

Computational Pyrolysis Consortium

2013 DOE Biomass Technologies Office (BETO) Project Peer Review

Biotechnology Area Review

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May 22, 2013



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Goal/Objective (1)

- **Through multi-lab collaboration, develop and implement computational tools that support R&D aimed at:**
 - Understanding and minimizing carbon losses during fast pyrolysis;
 - Improving bio-oil properties (e.g., reduce oxygen content, corrosivity, viscosity and increase stability) with vapor and liquid-phase catalysis;
 - Improving utilization of aqueous phase bio-oil components;
 - Improving understanding of scale-up and integration;
 - Improving predictions needed for TEA and LCA of the most advanced fast pyrolysis and oil upgrading technologies;



Achieve MYPP fuel cost target of \$3.00/gal by 2022

Goal/Objective (2)

- **Leverage and integrate experimental and modeling capabilities at multiple national labs to accelerate progress**
 - **ORNL**
 - Multi-phase and catalytic reactor modeling (e.g., MFIX, DIBS)
 - Coordination of lab-industry-university R&D collaborations (e.g., CLEERS)
 - **INL**
 - Feedstock characterization tools and data
 - Biomass pre-processing PDU and models
 - **NREL/ANL**
 - Multiple micro-to-pilot-scale experimental pyrolysis reactors
 - Multi-scale biomass reaction and transport measurement capabilities
 - Catalyst screening and characterization
 - Vapor-phase H-donor catalyst modeling
 - **PNNL**
 - Build database and code for constructing, tuning, archiving and reusing microkinetics mechanisms in a form useful to experimentalists
 - Quantum and MD catalysis mechanisms (in partnership with U Del and TUM)
 - Reaction mechanism reduction

Project QUAD Chart Overview

Timeline

- Start Date: May 1, 2013 (Just started)
- End Date: September 30, 2017
- (Go/No-Go decision March 31, 2014)

Budget

Funding received in FY 2011: \$0

Funding in FY 2012: \$0

Expected Funding for FY 2013:

Total DOE - \$2.2MM

- ORNL- \$550K
- NREL- \$621K
- PNNL/U Del - \$360K/\$250K
- INL- \$115K
- ANL- \$300K

Years funded & avg. funding/yr:

NEW PROJECT

Barriers Addressed

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

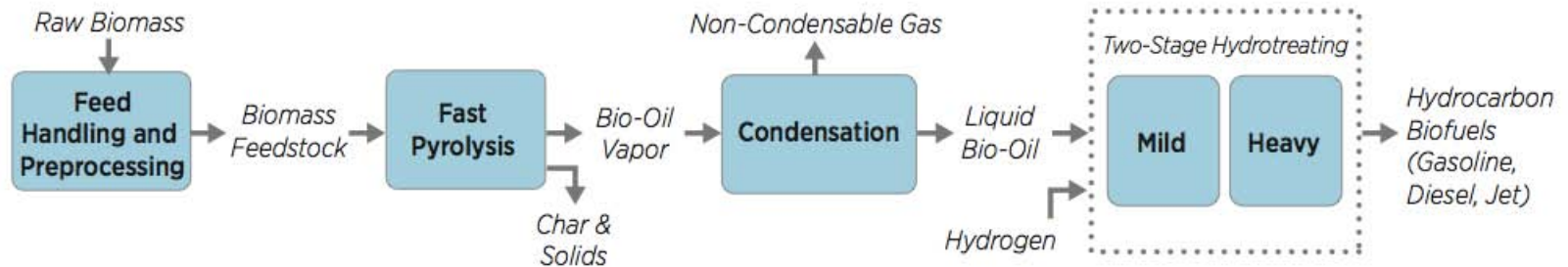
Partners & Roles

- ORNL
 - Overall coordination
 - Global reactor models
 - Model interfacing/integration
- NREL/ANL
 - Pyrolysis & catalysis data
 - Vapor-phase catalysts & models
 - Biomass reaction models
- PNNL/U Delaware/TU Munich
 - Hydrotreating & aqueous catalysts
 - Reduced order upgrading kinetics
- INL
 - Detailed feedstock characterization

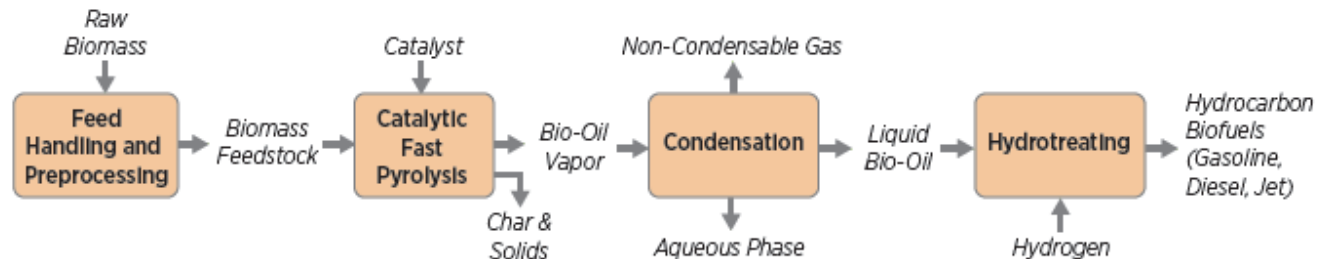
Project Overview (1)

