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

Catalytic Fast Pyrolysis

WBS: 2.3.1.312/314/315

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

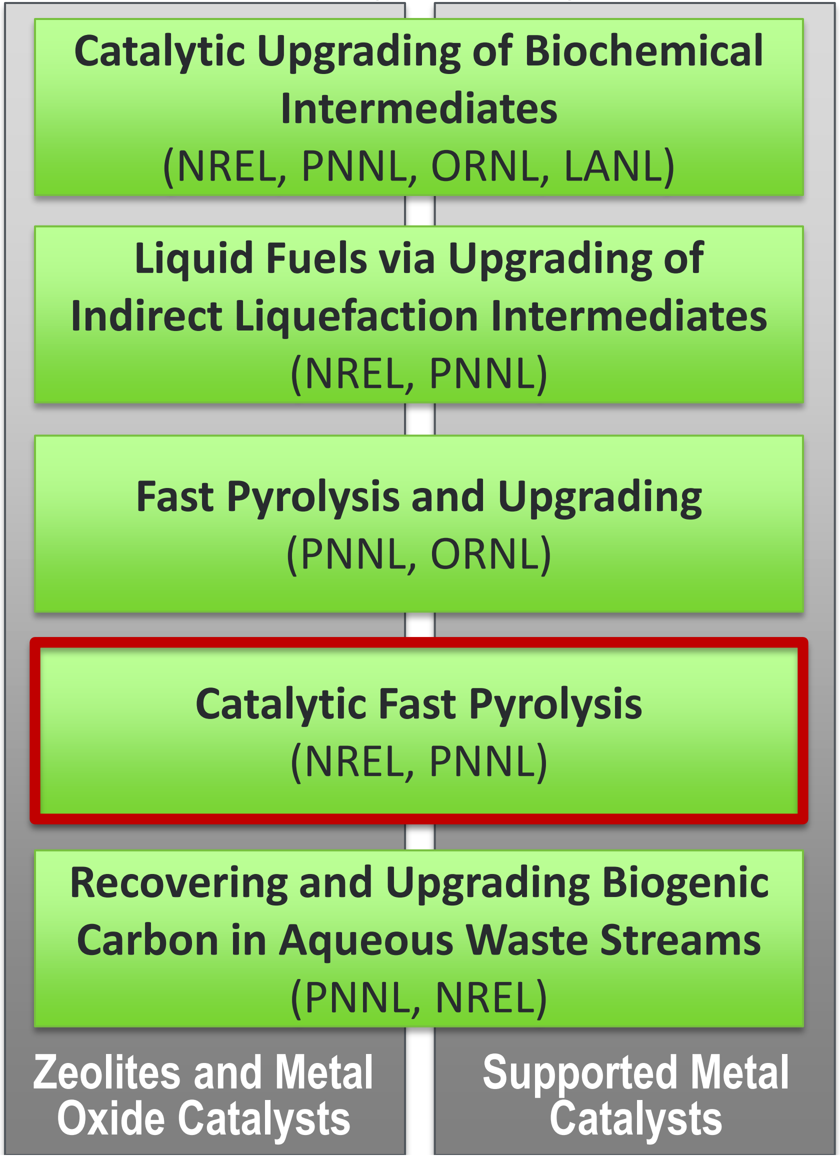
Thermochemical Conversion

March 7th, 2017

Project Leads:
Josh Schaidle – NREL
Kim Magrini – NREL
Huamin Wang – PNNL

ChemCatBio Structure

Core Catalysis Projects



Catalytic Upgrading of Biochemical Intermediates
(NREL, PNNL, ORNL, LANL)

Liquid Fuels via Upgrading of Indirect Liquefaction Intermediates
(NREL, PNNL)

Fast Pyrolysis and Upgrading
(PNNL, ORNL)

Catalytic Fast Pyrolysis
(NREL, PNNL)

Recovering and Upgrading Biogenic Carbon in Aqueous Waste Streams
(PNNL, NREL)

Zeolites and Metal Oxide Catalysts

Supported Metal Catalysts

Cross-cutting Discussion Groups

Enabling Projects

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

Catalyst Cost Model Development
(NREL, PNNL)

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

Consortium Integration

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

Goal Statement

Goal: Develop a market-responsive biorefinery concept based on catalytic fast pyrolysis (CFP), which is capable of producing both cost-competitive biofuels and high-value co-products with targeted yields and compositions.

Outcome: Advance the state of technology by demonstrating the production of fuel blendstocks (<1wt% O) from ***optimized processes for both in-situ and ex-situ CFP coupled with hydroprocessing*** that achieve a minimum fuel selling price of ***less than $4*** GGE with greater than **25% of the fuel in the diesel range**

- Develop next generation catalysts with ChemCatBio consortium
- Evaluate catalysts at multiple scales (mg – kg) in selected process configurations
- Leverage existing relationships with industrial partners (VTT, WR Grace, and JM)
- Hydroprocess CFP oils at PNNL

Advancing the State of Technology in Catalytic Fast Pyrolysis

Process Parameter	**2014 SOT**	**2016 SOT**	***2019 Target***	***2022 Target***
CFP C Efficiency	27%	33%	***39%***	***44%***
Overall Process C Efficiency	23%	28%	***36%***	***42%***
Selectivity to Diesel	15%	15%	***35%***	***55%***
MFSP	$6.61	$5.19	***$4.00***	***$3.38***

**Ex-situ* CFP Case

Quad Chart Overview

Timeline

- Project start date: 10/1/2016
- Project end date: 9/30/2019
- Percent complete: 17%

Budget

	FY15 Costs	FY16 Costs	Total Planned Funding (FY17-Project End Date)
DOE Funded	$5.2M	$5.9M	$17.5M

*FY17 operating budget reduced to $4.65M

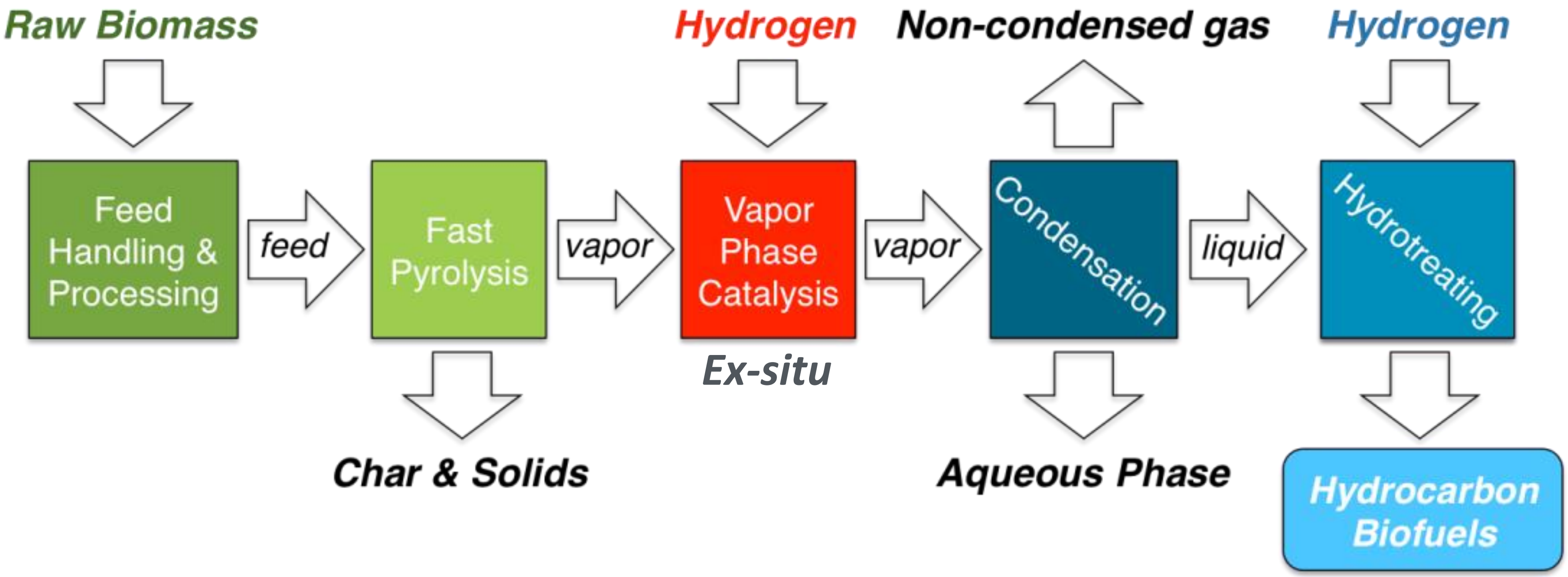
Barriers addressed & Actions

- Ct-F. Efficient High Temperature Deconstruction of Biomass
  - ***Developing in-situ and ex-situ CFP technologies and co-optimizing catalyst and process configuration***
- Ct-H. Efficient Catalytic Upgrading of Bio-oil Intermediates
  - ***Developing next generation catalysts for both CFP and HT***

Partners

- **National Labs**
  - NREL (83%)
  - PNNL (17%)
- **Industry**
  - Johnson-Matthey, WR Grace, VTT, BASF, Pall, CoorsTek
- **University**
  - Utah State, Georgia Tech, U. of Michigan, U. of Southern California, Colorado School of Mines

Project Overview: Catalytic Fast Pyrolysis (CFP)



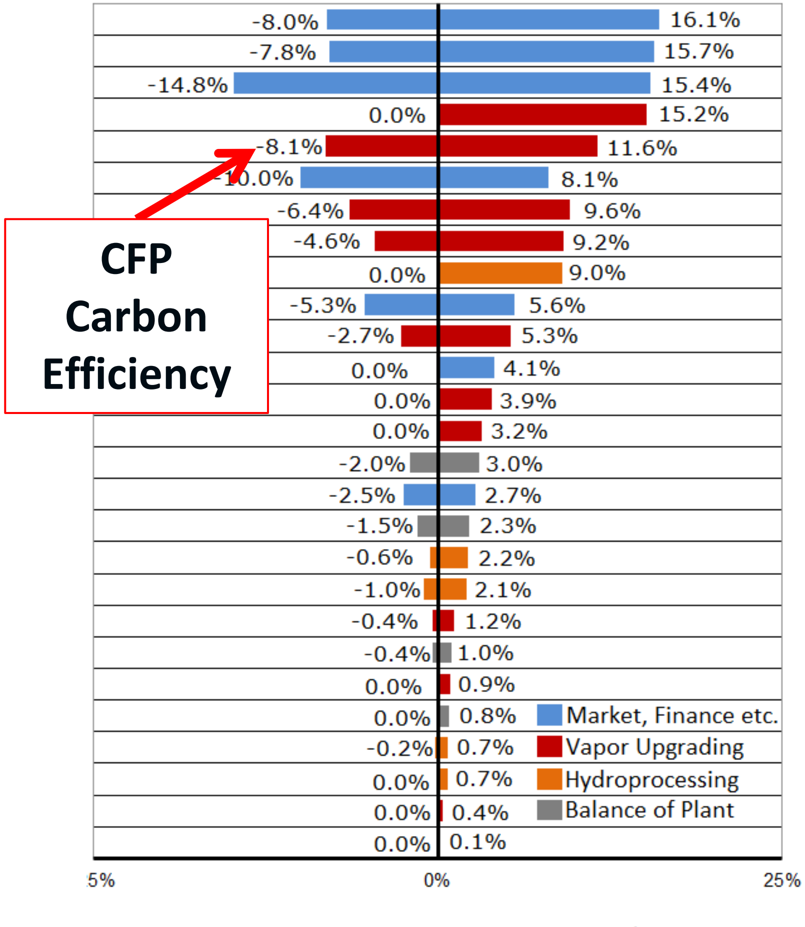
D. Ruddy, et al. *Green Chem* 16 (2014) 454

The goals of CFP are to improve the fuel quality and stability of the resulting pyrolysis bio-oil and reduce hydrotreating costs by:

- Reducing organic oxygen content (deoxygenation)
- Increasing hydrogen content (hydrogenation)
- Increasing carbon number to a range suitable for gasoline, diesel, or jet fuel (C-C coupling)

