ChemCatBio
Chemical Catalysis for Bioenergy

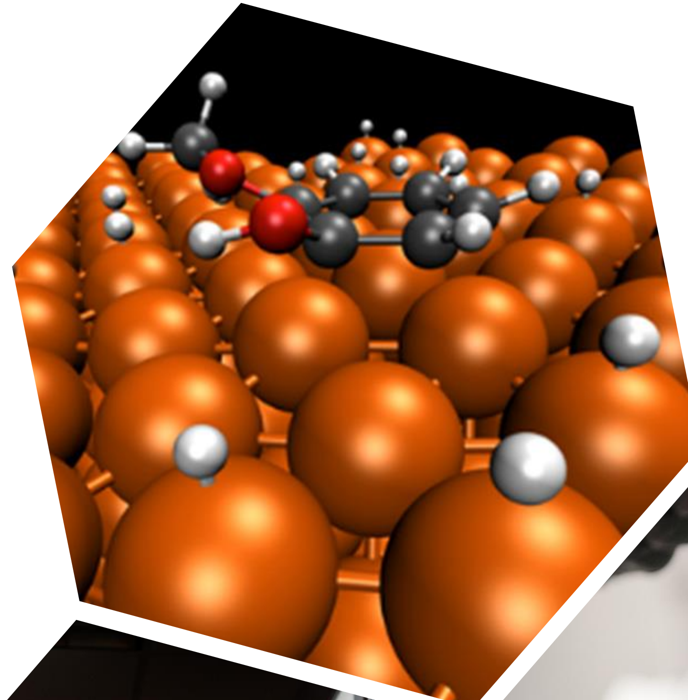
DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review

Catalytic Upgrading of Pyrolysis Products

Josh Schaidle, Kim Magrini, and Huamin Wang

Catalytic Upgrading

March 2019



Goal Statement

Goal: Develop a ***catalytic fast pyrolysis (CFP) technology platform*** for an integrated biorefinery concept, which is capable of producing both ***cost-competitive biofuels*** at greater than 75 gasoline gallon equivalent (GGE)/dry ton of biomass and ***high-value co-products***, and can be market-responsive by controlling the product distribution to meet market demand

Outcome: Advance CFP state-of-technology and reduce commercialization risk by (1) ***demonstrating production of a fuel blendstock at a modeled minimum fuel selling price (MFSP) of $3.0/GGE*** and (2) developing strategies to reduce MFSP to $2.5/GGE

- Vertically-integrated, collaborative approach spanning from catalyst design to integrated bench-scale CFP with downstream hydrotreating (HT)
- Combined experimental-computational approach to catalyst design, coupled with catalyst evaluation across scales
- Evaluation of co-product and co-processing opportunities

Relevance to Bioenergy Industry: Addressing ***critical technical challenges*** limiting commercialization of CFP technologies: carbon efficiency and product diversity/quality

ChemCatBio Foundation

Integrated and collaborative portfolio of catalytic technologies and enabling capabilities

Catalytic Technologies

- Catalytic Upgrading of Biochemical Intermediates (NREL, PNNL, ORNL, LANL, NREL*)
- Catalytic Upgrading of Indirect Liquefaction Intermediates (NREL, PNNL, ORNL)
- **Catalytic Fast Pyrolysis (NREL, PNNL)**
- Electrocatalytic and Thermocatalytic CO_2 Utilization (NREL, ORNL*)

*FY19 Seed Project

Enabling Capabilities

- Advanced Catalyst Synthesis and Characterization (NREL, ANL, ORNL, SNL)
- Catalyst Cost Model Development (NREL, PNNL)
- Consortium for Computational Physics and Chemistry (ORNL, NREL, PNNL, ANL, NETL)
- Catalyst Deactivation Mitigation for Biomass Conversion (PNNL)

Industry Partnerships (Directed Funding)

- **Gevo** (NREL)
- **ALD Nano/JM** (NREL)
- **Vertimass** (ORNL)
- **Opus12**(NREL)
- **Visolis** (PNNL)
- **Lanzatech** (PNNL) - Fuel
- **Gevo** (LANL)
- **Lanzatech** (PNNL) - TPA
- **Sironix** (LANL)

Cross-Cutting Support

- **ChemCatBio Lead Team Support** (NREL)
- **ChemCatBio DataHUB** (NREL)

Quad Chart

Timeline

- Project start date: October 1st, 2016
- Project end date: September 30th, 2019
- Percent complete: 83%