We are targeting 3 key pyrolysis pathways in the MYPP

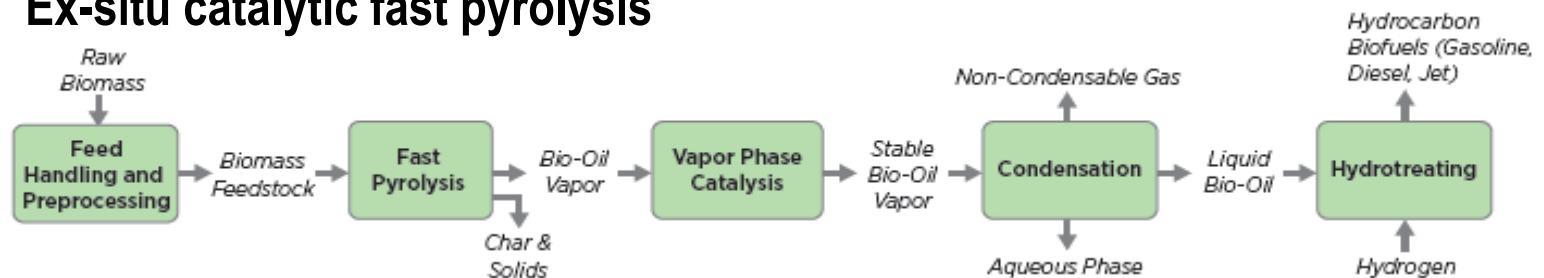
Fast pyrolysis and hydroprocessing



In-situ catalytic fast pyrolysis



Ex-situ catalytic fast pyrolysis



Project Overview (2)

Each pathway involves specific and general barriers:

Specific

- **Fast pyrolysis & hydroprocessing**
 - New catalysts for multi-step raw oil upgrading
 - High char yields
- ***In situ* fast pyrolysis**
 - New catalyst development for *in situ* & raw oil upgrading
 - Biomass/catalyst/vapor mixing during pyrolysis
 - Time-temperature effects during pyrolysis
- ***Ex situ* fast pyrolysis**
 - New catalyst development for *ex situ* and raw oil upgrading catalyst development
 - Catalyst/vapor contacting in post-pyrolysis reactor
 - Post-pyrolysis time-temperature effects

General

- Sensitivity to feed properties & blends
- Internal biomass reaction & transport
- Inter-phase heat & mass transfer
- Raw oil is unstable, has high O
- Catalyst coking & deactivation
- Reaction mechanism reduction
- C loss to aqueous phase
- Oil contamination by particulate
- Multi-component process integration
- Carbon yields are low
- High demand of H₂, reaction severity

These are being addressed by the consortium team members in the following tasks...

Approach (Task 1): All lab collaboration

- ORNL Lead/ All Labs Partner
- Establish informal, pre-competitive collaboration among the lab partners
 - Regular telecoms/webinars among team members
 - Shared experimental and reference databases
 - Protocols for input/output data exchange between component models
- Establish industry advisors to provide feedback and guidance
 - 4-6 technically knowledgeable representatives
 - Occasional summary reports/webinars provided by lab team for comment
 - Most important input will be to keep priorities on target (relevant to industry)