Project Overview: Carbon Efficiency is Key to Commercial Viability

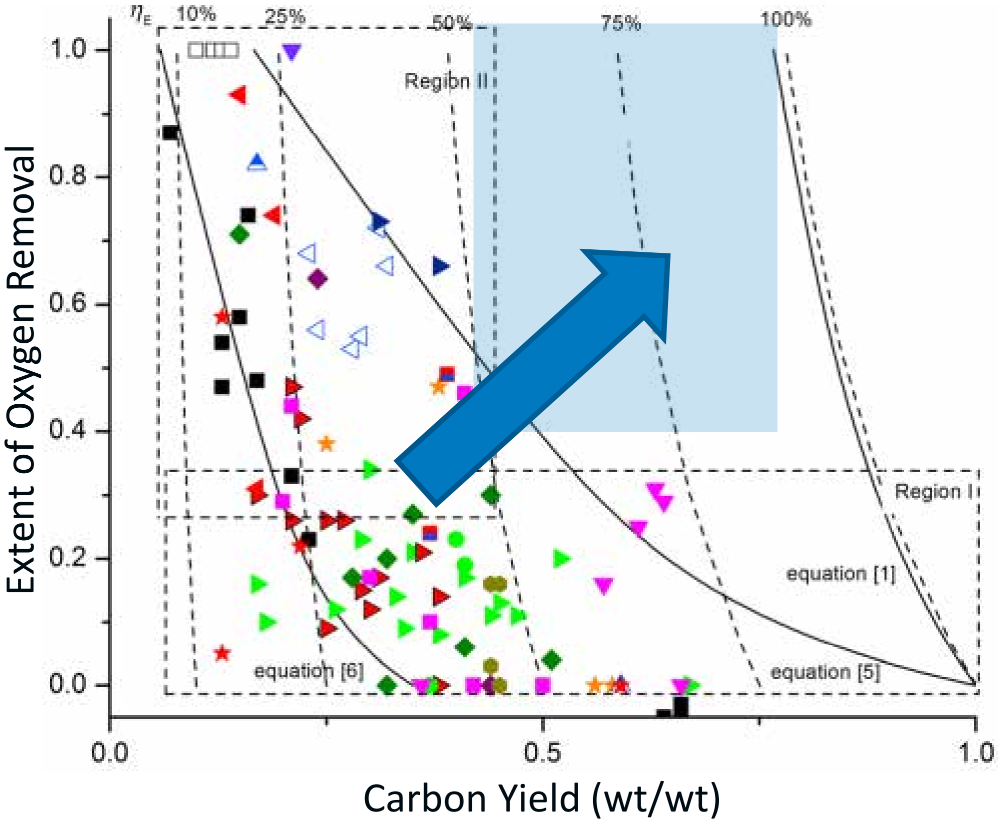
Process Sensitivity Analysis



CFP Carbon Efficiency

A. Dutta, et al., CFP Design Report, 2015

Relationship between Carbon Yield and Oxygen Content for CFP

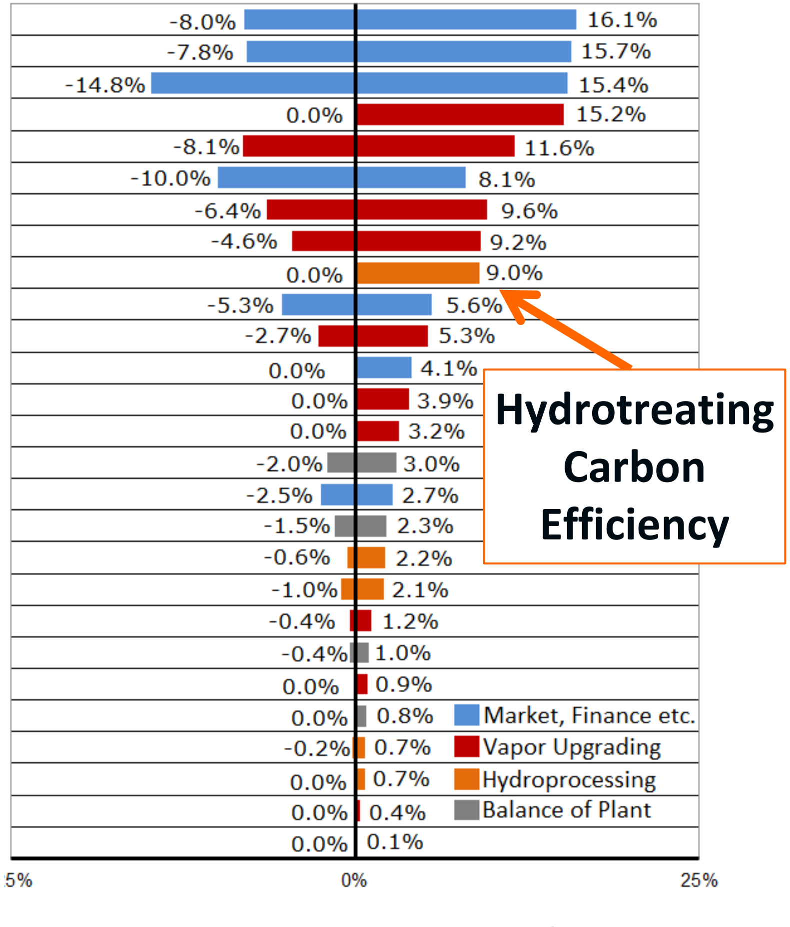


R. Venderbosch, *ChemSusChem* 8 (2015) 1306

CFP catalysts need to achieve extensive deoxygenation AND high carbon yields

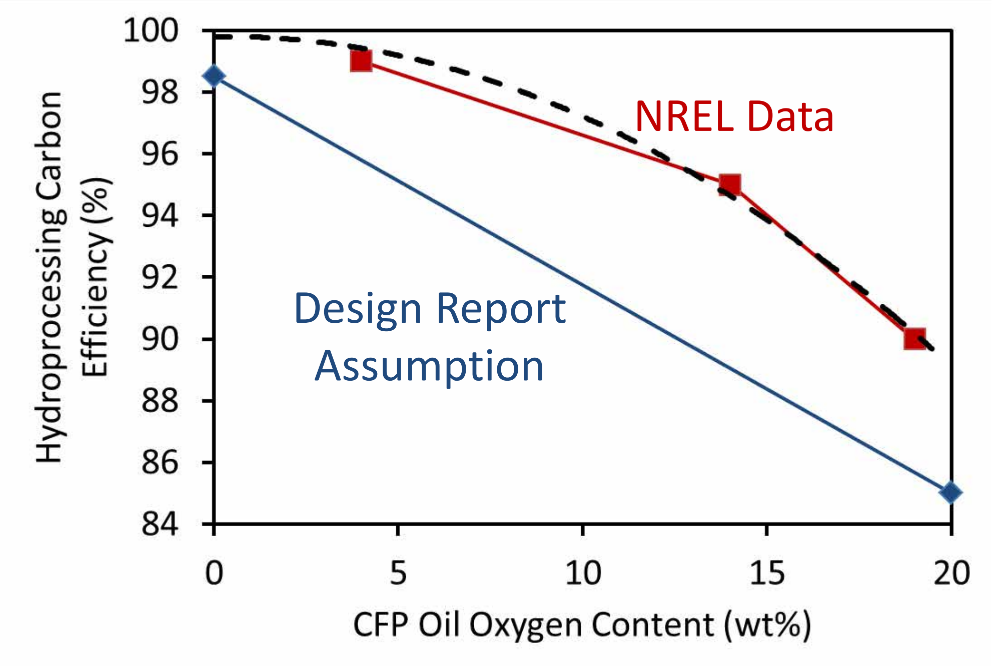
Project Overview: Carbon Efficiency is Key to Commercial Viability

Process Sensitivity Analysis



A. Dutta, et al., CFP Design Report, 2015

Hydrotreating Carbon Efficiency

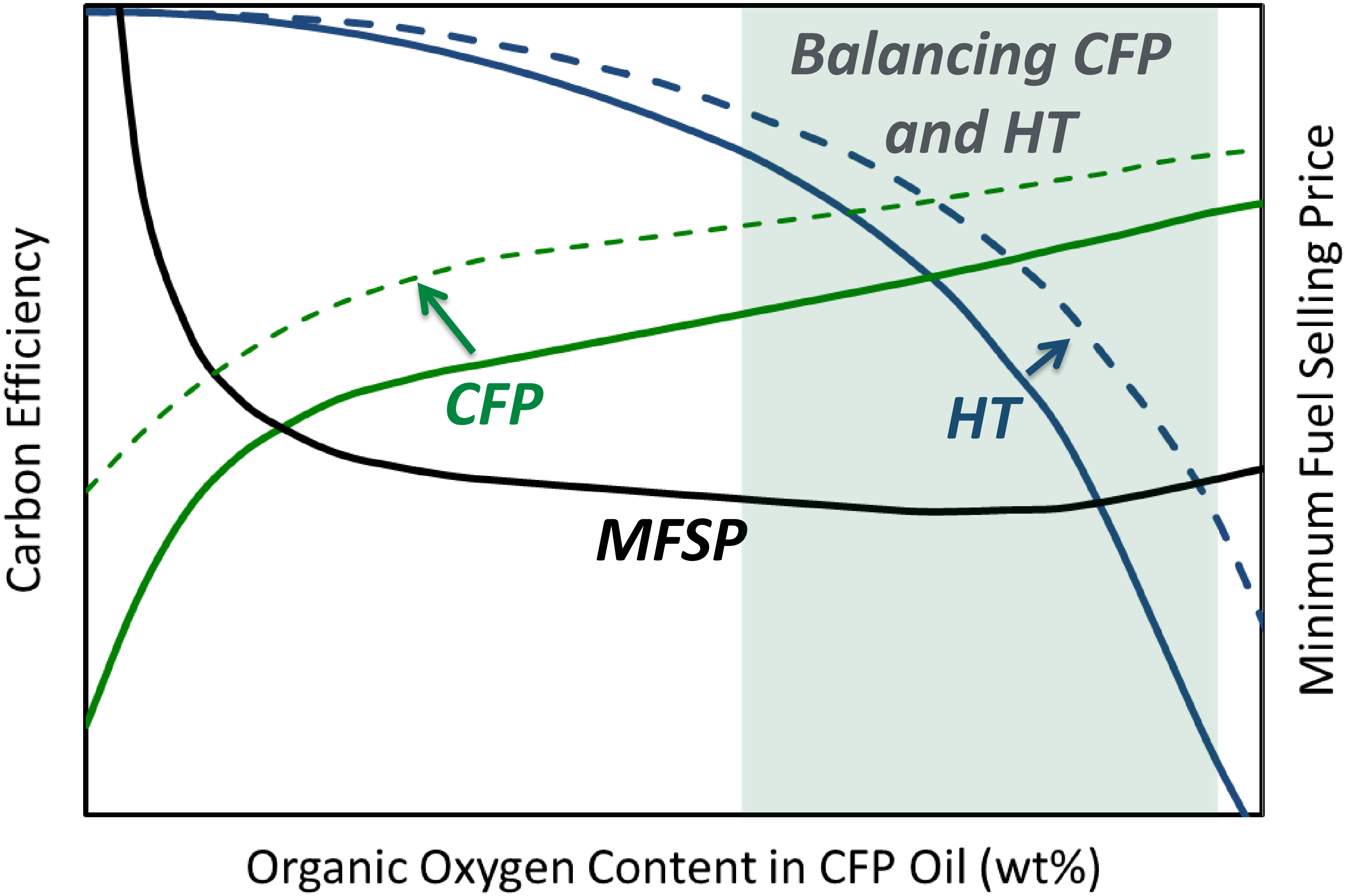


CFP: HZSM5, 500°C, B/C: 0.5-1.5

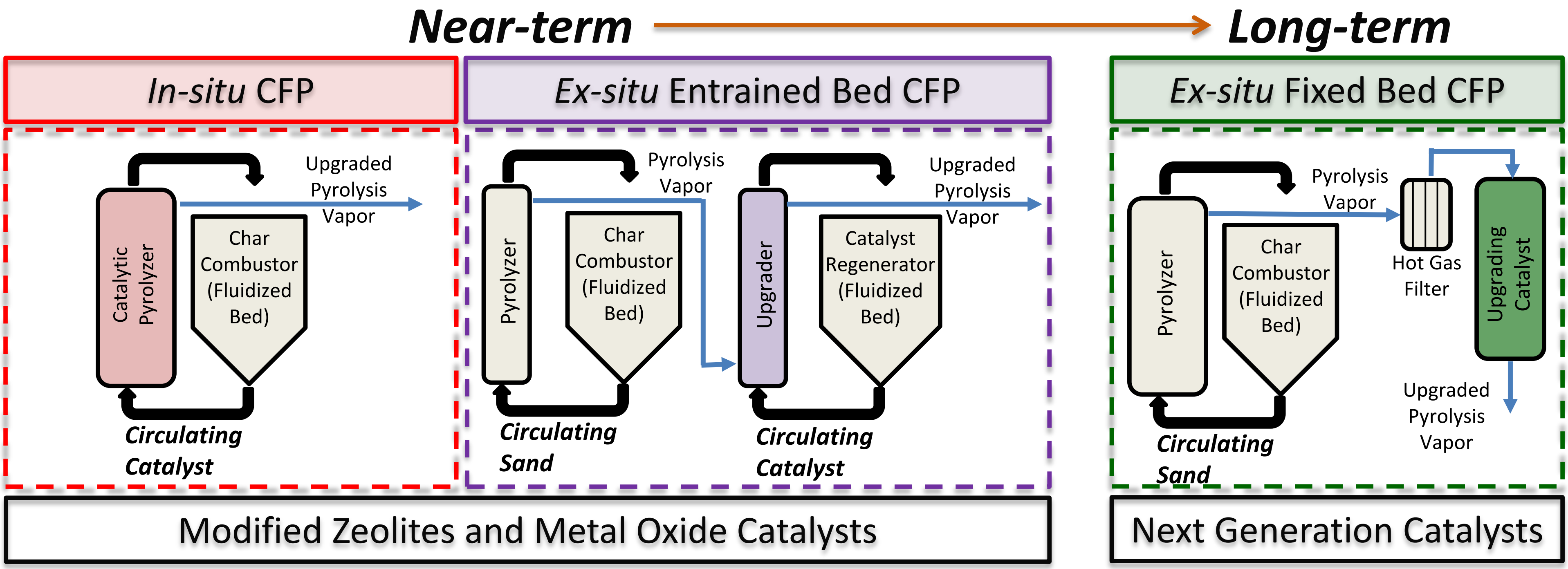
HT: Batch Parr Reactor, CoMoS catalyst, 2500psi, T: 350-410°C

