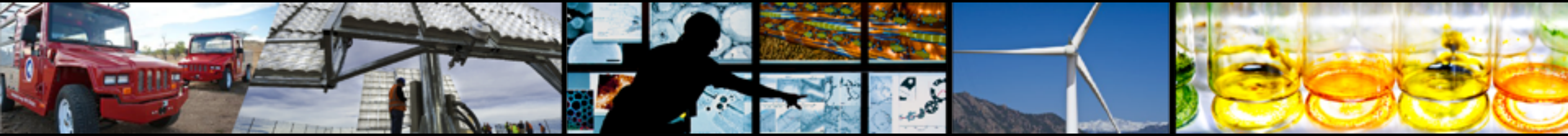
2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

Catalytic Pyrolysis Sciences



Bio-oi Technolog Are Revie

Goal/Objective Statement

- Goal: Improve catalytic fast pyrolysis (CFP) through laboratory exploration and modeling
  - Understand carbon loss to char, coke on catalyst
  - Improve predictability of pyrolysis
  - Understanding of products from CFP
  - Investigate catalytic processes during CFP
- WBS 3.6.1.6 Catalytic Pyrolysis Science

Goal/Objective Statement (cont.)

Supports *in-situ* and *ex-situ* CFP BETO pathways

- **Improve overall carbon efficiency**
- **Process intensification/utilize existing infrastructure**
- **Understanding to develop improved catalysts and processes**
    - Improve yields
    - Reduce oxygen in resulting oil
    - Improve oil properties (stability, viscosity, miscibility, corrosivity)
    - Products in the diesel fuel range
- **Obtain reaction conditions for techno-economic analysis (TEA) and life-cycle analysis (LCA)**
- **Develop understanding for scaling up processes**

Project Quad Chart Overview

Timeline

- **Start Date:** October 1, 2012
- **End Date:** September 30, 2017
- **13% percent complete**

Budget

Total project funding: DOE - $10MM; cost share, JM - $2MM

Funding received in FY 2011: $0

Funding in FY 2012: DOE - $2MM; cost share, JM - $400K

Funding for FY 2013: DOE - $2MM; cost share JM - $400K

ARRA Funding: $0

Years the project has been funded & average annual funding: New project

Barriers

Barriers addressed

Tt-E Improve bio-oil quality, improve carbon efficiency

Tt-G Improve upgrading catalysts

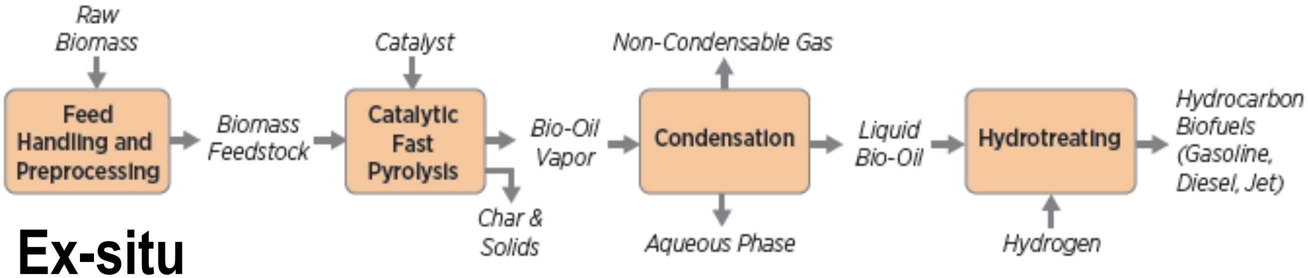
Tt-K Characterize feedstock products and CFP oil for downstream processing

Partners & Roles

- Johnson Matthey: Catalyst development and characterization (Vapor Phase Upgrading)
- Colorado School of Mines (Richards): Catalyst development and characterization
- University of Colorado (Ellison): mechanisms of pyrolysis
- LBL - Advanced Light Source (Ahmed): pyrolysis
- ORNL (Daw), PNNL (Weber), ANL (Snyder), INL (Westover): Computational modeling

Project Overview: Catalytic Fast Pyrolysis

In-situ

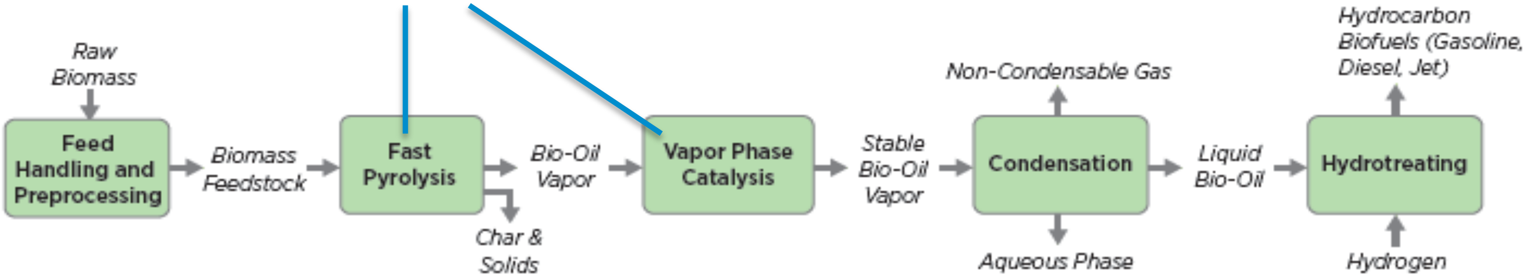


Raw Biomass → Feed Handling and Preprocessing → Biomass Feedstock → Catalytic Fast Pyrolysis (Catalyst) → Bio-Oil Vapor; Char & Solids

Bio-Oil Vapor → Condensation → Liquid Bio-Oil; Non-Condensable Gas; Aqueous Phase

Liquid Bio-Oil → Hydrotreating (Hydrogen) → Hydrocarbon Biofuels (Gasoline, Diesel, Jet)

Ex-situ



Raw Biomass → Feed Handling and Preprocessing → Biomass Feedstock → Fast Pyrolysis → Bio-Oil Vapor; Char & Solids

Bio-Oil Vapor → Vapor Phase Catalysis → Stable Bio-Oil Vapor → Condensation → Liquid Bio-Oil; Non-Condensable Gas; Aqueous Phase

Liquid Bio-Oil → Hydrotreating (Hydrogen) → Hydrocarbon Biofuels (Gasoline, Diesel, Jet)

Unit Operation	Barriers Addressed
Pyrolysis	1) 10 - 20 % char yield, 2) effects of metals and particulates, 3) prediction of products
Vapor Phase Upgrading	1) Low carbon yields in oils, 2) effects of products on downstream operations, 3) catalyst maintenance 4) unknown reactor design and operation, 5) catalyst development

- Cost target: \$3.00 gal^{-1} by 2022
- Largest cost contributors: feedstock and capital
- Diesel and Jet fuels are more desirable

1 - Approach

- Conduct laboratory experiments of catalytic upgrading of pyrolysis vapor
  - Measure products, determine yields
  - Design catalysts, screen catalysts and reactor conditions, investigate deactivation and regeneration, characterize catalysts
- Investigate pyrolysis and effects of composition and structure
  - Pyrolysis experiments, Biomass Surface Characterization Lab (BSCL)

Subtasks:

- Biomass Pyrolysis Characterization and Optimization (Donohoe)
- Catalyst Screening and Development for Johnson Matthey CRADA (Mukarakate)
- Catalyst Design and Small-Scale Experiments (Robichaud)
- Catalyst Deactivation and Regeneration (Iisa)