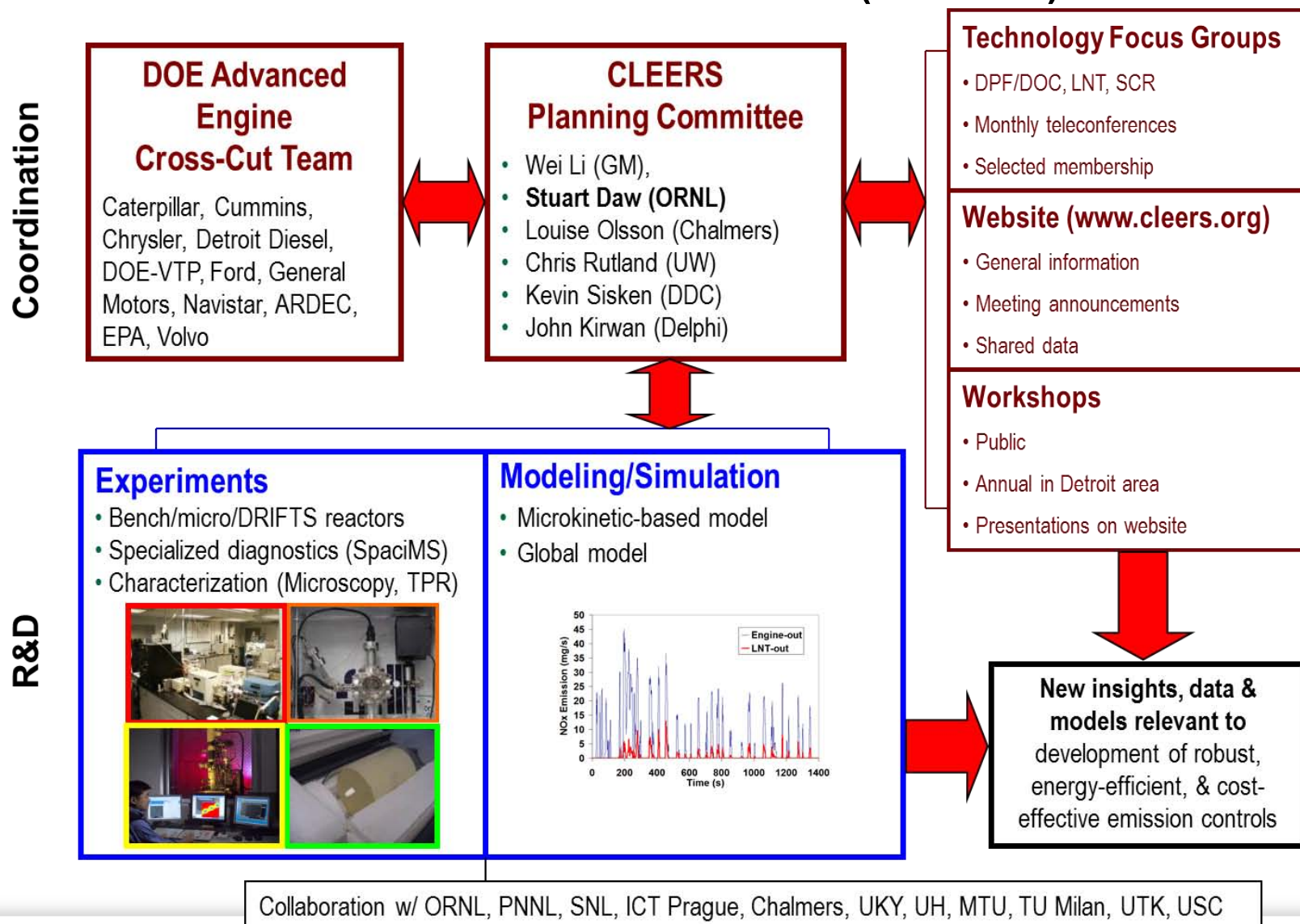
Sreekanth Pannala



Stuart Daw

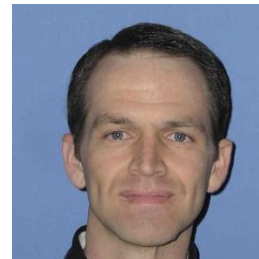
Approach (Task 1 continued)

ORNL is drawing on experience with the DOE Crosscut Lean Exhaust Emissions Reduction Simulation (CLEERS) Consortium



Approach (Task 2): Biomass characterization and data development

- INL Lead/NREL and ORNL Partner
- Establish a database within the Biomass R&D Library targeted at the pyrolysis feedstock
 - Identify key physical and chemical properties for 3 reference biomass feedstocks needed for computational pyrolysis modeling
 - Make property measurements where required data are currently not available (thermal conductivity, specific heat, gas diffusion rates, etc.)
- Assist NREL and ORNL in establishing standard input data formats for pyrolysis computational models
- Assist NREL and ORNL in establishing correlations between standard biomass measurements and micro and mesoscale biomass transport and kinetic properties



Tyler Westover



David Muth

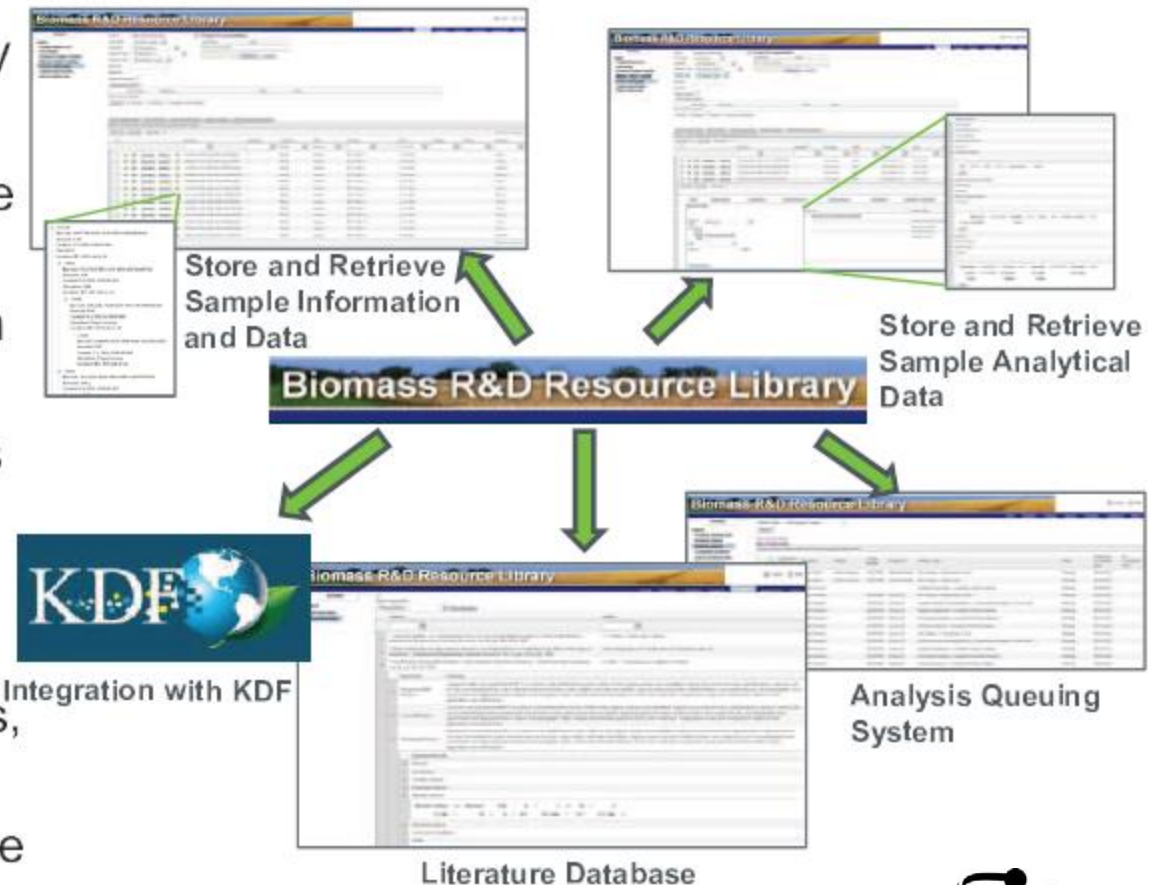


Shahabaddine
Sokhansanj

Approach (Task 2 continued)

