ChemCatBio
Chemical Catalysis for Bioenergy

BETO 2021 Peer Review: Catalytic Upgrading of Pyrolysis Vapors 2.3.1.314

Mike Griffin

March 9, 2021

U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY
BIOENERGY TECHNOLOGIES OFFICE

Project Overview: ChemCatBio

Catalytic Technologies

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

Upgrading of C1 Building Blocks
(NREL)

Upgrading of C2 Intermediates
(PNNL, ORNL)

Catalytic Fast Pyrolysis
(NREL, PNNL)

Electrocatalytic CO_2 Utilization
(NREL)

Enabling Capabilities

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

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

Catalyst Deactivation Mitigation for Biomass Conversion
(PNNL)

Industry Partnerships (Phase II Directed Funding)

Opus12 (NREL)

Visolis (PNNL)

Sironix (LANL)

Cross-Cutting Support

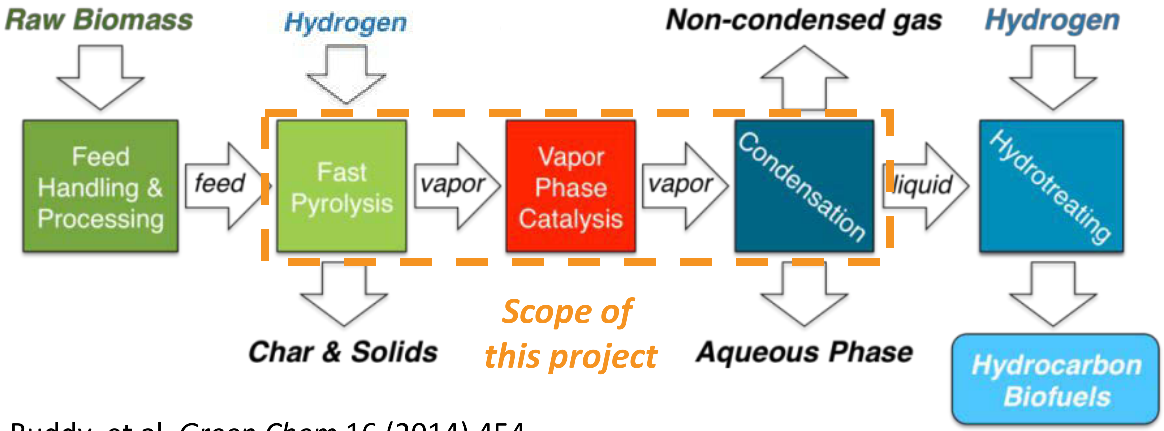
ChemCatBio Lead Team Support (NREL)

ChemCatBio DataHUB (NREL)

Project Overview

Catalytic fast pyrolysis is a versatile technology pathway for the direct liquefaction of biomass and waste carbon sources

- Potential for high carbon yields to fuel blendstocks
- Ability to control the product slate through vapor phase catalytic upgrading
- Opportunities for co-processing using existing refinery infrastructure



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

Advantage over petroleum fuels:
Reduces greenhouse gas emissions and qualifies for advanced regulatory incentives

Advantage over non-catalytic fast pyrolysis:
Generates a stabilized bio-oil with lower acidity, lower viscosity, and reduced oxygen content

Project Overview

Project Objectives

- Maximize yields and minimize costs through integrated catalyst and process development
- Expand market responsiveness by developing routes to produce co-products
- Provide experimental data to inform process modelling and scale-up activities
- Support BETO goals of meeting 2022 verification cost and carbon intensity targets: ≤$3/GGE MFSP, ≥60% reduction in GHG emissions.

Vision:

A circular carbon economy in which biomass and waste carbon sources can be readily recycled into renewable fuels, chemicals, and materials.

GGE: Gasoline gallon equivalent, MFSP: Minimum fuel selling price, GHG: Greenhouse gas

Management Plan: Structure and Implementation

The management plan leverages an integrated task structure that spans key elements of CFP catalyst and process development

Task 1: Project Management
Lead: Mike Griffin

Task 2: Catalyst Synthesis and Characterization
Lead: Susan Habas

Task 3: Performance Evaluation
Lead: Calvin Mukarakate

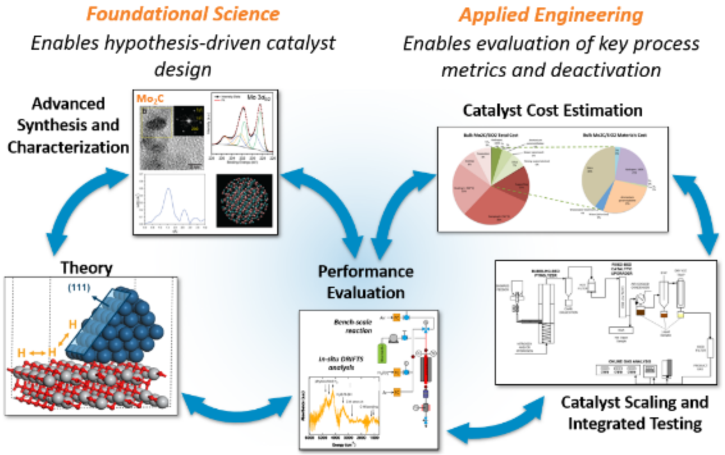
Task 4: Catalyst and Process Durability
Lead: Matt Yung

Task 5: CFP-Oil Production using FCC-Systems
Lead: Kim Magrini

Task 6: CFP-Oil Fractionation
Lead: Kristiina Iisa

Task 7: Co-Product Formation
Lead: Mark Nimlos

The implementation strategy combines advancements in foundational science and applied engineering to meet overarching project objectives



Integrated **risk assessment** and **stage-gates** to track progress and inform strategy

Risk Assessment: *March 2020 Comprehensive Pathway Review*

Stage Gate: *June 2020 Verification Go No-Go Decision Point*

Management Plan: Collaboration

Collaboration across projects, consortia, and industry partners promotes integrated R&D

Feedstock-Conversion Interface Consortium
Establishing critical feedstock attributes and pre-processing strategies for FP and CFP

ChemCatBio Enabling Projects
Improving catalyst performance and durability with support from enabling projects

Consortium for Computational Physics and Chemistry
Informing process development and scale-up through atomistic, particle, and reactor-scale modeling

