ChemCatBio
Chemical Catalysis for Bioenergy

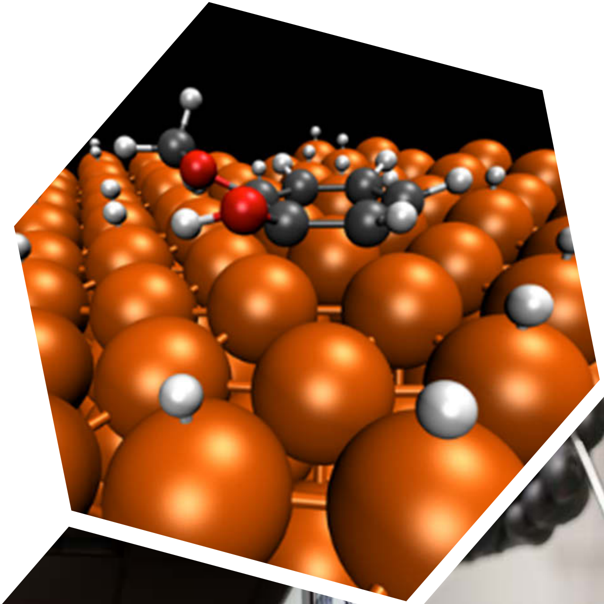
Recent Advancements in Catalytic Fast Pyrolysis for the Production of Fuels and Chemicals from Biomass

Joshua A. Schaidle, NREL

ePYRO 2021

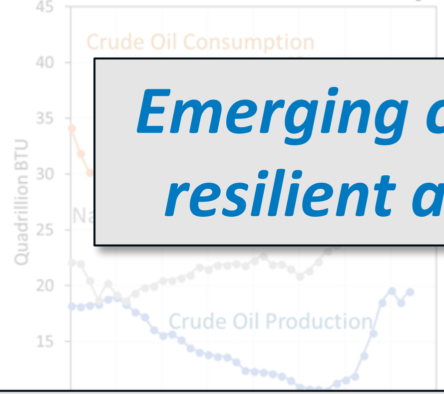
April 13th, 2021

NREL/PR-5100-79564



Trends in Carbon Management

Major Shifts in US Fossil Fuel Production and Consumption



Increased Electrification

Decreasing costs for renewable electricity

International Maritime Organization

Reduce sulfur in marine bunker fuel from 3.5% to 0.5% as of 2020

Emerging carbon conversion technologies need to be resilient and responsive to market and policy shifts

Need for Carbon-Negative

Challenge: How do we design carbon conversion technologies, including capex-intensive facilities, to succeed in tomorrow's dynamic economy?

National Geographic

Airlines for America

National Academy of Sciences

Opportunity: Designed Resilience

"It is not the strongest of the species that survives, nor the most intelligent, but the one most adaptable to change" *Leon C. Megginson*

National Academy of Sciences Definition of Resilience: "The ability to prepare and plan for, absorb, recover from, and more successfully adapt to adverse events"

I. Linkov, et al., Changing the Resilience Paradigm, *Nature Climate Change* 4 (2014) 407.

Goal: Enable the design of *versatile catalytic carbon conversion technology platforms* capable of nimbly responding to external stimuli

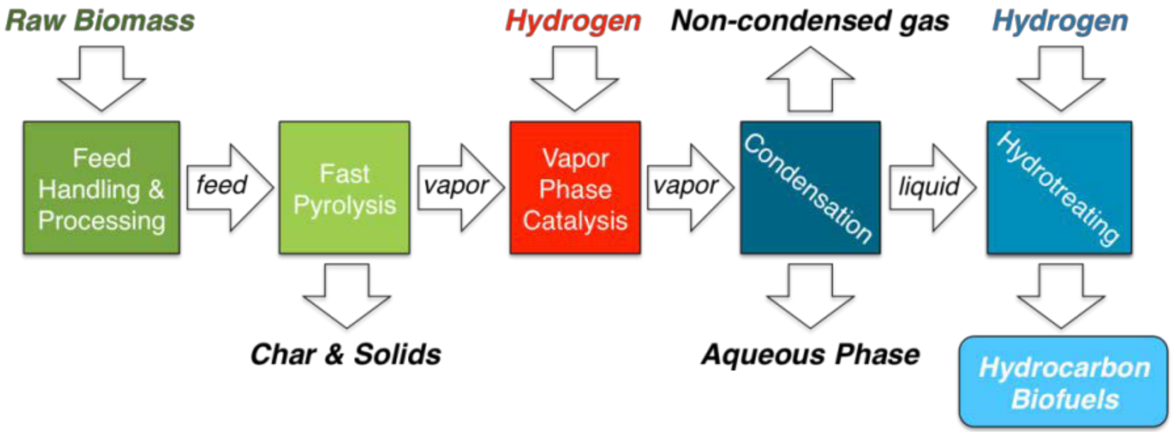
Critical Needs:

- Feedstock flexibility
- Adaptive process design and control
- Low conversion costs
- Product tunability

Porter's Five Forces

Catalytic Fast Pyrolysis (CFP) Technology Platform

Potential for whole biomass conversion to drop-in hydrocarbon fuels at high yields (>75 gal/ton)



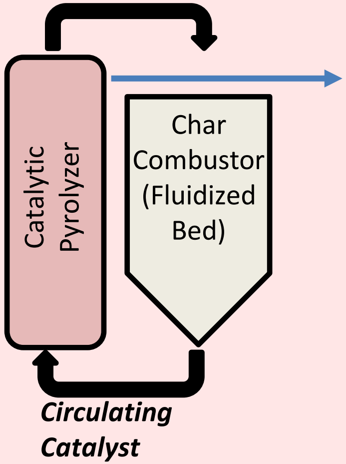
D. Ruddy, et al. *Green Chem* 16 (2014) 454