The Biomass R&D Library at INL is a major asset

- Enhanced query capability
 - Analytical data points
 - Samples and literature simultaneously
- Export sample information and analysis
- Sample hierarchy enables tracking of sample history
- Self-managed sample templates
- Attach documents, reports, raw analysis
- Security measures in place



Approach (Task 3): Simulate Fast Pyrolysis and Interface to Upgrading

- ORNL Lead/NREL Partner
- **Construct baseline low-order integral models for fast pyrolysis reactors (w and w/o catalyst)**
 - Develop and incorporate NREL biomass particle evolution models
 - Calibrate/validate models as data become available
 - Utilize models for interpreting and planning NREL experiments
 - Utilize models to correlate/predict raw oil composition changes that impact downstream upgrading (report to PNNL)
- **Utilize CFD models (e.g., MFIX, DEM) to supplement experiments**
 - Identify quality/rate limiting processes not accessible to direct measurement or low-order models
 - Selectively use CFD to fill knowledge gaps



Sreekanth Pannala



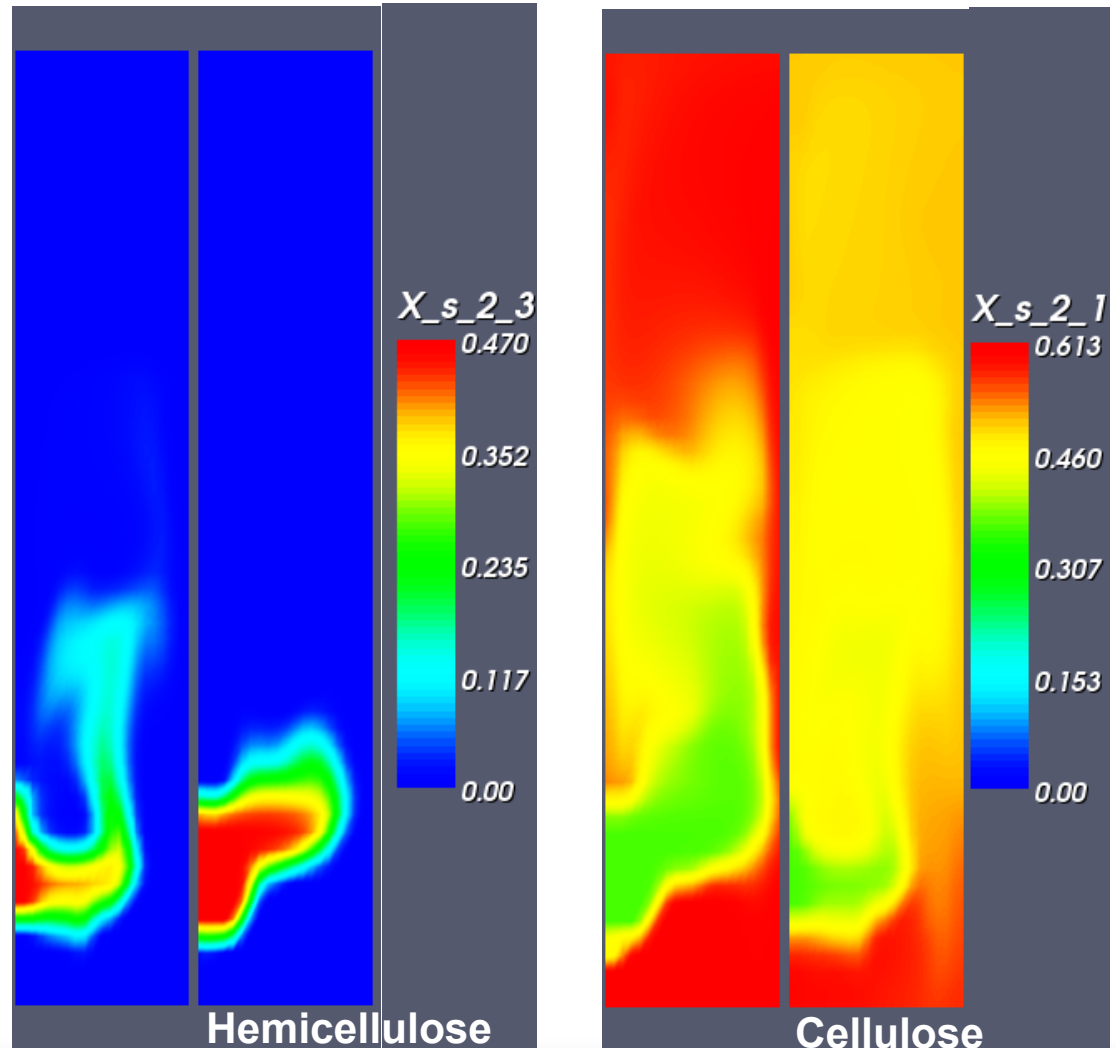
Stuart Daw

Approach (Task 3 continued)