Hydrotreating carbon efficiency improves at lower CFP oil oxygen content, but validation of trend is required

Technical Approach: Process Optimization



Technical Approach: CFP Process Design Options



Near-term → ***Long-term***

In-situ CFP

Ex-situ Entrained Bed CFP

Ex-situ Fixed Bed CFP

Modified Zeolites and Metal Oxide Catalysts

Next Generation Catalysts

- Operating conditions tied to fast pyrolysis
- Catalyst mixed with biomass, char, and ash
- Lower capital investment
- Higher catalyst replacement rates

- Operating conditions can differ from fast pyrolysis
- Biomass, ash, and char are reduced or removed; more benign environment for catalyst
- Higher capital investment
- Lower catalyst replacement rates

- More diverse catalysts are feasible
- Access to greater catalytic chemistry
- Long catalyst lifetimes required
- Hot gas filter required

Technical Approach: Challenges and Success Factors

Grand Challenges

- *Co-optimize catalyst-process configuration combination* to balance yield and product quality of bio-oil intermediate with down-stream hydrotreating steps

Goal: ***Maximize carbon efficiency***

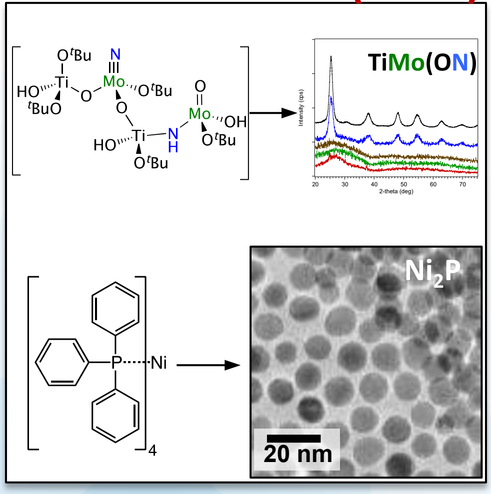
- Develop scalable, cost-effective, selective and durable catalysts that provide *control over product distribution*
- *Mitigate catalyst deactivation* and develop efficient *regeneration protocols*

Critical Success Factors

- *Achieve carbon efficiency and product distribution targets for 2019*
  - 39% CFP C efficiency and 35% product selectivity to distillates
- Demonstrate that CFP *reduces cost of downstream hydrotreating*
  - Validate design report assumptions
- Develop *relationships linking CFP and hydrotreating*

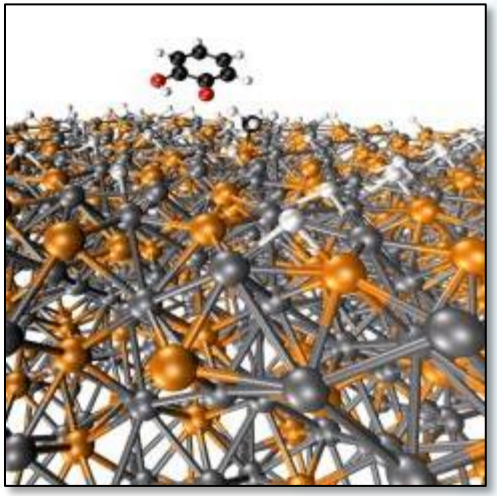
Technical Approach: From Catalyst Design through Demonstration

Synthesis & Characterization (ACSC)



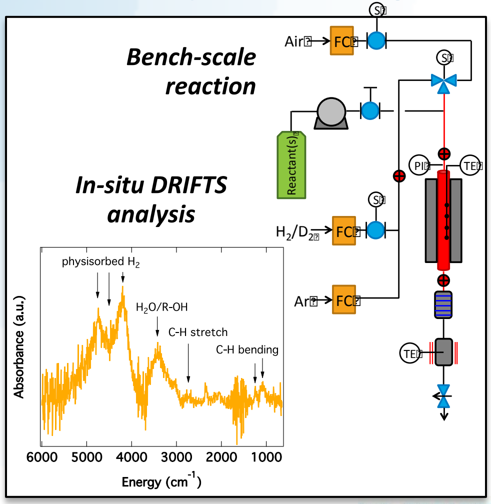
- *Reliable, versatile methods*
- *Target new, tailored structures*
- *Metastable phases*
- *Solid-state analogs of solution spectroscopies*
- *Understand surface chemistry*

Theory (CCPC)



- *Structure & energetics*
- *Performance descriptors*
- *Predictive capability*

Catalytic Testing

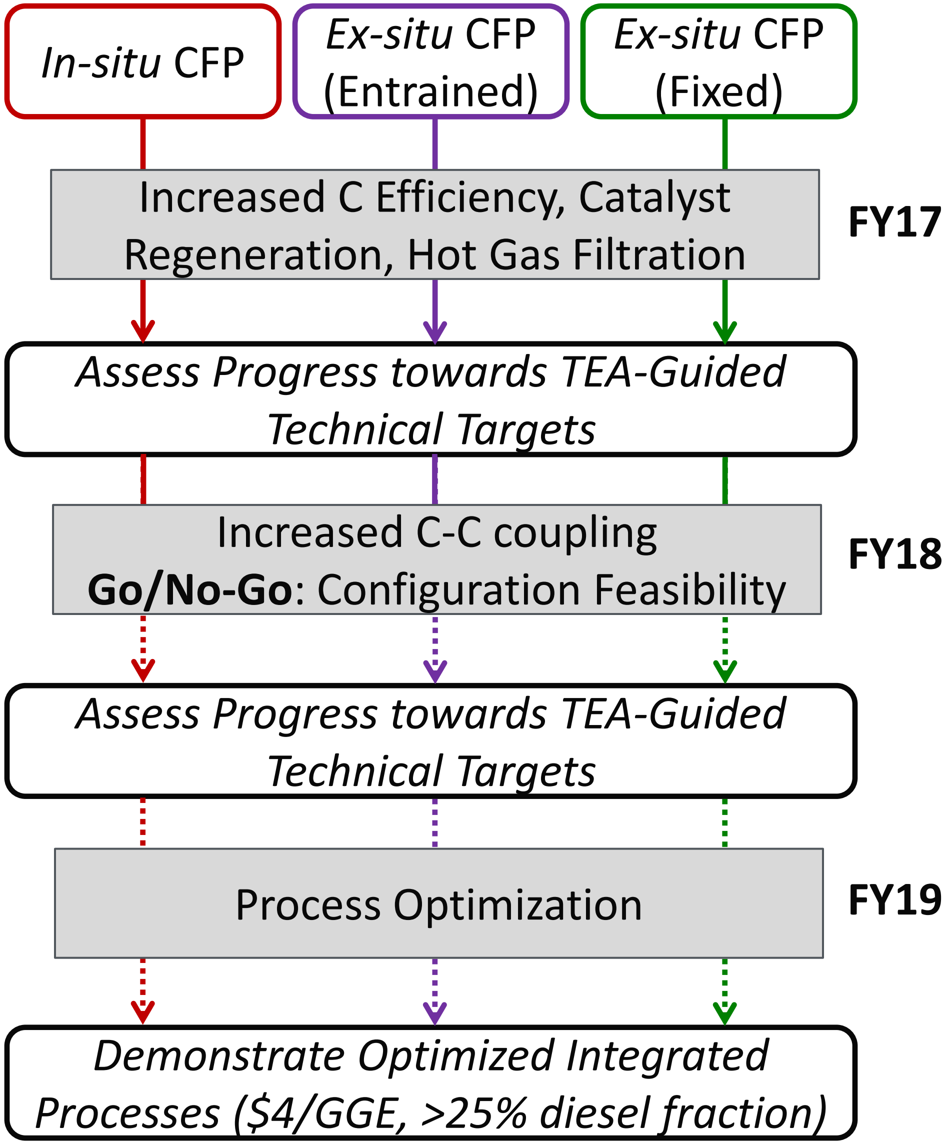


Catalyst scaling & Pilot-scale testing (CCM)

- *Activity & selectivity*
- *Mechanisms*
- *In-situ spectroscopies*
- *Structure-function relationships*

Management Approach

Research Management



Project Management

Catalyst Design and Development and Small-Scale CFP

PI: Josh Schaidle (NREL)

- Task 1: Catalyst Design and Development
- Task 2: CFP with Model Compounds
- Task 3: CFP with Biomass Pyrolysis Vapors

Ex-situ CFP Process Evaluation and Configuration Optimization

PI: Kim Magrini (NREL)

- Task 4: CFP with Coupled Pyrolyzer-Davison Circulating Riser

In-situ CFP and Hydrotreating

PI: Huamin Wang (PNNL)

- Task 5: *In-situ* CFP (USU/VTT)
- Task 6: Hydrotreating of CFP Bio-oils

Research Progress: *In-situ* CFP

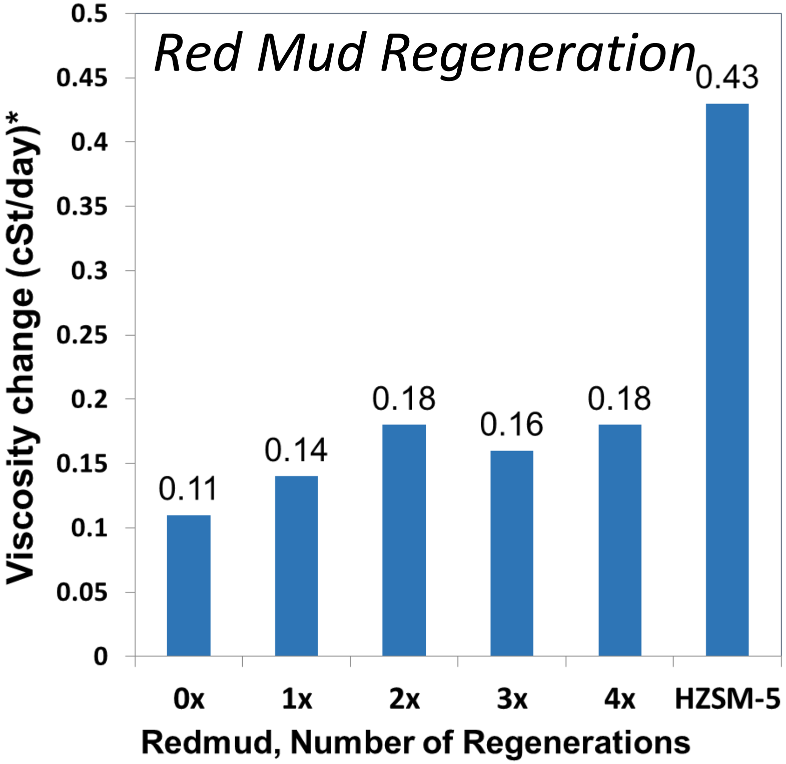
Low-cost red mud is a promising catalyst for in-situ CFP

	Bio-oil yield wt%, dry	C/H/O wt%, dry	H_2O wt%	Carbonyl mmol/g	TAN mg KOH/g
FP Bio-oil (typical)[1]	63	53/6.5/40	24	5.3	71
VTT ZSM-5 catalyzed[2]	32	72/6.5/22	6	3.5	57
USU Red mud catalyzed[3]	21-28	68/7/25	3.5	2.6	47

*Oil characterization joint with bio-oil analysis standardization project (2.5.2.301/302)

[1] *Energy Fuels* 2010, 24, 1380; [2] *Green Chem*. 2014, 16, 3549; [3] *Energy Fuels* 2016, 30, 7947

- *In-situ* CFP resulted in lower O content, carbonyl content, and TAN than FP
- Red mud (low-cost waste product from alumina process, contains Fe_2O_3, Al_2O_3, TiO_2, SiO_2, MgO, CaO) showed comparable performance to H-ZSM-5
- Lower pyrolysis T increased bio-oil yield