Other collaborating tasks

Computational Pyrolysis Consortium (Fluid dynamics and and catalyst modeling)

3.3.1.12 Catalytic Upgrading of Pyrolysis Products

3.6.1.1 Thermochemical Platform Analysis

3.3.1.14 Catalyst Development/Testing: Deconstruction

3.3.1.13 Integration and Scale Up

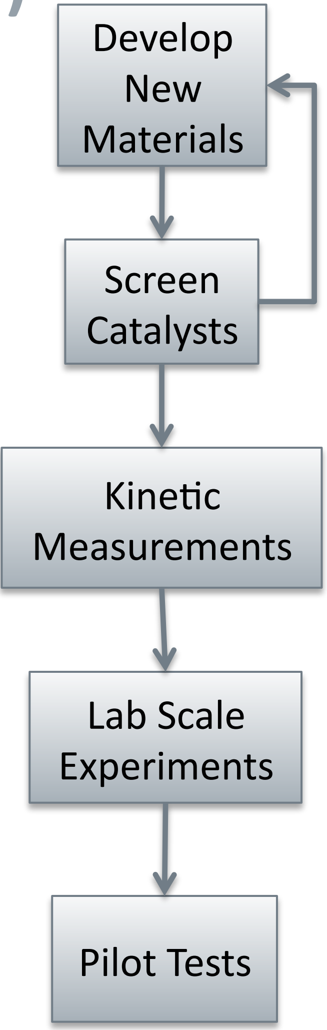
2 - Technical Accomplishments/ Progress/Results

- **Catalyst testing**
- **Catalyst deactivation**
- **Hot gas filtration**
- **Hydrogen donor molecules**
- **Imaging and particle dynamics**
- **Impact of salts**
- **Pyrolysis mechanisms**

Johnson Matthey/NREL CRADA

NREL ($5M)

JM ($2M)



Develop New Materials

Screen Catalysts

Kinetic Measurements

Lab Scale Experiments

Pilot Tests

Y1-Y5

- Composition of pyrolysis vapor
- Chemical mechanisms
- Test in small reactors

- Catalyst synthesis and screening
- Catalyst screening and characterization

1-10 g catalyst

This CRADA will allow NREL to work closely together throughout the entire catalyst development chain

Y2-Y5

- Entrained flow reactor

10-100 g catalyst

- Catalysts down selected at each step
- Less expensive experiments used to screen catalysts
- Each scale provides different information

Y3-Y5

- Experiments in Riser Reactor
- Attrition tests

- Develop supports

1-10 Kg catalyst

Y3-Y5

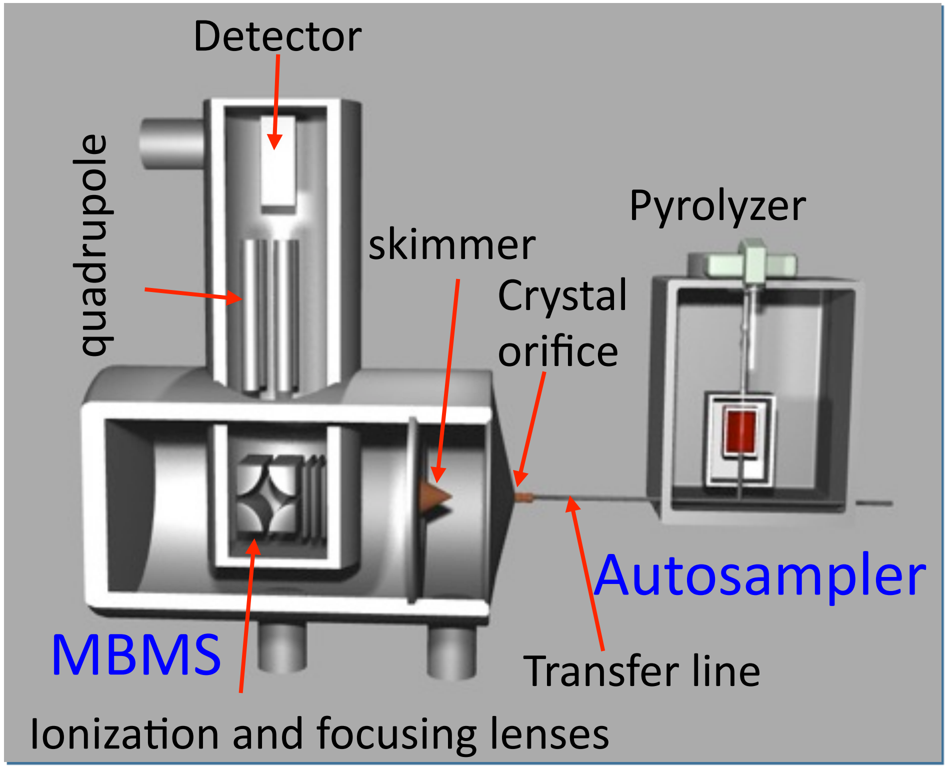
- Integration
- Test suitability of oil

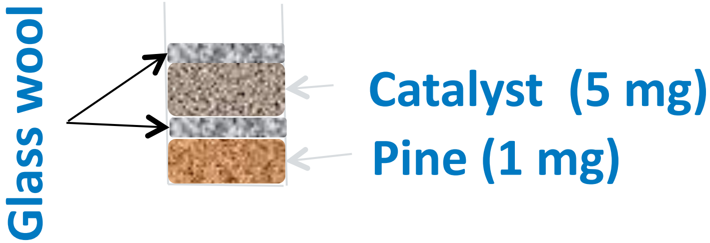
1-10 Kg catalyst

Y1-Y5

- **Technoeconomic Analysis**

Catalyst Development and Screening





Sample Holder

Autosampler Molecular Beam Mass Spectrometer (MBMS)

- Rapid sampling (~20 samples/hr)
- Direct sampling
- Universal detection (MS)

Screening to date:

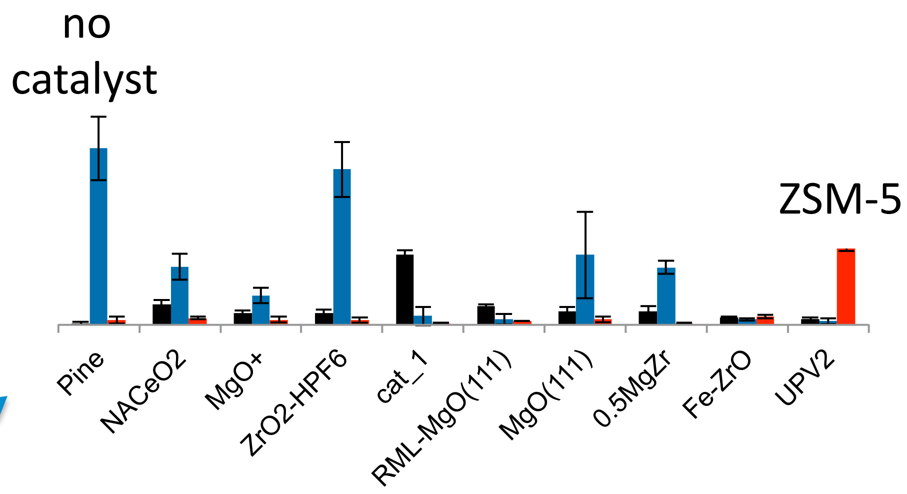
- Over 70 catalysts screened
- Various metal oxides and metals
- Catalysts supplied by CSM, JM and commercial vendors
- Results analyzed using Multivariate analysis of MBMS spectra