ORNL is drawing on extensive experience with computational multi-phase reactor modeling and CFD

Example dynamic simulation of biomass pyrolysis in a 0.1 m-ID bubbling bed with MFIX:

- Left and right frames are snapshots in time
- Biomass feed enters at lower left
- Hemicellulose component reacts quickly
- Cellulose component reacts more slowly
- Both components exhibit large radial mixing gradients



Approach (Task 4): Computational modeling of fast pyrolysis oil upgrading

- PNNL Lead/U Delaware Partner
- Focus on catalytic hydro-upgrading of monomeric oxygenates
 - Addition of H to open aromatic rings and remove O
 - Stabilize unsaturated intermediates to reduce gums and tars
- Construct 1st principles kinetic model on an archetypal catalyst (e.g., Ru/C)
 - Reuse mechanisms and kinetics from previous NSF and BES studies
 - Use results to develop shareable practices for manipulating and interpreting complex biomass reaction data
 - Adapt recently developed methods for reaction order reduction leading to more tractable rate expressions for process modeling



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Roger Rosseau



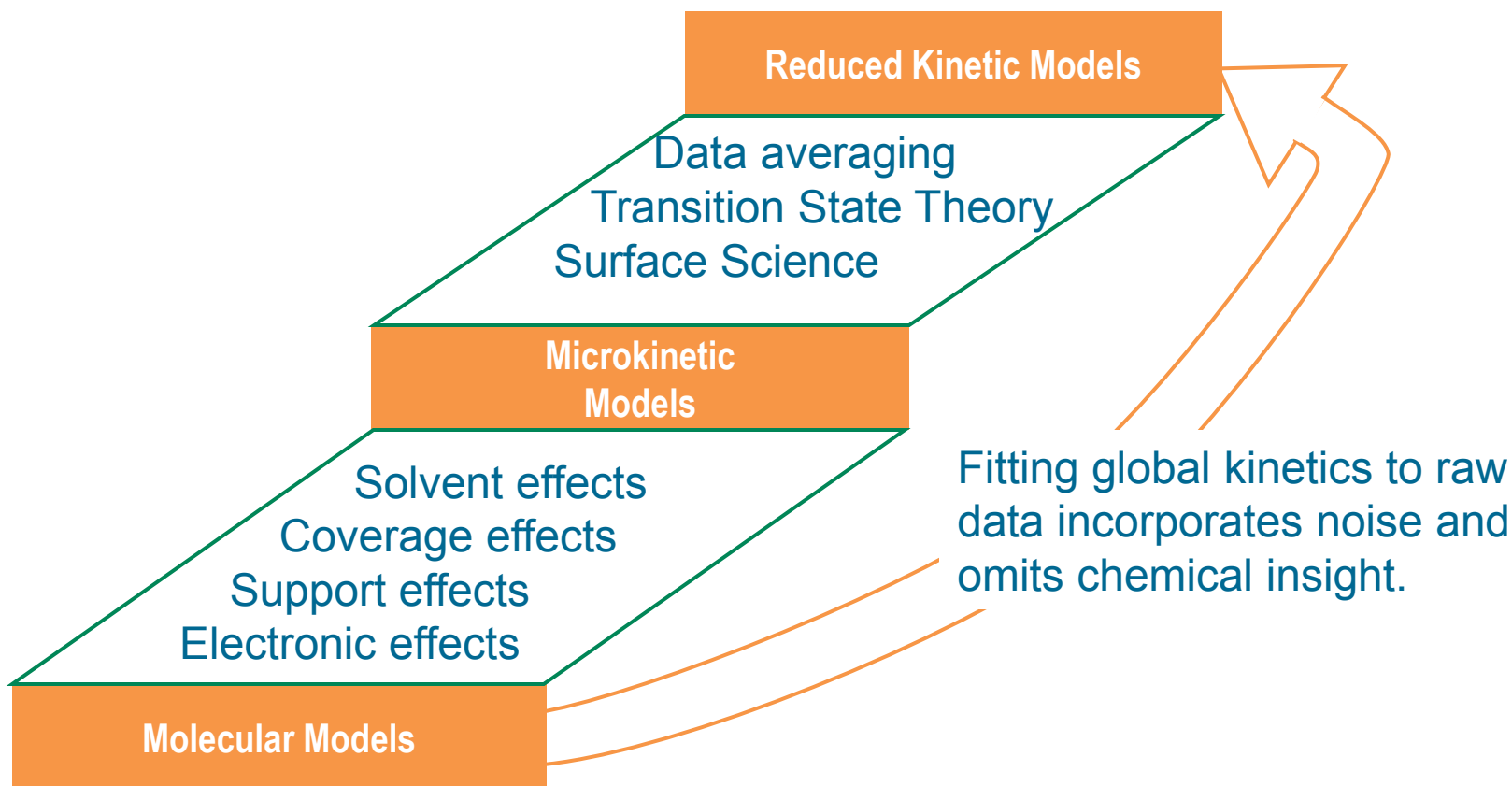
Bob Weber



Dion Vlachos

Approach (Task 4 continued)

PNNL's approach utilizes molecular models and microkinetics to make the catalytic upgrading kinetics more physically sound and predictive