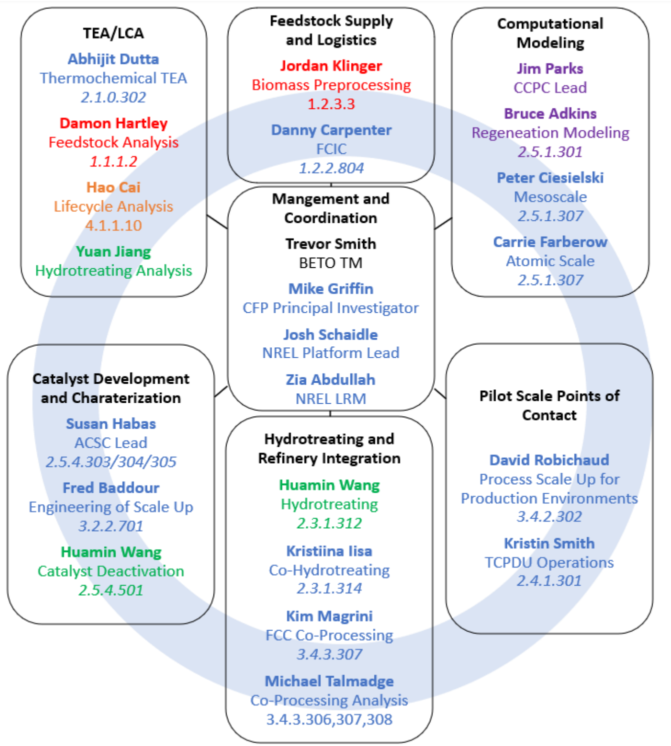
ChemCatBio Industrial Advisory Board
Guiding R&D towards commercially impactful outcomes

ExxonMobil CRADA
Advancing biomass pyrolysis technologies through collaborative R&D

Johnson-Matthey CRADA
Advancing CFP catalyst and process development through collaborative R&D

CRADA: Cooperative Research and Development Agreement

Streamlined communication enabled through the development of a multi-lab organizational structure

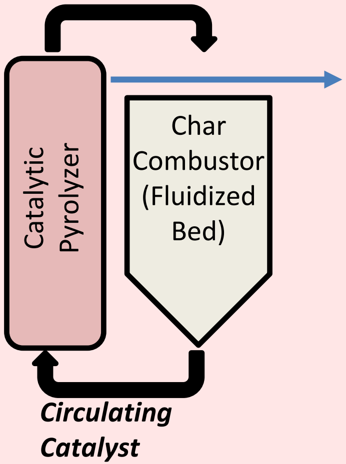


NREL | Pacific Northwest National Laboratory | Oak Ridge National Laboratory | INL Idaho National Laboratory | Argonne National Laboratory

Approach: Pathway Assessment

Early efforts within this project focused on benchmarking performance for several CFP catalysts and reactor configurations

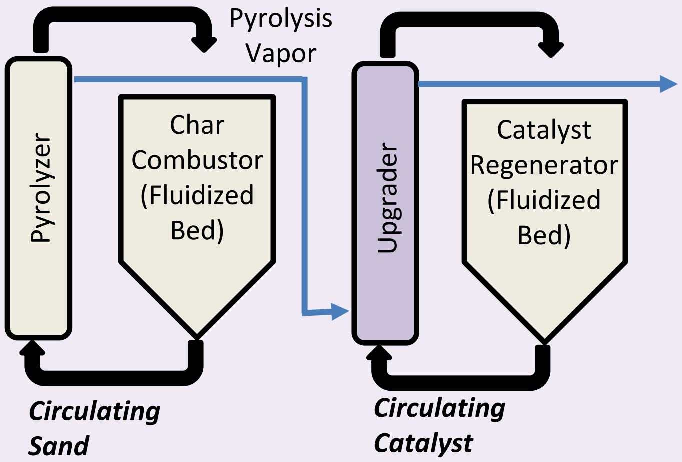
In-Situ CFP
Metal Oxide Catalysts



Low capex requirements

Harsh upgrading environment

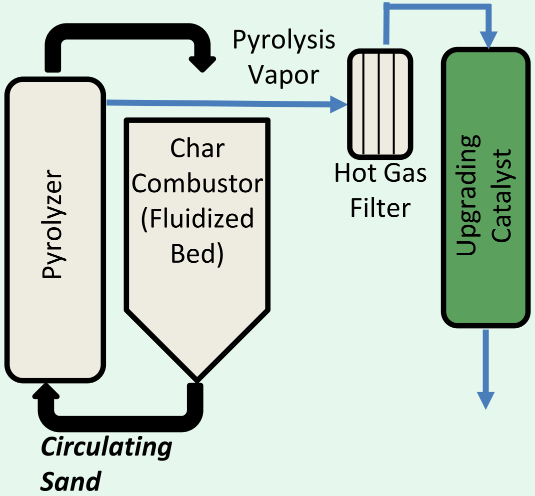
Ex-Situ Entrained Bed CFP
Zeolite Catalysts



Controlled upgrading environment

Higher capex required

Ex-Situ Fixed Bed CFP
Metal-Acid Catalysts



More diverse catalysts and chemistries possible

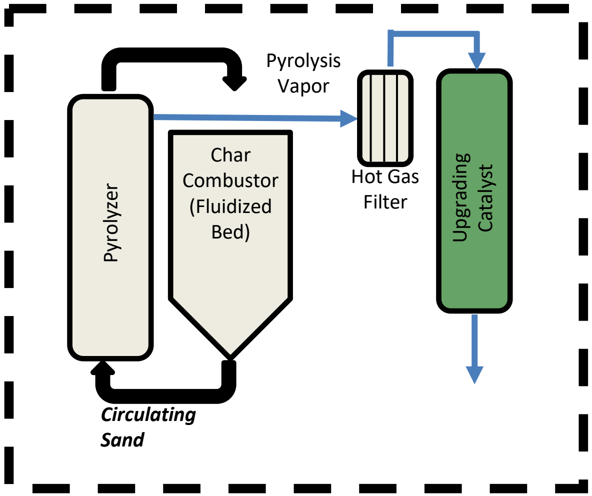
Longer catalyst lifetimes required

Approach: 2017 Down-Selection

A down-selection was informed by a first-of-its kind performance evaluation under a controlled set of conditions

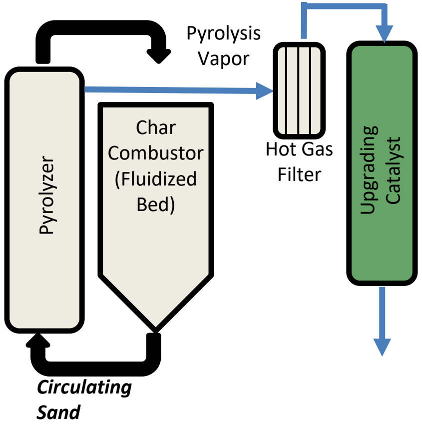
Process	***In-situ* CFP**	***Ex-situ* Riser CFP**	***Ex-situ* Fixed-Bed CFP**
Catalyst (Conditions)	Red Mud (400°C)	ZSM-5 (550°C)	2 wt% Pt/TiO_2 (400°C, H_2 co-feed)
Reactor	Utah State's Fluidized Bed Pyrolyzer	NREL's 2" Fluidized Bed Pyrolyzer + Catalytic Upgrading System	
CFP Carbon Efficiency* (%)	42	33	42
CFP O Content (wt%)	28	17	17
HT Carbon Efficiency* (%)	85	96	93
HT Oil O Content (wt%)	0.9	1.2	0.4
Overall Carbon Efficiency* (%)	***36***	***32***	***38***

Due to the comparatively high CFP yields, low oil-oxygen content, and improved overall carbon efficiency, the ex-situ fixed bed CFP approach was down-selected as a leading pathway for the BETO 2022 Verification