Strategy:

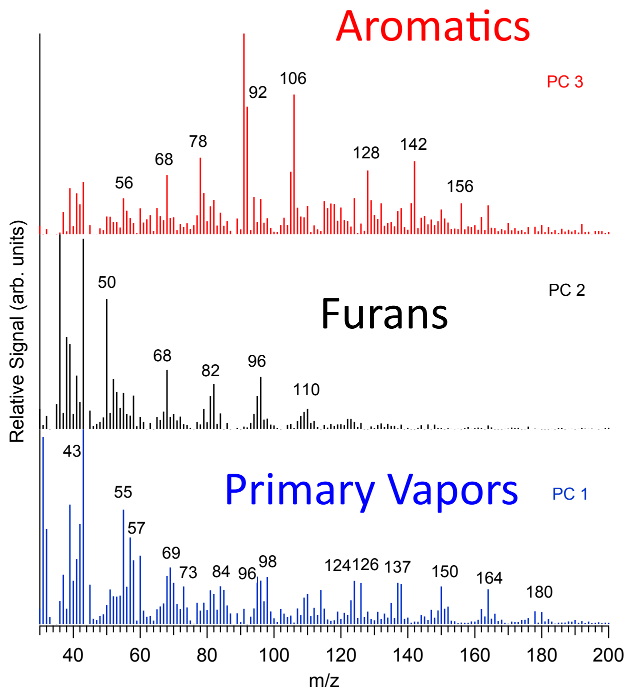
- Search for oxygen rejection
- Carbon efficiency
- Identify suites of products

Sample Catalyst Screening Results

- 9 catalysts studied
- 3 principal components found
- Identify product suites from each catalyst



Principal Components

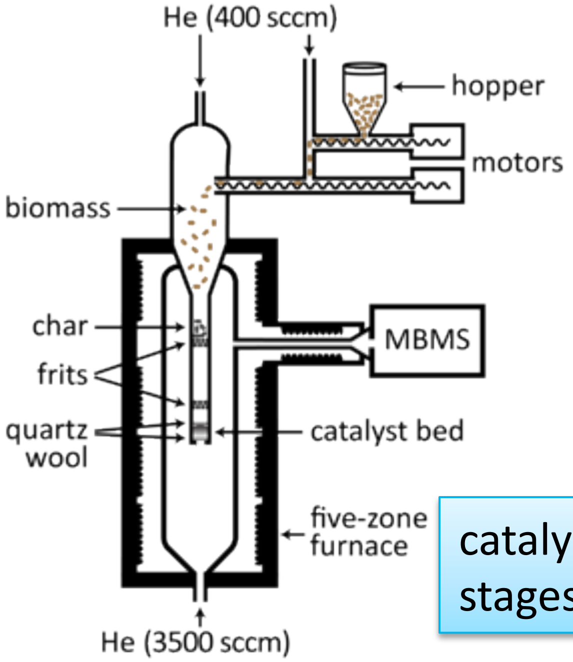


- Investigated effects of metals and supports
- Down selected catalysts for further study
- Identified catalysts that produce unique products (furans)

➢ **New products can be investigated for down-stream processing (Hydrotreating, etc)**

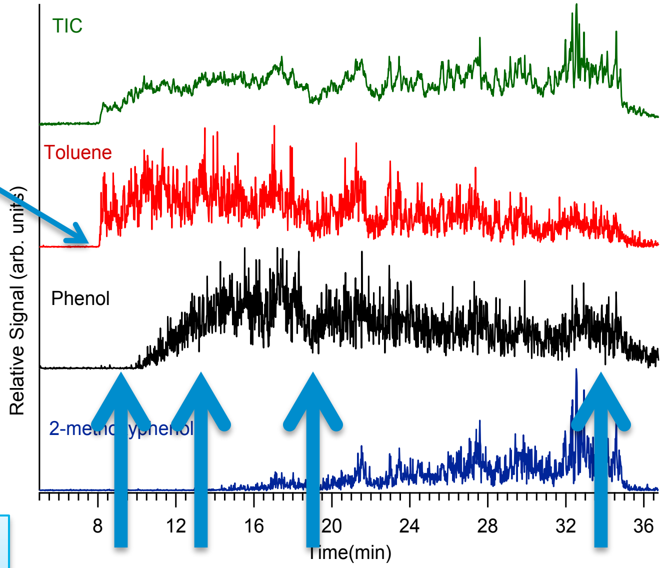
Catalyst Deactivation

Batch-fed Microreactor



Real time analysis of products with MBMS

start biomass feed



ZSM-5

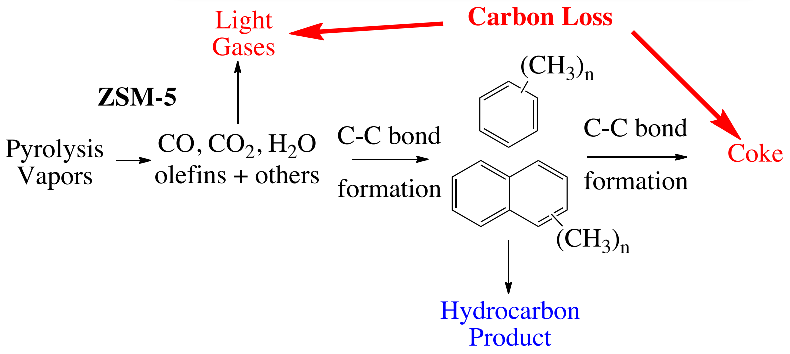
catalyst sampled at stages of deactivation

1 2 3 4

fully active

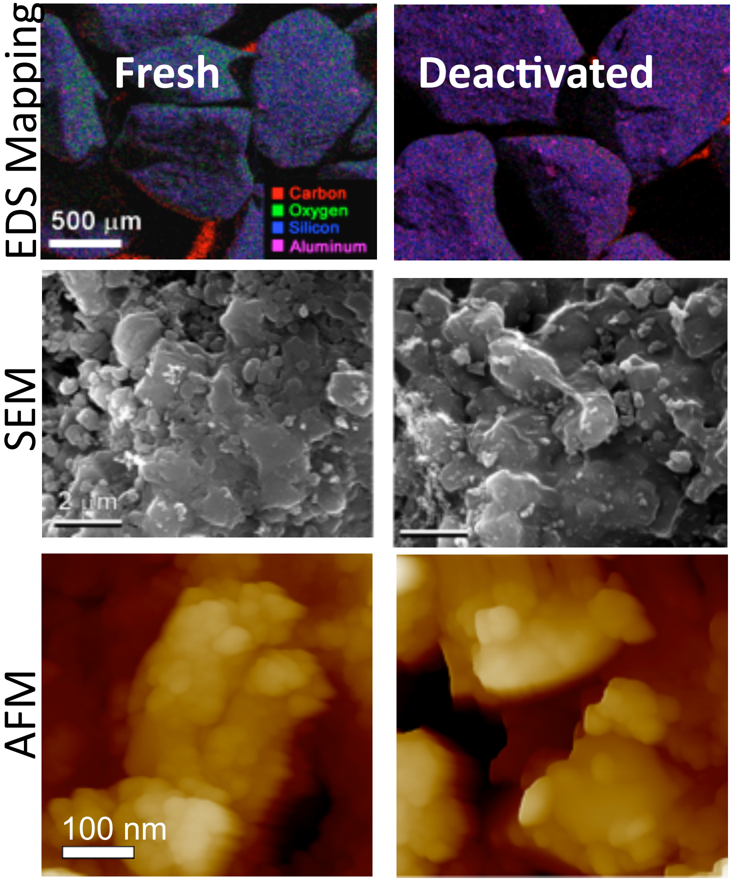
deactivated

Proposed Mechanism

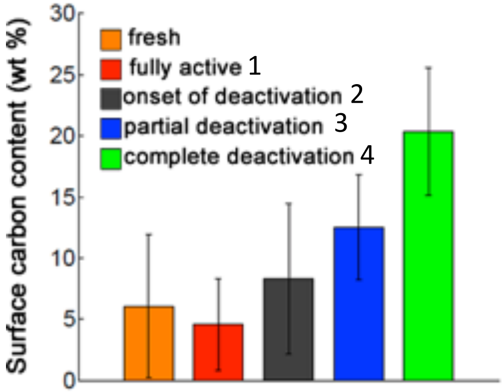


- ZSM-5 produces aromatic hydrocarbons
- Deactivates quickly
- ➢ **Acid sites on ZSM-5 make it too active, does not stop at aromatic compounds**