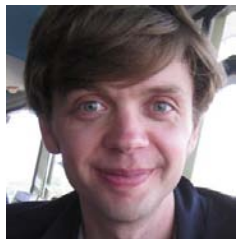


Approach (Task 5): Modeling of vapor phase upgrading*

- NREL Lead/ANL Partner
- NREL and ANL will investigate H donor catalysts at a fundamental level for both *in situ* and *ex situ* catalytic fast pyrolysis
 - Multiple atomistic and quantum chemistry computational approaches
 - Compare coke build-up to deoxygenation reactions
 - Optimize furan yields from carbohydrates
 - Optimize furan conversion to diesel HCs
- NREL will develop low-order kinetics for reactor context
 - Heat transfer, mixing, multi-phase flow, biomass particle evolution
 - Low-order kinetics will be utilized in integral reactor models to understand fundamental catalyst interactions that can affect reactor design and scale-up and potentially impact downstream upgrading.



Mark Nimlos



Gregg Beckham



Thomas Foust



Larry Curtiss



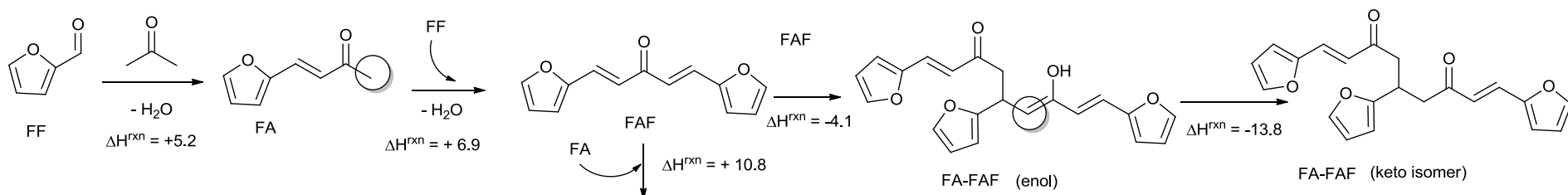
Rajeev Assary

* See also presentation 3.6.1.6 by Mark Nimlos

Approach (Task 5 continued)

NREL and ANL will apply unique computational methodologies to H donor catalyst modeling

- ❑ Reaction pathway landscape investigations
 - Thermodynamics of intermediates
 - Transition states, barriers, and kinetics
 - Identification of undesired reactions
- ❑ Theoretical Methods
 - High-level ab initio theory: CCSD(T), G4
 - Density Functional Theory (DFT)
 - Ab-Initio Molecular Dynamics (AIMD)
- ❑ Feedback loop with experimental efforts at ANL, NREL

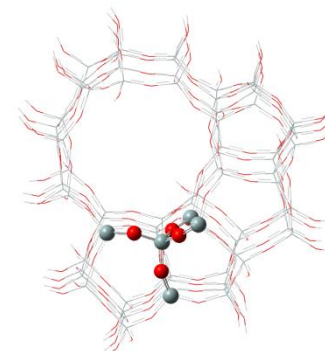


Example Scheme : C5 to C21 via cross Aldol reactions

Approach (Task 5 continued)

NREL will investigate the competition between coking reactions and deoxygenation in catalytic vapor phase upgrading

- ❑ **Reactions on catalysts that lead to aromatic compounds**
 - **Characterization of catalyst sites (i.e. Bronsted acid sites)**
 - **Investigate C-O breaking reactions (barriers, thermodynamics)**
 - **C-C coupling reactions**
 - **Effects of hydrogen donor molecules**
- ❑ **Theoretical Methods**
 - **Density Functional Theory (DFT)**
 - **Quantum Molecular Dynamics (VASP, CPMD)**
- ❑ **Collaborate with experimental work at NREL**



T12 active site in
ZSM-5

Approach (Task 6): Modeling upgrading of aqueous phase pyrolysis products

- PNNL Lead/U Delaware, TU Munich Partners
- Tune and deploy micro-kinetic modeling to guide recovery of aqueous phase carbon to capture its fuel value and avoid waste
 - Construct aqueous microkinetics and tune with experiments
 - Use microkinetics for sensitivity analysis and guide other experiments
 - With quantum chemistry, relate rates and solvent effects with molecular structure
 - Build on modeling experience and experimental data of University of Delaware and Technical University of Munich
 - As in task 4, use results to develop shareable practices for manipulating and interpreting complex reaction data
 - Develop reduced reaction mechanisms for tractable process modeling



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Roger Rosseau



Bob Weber

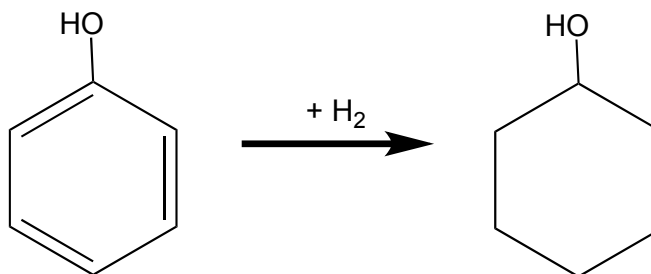


Dion Vlachos

Approach (Task 6 continued)

- Previous QM/MD modeling by PNNL has predicted important effects of reaction medium polarizability

The prototypic reaction:

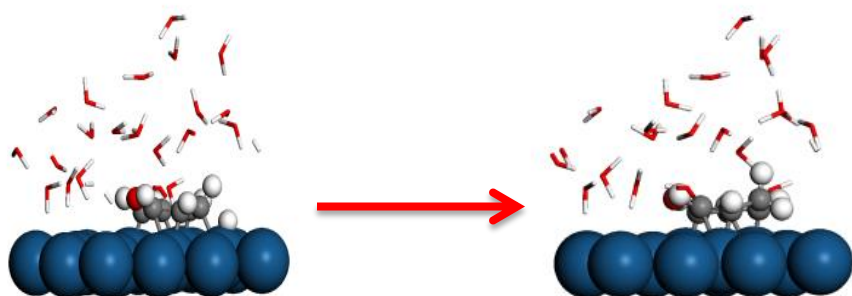


- In polar medium:

- H species have cationic character and react via electrophilic attack on phenol leading to preference for *ortho* and *para* sites for initial hydrogenation steps

- In nonpolar medium:

- H species on the surface of the catalyst are neutral and therefore do not react preferentially with any site on phenol, a prototypic intermediate



Approach (Task 6 continued):

- **PNNL and U Del will generate the first, 1st-principles microkinetic models for acid & metal catalysis in the aqueous phase**
- **Initial reaction networks will represent literature-based hypotheses on PGM-catalyzed initially for the conversion of glucose to H₂**
- **The reaction network will consist of ring opening and C-C, C-O, C-H and O-H metal catalyzed reactions**
- **The next reaction network will add acid-catalyzed reactions**
- **The work will proceed from mean-field microkinetics to QM/MM MD as appropriate.**
- **DFT will be used to estimate rate constants in the absence of solvent first and in water next.**
- **Simulation activities will be coordinated to share methodologies and, where possible, code.**

Technical Accomplishments/Status

- **Project just started at the end of March**
- **Two telecoms involving all the lab team members have been held to coordinate lab roles**
- **INL has established a SharePoint site for data exchanges**
- **Advisory panel candidates are being contacted**
- **Individual labs are consulting with their partners regarding their specific tasks**

Relevance

- **Addresses multiple MYPP barriers:**
 - Tt-E Bio-oil Stabilization, Tt-G Catalysts Development, Tt-K Integration, Tt-H Validation of 2017 Cost Target
- **Addresses key risk/uncertainty areas identified in fast pyrolysis and catalytic fast pyrolysis pathway design reports:**
 - Pyrolysis C yields and prediction of *in situ* and *ex situ* catalyst performance based on feedstock properties;
 - Reduction of aqueous phase C losses.
 - Integrated predictions of yields, production rates, catalyst life and regeneration, and reactor conditions and process configurations that inform techno-economic analysis
 - Improve carbon yields during catalytic vapor phase upgrading
 - Increase production of more valuable products (diesel and jet fuels)

Critical success factors

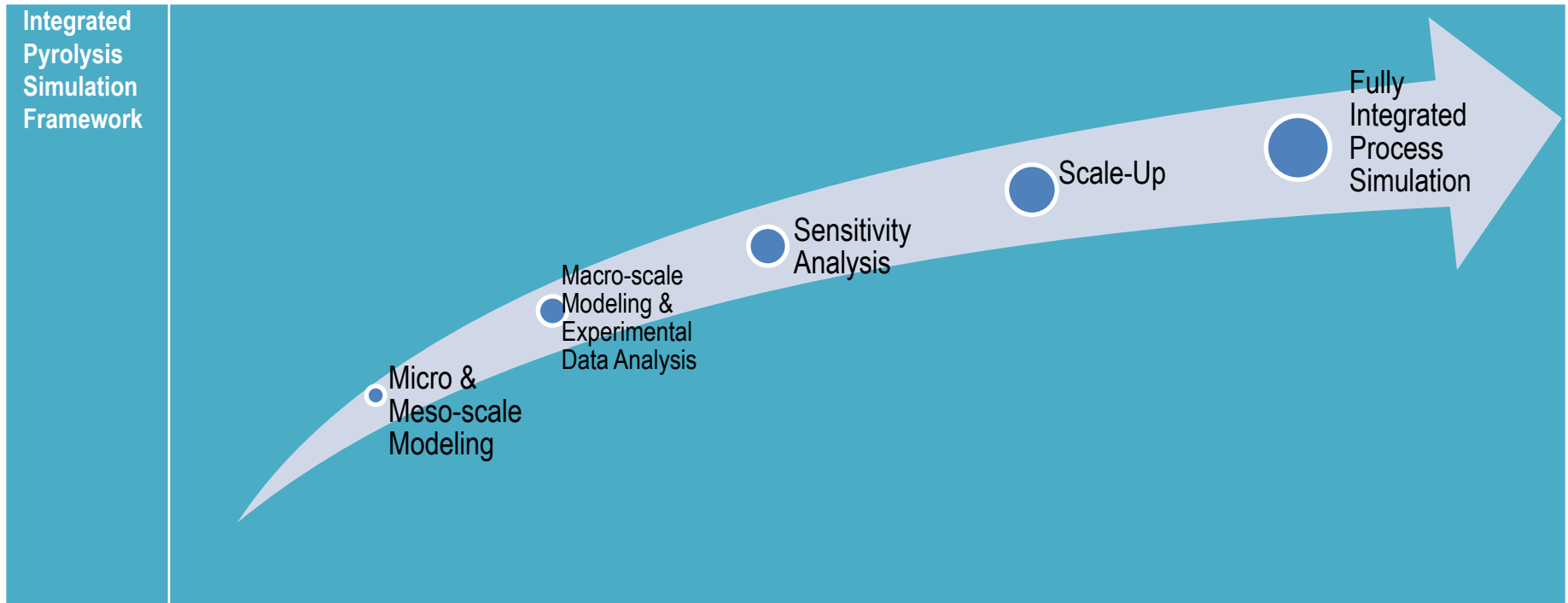
Factor	Goal	Approach
Improve yields and properties of pyrolysis oil	C yields ~ 40% ~ 10% oxygen in oil	<ul style="list-style-type: none">• Decrease char yields• Vapor-phase catalyst development• Reactor development
Predict global pyrolysis reactor performance	Validated over full range of pyrolysis conditions	<ul style="list-style-type: none">• Inclusion of detailed biomass properties• Transport modeling• Reduced global chemical kinetics• Inclusion of scaling effects
Recover carbon in aqueous streams	Suggest catalyst modifications and effective reaction conditions	<ul style="list-style-type: none">• Multi-scale catalyst modeling• Model guided experiments and sensitivity analysis
Improve hydrogen efficiency in upgrading oils	Suggest catalyst modifications and effective reaction conditions	<ul style="list-style-type: none">• Multi-scale catalyst modeling• Model guided experiments and sensitivity analysis
Process integration	Accurate mass and energy balances for TEA, LCA	<ul style="list-style-type: none">• Compatible process component models• Seamless input/output data transfer between components