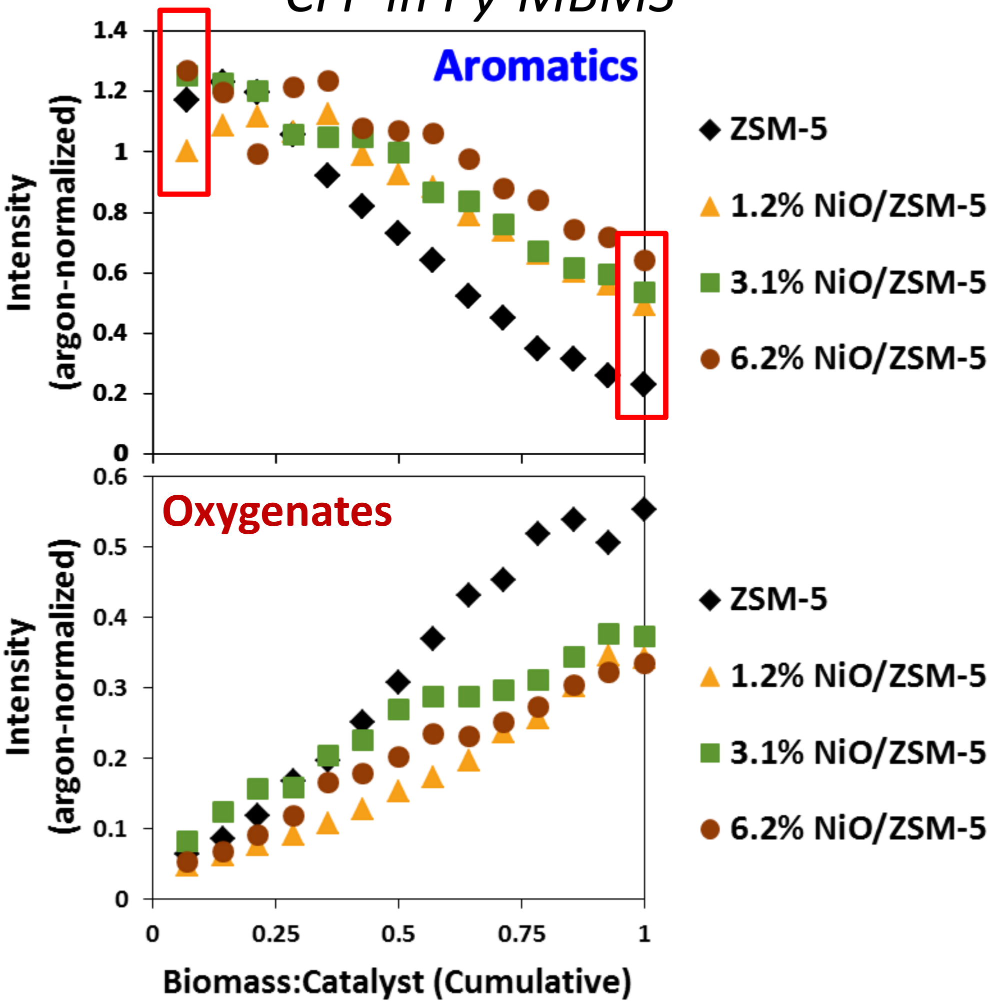
* Daily change of bio-oil viscosity used as an indicator of bio-oil stability

- Red mud catalyst is regenerable for at least 20 cycles

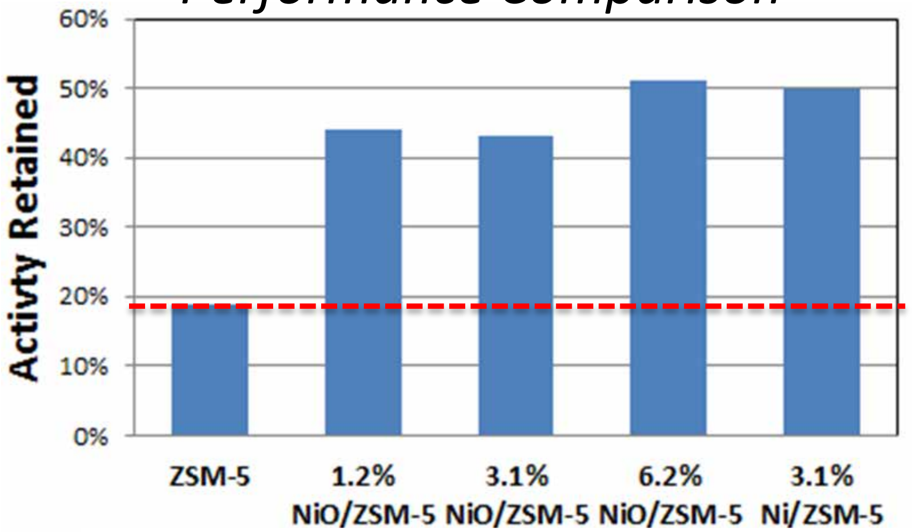
Research Progress: *Ex-situ* CFP with Zeolite-based Catalysts

Ni-modification of HZSM-5 improves performance for ex-situ CFP

CFP in Py-MBMS



Performance Comparison



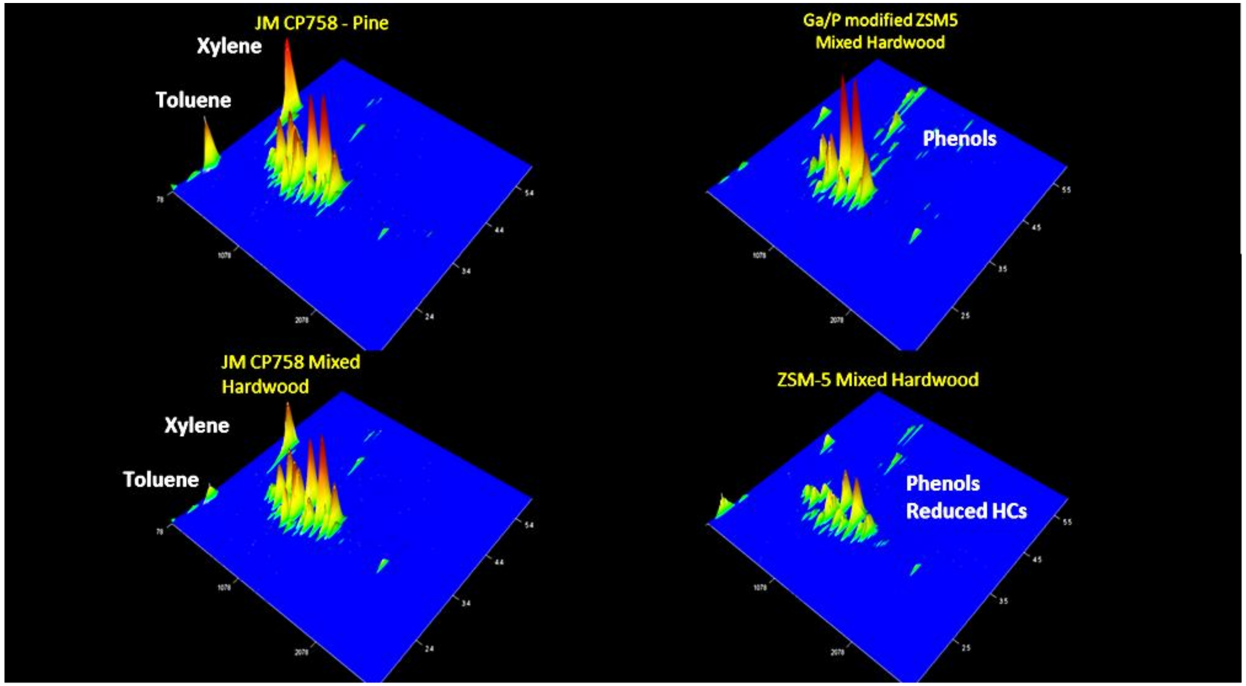
- Aromatic yield increased with higher NiO loading
- Ni addition increased stability
- NiO/HZSM-5 is regenerable; H_2 not required

M. Yung, et al., *Energy & Fuels* 30 (2016) 5259

Research Progress: *Ex-situ* CFP with Zeolite-based Catalysts

Pyrolyzer-DCR enables catalyst evaluation in an industry-standard system

2D GCxGC TOF-MS of CFP Bio-Oil



*Pyrolyzer: 500°C, 25psig, 2s RT; DCR: 1kg/h feed, 1.8kg cat, riser T = 550°C

- Evaluated both in-house and commercial catalysts (JM)
- JM CP758 showed enhanced selectivity to toluene and xylene, with significantly reduced phenolics

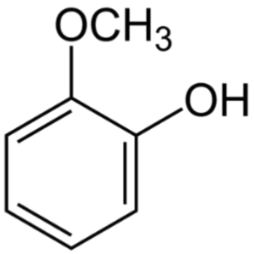
Catalyst ID	Type	Performance
ZSM-5	ZSM-5 additive	Enhanced olefins, aromatics
JM CP758	Johnson Matthey CP758	Enhanced toluene and xylene, reduced phenolics
P-ZSM-5	Phosphorus-stabilized ZSM-5	Enhanced olefins, aromatics
Ga/P-ZSM-5	Gallium impregnated phosphorus-stabilized ZSM-5	Enhanced heavy HCs, phenolics

Research Progress: *Ex-situ* CFP with Non-Zeolite Catalysts

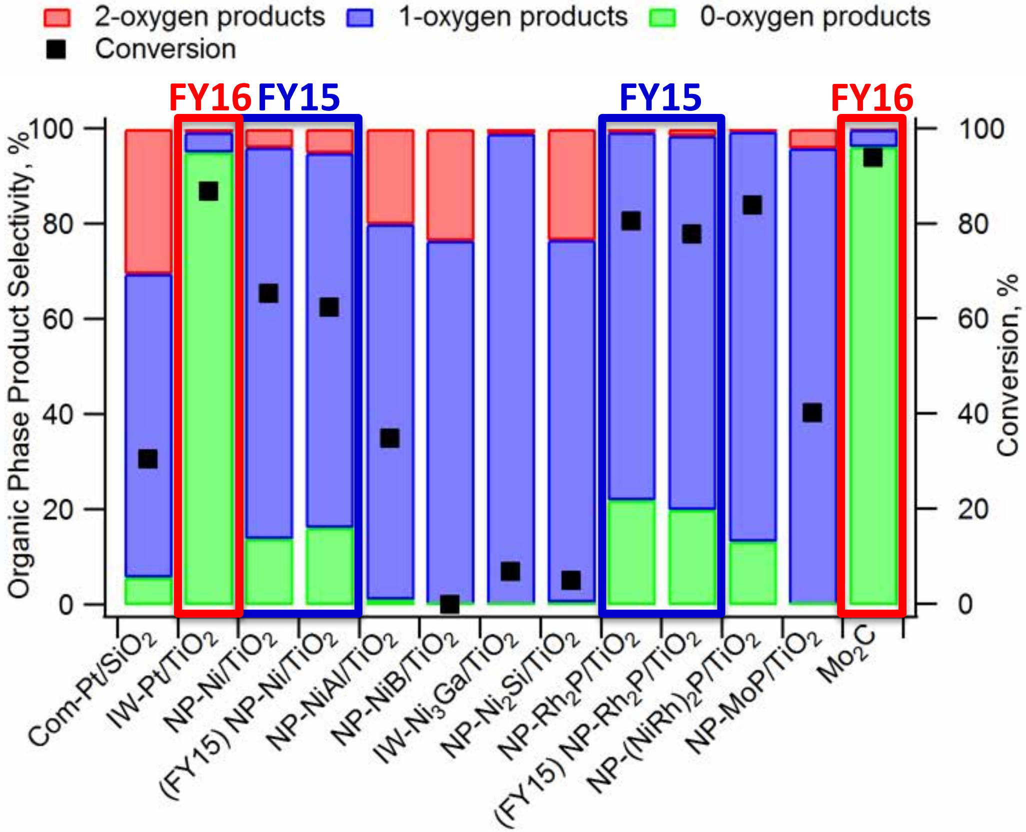
Identified high-performing next generation catalyst formulations

Model Compound Studies

- Feed: Guaiacol
- Bench-scale fixed-bed isothermal reactor
- 350°C, 0.5MPa
- 12:1 H_2:Guaiacol
- WHSV = $10h^{-1}$, 8h TOS