	Total Costs Pre FY17	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded	$6M	$2.7M	$3M	$3.2M
Project Cost Share	N/A			

National Lab Partners: NREL: 85%; PNNL: 15%

Industry Partners: Johnson Matthey, WR Grace, VTT, ExxonMobil

University Partners: Utah State, Georgia Tech, University of Michigan, University of Southern California

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

Objective

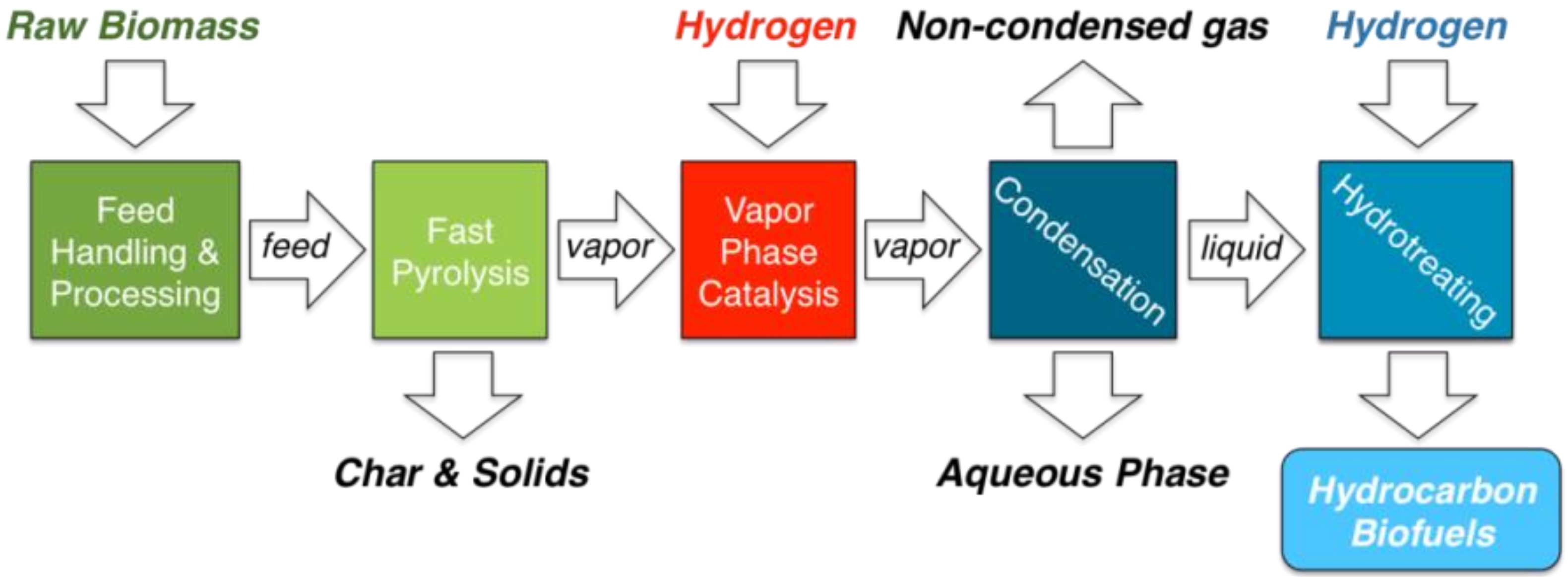
Develop a catalytic fast pyrolysis (CFP) technology platform for an integrated biorefinery concept, which is capable of producing both cost-competitive biofuels at greater than 75 gasoline gallon equivalent (GGE)/dry ton of biomass and high-value co-products, and can be market-responsive by controlling the product distribution to meet market demand

End of Project Goal

By September 2019, this project will (1) produce fuel blendstocks from at least one advanced CFP process that achieves a minimum fuel selling price of $3.0/GGE in 2016$ with greater than 25% (GGE basis) of the fuel in the diesel/jet range, and (2) identify viable routes to $2.5/GGE for further development in 2020-2022.