*Normalized carbon efficiencies based on >500mL of CFP oil generated

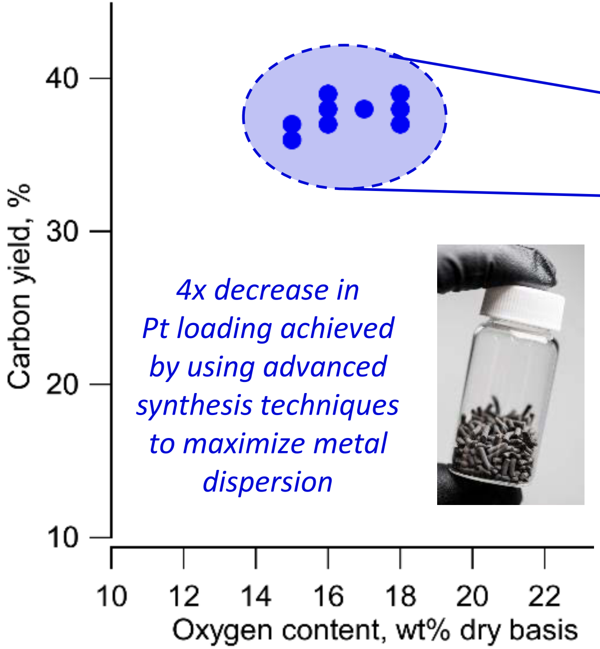
Approach: 2018 Baseline

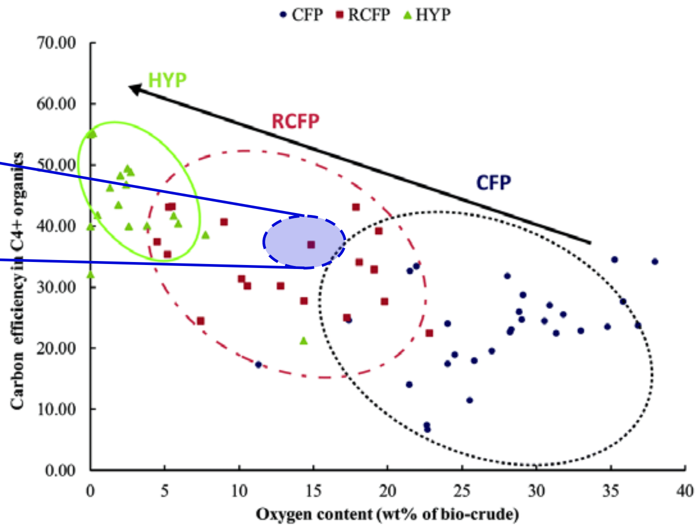


Standard Conditions
Feedstock: Loblolly Pine
Catalyst: 0.5 wt% Pt/TiO_2
Support: 1.7 mm TiO_2 Pellets
Pyrolysis Temperature: 500 °C
Upgrading Temperature: 435 °C
Catalyst Mass: 100 g
WHSV: 1.4 g biomass/gcat*h
Near Atmospheric Pressure
Hydrogen Concentration: 83%
Biomass:Catalyst Ratio: 3-13.2

Griffin, M. et al., Energy Environ Sci, 2018

Integrated experiments demonstrate potential for high carbon yields using 0.5 wt% Pt/TiO_2





Data are consistent with literature benchmarks performed under hydrodeoxygenation conditions

K. Wang, et al., *Green Chem.* 19 2017

Approach: FY19-FY20 Research Priorities

With the potential benefits of the chemistry established, research in FY19-FY20 targeted technical objectives associated with reducing risks, diversifying feedstocks, and informing scale up:

- Reducing analytical uncertainty by improving material balances
- Assessing catalyst and process durability
- Increasing catalyst cycle length and regeneration efficiency
- Demonstrating compatibility with waste feedstocks (e.g., forest residues)
- Informing process scale up and supporting BETO Verification goals

Impact

Impact Section Will Follow Progress and Outcomes
(Slides 20-21)

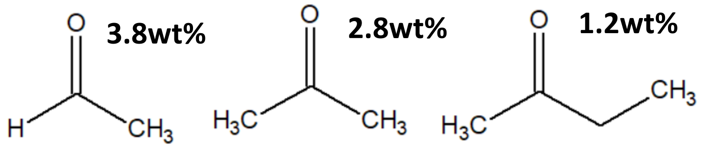
Progress and Outcomes: Improved Analytics

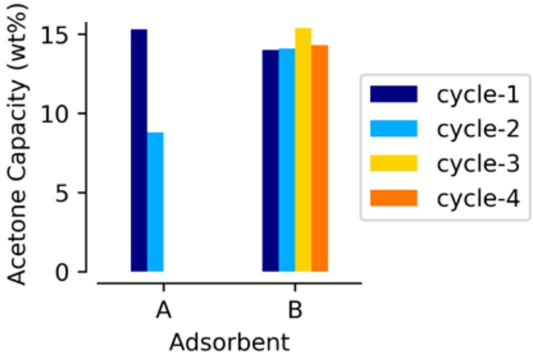
Progress: modifications to the system and methods resulted in improved carbon balance closure and reduced uncertainty in the product distribution

	FY18	FY19
CFP Carbon Balance (%)	88	100
CFP Oil Carbon Yield	45	35
CFP Oil Oxygen (wt%, dry)	19	15
HT Carbon Yield (%)	89	95
CFP + HT Carbon Yield (%)	36	33
Co-Product Credit	-	$0.52
MFSP, $/GGE	3.50*	3.33

**This added level of analytical detail resulted in downward revisions to the 2018 normalized CFP oil carbon yield and increase in MFSP to $3.80*

***Co-Product Opportunity:** high yields were observed for acetaldehyde, acetone, and 2-butanone*

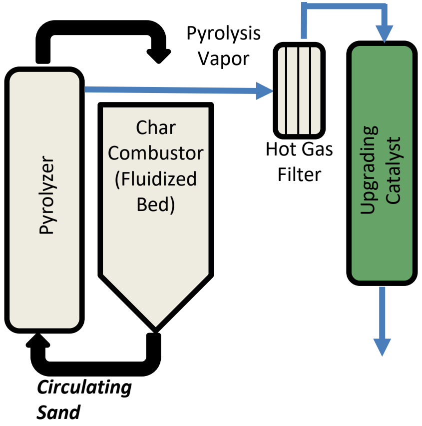




Preliminary model compound data demonstrate acetone adsorption capacity. Ongoing research aims to confirm these results under realistic reaction conditions.