Advanced imaging correlate changes in catalyst structure and composition to deactivation and product distribution

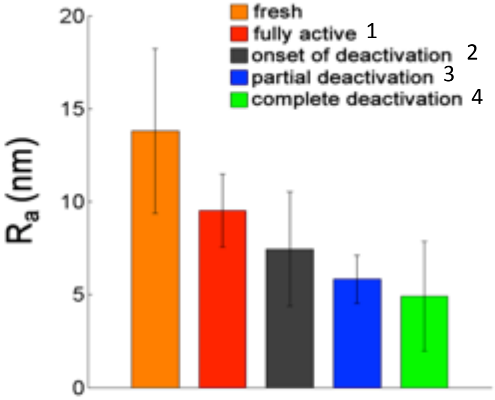


Energy Dispersive X-ray Spectroscopy (EDS)
quantify deposition of carbonaceous film



SEM imaging
decrease in surface roughness with de-activation

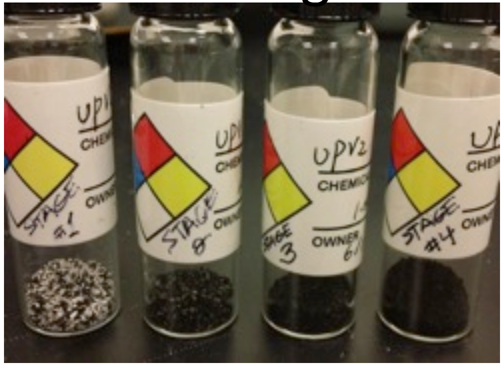
AFM
roughness reduction measured directly



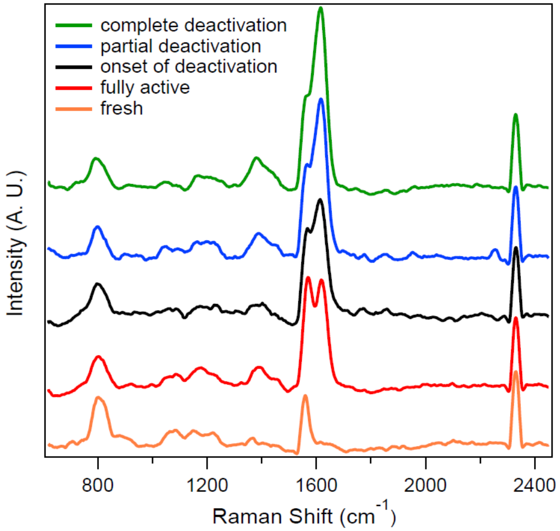
Catalyst deactivation correlated with carbon build up and smoothing of catalyst surface