Project Overview: Catalytic Fast Pyrolysis

Potential for whole biomass conversion to drop-in hydrocarbon fuels at high yields (>80 gal/ton)



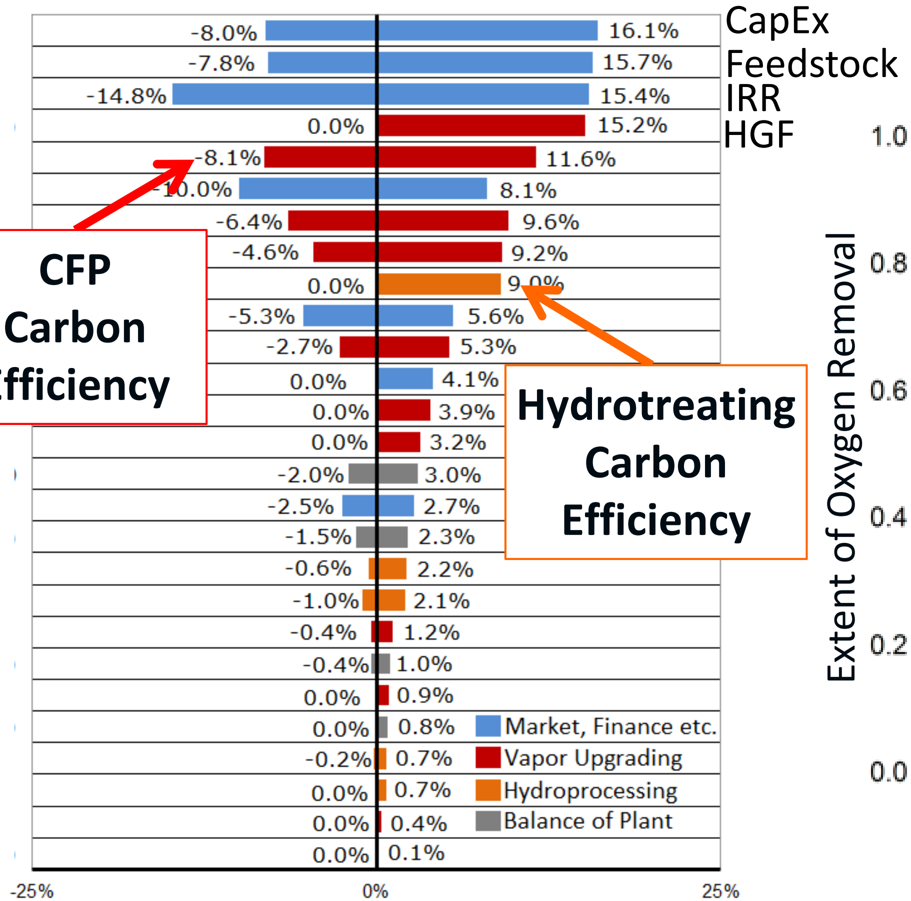
D. Ruddy, et al. *Green Chem* 16 (2014) 454

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 (HT) 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