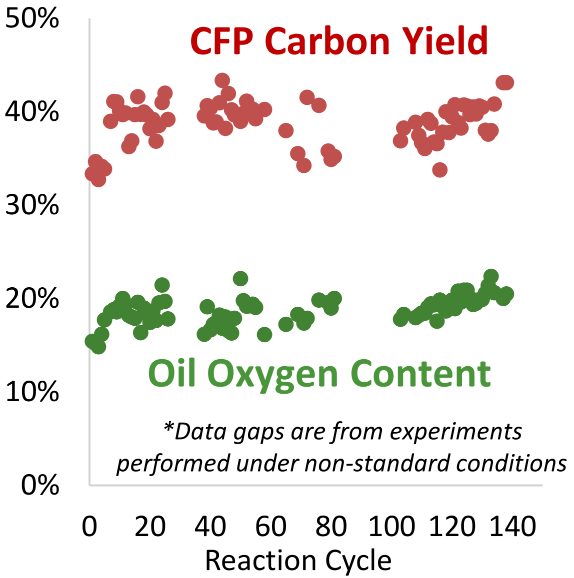
Outcome: Reduction in risk and analytical uncertainty, **$0.30/GGE** increase in MFSP, potential for ~**$0.50/GGE** reduction through valorization of acetone and 2-butanone

Progress and Outcomes: Process Durability

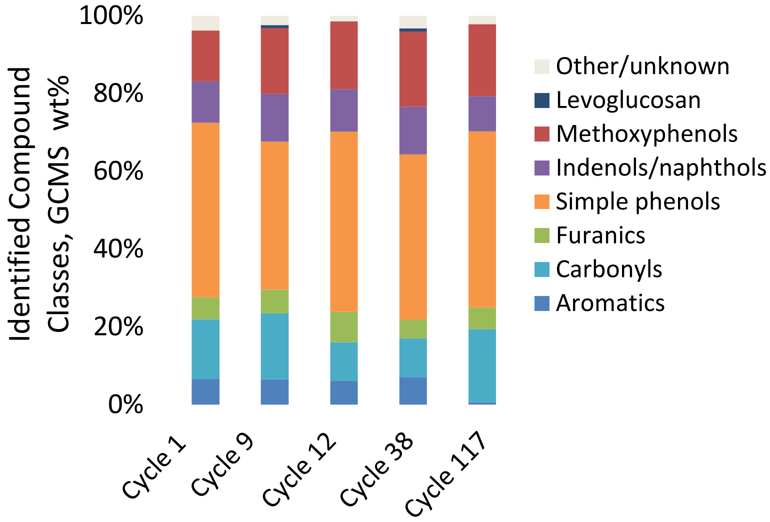


Standard Conditions
Feedstock: Loblolly Pine
Catalyst: 0.5 wt% Pt/TiO_2
Pyrolysis Temperature: 500 °C
Upgrading Temperature: 435 °C
Catalyst Mass: 100 g
WHSV: 1.4 g biomass/gcat*h
Near Atmospheric Pressure
Hydrogen Concentration: 83%
Biomass:Catalyst Ratio: 3

Progress: integrated experiments performed for 100+ reaction cycles reveal minimal impact on yields, oil-quality, and product composition

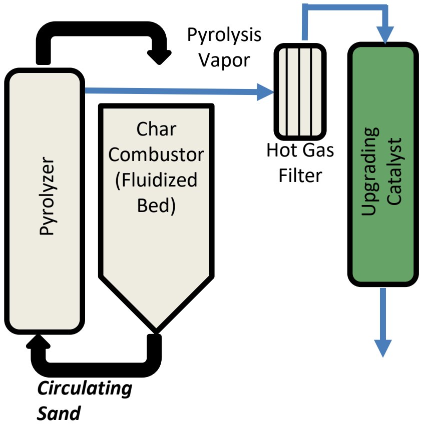


> 10 L of CFP oil was distributed to support research across BETO programs



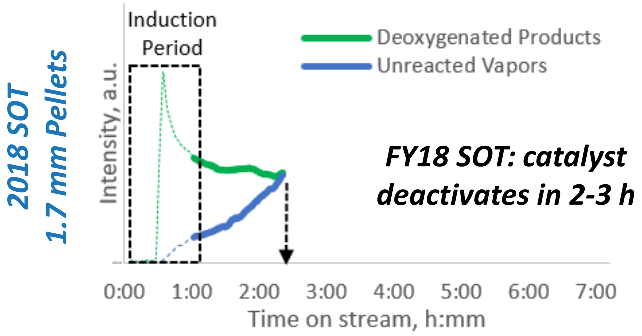
Outcome: improved confidence in catalyst and process durability, reduced risk for process model inputs, and support for technology transfer efforts

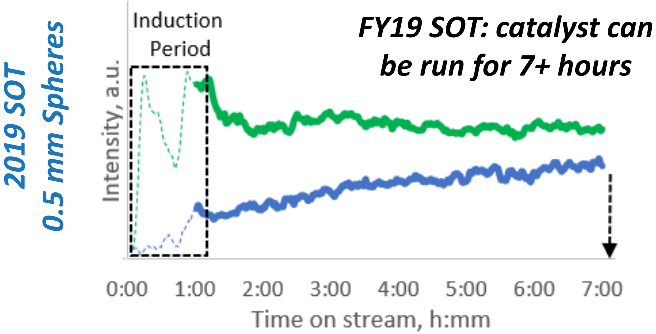
Progress and Outcomes: Increased Cycle Length

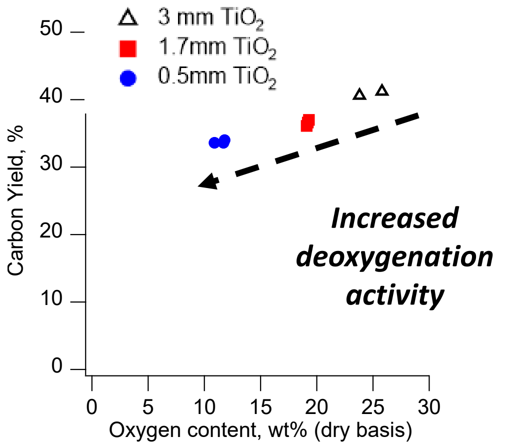


Conditions
Feedstock: Loblolly Pine
Catalyst: 0.5 wt% Pt/TiO_2
Pyrolysis Temperature: 500 °C
Upgrading Temperature: 435 °C
Catalyst Mass: 100 g
WHSV: 1.4 g biomass/gcat*h
Near Atmospheric Pressure
Hydrogen Concentration: 83%
Biomass:Catalyst Ratio: 3-12

Progress: reducing the size of the catalyst support reveals potential for improved deoxygenation activity and increased cycle length