Future Work: The Near Term

Task/Sub-task	Owner (s)	FY13 Quarters				FY14 Quarters			
		1st	2nd	3rd	4th	1st	2nd	3rd	4th
1. Multi-lab consortium									
Regular lab telecoms/web meetings	ORNL/All			●	◆				◆
Industrial advisory panel	ORNL/All			●	◆				◆
Review results/benefits- Go/No Go decision	All							●	◆
2. Computational database									
Multi-lab data sharing	INL/ORNL			●	◆				
Biomass parameters for pyrolysis	INL/NREL/ORNL			●	◆				
3. Pyrolysis-Oil Interface									
Integrated process simulation	ORNL/NREL/PNNL			●					◆
4. Model liquid oil upgrading									
Micro-kinetic models for aqueous C constituents	PNNL/U Del			●	◆				
5. Model vapor phase upgrading									
H donor catalyst mechanisms & kinetics	NREL/ANL			●					◆
Coke formation & deoxygenation models	NREL/ANL/ORNL			●					◆
Furan/pyran coupling & anhydrosugar energetics	ANL/NREL			●				◆	
Catalytic furan formation model	NREL/ANL			●					◆
Biomass intra-particle transport model	NREL/ORNL			●					◆
Reduced-order integrated fast pyrolysis model	NREL/ORNL			●					◆
6. Model aqueous phase oil upgrading									
Reduced-order aqueous reaction kinetics	PNNL/U Del/TUM			●			◆		

- Rapid ramp-up this FY
- Go/No Go decision on 3/31/2014 based on demonstrated results

Future Work: Our Longer Range Vision



	Year 1	Year 2	Year 3	Year 4	Year 5
ORNL	Organize consortium	Baseline pyrolysis simulations	Refined vapor phase upgrading simulations	Linked vapor & liquid-phase upgrading simulations	Collaborative full plant simulations of conventional, in situ, & ex situ fast pyrolysis with advanced vapor & liquid-phase catalysts & multiple feedstock blends in support of refined TEA and LCA
INL	Identify reference feedstocks & set up database	Refine feedstock data per NREL/ORNL feedback	Develop property models for feedstock blends	Interface feedstock prep models with pyrolysis inputs	
NREL	Baseline coke formation & particle transport models	Link coke & particle models with pyrolysis reactor model	Vapor catalyst kinetics & deactivation/regen models, lab validations	In situ & ex situ kinetics refinement with lab & PDU experimental validations	
PNNL	Micro-kinetic catalysis models for aqueous carbs with oxide support metals	Procedures for liquid phase reaction network mapping & mechanism reduction	Refine aqueous & organic liquid phase catalyst formulations	Reduced liquid phase catalyst mechanism & kinetics for aqueous & organic phases	
ANL	Vapor catalysts for furan & pyran coupling; energetics for anhydrosugars	Baseline vapor phase catalyst formulations and kinetics	Mechanisms for vapor phase catalyst deactivation, regeneration	Reduced models for vapor catalysis kinetics and deactivation/regeneration	

Summary

- **Goal/Objective:** Through multi-lab collaboration with industry feedback, develop and implement computational tools aimed at major technical barriers and risks for compatible bio-fuels production via pyrolysis oil upgrading.
- **Key Barriers Addressed:** **Tt-E** Improve bio-oil quality, improve carbon efficiency; **Tt-G** Improve upgrading catalysts; **Tt-K** Improve process integration and scale-up.
- **Approach:** Apply and integrate multiple computational approaches for modeling and improving key process steps and components based on the latest chemical and physical information coming from (and guiding) ongoing experiments at the national labs.
- **Accomplishments and Progress:** Project just started in April, 2013.
- **Relevance:** By targeting key risks and uncertainties in latest biomass pyrolysis design studies, supports the BETO MYPP goal of identifying viable pyrolysis pathway options for producing \$3.00/gal bio-diesel and bio-gasoline by 2022.
- **Future Plans:** Continue with full process simulations using advanced catalysts pending Go/No Go decision in 3rd quarter 2014.