Project Overview:
Carbon Efficiency is Key to Commercial Viability

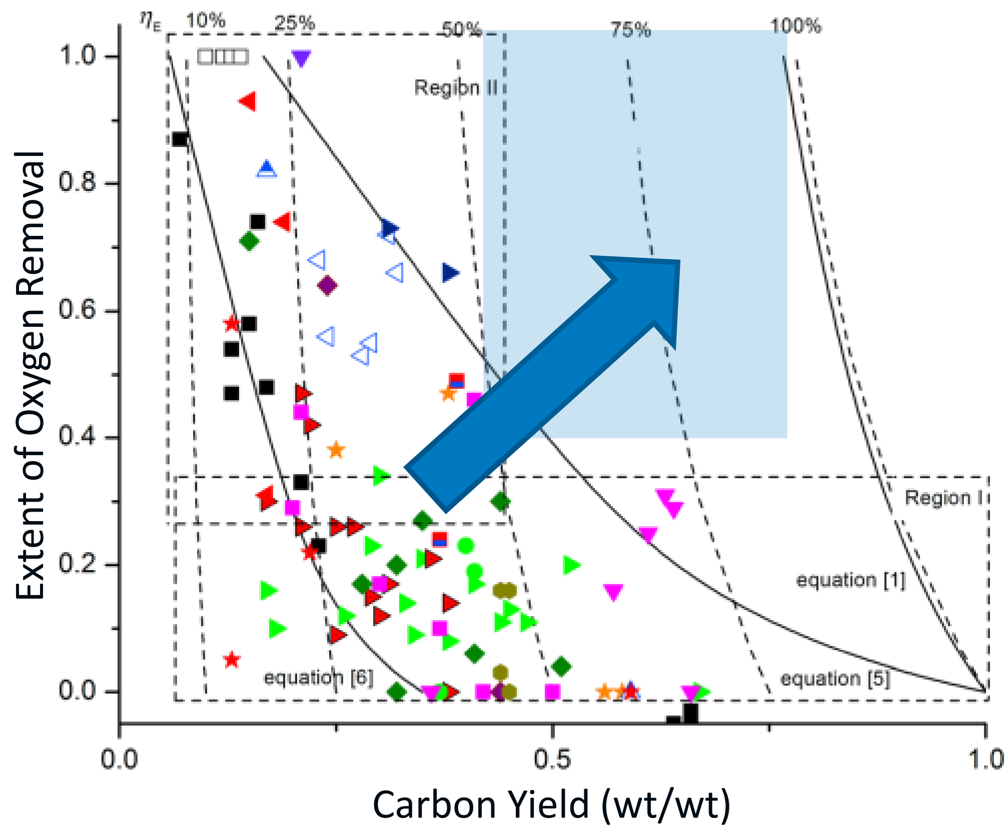
Process Sensitivity Analysis



% Change to MFSP from the ex situ base case ($3.31/GGE)

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

Relationship between Carbon Yield and Oxygen Content for CFP

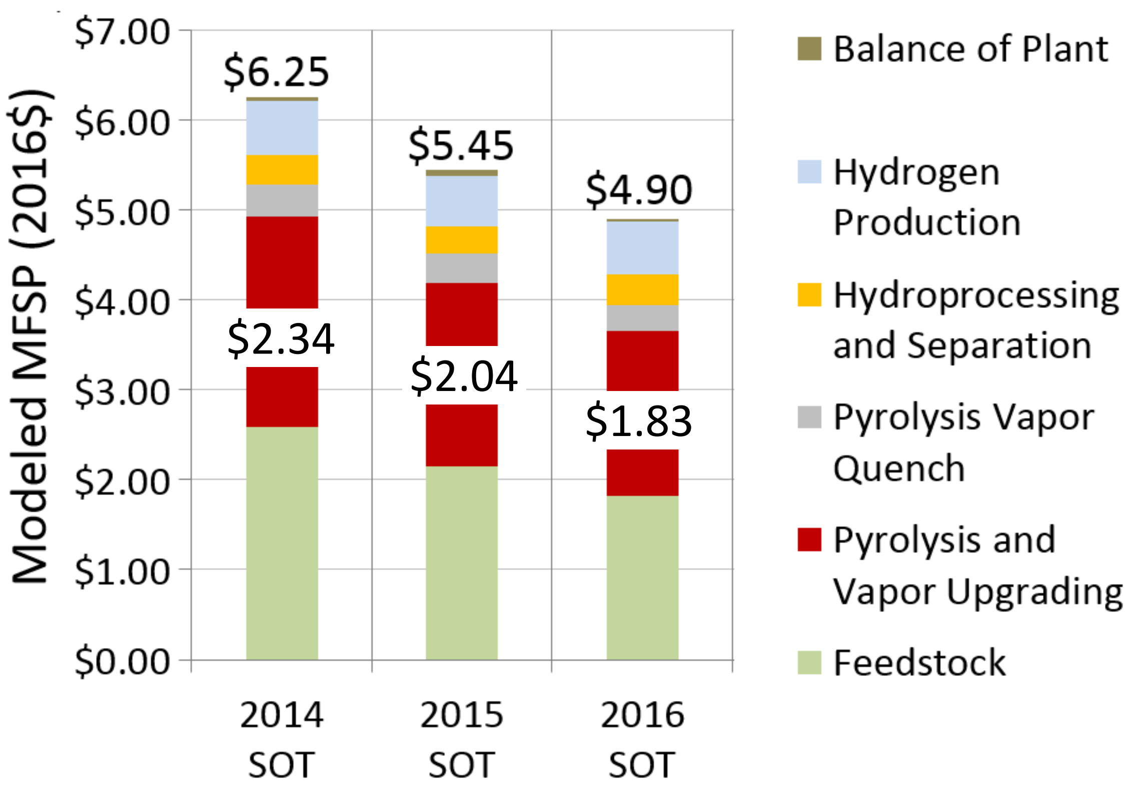


R. Venderbosch, *ChemSusChem* 8 (2015) 1306

CFP catalysts and processes need to achieve extensive deoxygenation AND high carbon yields