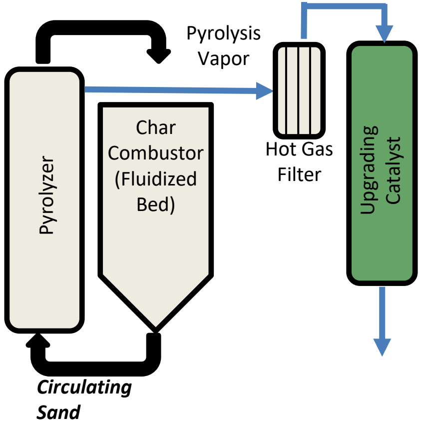






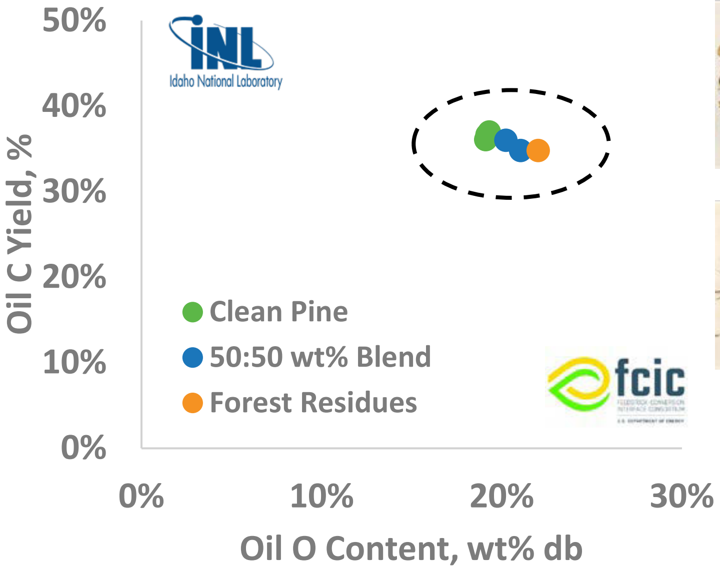
Outcome: 3.5 MM reduction in capital costs and improved process efficiency

Progress and Outcomes: Waste Feedstocks



Standard Conditions
Feedstock: Loblolly Pine + Forest Residues
Catalyst: 0.5 wt% Pt/TiO_2
Pyrolysis Temperature: 500 °C
Upgrading Temperature: 435 °C
Catalyst Mass: 100 g
WHSV: 1.4 g biomass/gcat*h
Near Atmospheric Pressure
Hydrogen Concentration: 83%
Biomass:Catalyst Ratio: 3

Progress: reaction testing data demonstrates minimal impact of waste feedstocks on carbon yield or oil quality



Clean Pine
Debarked stem-wood

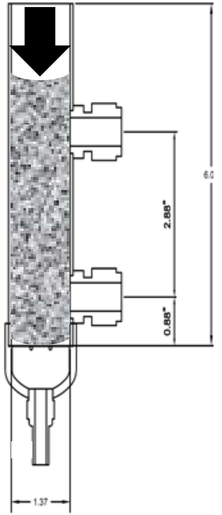
Forest Residues
Harvest waste including bark, needles, branches

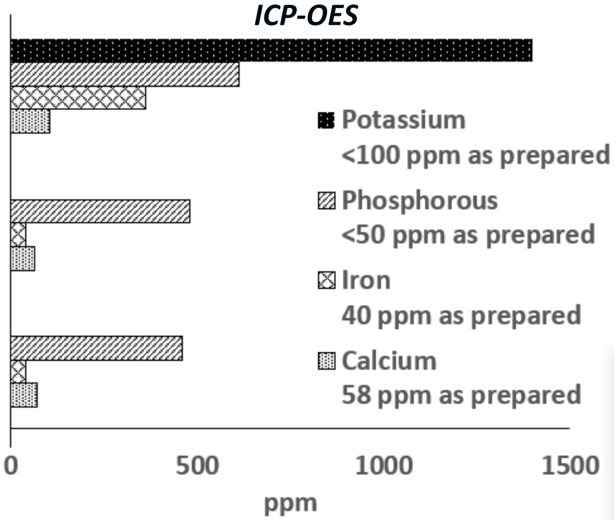
Ongoing Research: *establish critical feedstock attributes for CFP. FCIC: 1.2.2.804*

Outcome: 20% reduction in feedstock costs, translating to a **$0.33/GGE** improvement in MFSP

Progress and Outcomes: Tracking Inorganic Deposition

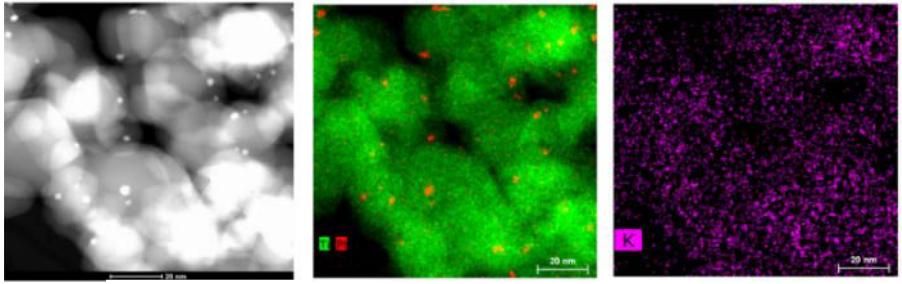
Progress: catalyst characterization after reaction with forest residues tracks potassium deposition at the leading edge of the catalyst bed

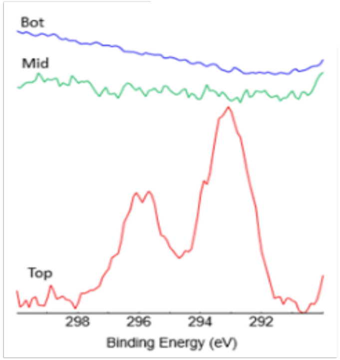




Experiments performed with a 50:50 wt% blend of clean pine and forest residues for a cumulative time on stream of 32 h

Dark field STEM images and EDS maps indicate well-dispersed K on the surface of the post-reaction samples from the top of the bed





XPS Spectra of K 2p Region confirm K deposition

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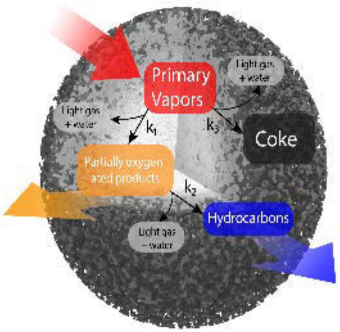
Ongoing Research:
CDM: 2.5.4.501
ACSC: 2.5.4.303/304/305

Outcome: building foundational knowledge of critical deactivation mechanisms and mitigation strategies for biomass conversion pathways

Progress and Outcomes: Informing Scale Up

Progress: collaborative development of a new simulation frameworks for multiscale modeling to inform in-silico optimization and process scale up



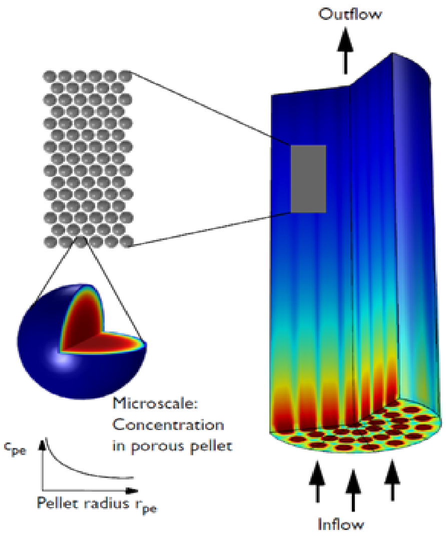
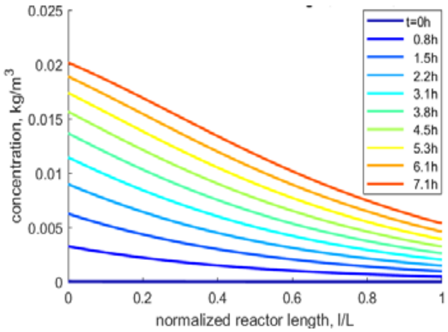
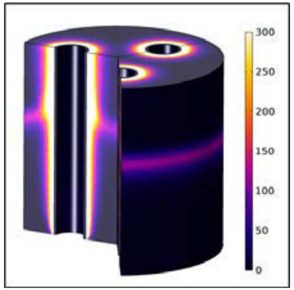