Aromatic Formation and Micro-Pores

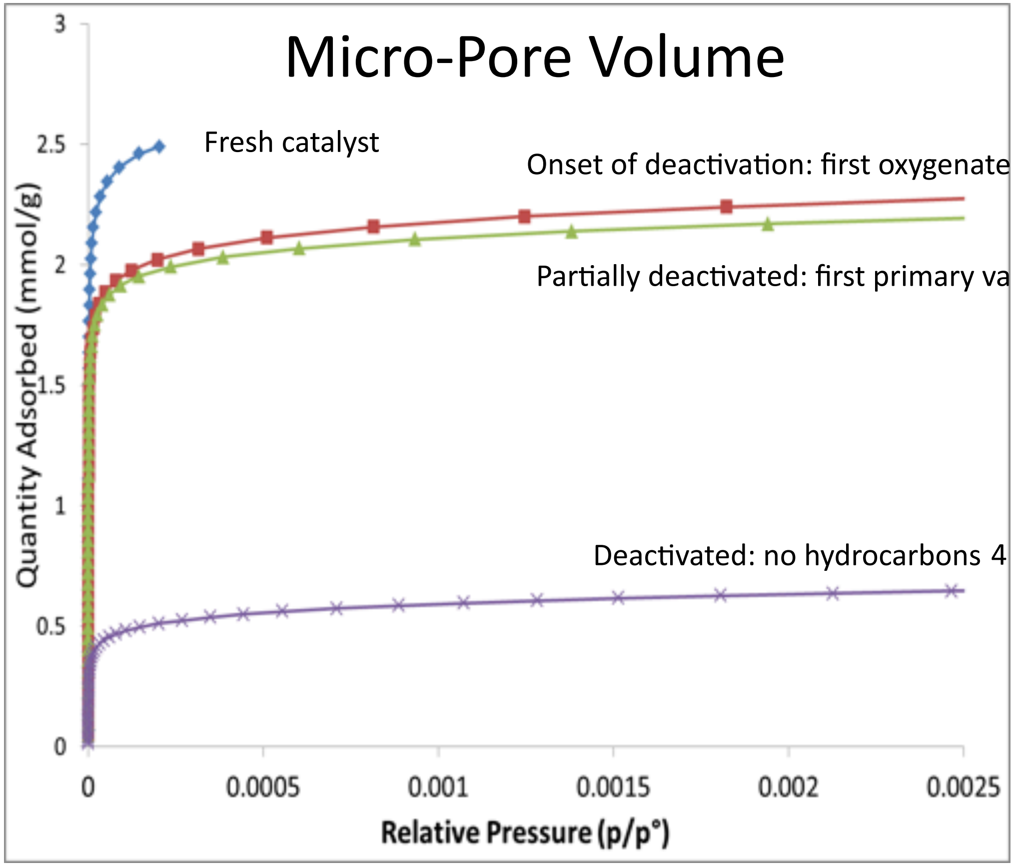
Four Stages



Surface Raman



Increase in polyaromatics

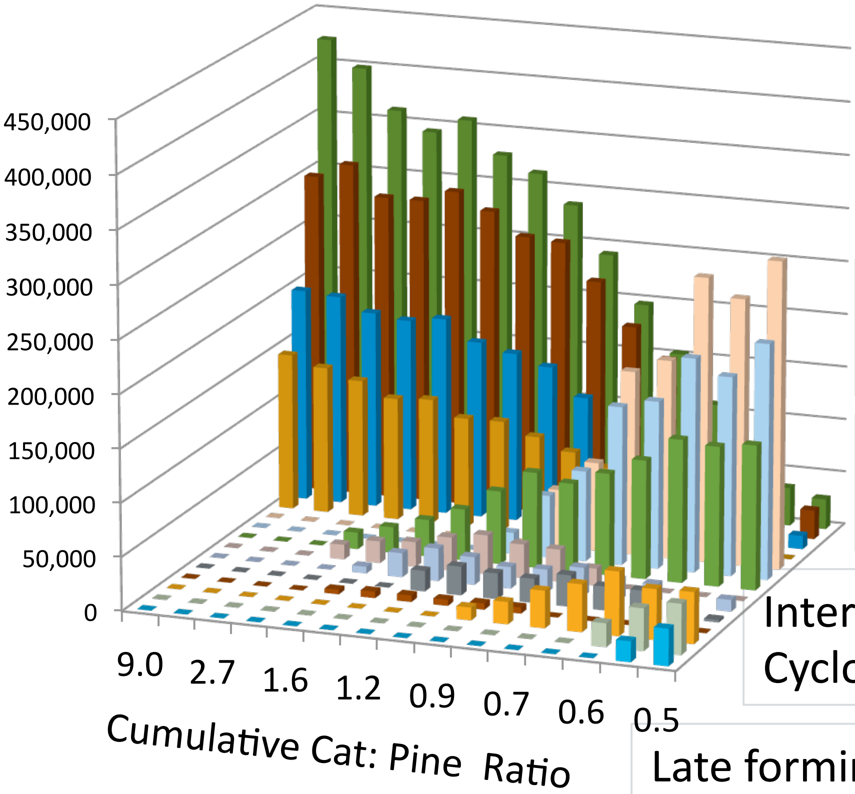


Decrease in micro-pore volume as catalyst deactivates

Catalyst deactivation also correlated with aromatic formation and plugging of pores

Deactivation and Products Formed

Pyro-probe Experiments



Identification of product changes during catalyst deactivation

Hydrocarbons decreasing:
Toluene, xylene, naphthalenes, benzene

Oxygenates increasing:
Methoxy phenols, Furans

Intermediate compounds with maxima:
Cyclohexadiene, phenols, benzofurans

Late forming compounds:
Cyclopentenones, furfural, acids

Py-GC/MS, 500°C, pine, ZSM-5

A different suite of products formed during partial deactivation

Hot Gas Filtration

Number of frits	Catalyst	Biomass fed until deactivation
0	1.0 g	1.0 g
1 coarse	1.0 g	1.0 g
2 coarse	1.0 g	1.5 g
2 fine	1.0 g	≥ 6.0 g

Pore sizes

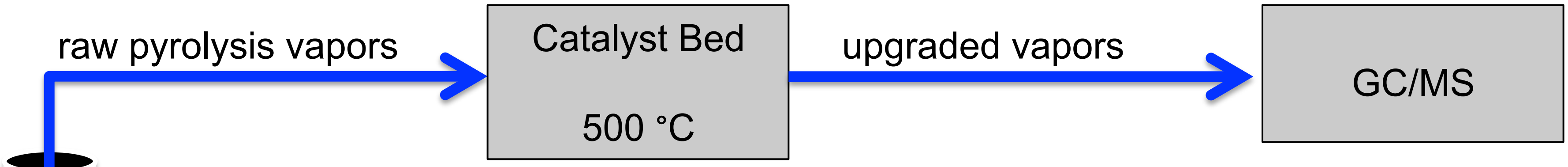
Fine: 90-150 µm

Coarse: 150-200 µm

- Micro reactor experiments with filters
- Used one or two ceramic filters between pyrolysis and upgrading
- Filtering removes mineral and particulate materials and heavy lignins

➢ **Filtering of pyrolysis vapors increases the life of the catalyst**

Addition of Hydrogen Donor Molecules



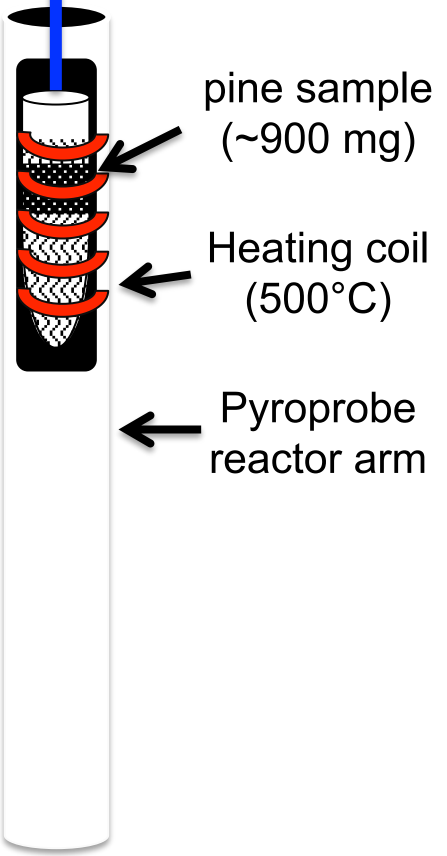
raw pyrolysis vapors

Catalyst Bed

500 °C

upgraded vapors

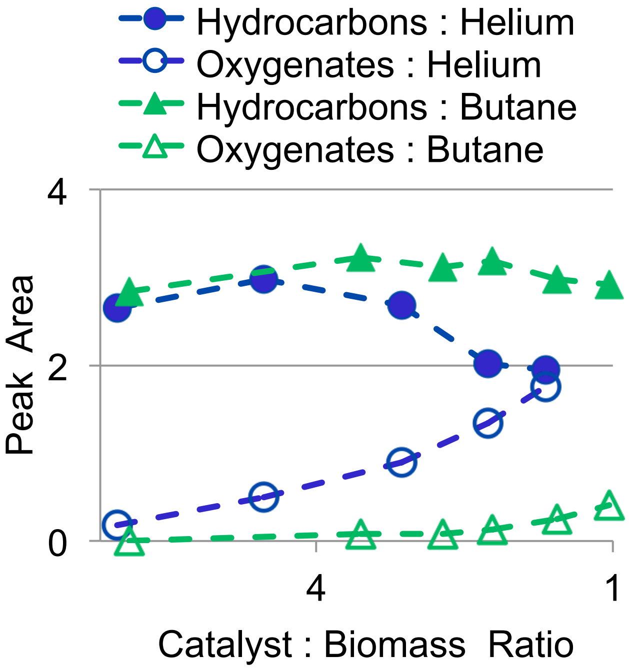
GC/MS



pine sample (~900 mg)

Heating coil (500°C)