Guaiacol Deoxygenation

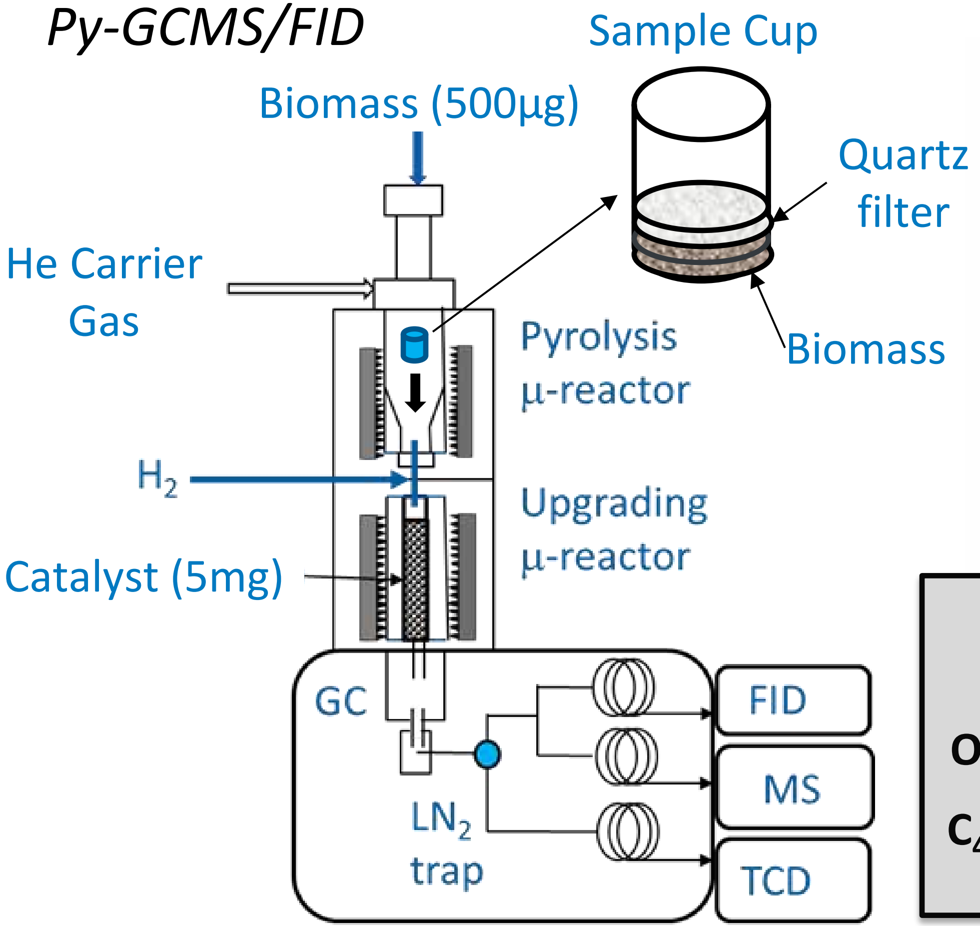


Mo_2C and Pt/TiO_2 have exhibited the best performance to date for deoxygenation of guaiacol

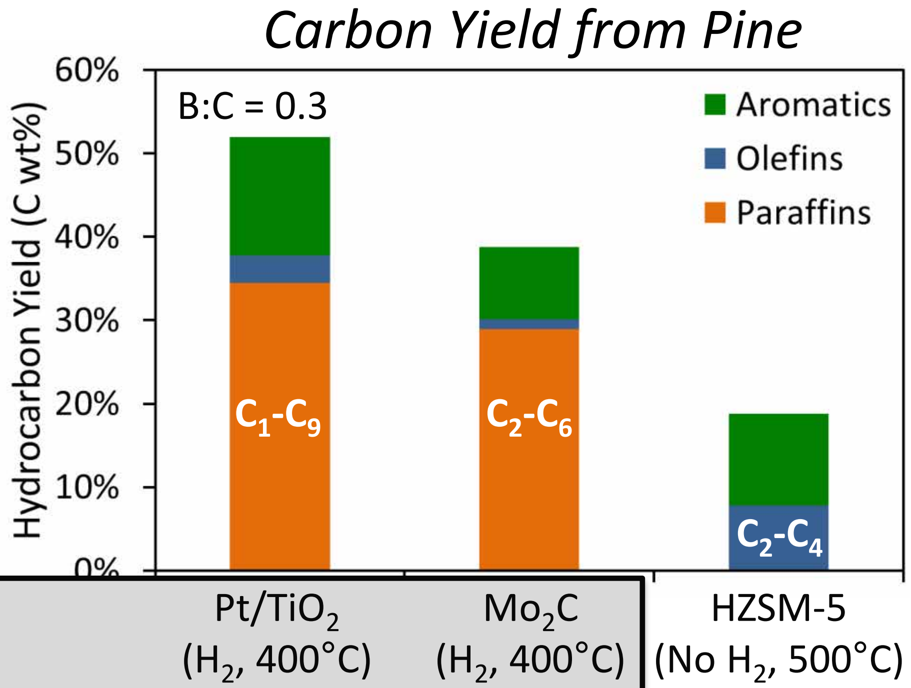
Research Progress: *Ex-situ* CFP with Non-Zeolite Catalysts

Evaluated next generation catalysts with biomass vapors

Py-GCMS/FID



Carbon Yield from Pine



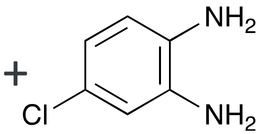
	Pt/TiO_2 (H_2, 400°C)	Mo_2C (H_2, 400°C)
O Content	1.5wt%	~0wt%
C_{4+} Carbon Yield	40wt%	29wt%

Mo_2C and Pt/TiO_2 efficiently deoxygenated pine pyrolysis vapors to produce hydrocarbons and exhibited different product selectivity than HZSM5

Research Progress: *Ex-situ* CFP with Non-Zeolite Catalysts

Synthesized Supported Mo_2C Nanoparticles using a Hard Template Approach

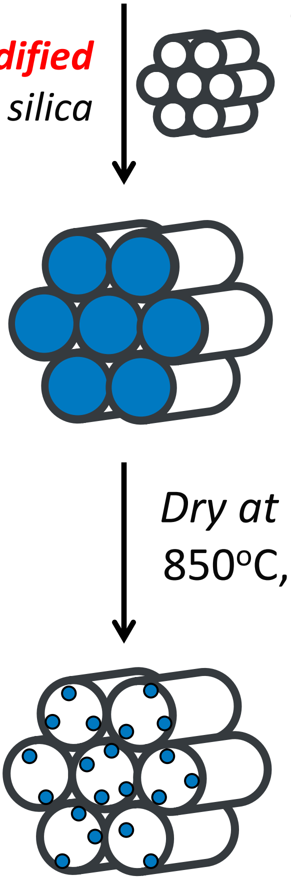
$MoCl_5$ + EtOH +



Mix at RT →

[Amine-Mo solution]

B.M. Leonard *et al.*, *Chem. Commun.* **2013**, *49*, 10409; *Chem. Mater.* **2015**, *27*, 4281.

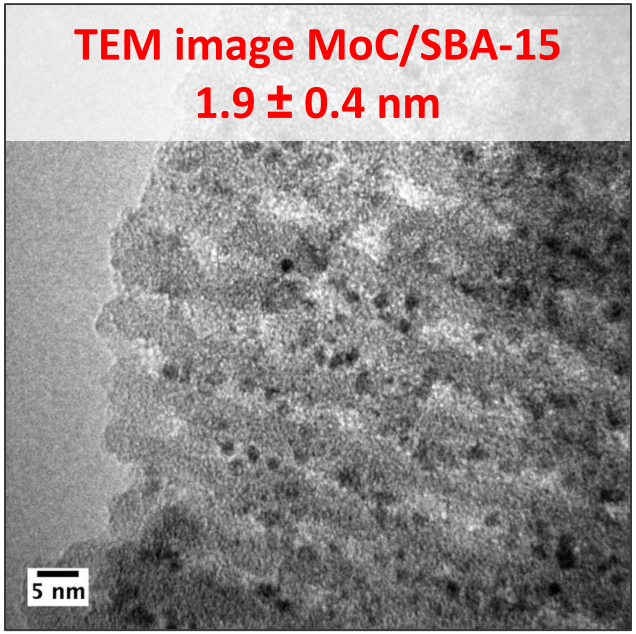


Surface-modified *SBA-15 silica*

'Amine-Mo' impregnated SBA-15

Dry at RT
850°C, N_2

Supported nano-MoC



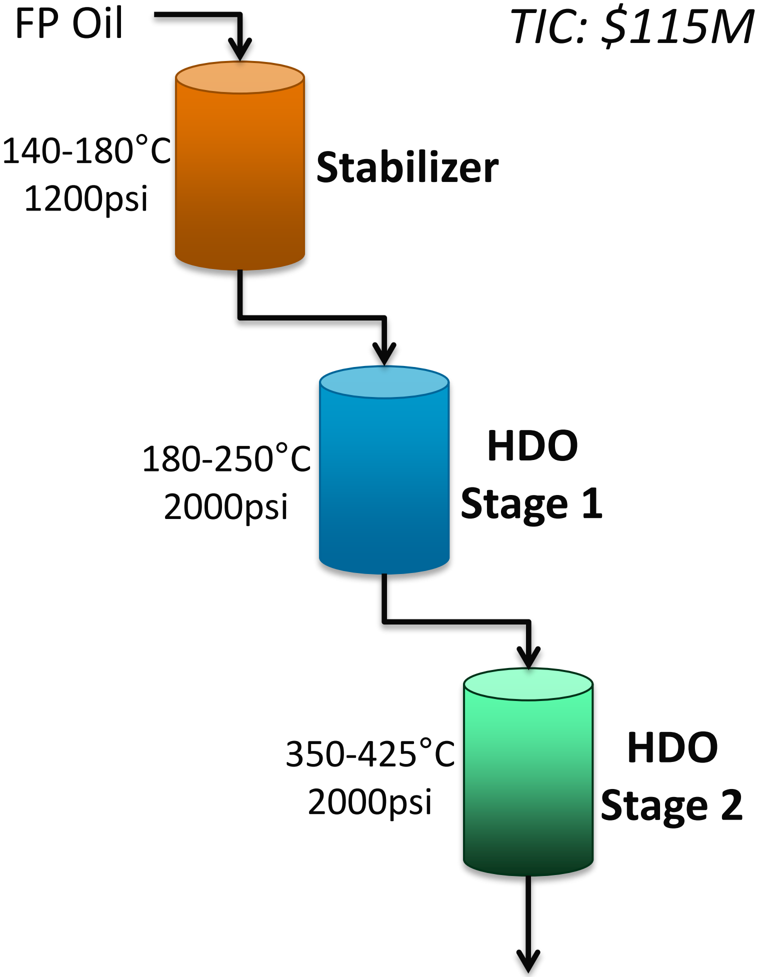
TEM image MoC/SBA-15
1.9 ± 0.4 nm

- NPs inside the SBA-15 pores
- 1.9nm diameter
- XRD matches α-MoC
- Similar reactivity to bulk Mo_2C
- Method transferrable to other supports

F. Baddour *et al.*, *Angewandte Chemie* 55 (2016) 9026

Research Progress: Hydrotreating

Fast Pyrolysis Oil



FP Oil

TIC: $115M

140-180°C
1200psi

Stabilizer

180-250°C
2000psi

**HDO
Stage 1**

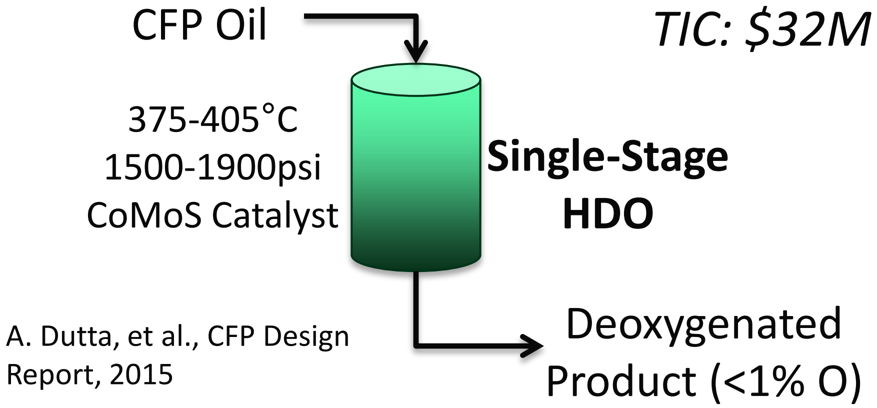
350-425°C
2000psi

**HDO
Stage 2**

Deoxygenated
Product

S. Jones, et al., Fast Pyrolysis and Hydrotreating Bio-oil Pathway, 2013

Catalytic Fast Pyrolysis Oil



CFP Oil

TIC: $32M

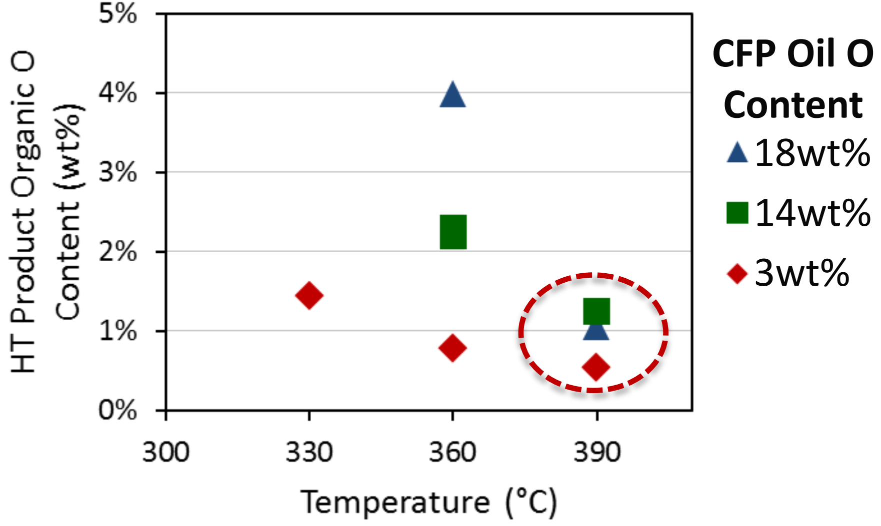
375-405°C
1500-1900psi
CoMoS Catalyst

**Single-Stage
HDO**

Deoxygenated
Product (<1% O)