Image made using COMSOL Multiphysics® software and provided courtesy of COMSOL.[26]

Predicted catalyst coke profile as a function of time on stream



Thermal excursions during regeneration at pilot-scale



∇T, °C/cm

Outcome: early identification of potential process disruption at the pilot scale. Ongoing efforts target improve heat transfer capabilities through catalyst development and reactor design: *CCPC: 2.5.1.301*

Consortium for Computational Physics and Chemistry
U.S. DEPARTMENT OF ENERGY
BIOENERGY TECHNOLOGIES OFFICE

Pecha, B.; et al. *Reaction Chemistry and Engineering*, 2020
Adkins, B. D.; et.al, *Reaction Chemistry and Engineering, Submitted*

Progress and Outcomes: Verification Go/No Go

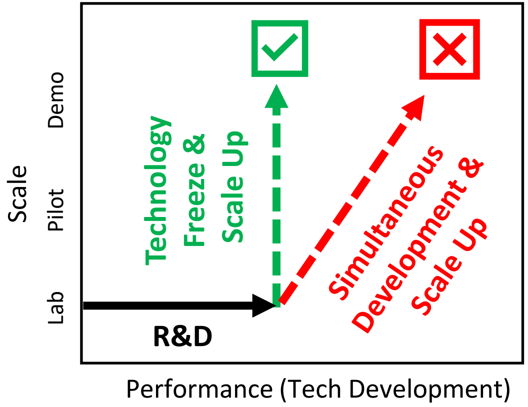
Progress: data from this project informed a comprehensive pathway review performed with an independent engineering team to serve as a scale-up stage gate for the 2022 BETO Verification

A detailed **block flow diagram** which clearly defines all inputs/outputs for pilot scale unit operations

A **process indicator matrix** that provides a row-by-row comparison across scales

An overarching **risk assessment** to identify research needs and inform forward looking decision making

Determination: successfully meeting the verification goals by 2022 would **require simultaneous technology development and scale-up.** This exceeded risk tolerances and motivated a no-go decision for the pathway.



Needed: additional experimental data to meet \$3/GGE cost target and de-risk process scale-up

Outcome: early risk assessment and proactive project management to guide decision making for the BETO 2022 Verification

Progress and Outcomes: Project Direction

Near term research addresses technical risks and data gaps through four targeted experimental campaigns:

Feedstock Risks
Establish critical material attributes for CFP feedstocks and identify pre-processing requirements
FCIC: 1.2.2.805

Catalyst Risks
Tailor catalyst support morphology to increase cycle length and minimize pressure drop
ACSC: 2.5.4.303/304/305
EOS: 3.2.2.701

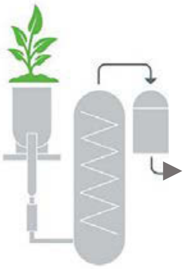
Integration Risks
Link CFP reaction conditions to bio-oil quality and down-stream processing requirements
PSUPE: 3.4.2.302

Durability Risks
Assess durability during prolonged exposure to reaction environments
PSUPE: 3.4.2.302

Assessment of Co-Product Recovery and Separation

Project Direction

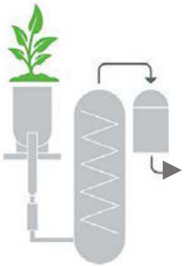
FY21: facilitate a constructure closeout of the fixed bed CFP + standalone hydrotreating pathway



Stand Alone Hydrotreating to Fuel Blendstocks

Outcome:
communicating advancements and R&D needs through a comprehensive closeout report

FY22+: produce application specific CFP-oil for refinery integration



Co-Processing with Fossil Streams

Outcome:
adapting CFP to address emerging demand for biogenic refinery feedstocks

Impact: Pathway to Market

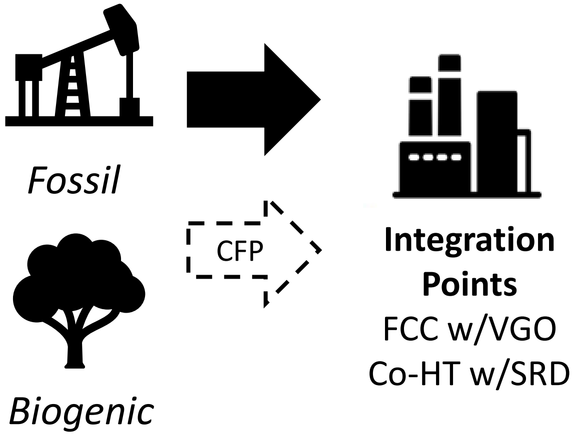
Opportunity

>$2 billion invested to produce renewable diesel from fats, oils, and greases (FOG)

However, the supply of FOG is limited, and further growth in this sector will be inhibited by feedstock availability

CFP can help fill this gap by proving a stable biogenic liquid for refinery co-processing

FCC: Fluid Catalytic Cracking
VGO: Vacuum Gas Oil
HT: Hydrotreating
SRD: Straight Run Diesel



CFP Co-Processing Targets:

Increase biogenic carbon incorporation

Reduce carbon intensity

Mitigate potential for process disruption

Impact: establishing a **pathway to market** that allows refiners and chemical companies to diversify feedstock sources, leverage existing capital, and reduce the cost of regulatory compliance

Impact: Science and Partnerships

Impact: Development of Industrial Partnerships

Johnson Matthey — Inspiring science, enhancing life

CRADA: Catalyst Development

ExxonMobil

CRADA: Biomass Pyrolysis

Impact: Spin-Off Projects (TCF, SBIR, DOE, USDA)

Aditya Birla – Birla Carbon, BIC Battery Innovation Center, NC State, Ensyn

Carbon Co-Products For Energy Storage Applications

Marrone Bio Innovations

Chemical Co-Products for Bioinsecticide Applications

LUNA

Chemical Co-Products for Biopolymer Applications

Impact: Generation of Scientific Knowledge

14 Peer Reviewed Publications Since 2019
Average Journal Impact Factor of 7
See Supporting Slides 26-27

18+ External Presentations Since 2019
Spanning CFP Catalyst and Process Development
See Supporting Slides 28-29

2 Issued Patents
6 Pending Patent Applications
Novel catalysts, processes, and co-products

CRADA: Cooperative Research and Development Agreement
TCF: Technology Commercialization Fund
SBIR: Small Business Innovation Research

Acknowledgements

CFP

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Connor Nash (NREL)
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Jessica Olstad (NREL)
Brady Petersen (NREL)
Mike Sprague (NREL)
Rebecca Jackson (NREL)

CFP

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Kristin Smith (NREL)
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Matt Oliver (NREL)