Pyroprobe reactor arm

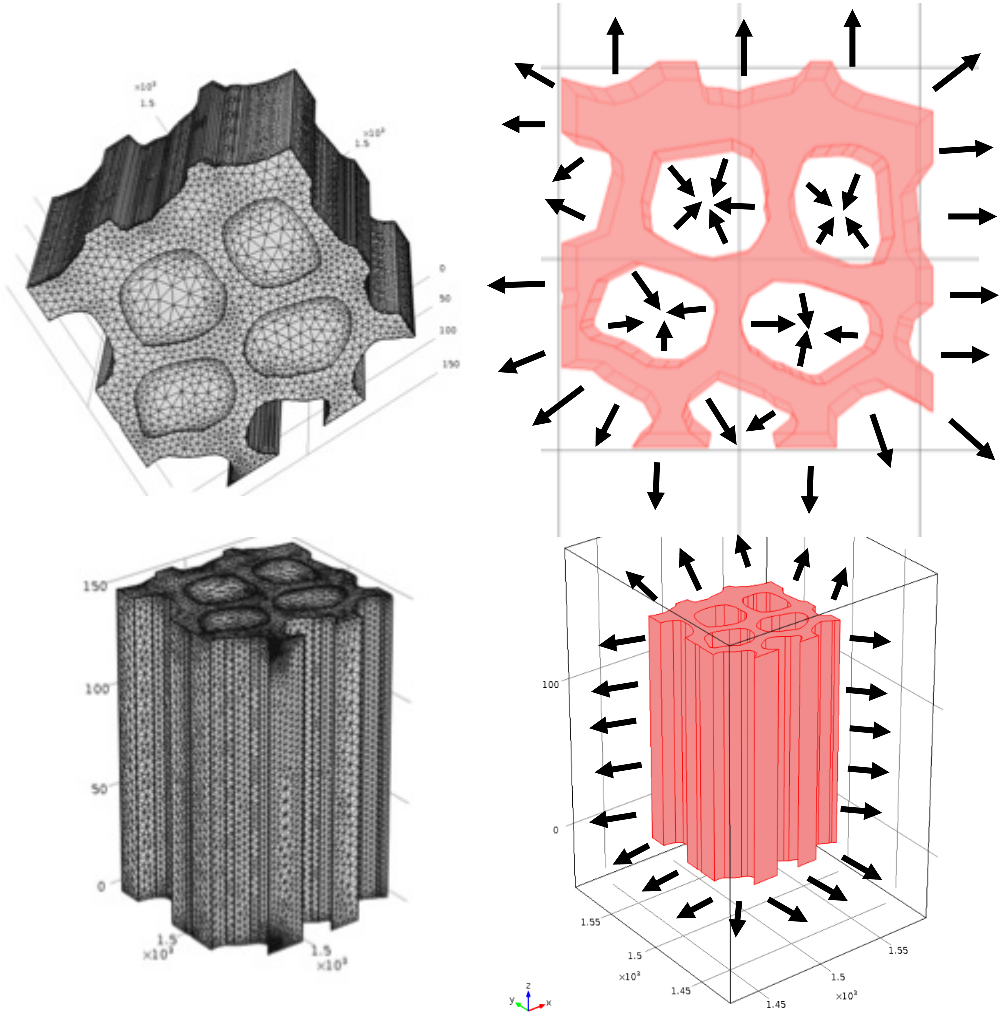


- Studied H_2, Butane, and MeOH
- Provides a pool of hydrogen atoms
- Can decrease coking rates
- With ZSM-5 showed decrease in deactivation rate

➢ **Addition of hydrogen can delay deactivation of catalysts, improve yields.**

Imaging and Particle Dynamics

3D modeling based on experiments



- Obtain geometries and densities from imaging
- Measure physical properties
- Chemical properties from spectroscopy and gas sampling

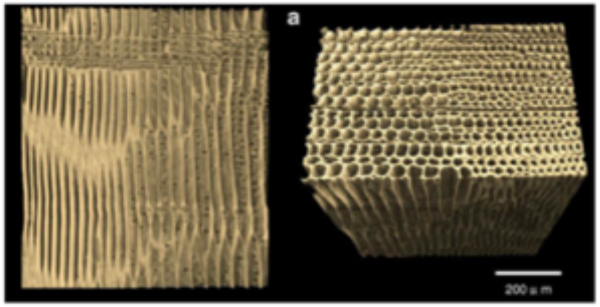
➢ **Understand product evolution and transport**

➢ **Investigate effects of pretreatment, composition and reactor conditions**

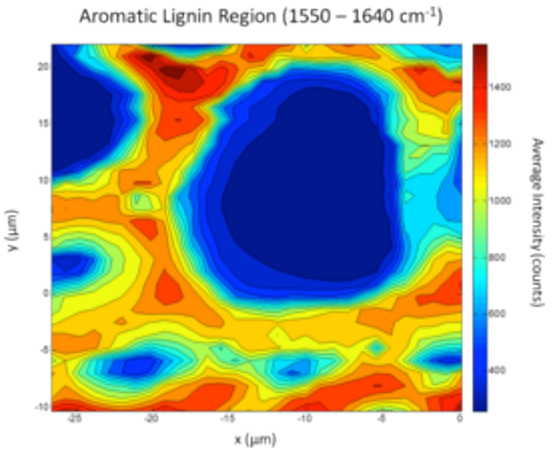
➢ **Modeling work will be continued under Computational Pyrolysis Consortium**

Modeling biomass with realistic geometry and composition derived from microscopy data

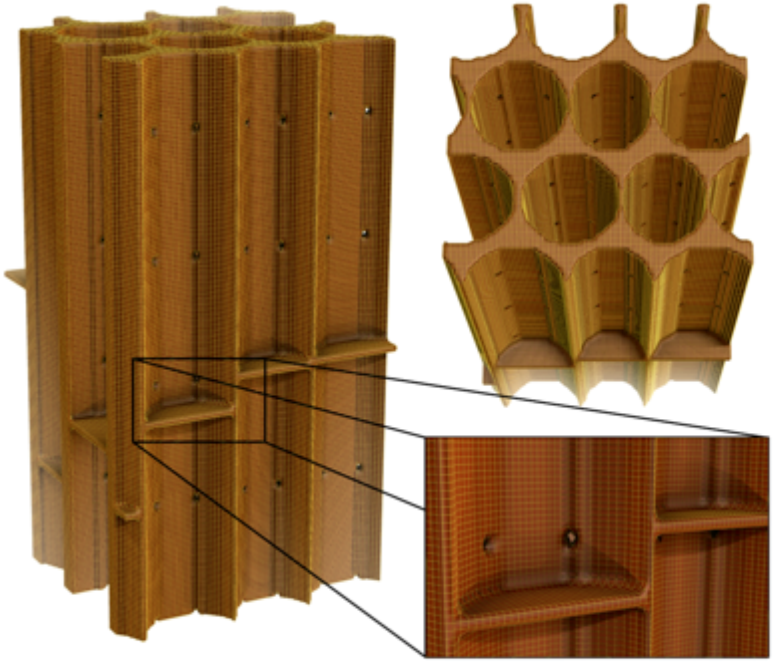
How are heat and mass transfer during pyrolysis affected by biomass geometry and composition? How do these affect the product distribution and char formation?



Biomass geometry obtained by multi-modal imaging (Mayo, S.C., 2010)



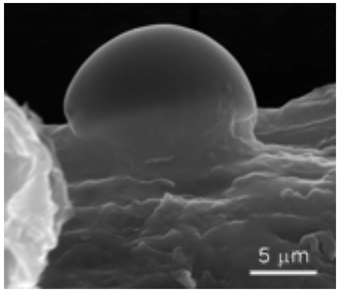
Localized biomass composition from Confocal Raman Microscopy



Computer model generated from microscopy data with representative geometry and composition