Project Overview: Baseline

2016 state-of-technology for CFP + HT pathway resulted in 28% carbon efficiency to fuel products and a modeled MFSP of $4.90/GGE



- Zeolite-based catalyst in an ex-situ riser reactor
- Feedstock: clean pine at $92/dry us ton

Project Overview: Value Proposition

Value Proposition: *Reduce conversion costs for biofuel production by developing and advancing a versatile CFP technology platform that achieves high yields (>40% C yield) to biofuels and bioproducts*

Objectives and *Success Factors*:

- Evaluate CFP process configurations using a common basis
- Leverage ChemCatBio enabling capabilities to develop catalysts and processes that achieve >40% overall carbon efficiency to products
- Demonstrate bench-scale production of fuel blendstocks at a modeled MFSP of $3.0/GGE with greater than 25% of the fuel in the diesel/jet range
- Provide early-stage R&D to enable BETO 2022 engineering-scale verification
- Identify and demonstrate viable routes to co-products and $2.5/GGE MFSP

Differentiators:

- Vertically-integrated approach coupling hypothesis-driven catalyst design with multi-scale process evaluation, guided by TEA
- Leveraging deep expertise in CFP and HT at NREL and PNNL
- Cross-disciplinary partnerships with industry, academia, and BETO consortia

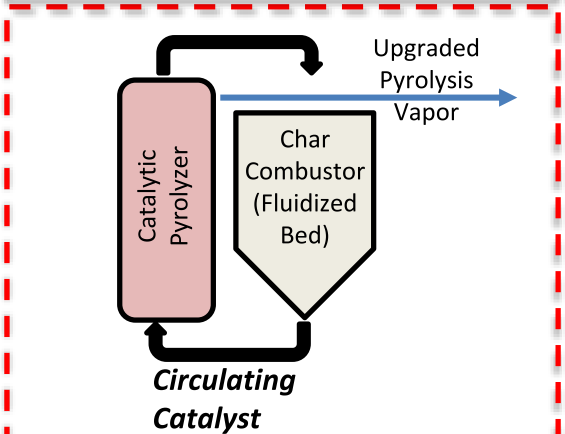
Technical Approach:
Evaluation of CFP Process Configurations

Challenge: Numerous CFP process configurations exist, each with advantages and disadvantages

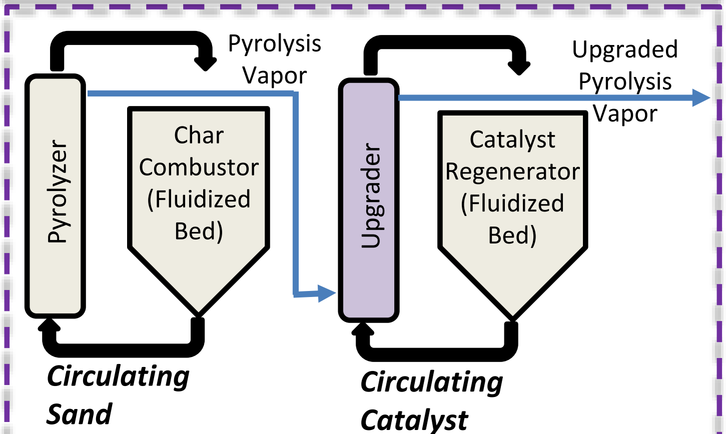
Approach: Evaluate each configuration and prioritize R&D based on opportunities for cost reduction

Near-term → ***Long-term***

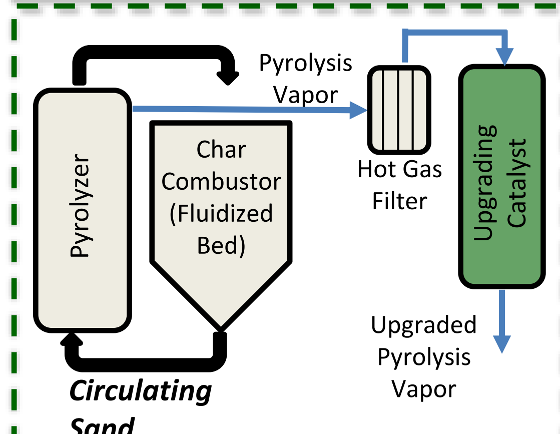
In-situ CFP



Ex-situ Entrained Bed CFP



Ex-situ Fixed Bed CFP



Modified Zeolites and Metal Oxide Catalysts | **Next Generation Catalysts**

- Low capex
- Harsh conditions (catalyst mixed with biomass/char/ash)