Advantages of the Technology:

- Cost of wood-based feedstock is de-coupled from petroleum price
- Vapor-phase catalytic upgrading provides control over product slate
- Reduces downstream hydrotreating costs as compared to fast pyrolysis
- Upgraded bio-oil could be co-processed in existing refinery infrastructure
- Produces a drop-in fuel blendstock, with co-product opportunities

CFP Process Design Options

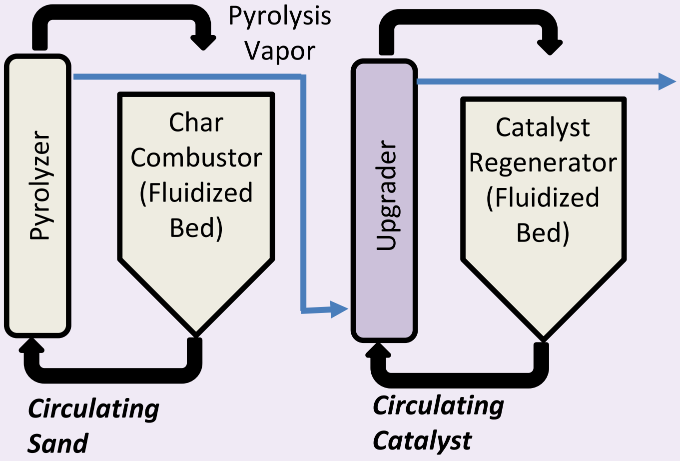
In-Situ CFP
Metal Oxide Catalysts



Low capex requirements

Harsh upgrading environment

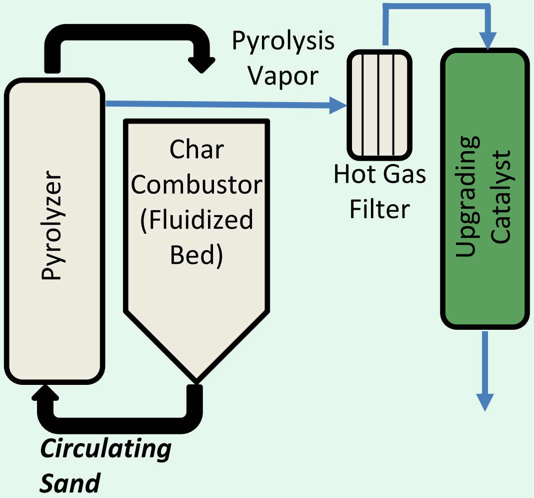
Ex-Situ Entrained Bed CFP
Zeolite Catalysts



Controlled upgrading environment

Higher capex required

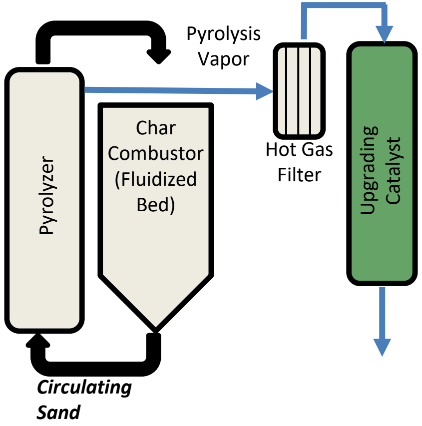
Ex-Situ Fixed Bed CFP
Metal-Acid Catalysts



More diverse catalysts and chemistries possible

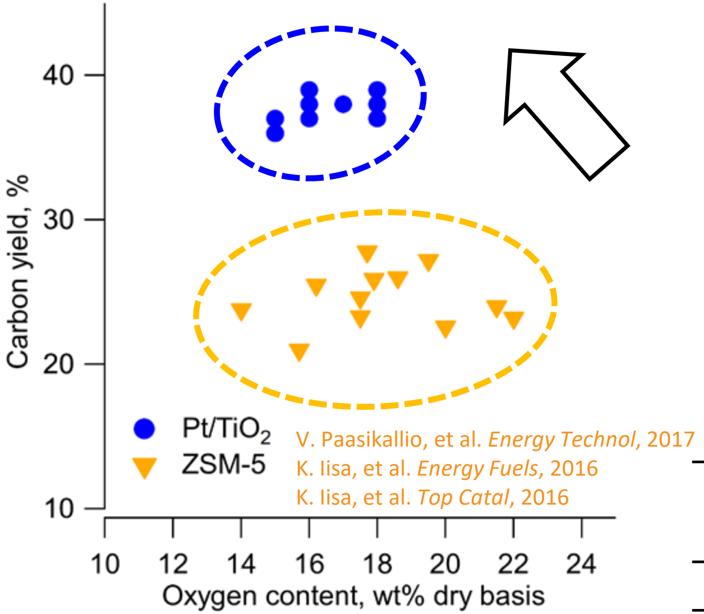
Longer catalyst lifetimes required

Ex-situ Fixed Bed CFP: 2018 State-of-Technology

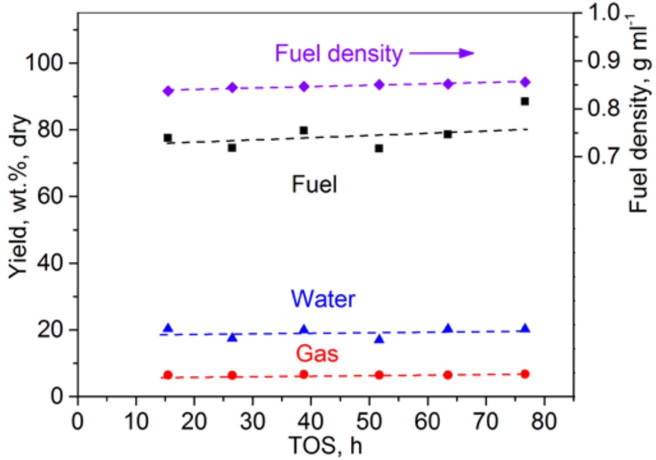


Standard Conditions
Feedstock: Loblolly Pine
Catalyst: 0.5-2.0 wt% Pt/TiO_2
Pyrolysis Temperature: 500 °C
Upgrading Temperature: 435 °C
Catalyst Mass: 100 g
WHSV: 1.4 g biomass/gcat*h
Near Atmospheric Pressure
Hydrogen Concentration: 83%
Biomass:Catalyst Ratio: 3-13.2