A. Dutta, et al., CFP Design Report, 2015

Hydrotreating CFP Oil



CFP: HZSM5, 500°C, B/C: 0.5-2.1

HT: Batch Parr Reactor, CoMoS catalyst, 2000psi H_2

Research Progress: Hydrotreating

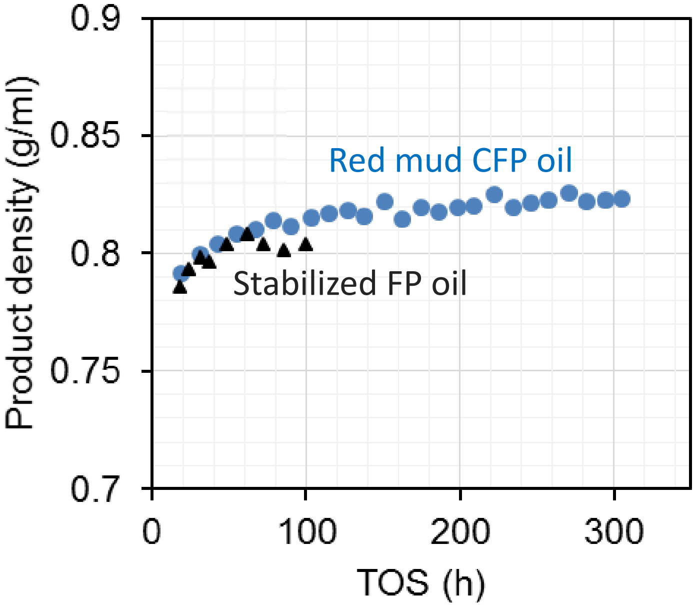
Hydrotreating assumptions validated with in-situ CFP oil

PNNL has demonstrated *greater than 300h of time on stream hydrotreating* of *in-situ* CFP oil from Utah State University, with product densities similar to stabilized fast pyrolysis oil

	Catalyst bed	Oil Yield g/g, dry	O in Product	TOS
Bio-oil (typical)[1]	Reduced Ru + CoMo sulfide	0.40-0.45	<2.0 wt.%	>1000 h
Red mud catalyzed[2]	Single CoMo sulfide	0.72-0.76	1.0-1.2 wt.%	Stable for 300 h

[1] 2016 SOT; Stabilized over Ru catalyst at 140 °C; Hydrotreated over commercial CoMo catalyst at 400°C, 1800 psig, 0.22 h^{-1} LHSV

[2] Hydrotreating test: CoMo sulfide catalyst, 400°C, 1800 psig, 0.20 h^{-1} LHSV



Agblevor et al. *Energy Fuels* 2016, 30, 7947

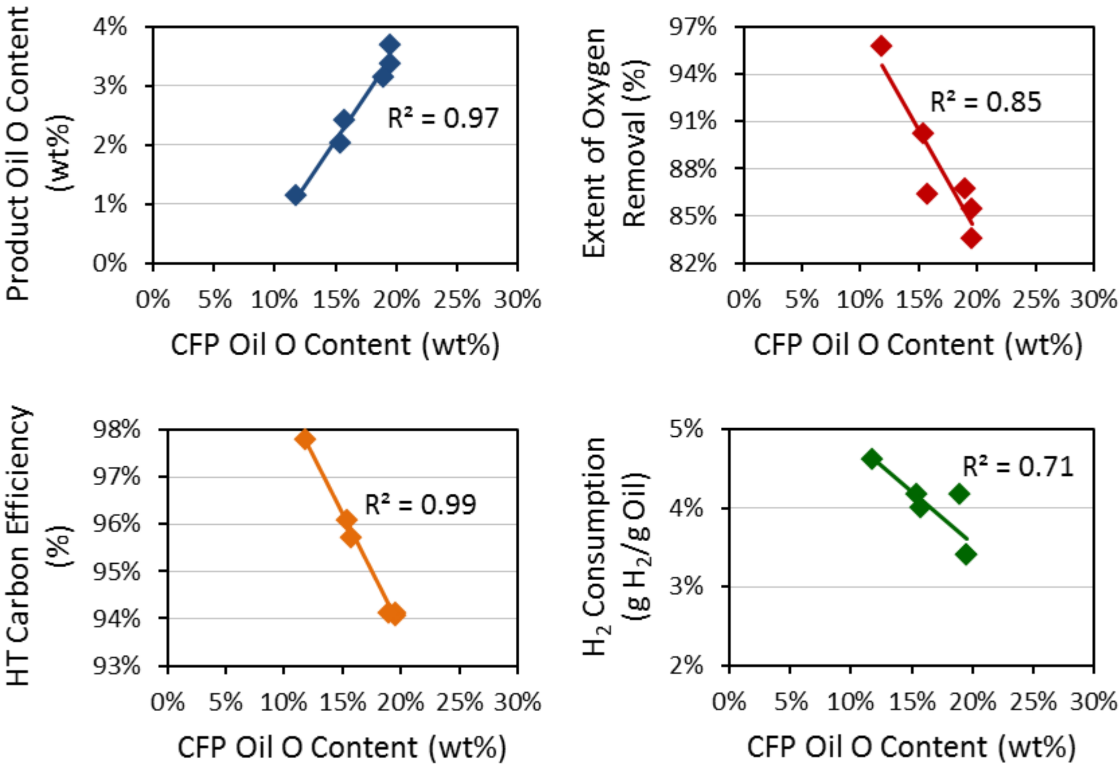
CFP enables single-stage bio-oil hydrotreating without stabilization

Research Progress: Hydrotreating

Developed relationships between CFP and HT

Experimental Plan:

- Produce CFP oils under varying conditions
  - Upgrading T: 500-550°C
  - Catalysts: ZSM-5, Ni/ZSM-5, Ga/ZSM-5, JM ZSM-5
  - Reactor Systems: 2” Fluidized bed reactor and DCR
  - Oil O content: 12-20%
- Hydrotreat all oils under same conditions
  - Batch Parr reactor, 390°C, CoMoS catalyst, 2000psi H_2

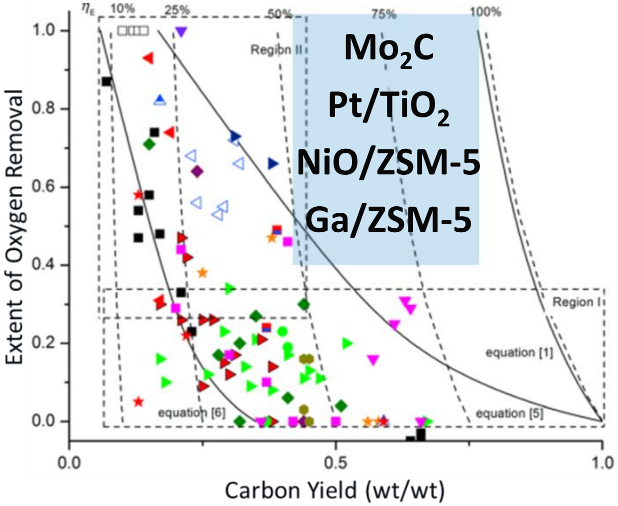


Hydrotreatability of CFP oils is well-correlated with the CFP oil O content

Relevance

Decrease Biomass Conversion Costs for CFP by Developing Catalysts and Integrated Processes that *Improve Yield and Enhance Fuel Quality*

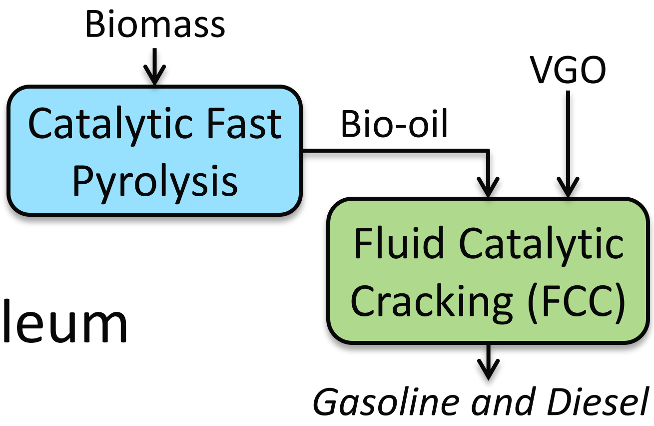
- Advances CFP SOT by targeting the primary cost driver: ***carbon efficiency***
  - ***Carbon efficiency is the key to commercial viability***
  - Improvements are realized through co-optimization of catalyst and process configuration
  - 2014 - 2016: Increased C Eff. from 23% to 28% resulting in ***>$1.4/GGE reduction in MFSP***
- Establishes CFP to meet BETO's 2022 goal of producing hydrocarbon biofuel at an MFSP of $3/GGE and GHG reduction of over 50%



- Fulfills a critical need for Conversion Enabling Technologies:
  - "Investment in ***early stage catalyst development*** ensures a consistent pipeline for breakthroughs in Conversion and is ***crucial to improving the economics of fuel and product production***." BETO MYPP
- Leverages industrial partnerships (VTT and JM) and industrially-relevant systems (DCR) to provide *directly transferrable knowledge to the bioenergy industry*

Future Work

- Continue ***catalyst development***
  - ***Increase carbon yield by 10%*** (relative) compared to 2016 SOT catalysts
  - Validate observed yield improvements in larger-scale systems
- ***Compare performance*** across all three CFP configurations
  - Produce at least 500mL of CFP oil utilizing the same feedstock (clean pine)
  - Hydrotreat CFP oils at PNNL and assess progress towards 2017 targets
- ***In-situ CFP technology demonstration*** at 20 kg/h scale using red mud catalyst from a scaled-up production
- Assess ***feasibility of fixed-bed ex-situ CFP system*** to meet BETO’s 2022 targets
  - MFSP and FY18 targets as decision criteria
  - Prepare pilot plant for 2022 verification
- Pursue ***co-product opportunities***
  - CRADA with petrochemical company (April)
- Evaluate ***co-processing*** CFP oil with petroleum


Biomass

Catalytic Fast Pyrolysis

Bio-oil

VGO

Fluid Catalytic Cracking (FCC)

Gasoline and Diesel

Summary

- ***Carbon efficiency*** is the key to commercial viability of CFP
  - 10% (relative) improvement in carbon yield results in a ~$0.25/GGE reduction in MFSP
- This project focuses on the ***co-optimizing catalyst and process configuration*** to maximize carbon efficiency
- Advancing the SOT by addressing key challenges:
  - Co-Optimization of Catalyst-Process Configuration
    - CFP facilitates ***single-stage hydrotreating***
    - Hydrotreatability of CFP oils is ***well correlated*** *with O content*
  - Catalyst development and mitigation of deactivation
    - *Red mud, **a low-cost waste product**,* is an effective catalyst for *in-situ* CFP and is regenerable
    - ***NiO/HZSM-5 demonstrated higher aromatic yields*** *than HZSM-5 and is regenerable*
    - Mo_2C and Pt/TiO_2 effective at ***deoxygenating pyrolysis vapors***
- Demonstrated carbon efficiency improvement from ***23% to 28% from 2014 to 2016***, resulting in a ***reduction in MFSP by over $1.4/GGE***

Acknowledgements

ChemCatBio
Chemical Catalysis for Bioenergy

Energy Materials Network
U.S. Department of Energy

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy
Bioenergy Technologies Office

NREL

Susan Habas
Calvin Mukarakate
Kristiina Iisa
Michael Griffin
Erick White
Fred Baddour
Dan Ruddy
Connor Nash
Mark Nimlos
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Rick French
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Kurt Van Allsburg
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Brady Peterson
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Jess Olstad
Glenn Powell
Stuart Black
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Daniel Santosa
Corinne Drennan
Doug Elliott
John Frye
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Ben Roberts
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Igor Kutnyakov
Bala Maddi
John Cort
Karl Albrecht
Mariefel Olarte

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Christian Lindfors

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

Catalytic Fast Pyrolysis

WBS: 2.3.1.312/314/315

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

Thermochemical Conversion

March 7th, 2017

Project Leads:

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Nomenclature

- ACSC: Advanced Catalyst Synthesis and Characterization project
- CCB: Chemical Catalysis for Bioenergy Consortium
- CCM: Catalyst Cost Model project
- CCPC: Consortium for Computational Physics and Chemistry
- CFP: Catalytic Fast Pyrolysis
- DCR: Davison Circulating Riser
- FP: Fast Pyrolysis
- GGE: Gasoline Gallon Equivalent
- GHG: Greenhouse Gas
- HDO: Hydrodeoxygenation/Hydrotreating
- HT: Hydrotreating
- JM: Johnson Matthey
- MFSP: Minimum Fuel Selling Price
- NP: Nanoparticle
- SOT: State of Technology
- TEA: Techno-Economic Analysis
- TIC: Total Installed Capital
- USU: Utah State University
- VTT: VTT Technical Research Centre of Finland

Responses to 2015 Peer Review Comments (2.3.1.315)

Reviewer Comment:

The project is ready to generate data that should show the efficacy of this approach. DOE needs to ensure that this expensive asset (the Davidson Circulating Reactor) is well-utilized to maximize return on its investment.