Computational Modeling

Vivek Bharadwaj (NREL)
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Brennan Pecha (NREL)
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Austin Ladshaw (ORNL)
James Parks II (ORNL)

TEA/LCA

Abhijit Dutta (NREL)
Michael Talmadge (NREL)
Kurt van Allsburg (NREL)
Sue Jones (PNNL)
Yunhua Zhu (PNNL)
Yuan Jiang (PNNL)
Hao Cai (ANL)
Damon Hartley (INL)

Feedstocks

Jordan Klinger (INL)
Danny Carpenter (NREL)

Oil Analysis

Jack Ferrell (NREL)
Steve Deutch (NREL)
Renee Happs (NREL)
Anne Starace (NREL)
Nolan Wilson (NREL)
Earl Christensen (NREL)
Lisa Fouts (NREL)

Hydrotreating (PNNL)

Huamin Wang (PNNL)
Mike Thorson (PNNL)
Daniel (Miki) Santosa (PNNL)
Suh-Jane Lee (PNNL)
Igor Kutnyahov (PNNL)
Douglas C. Elliott (PNNL)
Kristiina Iisa (NREL)

ChemCatBio
Chemical Catalysis for Bioenergy
Energy Materials Network
U.S. Department of Energy
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Bioenergy Technologies Office
NREL NATIONAL RENEWABLE ENERGY LABORATORY
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Summary/Q&A

Management

- **Clear management plan** with implementation strategy that advances foundational science and applied engineering
- **Established avenues for collaboration** including a well-defined multi-lab organizational structure to streamline communications
- **Active project management** through integration of risk identification and mitigation (comprehensive pathway review + go/no-go)

Approach

- **Advances the state-of-the-art** through innovative catalyst and process development
- **Builds on previous data with clear objectives** that reduce technical risk, diversify feedstock opportunities, and inform process scale-up
- **Supports BETO 2022 Verification goals** by evaluating pathways to meet cost and GHG reduction targets

Progress and Outcomes

- **Reduced analytical uncertainty** by closing carbon balances to 100 +/- 1%
- **Improved process efficiency** by achieving a 4x increase in catalyst cycle length
- **Demonstrated process durability** for 100+ reaction cycles (~275 h)
- **Demonstrated compatibility with waste feedstocks** (e.g., forest residues)
- **Identified risks and research needs for process scale up** to inform a proactive pivot for the 2022 verification

Impact

- **Generated broadly enabling scientific knowledge** (14 publications, 18+ presentations, 8 IP positions)
- **Considerable industry engagement** through partnerships across the value chain (e.g., CRADAs with Johnson Matthey and ExxonMobil)
- **Promising pathway to market** that addresses an emerging demand for biogenic refinery feedstocks

Supporting Information

Catalytic Fast Pyrolysis

Project Quad Chart

Timeline
Project start date: October 1st, 2019
Project end date: September 30th, 2021
Percent complete: 44%

	FY20	Active Project
DOE Funding	3.4 MM	6.8 MM

Project Partners
Industry: ExxonMobil, Johnson Matthey
Academia: University of Southern California (FY20)

Barriers addressed

Ot-B: Cost of Production
Reducing MFSP for CFP technology platform

Ct-F: Increasing the Yield from Catalytic Processes
Developing catalysts and process operations to enhance carbon efficiency

Project Goal
Develop CFP as a versatile deconstruction technology that is compatible with biomass and waste carbon sources and enables the production of application specific bio-oils with properties that can be tailored to meet dynamic market needs.

End of Project Milestone
Develop refinery integration approaches and feasible co-products from catalytic fast pyrolysis pathways. Establish CFP-oil quality specifications and blend ratios for FCC and/or co-hydrotreating integration points to meet an overall minimum fuel selling price of $3/GGE in $2016 dollars.

Funding Mechanism
National Laboratory AOP Project

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- M.M. Yung et al., “Characterization of Mo_2C used for Hydrodeoxygenation of Biomass Pyrolysis Vapors,” North American Catalysis Society NAM 26 Meeting - Chicago, IL, June 2019.
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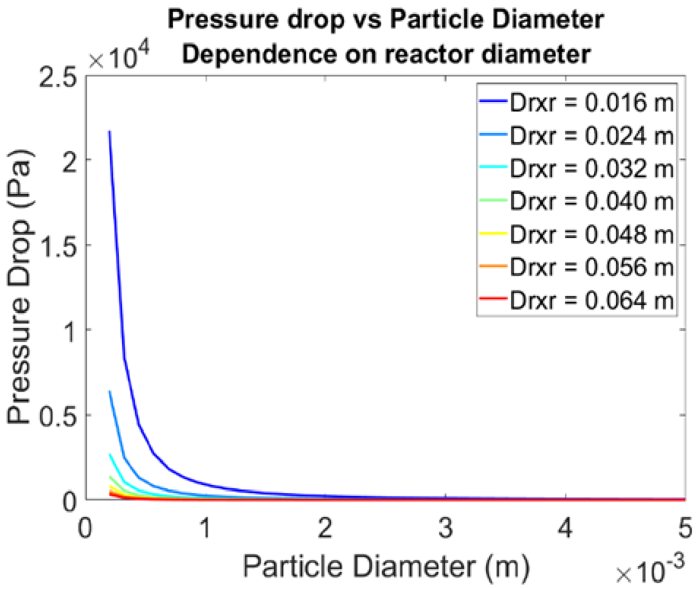
Other Research: Optimizing Catalyst Support Formulations



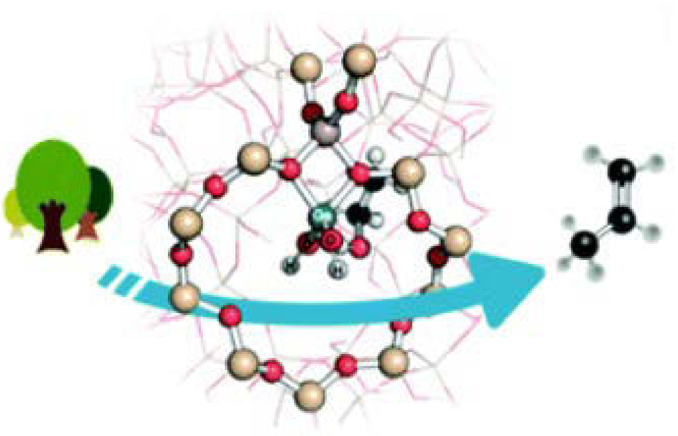
Ongoing collaborative research focuses on optimizing catalyst size and porosity using custom technical supports prepared at NREL (Engineering of Catalyst Scale Up: 3.2.2.701)

3 mm 1.6 mm 1 mm

Utilizing smaller TiO_2 supports improves deoxygenation performance but increases pressure drop and necessitates the use of low L/D reactors with limited heat transfer capabilities

Target outcome: achieve high catalyst activity while minimizing pressure drop to enable the use of reactor dimensions with improved heat transfer capabilities