Improved carbon yields compared to ZSM-5



The Pt/TiO_2 CFP-oil was hydrotreated using a **single stage** system for 80+ hours without fouling or plugging



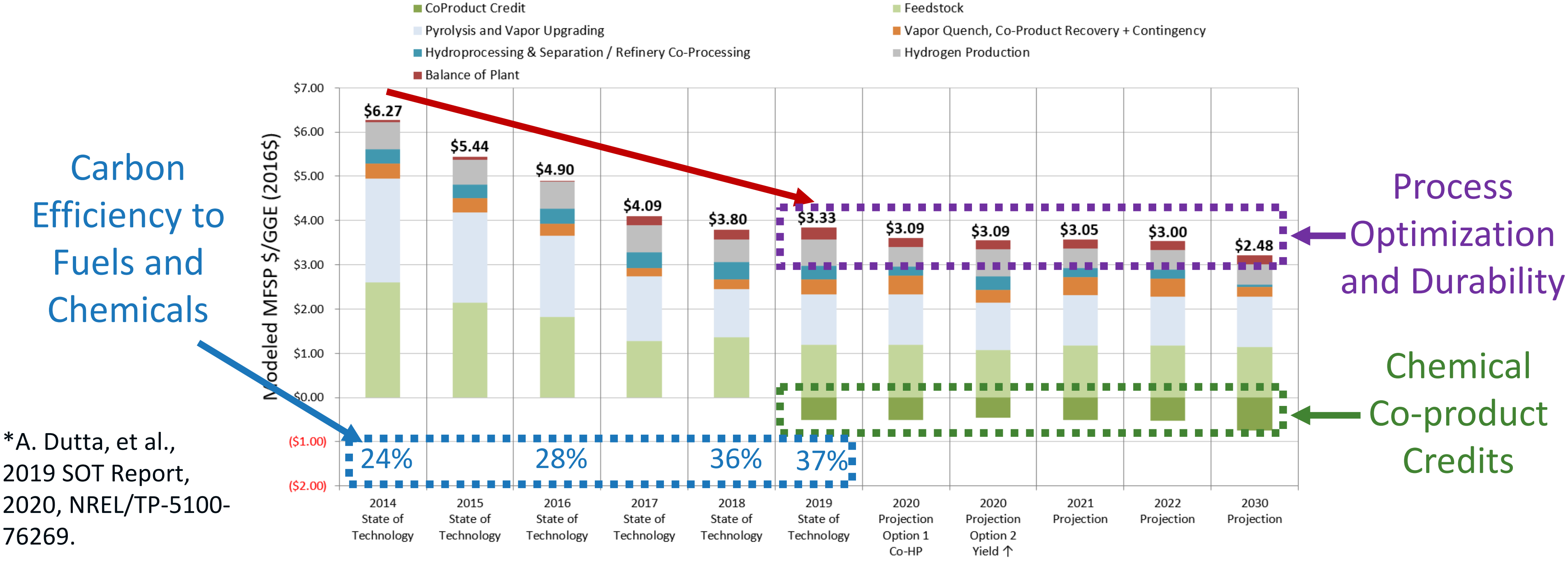
Carbon yield %	H/C mol/mol	O wt.% dry	Density g ml^{-1}
89	1.71	0.19	0.851

NiMo Sulfide, LHSV: 0.2-0.3, 13 MPa

M. Griffin, et al., *Energy Environ. Sci.*, 11 (2018) 2904-2918.
R. French, et al., *ACS Sustain. Chem. Eng.*, 9 (2021) 1235-1245.

Progress on Reducing Biofuel Production Costs from CFP

Reduced modeled biofuel production costs by ca. $3/GGE since 2014 by improving carbon efficiency

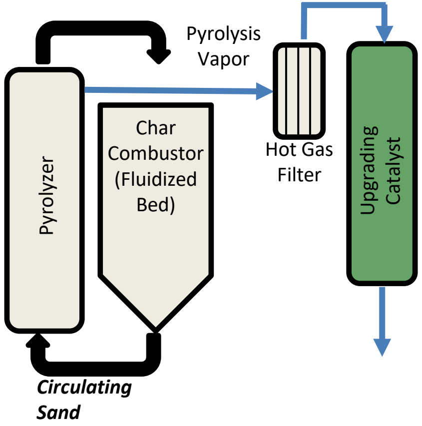


*A. Dutta, et al., 2019 SOT Report, 2020, NREL/TP-5100-76269.