PI Response:

We thank the reviewers for their comments and note that we are collaborating with commercial and other groups who want to use the DCR system for evaluating their catalysts, feedstocks, and process conditions.

Reviewer Comment:

This unit operation has a lot of “pots and pans.” I saw no review of conceptual economics to guide practicality of development.

PI Response:

The DCR unit is turnkey as designed by W.R. Grace and used by refineries worldwide, so we are not sure where the “pots and pans” are. The system is coupled with a biomass pyrolyzer to provide biomass pyrolysis vapors to the DCR for upgrading with FCC-type catalysts to hydrocarbon products. DCR operations are standardized to those used by the petroleum industry and process data is directly transferrable to the petroleum industry. Economic analyses and design reports for ex-situ CFP currently leverage an entrained flow reactor design, similar to a DCR, thus conceptual economics are integrated into this project.

Responses to 2015 Peer Review Comments (2.3.1.315)

Reviewer Comment:

How will aerosols be handled?

PI Response:

A hot gas filter removes residual char particles, aerosols and alkali species from pyrolysis vapors prior to upgrading in the DCR

Reviewer Comment:

Good luck with the issues of handling hydrogen at some point, removing vacuum gas oil (VGO) and working with 100% bio-oil, and overcoming catalyst attrition (need an inexpensive catalyst).

PI Response:

- We don't use hydrogen in the DCR
- We are working with biomass pyrolysis vapors (not bio oil)
- Near-term catalyst modifications focus on a "cheap" metal addition to FCC catalysts to improve deoxygenation and product yields, while reducing anti-coking properties

Responses to 2015 Peer Review Comments (2.3.1.314)

Consolidated Reviewers' Comments – Effect on Hydrotreating:

Effect of CFP on downstream hydrotreating was not clearly addressed. Does CFP processing result in reduced costs overall? If the downstream hydrotreater is being sized by the most difficult oxygenates and they still remain after the ex-situ step, the size of the hydrotreater remains the same PLUS an extra ex-situ processing step has been added. This does not sound too promising.

PI Response:

Over the last 2 years as part of this project, we have evaluated the effect of CFP on the requirements for downstream hydroprocessing (i.e., temperature, pressure, and number of reactors) and have demonstrated that CFP results in a reduction in the number of hydrotreater reactors required and the overall hydrotreating cost as compared to fast pyrolysis (see slides 19 and 20).

Consolidated Reviewers' Comments – Catalyst Evaluation and Metrics:

Metrics for catalyst success were given, but not tied to TEA. Researchers need to quantify the performance of existing catalysts to define the problem they're trying to solve.

PI Response:

The targets for catalyst performance (e.g., carbon efficiency, extent of deoxygenation, and extent of hydrogen incorporation) are directly derived from TEA based on our 2022 design case. Data generated from this project is incorporated into these TEA's yearly and provided in the MYPP. Catalyst performance is compared quantitatively to the prior year SOT or a baseline material (see slides 16 and 17 as examples).

Responses to 2015 Peer Review Comments (2.3.1.314)

Consolidated Reviewers' Comments – Scaled-up Technology Validations:
Not so clear that the large scale validation, at relatively high cost, will provide much additional information. The need for the large-scale validation in outyears is not clear. Reactor testing needs to be implemented. Investigators need to conduct experiments in a larger reactor to insure that results in small system correlate to a traditional reactor. The project needs to add accurate material balances to verify carbon yields. The effects of poisoning on catalyst activity needs to be assessed. Address catalyst life.

PI Response:
For many processes, there are often unforeseen issues during scale-up. By scaling up both catalyst synthesis and the CFP system, we hope to identify any of these issues at an early stage in the project so that they can be addressed prior to our FY22 integrated pilot-scale verification. In fact, our recent efforts to scale up the Pt/TiO_2 and Mo_2C catalysts and evaluate these materials in our 2" fluidized bed reactor (2FBR) provided insight into the desired physical properties. Moreover, larger-scale integrated operations provides insight into catalyst lifetime and stability that cannot be achieved at smaller scales. Achieving high mass balance closure is an ongoing effort. We recently made improvements to the 2FBR and DCR condensation trains and analysis systems to achieve more accurate mass balances and carbon yields.

Consolidated Reviewers' Comments – Computational Modeling:
The value of atomistic simulations for such a complex system is questionable.

PI Response:
We have seen good agreement so far between computational and experimental results with model compounds, and have also seen good agreement for catalyst performance when tested with either mixtures of model compounds or biomass pyrolysis vapors. By designing and developing catalysts to target the various functional groups present in pyrolysis vapors (e.g., carboxylic acids, ketones, aldehydes, and phenolics), we can pare down the complexity and use computational modeling (atomistic simulations) to guide development of next-generation materials.

Responses to 2015 Peer Review Comments (2.3.1.314)

Consolidated Reviewers' Comments – C-C Coupling:

Demonstrating C-C coupling is probably the economic key to cellulose conversion. We don't need C4's and C5's, we need diesel and jet.

PI Response:

As the reviewer states, the ability to produce diesel and jet fuel is key to this process being economically viable. Our TEA target cases for this process beyond FY17 shift towards making diesel-range products. Accordingly, C-C coupling through a variety of pathways (e.g., ketonization, hydroalkylation, and aldol condensation) is an active area of research within this project and will continue to be so throughout the lifetime of this project. In FY16, we demonstrated hydroalkylation in the vapor phase and identified support materials that enhance ketonization. In FY18, we have multiple milestones focused on improving C-C coupling.

Consolidated Reviewers' Comments – H_2 usage:

Desire to remove oxygen via water is not obvious. Hydrogen is normally VERY expensive compared to the cost of losing a single carbon. It is not clear if the new catalysts can result in reduction of total H2 demand. There needs to be a quick, iterative analysis to see how the results relate to process economics

PI Response:

Finding the optimal balance between removing oxygen as H_2O (consuming H_2) and removing oxygen as CO or CO_2 is based primarily on process/economic considerations. Based on our process designs, the *ex-situ* CFP pathway produces all of the required H_2 by reforming off-gases (light hydrocarbons) from the process, thus no additional natural gas is required. Additionally, the economics of the process are driven by the carbon yield. Accordingly, while some oxygen will be removed as CO by decarbonylation and CO_2 by decarboxylation/ketonization pathways, we are targeting to remove most of the oxygen as H_2O.

Publications (1 of 2)

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- M. M. Yung, A.K. Starace, C. Mukarakate, A.M. Crow, M.A. Leshnov, and K. A. Magrini, "Biomass Catalytic Pyrolysis on Ni/ZSM-5: Effects of Nickel Pretreatment and Loading," *Energy & Fuels* **2016** 30(7), 5259-5268.
- K. Magrini, Derek Vardon, Gregg Beckham, "Chapter 5: Catalysis's Role in Bioproducts Update", *Commercializing Biobased Products: Opportunities, Challenges, Benefits, and Risks*, **2016**, Edited by Dr. Seth W Snyder, Royal Society of Chemistry, London, England.
- C. Engtrakul, C. Mukarakate, A. Starace, K. Magrini, A. Rogers, M. Yung, "Effect of ZSM-5 acidity on aromatic product selectivity during upgrading of pine pyrolysis vapors", *Catalysis Today* **2016,** 269, 175-181.
- K. Magrini, "Converting Biomass Pyrolysis Vapors to Fungible Hydrocarbons using a Coupled Pyrolyzer Davison Circulating Riser System", IEA Newsletter Task 34 July **2016**.
- K. Magrini, "Refining Biomass Vapors into Fuels using an Industry-Standard Petroleum Refining Pilot Plant", BETO Success Story, September **2016**.
- S. Cheah, A. K. Starace, E. Gjersing, S. Bernier and S. Deutch, "Reactions of mixture of oxygenates found in pyrolysis vapors: deoxygenation of hydroxyacetaldehyde and guaiacol catalyzed by HZSM-5", *Topics in Catalysis*, **2016,** 59(1): 109–123.
- Iisa, K., French, R. J., Orton, K. A., Budhi, S., Mukarakate, C., Stanton, A. R., Yung, M. M., Nimlos, M. R., Catalytic pyrolysis of pine over HZSM-5 with different binders, *Topics in Catalysis,* **2016** (59) 94-108.
- G. S. Foo, A. K. Roger, M. M. Yung, and C. Sievers, "Steric Effect and Evolution of Surface Species in the Hydrodeoxygenation of Bio-oil Model Compounds over Pt/HBEA," accepted to ACS Catalysis, DOI: 10.1021/acscatal.5b02684.
- Iisa, K., French, R. J., Orton, K. A., Budhi, S., Mukarakate, C., Stanton, A. R., Yung, M. M., Nimlos, M. R., Catalytic pyrolysis of pine over HZSM-5 with different binders, *Topics in Catalysis,* **2016** (59) 94-108.
- M. M. Yung, A. R. Stanton, K. Iisa, R. J. French, K. A. Orton, and K. A. Magrini, "Multiscale Evaluation of Catalytic Upgrading of Biomass Pyrolysis Vapors on Ni- and Ga-Modified ZSM-5," *Energy &* Fuels, **2016**, *30* (11), pp 9471–9479.
- K. Magrini-Bair, W. Jablonski, M. Yung, Y. Parent, J. Olstad, S. Deutch, "Cleaning Biomass Derived Syngas with Fluid Bed Reforming Catalysts", pp. 39-42, extended abstract published in the Conference Proceedings of the 2nd International Conference on Renewable Energy Gas Technology, Barcelona, Spain (**2015)**, May 7-8, 2015.
- S. M. Schimming, O. D. LaMont, M. König, A. K. Rogers, A. D. D'Amico, M. M. Yung, and C. Sievers, "Hydrodeoxygenation of Guaiacol over Ceria-Zirconia Catalysts," *ChemSusChem* 8 (**2015)** 2073-2083.