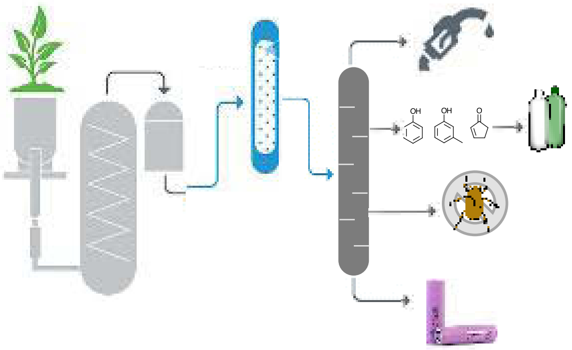
Catalyst development within this project has led to impactful outcomes for a wide range of CFP approaches and biomass conversion technologies



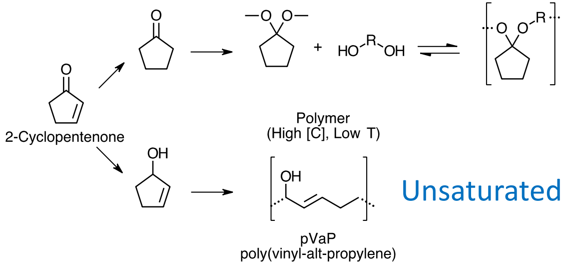
Improving hydrocarbon yields and increasing alkene selectivity using a Ga/ZSM-5 catalyst
Iisa, K., et al. Green Chemistry, 2020, 22, 2403

A novel and scalable solution phase synthesis route to produce molybdenum carbide nanoparticles
Baddour, F., et al. JACS, 2020, 142, 2, 1010

Other Research: Developing Co-Product Pathways with Commercial Partners



Chemicals for Polymers



Recyclable polymers

$1 - 3/kg

Unsaturated polyvinyl alcohols

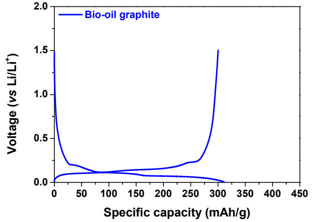
LUNA

ENSYN

BIC

ADITYA BIRLA
BIRLA CARBON

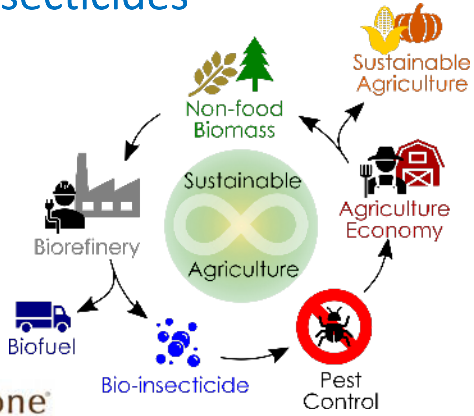
High Value Carbon

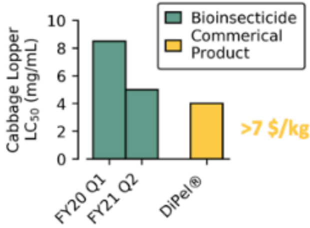


$5 - 10/kg

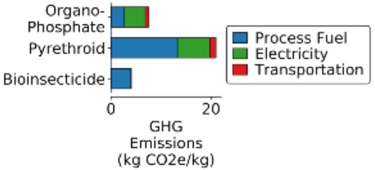
Anodes for Lithium and Sodium Ion Batteries

Bioinsecticides



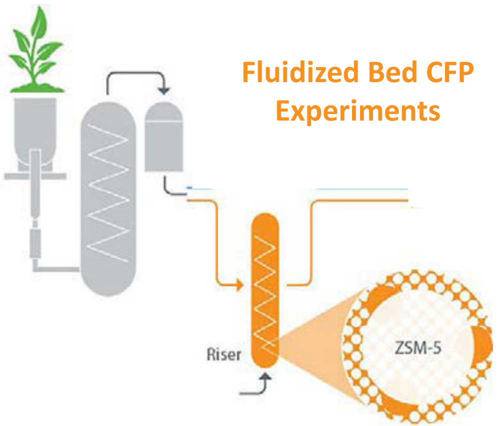


> $6/kg

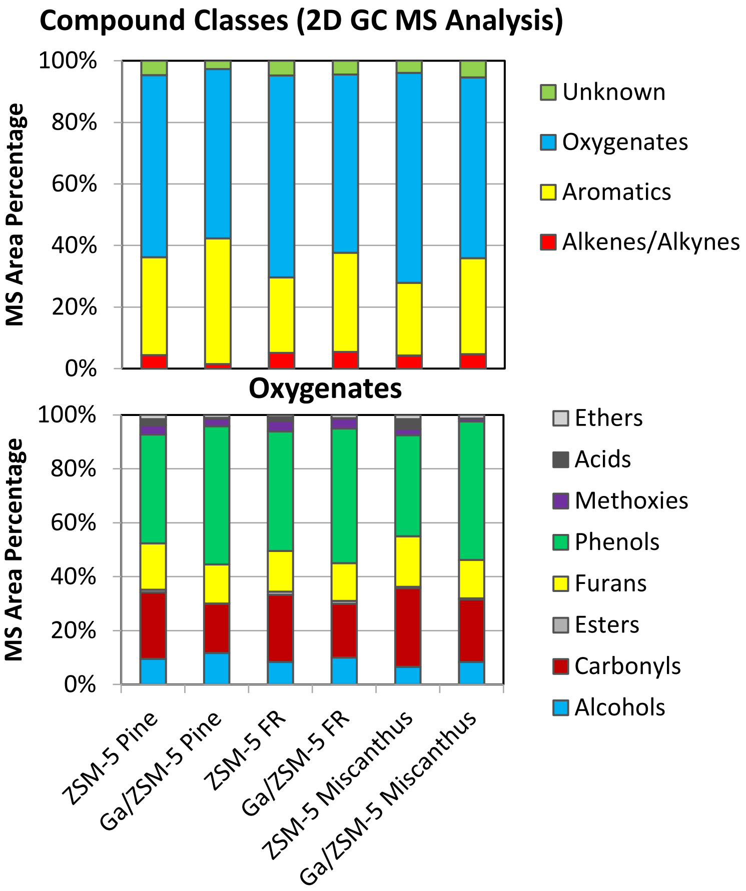


Marrone Bio Innovations

Other Research: Fluidized Bed CFP



Approach: Develop modified zeolites with Johnson Matthey that target biomass conversion and are compatible with refinery fluidized catalytic cracking (FCC) catalysts; prepare CFP oils using a coupled pyrolyzer/FCC plant; evaluate catalyst impact on oil composition; assess FCC co-processability to biogenic carbon containing fuels.



Feedstocks and Catalysts

- Pine (baseline feed)
- Pine forest residues (FR)
- Miscanthus
- ZSM-5
- Ga/ZSM-5

Feedstocks and ZSM-5

FR and Miscanthus

- Increased oxygenates, reduced aromatics

Miscanthus: reduced phenolics (less lignin)

Feedstocks and Ga/ZSM-5

- Increased aromatics, phenols for all feedstocks
- Reduced furans and carbonyls from cellulose deoxygenation