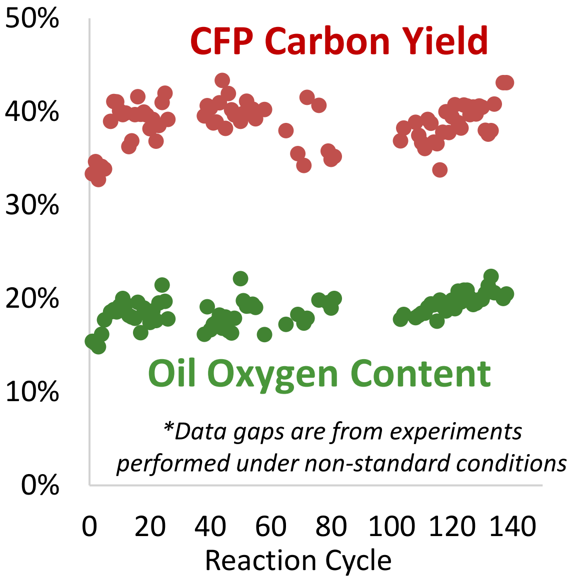
Targeted R&D on process optimization/durability and product diversification

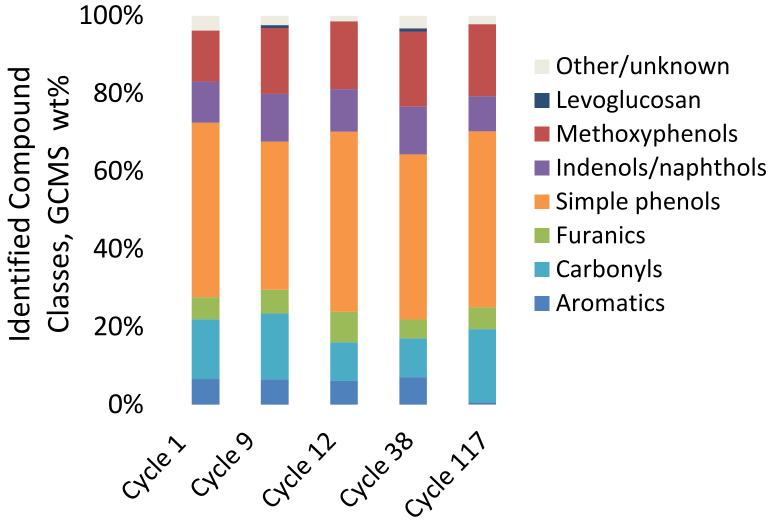
Process Optimization and Durability

Assessing Process Durability



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





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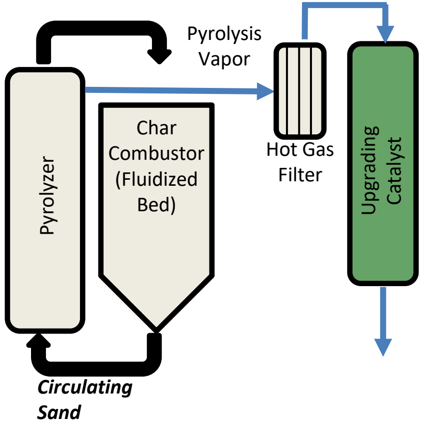
Catalyst Mass: 100 g
WHSV: 1.4 g biomass/gcat*h
Near Atmospheric Pressure
Hydrogen Concentration: 83%
Biomass:Catalyst Ratio: 3

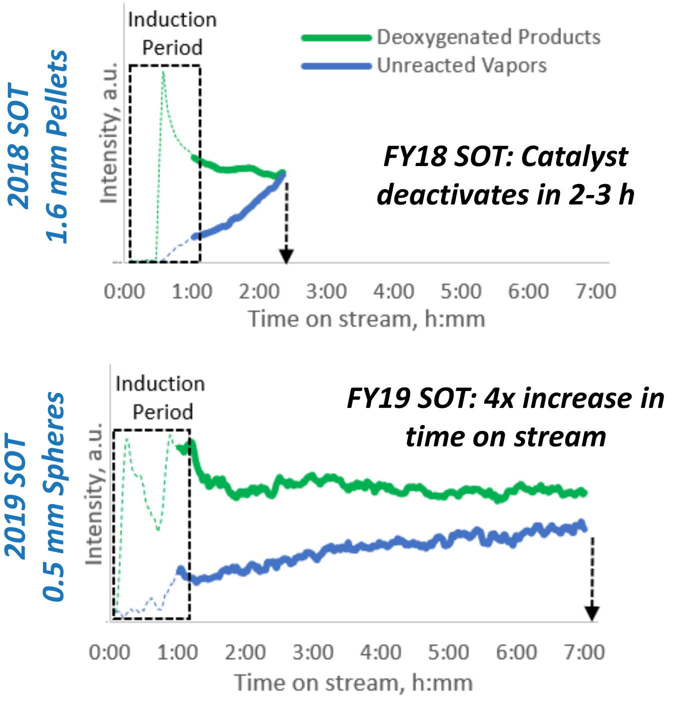
Outcome: improved confidence in catalyst and process durability, reduced risk for process model inputs, and support for technology transfer efforts

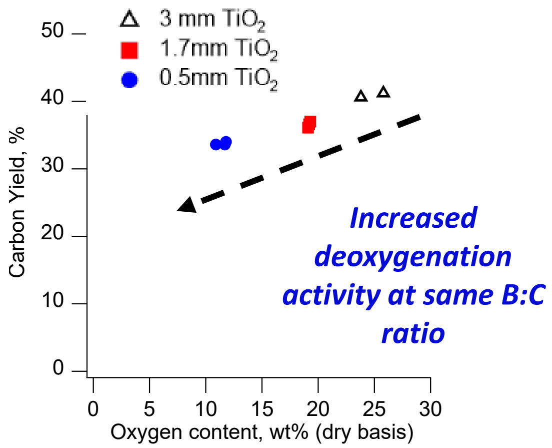
R. French, et al., *ACS Sustain. Chem. Eng.*, 9 (2021) 1235-1245.