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- Schimming, S. M., G. S. Foo, O. LaMont, A. K. Rogers, M. M. Yung, A. D. D’Amico, and C. Sievers, ”Kinetics of hydrogen activation on ceria-zirconia,” *Journal of Catalysis* 329 (**2015**) 335-347.
- S. Habas, F. Baddour, D. Ruddy, C. Nash, M. Pan, J. Wang, J. Hensley, J. Schaidle, “A Facile Molecular Precursor Route to Metal Phosphide Nanoparticles and their Evaluation as Hydrodeoxygenation Catalysts”, *Chemistry of Materials*, 27 (**2015**) 7580-7592.
- M. Griffin, F. Baddour, S. Habas, D. Ruddy, J. Schaidle, “Evaluation of Metal and Metal Phosphide Catalysts for the Hydrodeoxygenation of Guaiacol under *Ex-situ* Catalytic Fast Pyrolysis Conditions”, *Topics in Catalysis*, 59 (**2016**) 124-137. *Invited paper for a special issue on Catalytic Conversion of Biomass to Fuels and Chemicals.
- A. Dutta, J. Schaidle, D. Humbird, F. Baddour, A. Sahir, “Conceptual Process Design and Techno-Economic Assessment of Ex Situ Catalytic Fast Pyrolysis of Biomass: A Fixed Bed Reactor Implementation Scenario for Future Feasibility”, *Topics in Catalysis*, 59 (**2016**) 2-18. *Invited paper for a special issue on Catalytic Conversion of Biomass to Fuels and Chemicals.
- J. Schaidle, J. Blackburn, C. Farberow, C. Nash, K. Steirer, J. Clark, D. Robichaud, D. Ruddy, “Experimental and Computational Investigation of Acetic Acid Deoxygenation over Oxophilic Molybdenum Carbide: Surface Chemistry and Active Site Density”, *ACS Catalysis*, 6 (**2016**) 1181-1197. *Invited paper for Virtual Special Issue on Catalysis at U.S. Department of Energy National Laboratories.
- M. Pruski, A. Sadow, I. Slowing, C. Marshall, P. Stair, J. Rodriguez, A. Harris, G. Somorjai, J. Biener, C. Matranga, C. Wang, J. Schaidle, G. Beckham, D. Ruddy, T. Deutsch, S. Alia, C. Narula, S. Overbury, T. Toops, R. Morris Bullock, C. Peden, Y. Wang, M. Allendorf, J. Nørskov, T. Bligaard, “Virtual Special Issue on Catalysis at the U.S. Department of Energy’s National Laboratories”, Editorial, *ACS Catalysis* 6 (**2016**) 3227-3235. *Invited to provide overview of catalysis research at NREL for editorial in a Virtual Special Issue on Catalysis at U.S. Department of Energy National Laboratories.
- M. Griffin, G. Ferguson, D. Ruddy, M. Biddy, G. Beckham, J. Schaidle, “The Role of the Support and Reaction Conditions on the Vapor Phase Deoxygenation of m-Cresol over Pt/C and Pt/TiO_2 Catalysts”, *ACS Catalysis*, 6 (**2016**) 2715-2727.
- F. Baddour, C. Nash, J. Schaidle, D. Ruddy, “Synthesis of α-MoC_{1-x} nanoparticles using a surface-modified SBA-15 hard template and determination of structure-function relationships in acetic acid deoxygenation”, *Angewandte Chemie*, 55 (**2016**) 9026-9029.
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- K. Onarheim, Y. Solantausta, V. Paasikallio, D.C. Elliott, Technoeconomic assessment of fast pyrolysis concepts, Tcbiomass 2015, Chicago, IL, November 03, 2015.
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- M. M. Yung, “Heterogeneous Catalysis Research for Biofuel Production at NREL,” Florida American Vacuum Society – Surface Science Symposium, Orlando, Florida, March 2015 (invited).
- M. M. Yung, “Synthetic fuel production from biomass and catalysis research at NREL,” University of South Florida Chemical Engineering Department Seminar, Tampa, Florida, March 2015 (invited).
- M. Yung and T. Foust, “Symposium: Biomass Conversion to Fuels and Chemicals,” American Chemical Society National Meeting, Denver, Colorado, March 2015 (invited).
- M. M. Yung, C. Mukarakate, C. Engtrakul, K. A. Magrini, “Effects of Catalyst Acidity on Upgrading of Biomass Pyrolysis Vapors,” North American Catalysis Society NAM 24, Pittsburgh, PA, June 2015.
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- M. Yung, “Biomass Conversion to Fuels: Catalysis R&D at NREL,” University of Calgary Department of Chemical Engineering Seminar, Calgary, Canada, October 2015.
- A. K. Starace, M. M. Yung, K. A. Magrini, E. Chornet, “Low-cost Additives for Improved Char Gasification”, Gasification Technologies Conference, Colorado Springs, CO, October 11-14, 2015.
- K. Magrini, “Ex-Situ Catalytic Upgrading of Biomass Pyrolysis Vapors to Hydrocarbons”, BETO Conversion Catalysis Working Group Meeting, Denver, CO, October 20-21, 2015.

Presentations (2 of 5)

- K. Magrini, J. Olstad, M. Jarvis, Y. Parent, G. Powell, M. Sprague, “Upgrading Biomass Pyrolysis Vapors to Fungible Hydrocarbon Intermediates with a Coupled Pyrolyzer Davison Circulating Riser System, tcbBiomass 2015 – the International Conference on Thermochemical Conversion Science, Chicago, IL, November 2-5, 2015.
- M. Jarvis, J. Olstad, G. Powell, Y. Parent, S. Deutch, M. Sprague, “Co-feeding Biomass Pyrolysis Vapors and VFO foe Ex-Situ Upgrading of in a DCR”, oral presentation *tcbBiomass 2015* – the International Conference on Thermochemical Conversion Science, November 2-5, 2015, Chicago, IL.
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- Kristiina Iisa, Richard French, Kellene Orton, Mark Nimlos, “Ex-situ catalytic Pyrolysis of Pine in Fluidized Bed Reactor,” poster presented at TC-Biomass 2015: Technology for the Bioeconomy, Chicago, IL, November 2-5, 2015.
- K. Magrini, “Upgrading Biomass Pyrolysis Vapors to Fungible Hydrocarbon Intermediates with a Coupled Pyrolyzer Davison Circulating Riser System”, Biomass Program Weekly Update, NREL, November 17, 2015.
- K. Magrini, M. Jarvis, J. Olstad, Y. Parent, S. Deutch, G. Powell, M. Sprague, “Upgrading Biomass Pyrolysis Vapors to Fungible Hydrocarbons at the Small Pilot Scale”, C3E Ambassadors Meeting, Denver, CO, March 30, 2016.
- K. Magrini and M. Yung, “2.3.1.315 Project Go/No Go Decision Update”, presented to BETO program management, NREL, March 23, 2016.
- K. Magrini, “Upgrading Biomass Pyrolysis Vapors to Fungible Hydrocarbon Intermediates”, presented to Anellotech, NREL, May 31, 2016.
- K. Magrini, M. Jarvis, J. Olstad, Y. Parent, S. Deutch, G. Powell, M. Sprague, “Upgrading Biomass Pyrolysis Vapors to Fungible Hydrocarbon Intermediates”, 24th European Biomass Conference & Exhibition, Amsterdam, NE, June 6-9, 2016.
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- S. Cheah, T. O’Neill, W. Michener, M. Rabin, R. Evans, K. Magrini, “Synthesis of hydroxybutanone and chemicals from biomass”, Gordon Research Conference - Green Chemistry, Stowe, VT, July 31-August 5, 2016

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- M.M. Yung, “Thermochemical Conversion R&D at NREL: Current Projects and Catalysis Examples,” Chemical Engineering Department Seminar, Technical University of Munich, Munich, Germany, November 2016.
- M.M. Yung, K. Iisa, K.A. Magrini, “Biomass pyrolysis and catalytic upgrading for hydrocarbon fuel production: multi-scale catalyst evaluation and development,” 6th International Symposium on Energy from Biomass and Waste, Venice, Italy, November 2016.
- M.M. Yung, A.K. Starace, C. Mukarakate, K.A. Magrini, M.R. Nimlos, “Upgrading of Biomass Pyrolysis Vapors on Modified ZSM-5: Effects of Nickel Loading and Pretreatment,” AIChE Annual Meeting, San Francisco, CA, November 2016.
- K. Magrini, J. Olstad, M. Jarvis, Y. Parent, M. Sprague, G. Powell, “Upgrading Biomass Pyrolysis Vapors to Fungible Hydrocarbon Intermediates”, 6th International Symposium on Energy from Biomass and Waste, Venice, Italy, November 16, 2016.
- K. Magrini, J. Olstad, M. Jarvis, Y. Parent, S. Deutch, M. Sprague, G. Powell, “Upgrading Biomass Pyrolysis Vapors to Fungible Hydrocarbon Intermediates”, invited presentation to Enerkem, November 9, 2016, Sherbrooke, CA.
- M. Griffin, G. Ferguson, D. Ruddy, M. Biddy, G. Beckham, J. Schaidle*, “Role of the Support and Reaction Conditions on the Vapor-Phase Deoxygenation of m-Cresol over Pt/C and Pt/TiO_2 Catalysts”, AIChE Annual Meeting, San Francisco, CA. November 17th, 2016.
- C. Farberow*, C. Nash, J. Schaidle, “Mechanistic Insights into Carbon-Oxygen Bond-Breaking on Mo_2C Catalysts: Ethanol Dehydration”, AIChE Annual Meeting, San Francisco, CA. November 17th, 2016.
- S. Paleg*, J. Schaidle, L. Thompson, “Selective Hydrogenation of Bio-Oil Model Compounds over Molybdenum Carbide Supported Catalysts”, AIChE Annual Meeting, San Francisco, CA. November 14th, 2016.
- S. Habas*, F. Baddour, D. Ruddy, C. Nash, J. Schaidle, “A Facile Route to Nanostructured Metal Phosphide Catalysts for Hydrodeoxygenation of Bio-oil Compounds”, Frontiers in Biorefining Meeting, St. Simons Island, GA. November 11th, 2016.
- C. Mukarakate, M. Griffin, C. Nash, E. White, F. Baddour, D. Ruddy, J. Schaidle*, “From Catalyst Design to Technology Validation: The Role of Model Compound and Whole Biomass Vapor Experiments in Catalytic Fast Pyrolysis Research and Development”, Frontiers in Biorefining Meeting, St. Simons Island, GA. November 11th, 2016.
- J. Schaidle*, “Biomass Utilization: Opportunities and Challenges”, American Chemical Society Colorado Section Meeting, Golden, CO. October 20th, 2016. (Invited Talk)
- V. Vorotnikov*, F. Baddour, M. Griffin, S. Habas, D. Ruddy, G. Beckham, J. Schaidle, “Computational and Experimental Insights into the Shape and Faceting of Rh_2P Nanoparticles for Biomass Upgrading”, American Chemical Society Meeting, Philadelphia, PA. August 24th, 2016.
- E. White*, C. Mukarakate, M. Griffin, C. Nash, M. Yung, M. Nimlos, D. Ruddy, J. Schaidle, “Molybdenum Carbide Catalyzes the Conversion of Biomass Pyrolysis Vapors to Paraffinic and Aromatic Compounds”, American Chemical Society Meeting, Philadelphia, PA. August 21st, 2016.

Presentations (4 of 5)

- E. White*, C. Mukarakate, M. Griffin, C. Nash, M. Yung, M. Nimlos, D. Ruddy, J. Schaidle, "Molybdenum Carbide Catalyzes the Conversion of Biomass Pyrolysis Vapors to Paraffinic and Aromatic Compounds", American Chemical Society Meeting, Philadelphia, PA. August 21st, 2016.
- S. Habas*, F. Baddour, D. Ruddy, C. Nash, J. Schaidle, "Facile Molecular Precursor Route to Nanostructured Metal Phosphide Catalysts", American Chemical Society Meeting, Philadelphia, PA. August 21st, 2016.
- F. Baddour*, D. Ruddy, C. Nash, J. Schaidle, "Synthesis of Molybdenum Carbide Nanoparticles within the Pores of a Surface-Modified SBA-15 Hard Template for Bio-Oil Upgrading", American Chemical Society Meeting, Philadelphia, PA. August, 21st, 2016.
- J. Schaidle*****, "Biomass Utilization: Opportunities and Challenges", Summer School on Green Chemistry and Sustainable Energy, Golden, CO. June 23rd, 2016. (Invited Talk)
- S. Paleg*, J. Schaidle, L. Thompson, "Selective Hydrogenation of a Bio-Oil Model Compound via Promotion of Molybdenum Carbide", Michigan Catalysis Society Annual Spring Symposium, Midland, MI. May 4th, 2016.
- R. French*, K. Iisa, K. Orton, J. Schaidle, "Hydrotreating of Catalytically Upgraded Biomass Pyrolysis Oils", American Institute of Chemical Engineers Spring Meeting, Houston, TX. April 12th, 2016.
- G. Ferguson, M. Griffin*, D. Ruddy, M. Biddy, G. Beckham, J. Schaidle, "The Role of the Support and Reaction Conditions on the Mechanism of Vapor Phase m-Cresol Hydrodeoxygenation over Pt/TiO_2 and Pt/C Catalysts", Organic Reactions Catalysis Society, Miami, FL. March 31st, 2016.
- J. Schaidle*****, "Emerging Technologies for Biomass Utilization", Wyoming Forest Biomass Conference, Laramie, WY. March 29th, 2016. (Invited Talk)
- E. White*, C. Mukarakate, M. Griffin, C. Nash, M. Yung, M. Nimlos, D. Ruddy, J. Schaidle, "Molybdenum Carbide Catalyzes the Conversion of Biomass Pyrolysis Vapors to Paraffinic and Aromatic Compounds", Rocky Mountain Catalysis Symposium, Provo, UT. March 18th, 2016.
- C. Mukarakate, M. Griffin, C. Nash, E. White, M. Nimlos, D. Ruddy, J. Schaidle*****, "Vapor-Phase Upgrading over Oxophilic Molybdenum Carbide Catalysts: From Model Compounds to Biomass Pyrolysis Vapors", American Chemical Society Meeting, San Diego, CA. March 13th, 2016.
- D. Ruddy*, F. Baddour, C. Nash, M. Griffin, J. Hensley, J. Schaidle, "Development of Metal Carbide and Nitride Nano-Catalysts for Bio-oil Upgrading", Pacifichem, Honolulu, HI. December 19th, 2015.

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