Effects of Salts on Pyrolysis

Neat biomass after pyrolysis

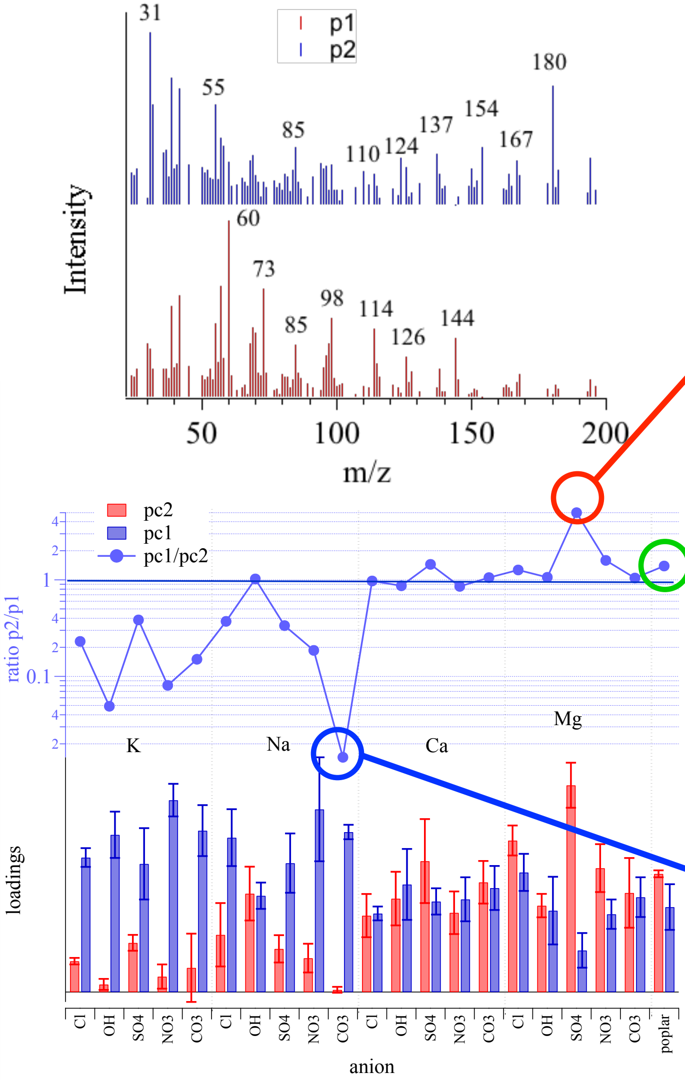


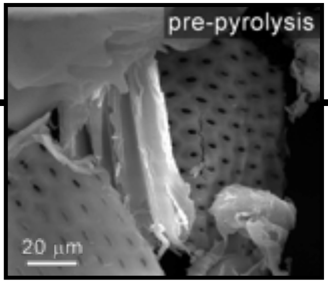
Bubbles trapped in softened biomass

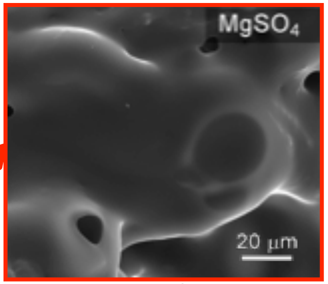
- Pyrolyze biomass with adsorbed salts
- Alkali metals change product slate, affect softening
- Alkaline earths have little effect
- MgSO$_4$???

➢ **Metals can affect structure and products**

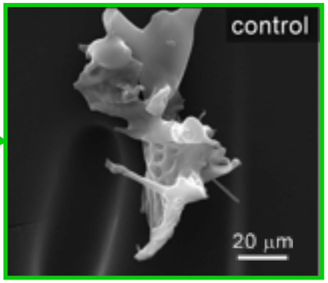
Multivariate Results



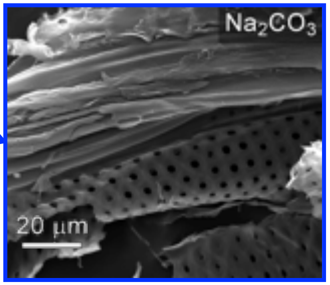




Super softening



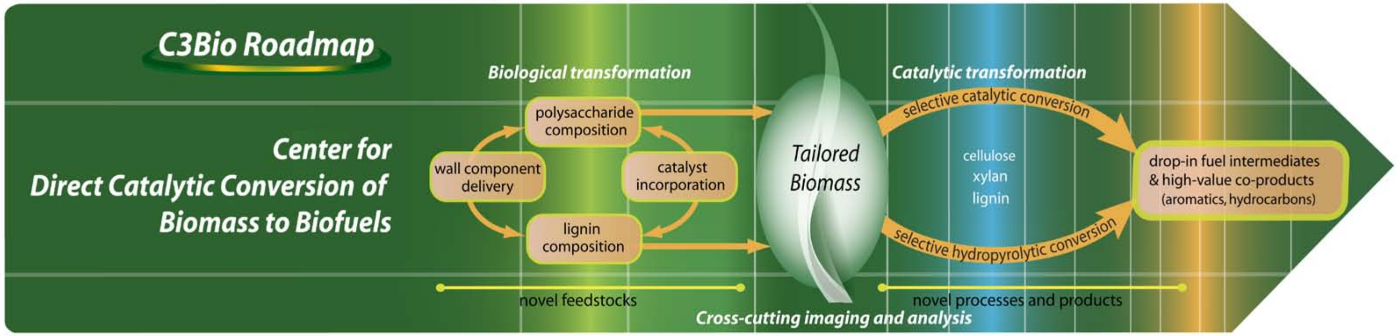
Softening of biomass



No change of structure

Collaboration with C3Bio EFRC

We are helping determine the impact metals have on product, tar, and char formation during catalytic fast pyrolysis



*The **Center for Direct Catalytic Conversion of Biomass to Biofuels (C3Bio)** is developing transformational knowledge and technologies to optimize the energy and carbon efficiencies of converting non-food biomass to advanced (drop-in) biofuels. **C3Bio** is conducting interdisciplinary fundamental research for the foundation of a renewable hydrocarbon industry.*

C3Bio

- Conducts high-risk, high-reward research for the future deployment of hydrocarbon-rich biofuels and other biobased products, currently derived from oil
- Develops transformational technologies for the direct conversion of plant biomass to minimize the agricultural footprint of bioenergy feedstock crops
- Uses chemical and thermal conversion processes that are scalable for industry
- One of 46 Energy Frontier Research Centers in the country funded by the U.S. Department of Energy, Office of Basic Energy Science

U.S. DEPARTMENT OF ENERGY | Office of Science

PURDUE UNIVERSITY

NREL NATIONAL RENEWABLE ENERGY LABORATORY

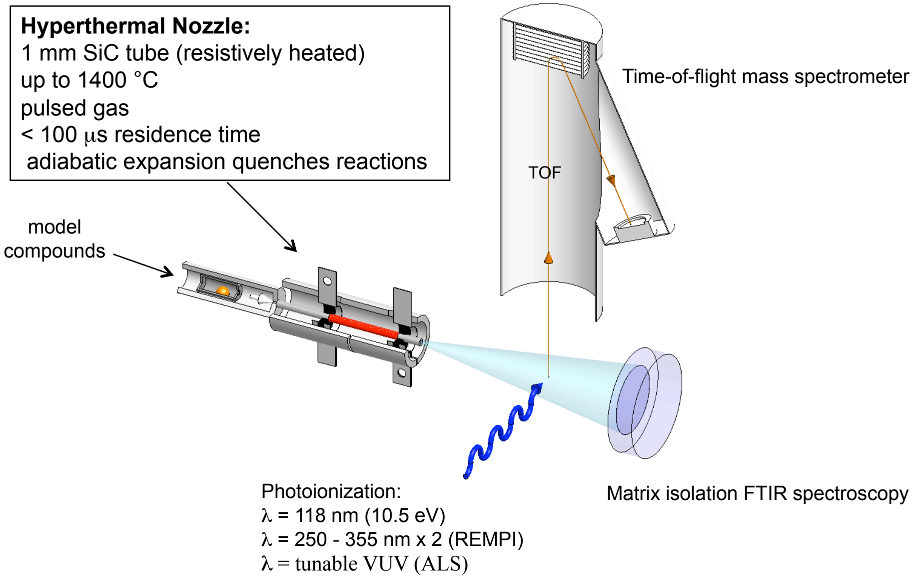
Argonne NATIONAL LABORATORY

THE UNIVERSITY of TENNESSEE UT KNOXVILLE

Northeastern University

http://C3Bio.org

Pyrolysis Mechanisms



Hyperthermal Nozzle:
1 mm SiC tube (resistively heated)
up to 1400 °C
pulsed gas
< 100 μs residence time
adiabatic expansion quenches reactions

model compounds

Time-of-flight mass spectrometer

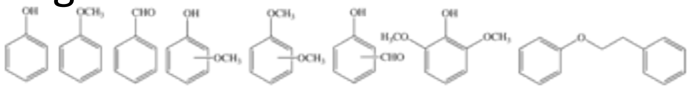
TOF

Photoionization:
λ = 118 nm (10.5 eV)
λ = 250 - 355 nm x 2 (REMPI)
λ = tunable VUV (ALS)