Increasing Cycle Length



Progress: optimizing the size and shape of the catalyst support reveals improved deoxygenation activity and increased cycle length





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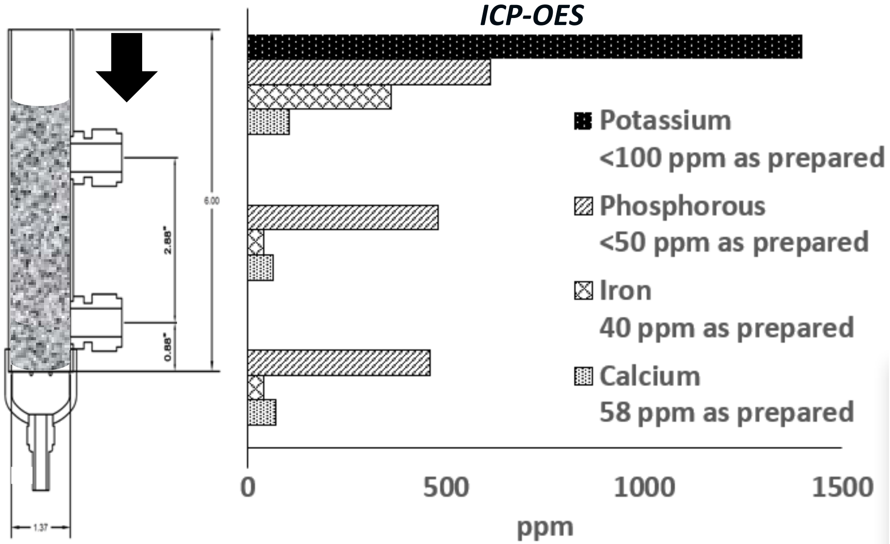
Catalyst Mass: 100 g
WHSV: 1.4 g biomass/gcat*h
Near Atmospheric Pressure
Hydrogen Concentration: 83%
Biomass:Catalyst Ratio: 3-12

Coke on catalyst reduced from 2.1 wt% to 1.9 wt%

Outcome: lower capital requirements, a **$0.05/GGE** reduction in MFSP, and improved operational efficiency

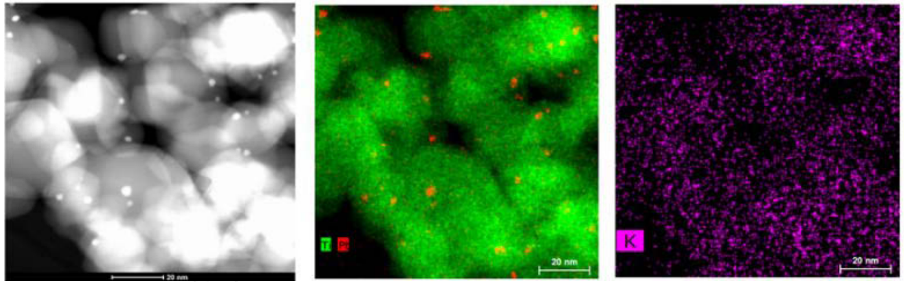
Tracking Inorganic Deposition

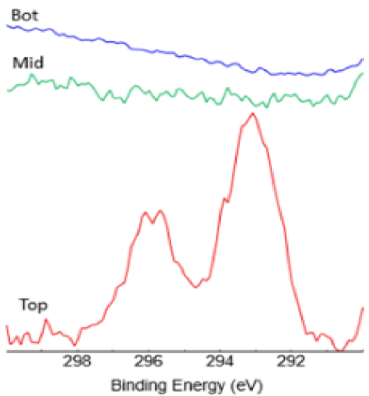
Catalyst characterization after reaction with forest residues revealed considerable potassium deposition at the leading edge of the catalyst bed



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



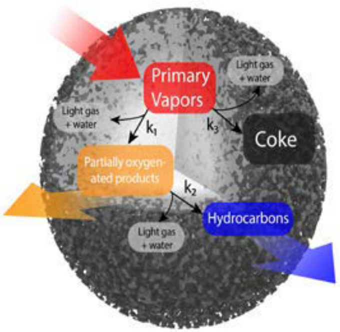


XPS Spectra of K 2p Region confirm K deposition

Ongoing Research:
Determine the impact of K on catalyst properties and performance

Informing Scale Up

Progress: development of a new simulation framework that leverages DOE high performance computing capabilities for multiscale modeling to inform in-silico optimization and process scale up



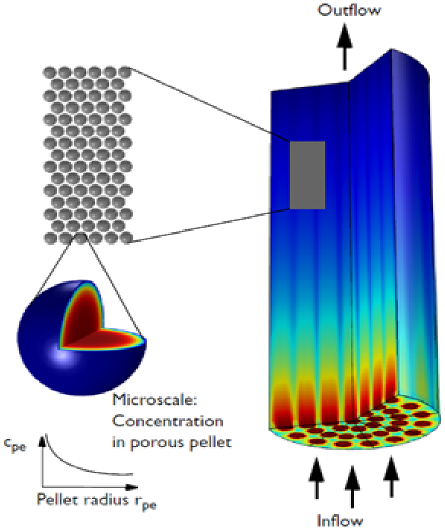
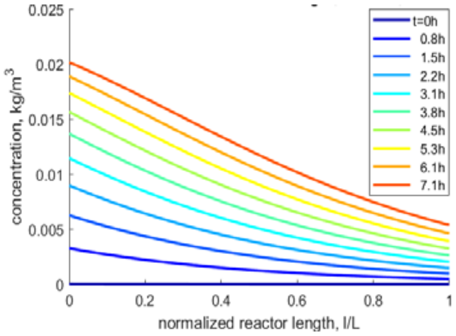
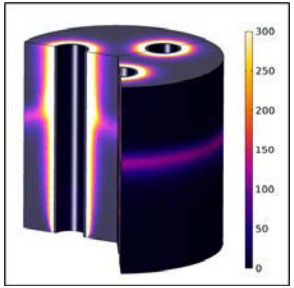


