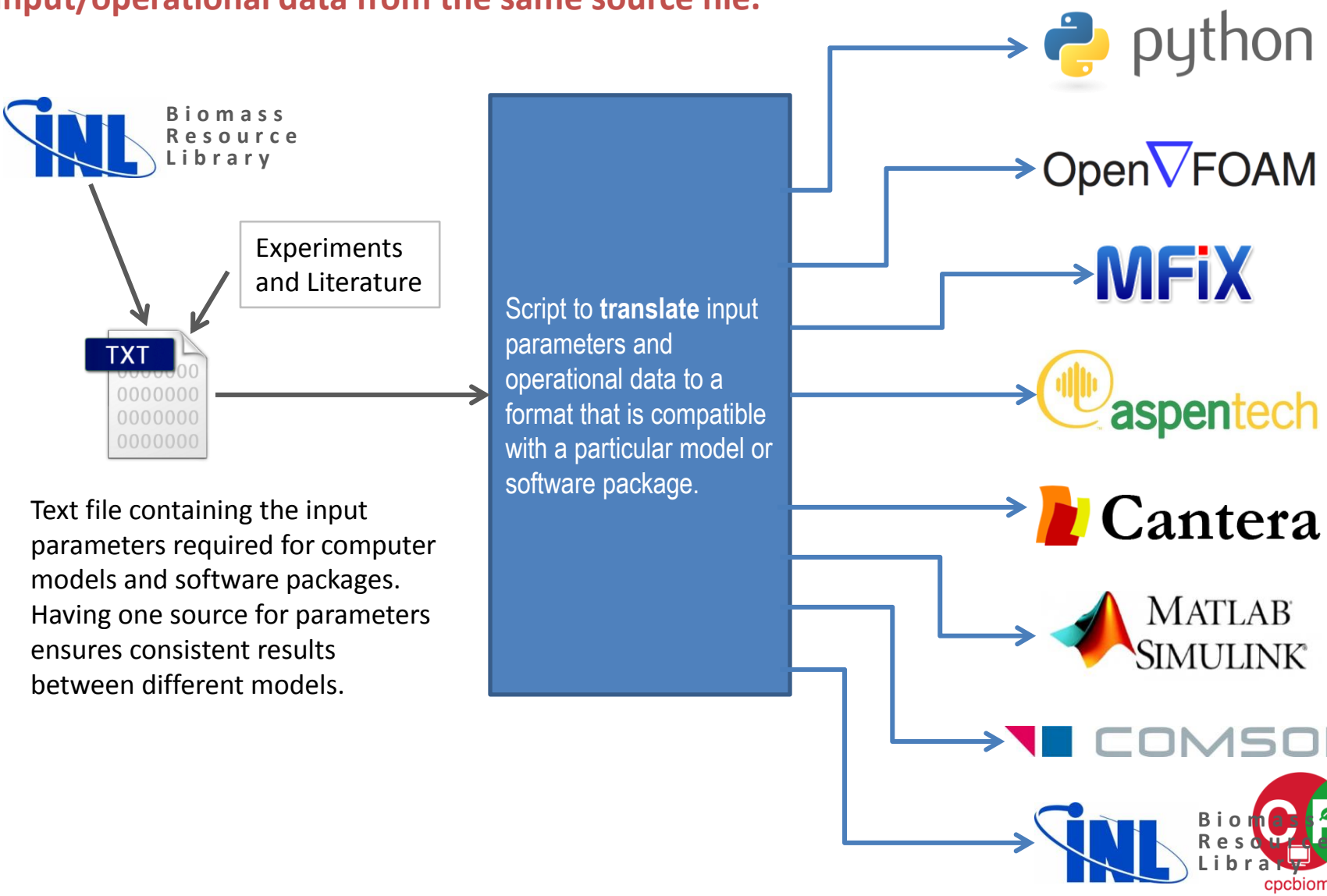
Interfacing between CPC component models

Goal is to have different types of models acquire their input/operational data from the same source file.



Text file containing the input parameters required for computer models and software packages. Having one source for parameters ensures consistent results between different models.