Matrix isolation FTIR spectroscopy

- Measuring the thermal decomposition of pyrolysis products
- Determining mechanisms
  - ➢ Help understand pyrolysis and upgrading chemistry

Lignin Products Studied



Carbohydrate Products Studied

Collaborators
Prof. G. Barney Ellison and John W. Daily at University of Colorado
John F. Stanton at University of Texas
Musahid Ahmed at Advanced Light Source
Leveraged with NSF funding at CU: (CHE-0848606) and (CHE-154-8379)

3 - Relevance

- **MYPP barriers addressed:**
  - Tt-E Bio-oil Stabilization, Tt-G Catalyts Development, Tt-K Integration, Tt-H Validation of 2017 Cost Target
- **Pyrolysis work: improve yields and allow prediction of catalyst performance based on feedstock (upstream and downstream)**
- **Catalyst mechanisms: have identified catalysts that produce different suites of products. Identified mechanisms of deactivation. Next we will produce oils and test properties**
- **The results from this work will provide much needed information (about yields, rates, reactor and processes configurations) to inform techno-economic analysis**

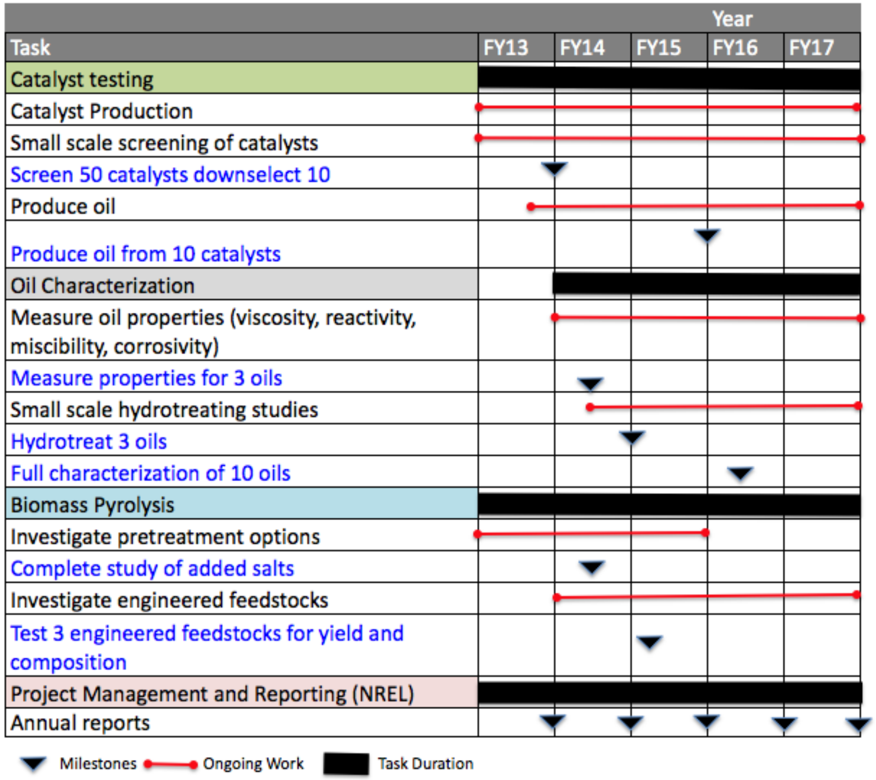
4 - Critical Success Factors

Factor	Goal	Approach
Improve yields of CFP oil	C yields ~ 40%	• Decrease char formation • Catalyst development • Reactor development • Hydrogen donation
Improve properties (miscibility, corrosivity, stability and viscosity)	~ 10% oxygen in oil	• Catalyst development • Hydrogen donation • Hydrotreatment
Produce distillate range oils	> 40% in the distillate range	• Development of C-C formation chemistries

- Improved carbon yields are critical to reaching the cost targets for FY2017
- Removing oxygen improves the properties of the pyrolysis oil so that it can be incorporated into refineries or blended with fuel
- Producing diesel feedstocks and blendstocks provides higher value

5. Future Work

- This project will continue to focus on testing catalysts for CFP to improve understanding of mechanisms
- During the next 16 months will grow our efforts into testing the oils produced from CFP
- We will also continue to investigate kinetics and mechanisms of pyrolysis
- The task will work closely with the Computational Pyrolysis Consortium to validate and inform models.



Task	FY13	FY14	FY15	FY16	FY17
Catalyst testing	■	■	■	■	■
Catalyst Production	—	—	—	—	—
Small scale screening of catalysts	—	—	—	—	—
Screen 50 catalysts downselect 10	▼				
Produce oil	—	—	—	—	—
Produce oil from 10 catalysts			▼		
Oil Characterization		■	■	■	■
Measure oil properties (viscosity, reactivity, miscibility, corrosivity)		—	—	—	—
Measure properties for 3 oils		▼			
Small scale hydrotreating studies		—	—	—	—
Hydrotreat 3 oils		▼			
Full characterization of 10 oils				▼	
Biomass Pyrolysis	■	■	■	■	■
Investigate pretreatment options	—	—	—		
Complete study of added salts		▼			
Investigate engineered feedstocks		—	—	—	—
Test 3 engineered feedstocks for yield and composition			▼		
Project Management and Reporting (NREL)	■	■	■	■	■
Annual reports	▼	▼	▼	▼	▼

▼ Milestones — Ongoing Work ■ Task Duration

CFP oil will be generated with Laminar Entrained Flow Reactor and 2” fluidized bed reactor.

Summary

- Relevance: This project is addressing critical issues for the 2017 economic targets of CFP (yields, oil quality and product value)
- Approach: Relevant laboratory approaches are needed and used because much needs to be learned about technical aspects of these projects
- Technical accomplishments: In six months we have made significant progress in testing catalysts and understanding mechanisms of pyrolysis and upgrading.
- Future work: Future work will include studies of CFP oil
- Success factors and challenges: The goals will be to improve carbon yields, oil quality and product value
- Technology transfer: We are working with Johnson Matthey to provide understanding for the development of catalysts for CFP

Additional Slides

Publications

1. Vasiliou, A. K.; Kim, J. H.; Ormond, T. K.; Piech, K. M.; Urness, K. N.; Scheer, A. M.; Robichaud, D. J.; Mukarakate, C.; Nimlos, M. R.; Daily, J. W.; Carstensen, H.-H.; Ellison, G. B., Biomass Pyrolysis: Thermal Decomposition of Furfural and Benzaldehyde. *J. Chem. Phys* Submitted.
2. Urness, K.; Golan, A.; Daily, J.; Nimlos, M.; Stanton, J.; M.Ahmed; Ellison, G. B., Pyrolysis of Furan in a Microreactor. *J. Chem. Phys* In Press.
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