Image made using COMSOL Multiphysics® software and provided courtesy of COMSOL.[26]

Predicted catalyst coke profile as a function of time on stream



Sharp temperature gradients during regeneration at pilot-scale



∇T, °C/cm

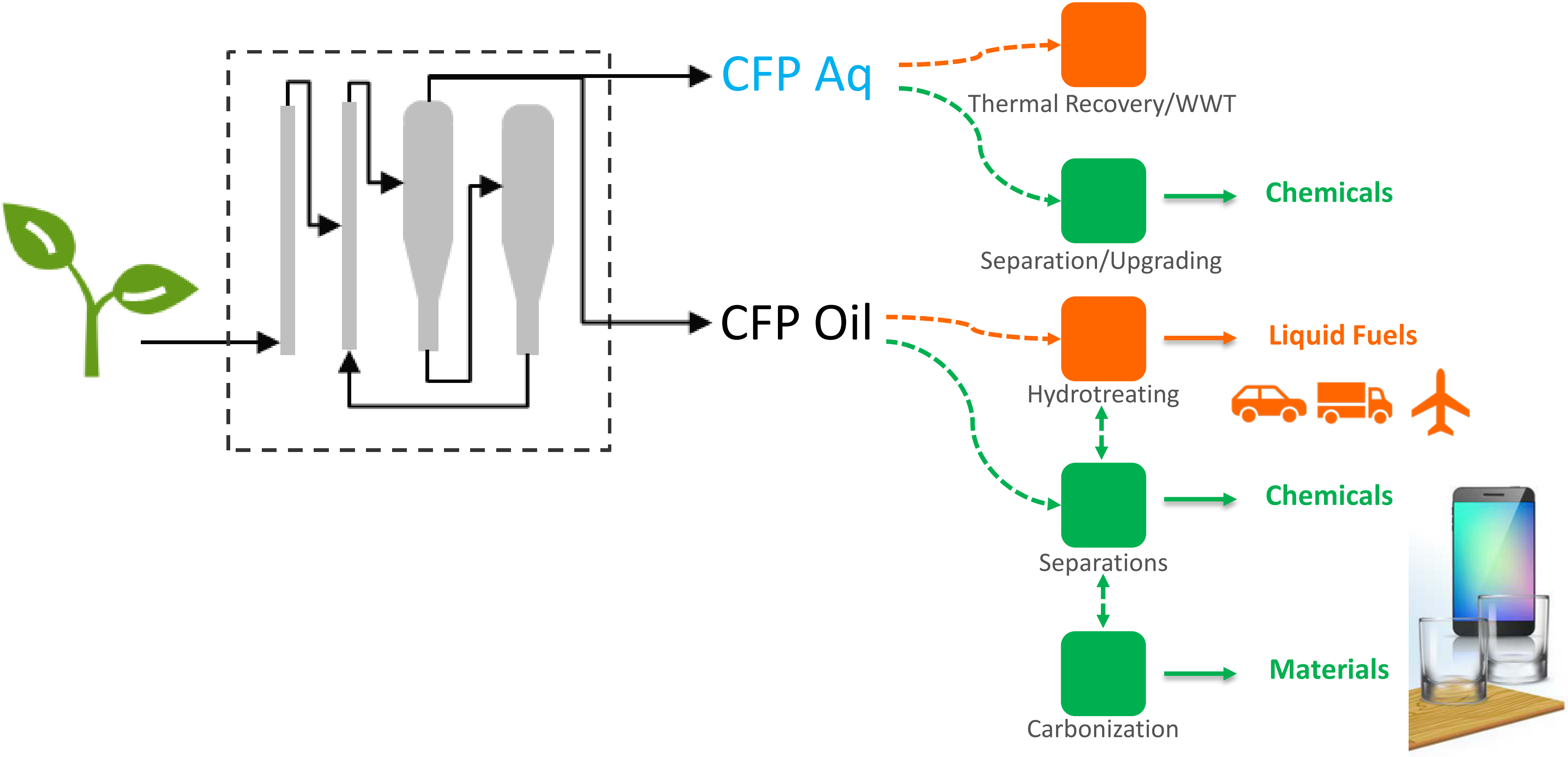
Outcome: early identification of potential process disruption at the pilot scale due to thermal excursions during regeneration. Ongoing collaborative research targets alternative reactor designs to improve heat transfer capabilities at scale

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

B. Pecha, et al., *Reaction Chemistry and Engineering*, 6 (2021) 125-137.
B. Adkins, et al., *Reaction Chemistry and Engineering*, (2021) in press

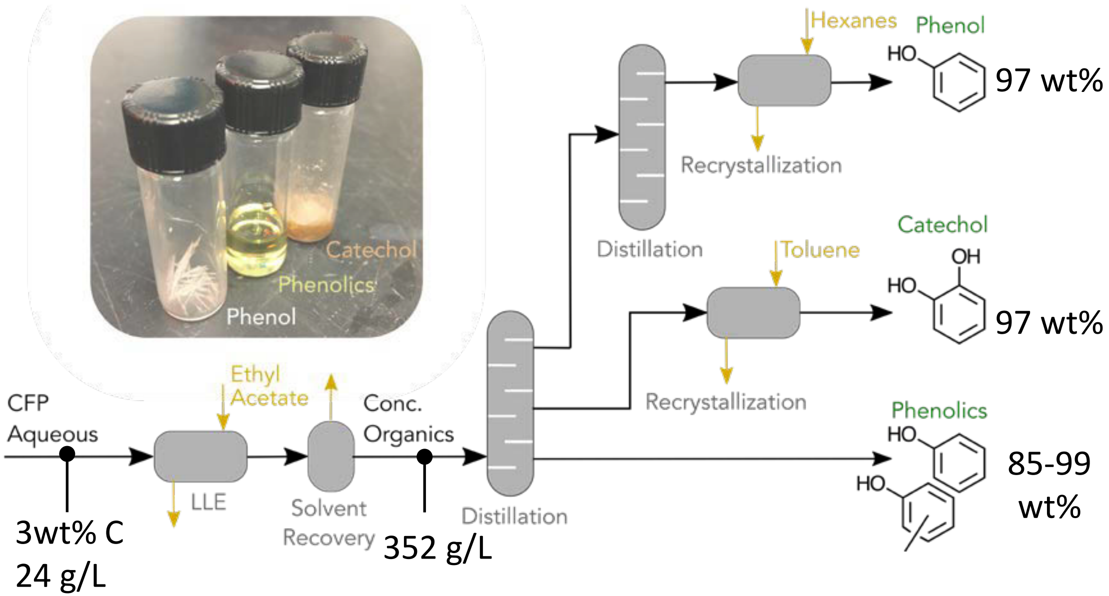
Product Diversification

Expanding the Product Slate from CFP

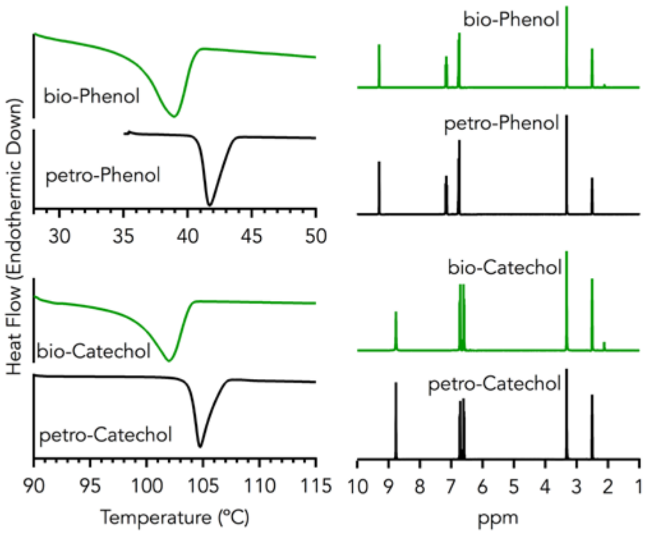


Expanding product slate from CFP technology platform by developing separation strategies for chemical precursors

Separations Approach



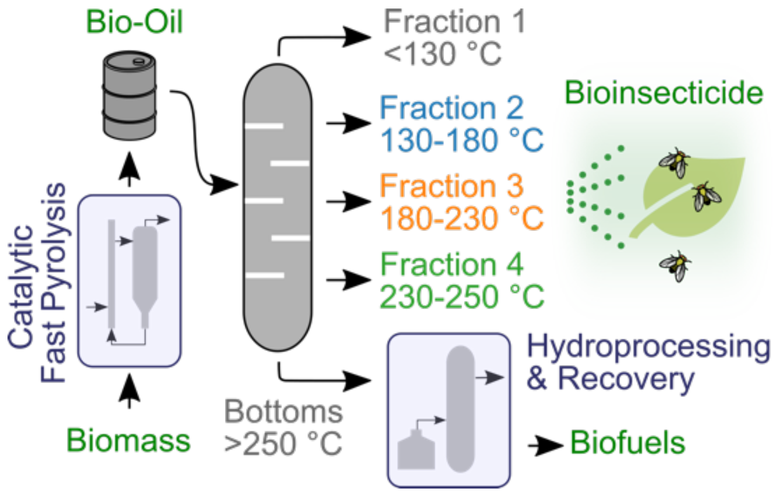
Product Characterization

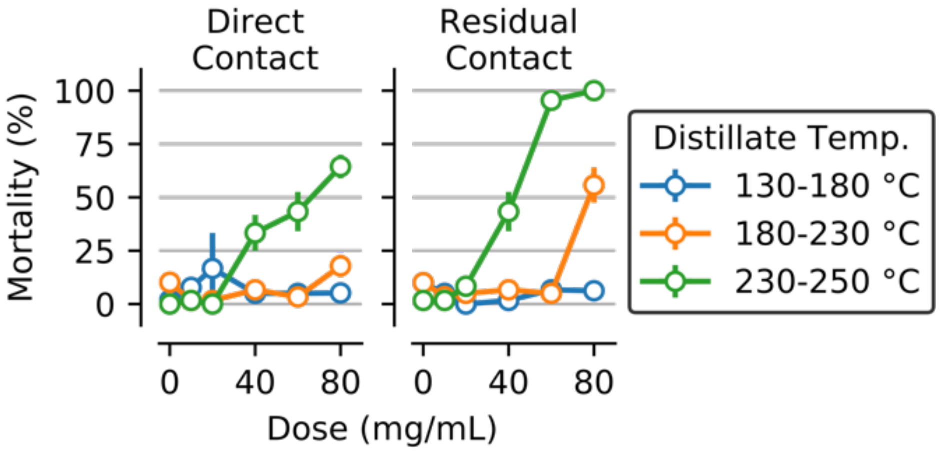


A. N. Wilson, et al., *Green Chemistry*, 21 (2019) 4217-4230

Bioinsecticides derived from CFP Bio-Oil

Fractions of CFP bio-oil exhibit activity as bioinsecticides, presenting an opportunity to improve sustainability in energy and food production sectors





(Spotted-wing Drosophila)

Extent of phenol alkylation appears to be correlated with mortality

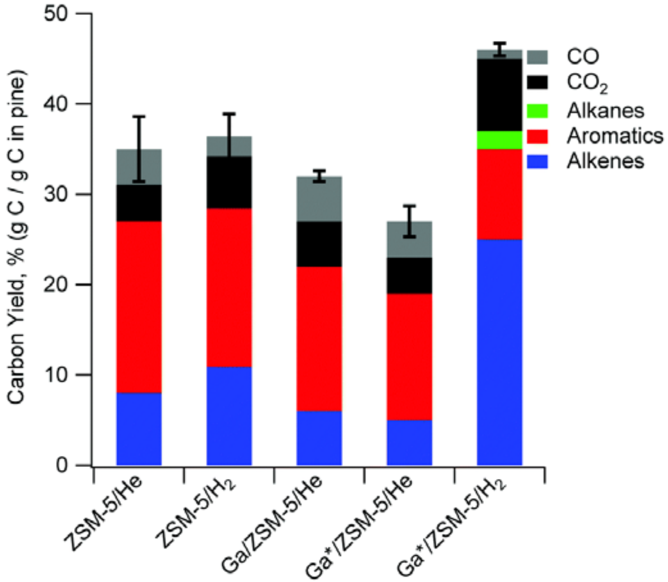
USDA

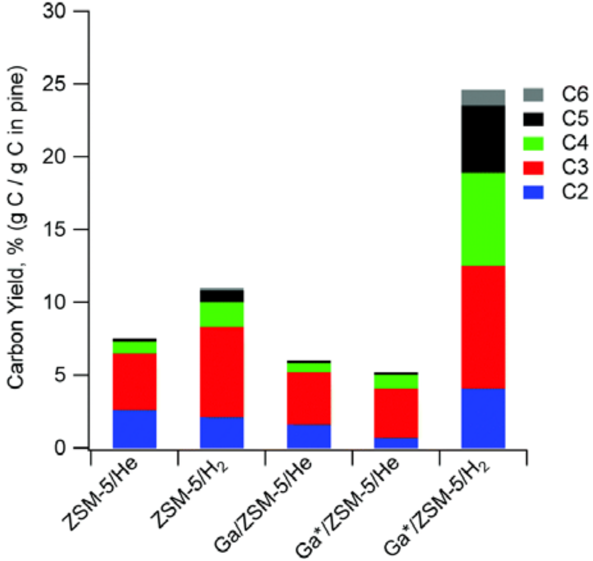
MICHIGAN STATE UNIVERSITY

Targeting Olefins as Primary CFP Products

Early-stage results suggest that modifying the catalyst and process conditions enables the CFP product slate to be tuned towards olefins

- Feedstock: Southern yellow pine
- Pyrolysis and catalysis temperature: 500°C
- Apparatus: Tandem micro-furnace pyrolyzer coupled to a GC-MS/FID
- Pressure: 115kPa
- B/C: 0.05
- Run in triplicate





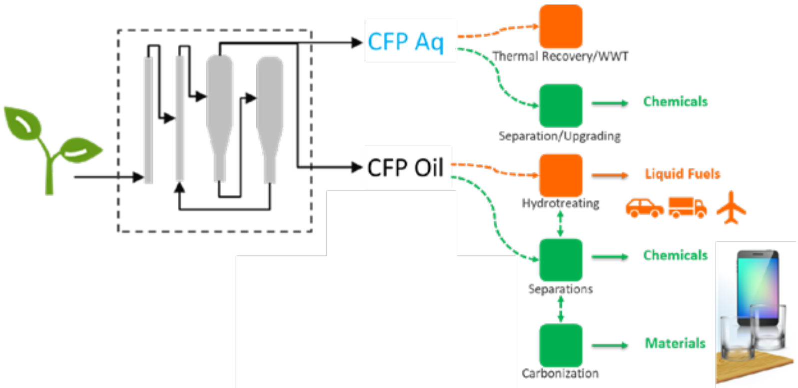
Ga* indicates Ga/ZSM-5 pretreated in H_2

Reduced Ga species (e.g., $[Ga(OH)_2]^+$ and $[GaH(OH)]^+$) appear to be responsible for improved olefin yield

K. Iisa, et al., *Green Chemistry*, 22 (2020) 2403-2418

Summary and Conclusions

- ***Designed resilience as a central theme*** for emerging carbon conversion and management technologies
- ***Critical Needs:***
  - Feedstock flexibility
  - Adaptive process design and control
  - Low conversion costs
  - Product tunability
- ***Catalysis enables the development of versatile technology platforms*** that meet these needs



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Earl Christensen
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John Dorgan (MSU)
David Chiaramonti (Turin)

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Thank you!

ChemCatBio Team

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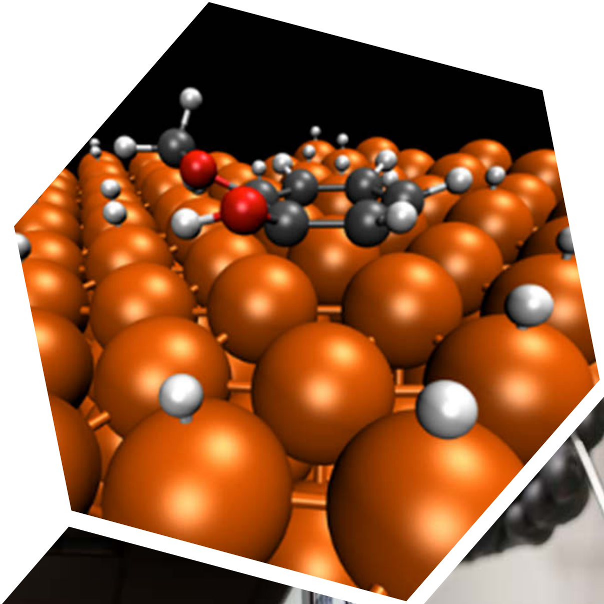

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