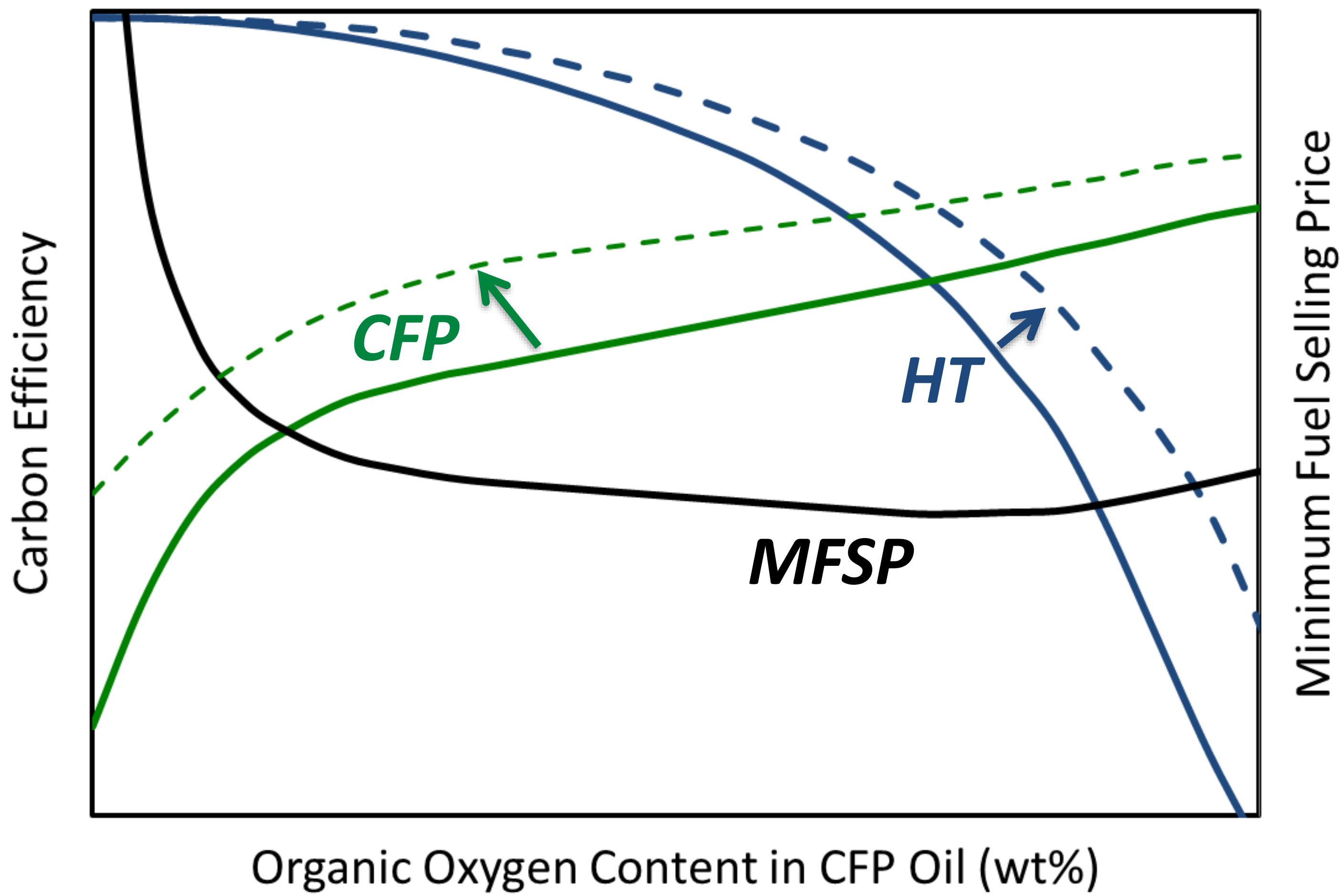
- Controlled catalytic environment (char/ash removed)
- Higher capex

- More diverse catalysts and chemistry
- Long catalyst lifetimes required

Technical Approach:
Hypothesis-Driven Catalyst and Process Development

Challenge: Low carbon efficiency due to coking and light gas formation

Approach: Improve carbon efficiency for CFP and HT through foundational catalyst and process R&D



Technical Approach:
Foundational Catalyst-Process Development

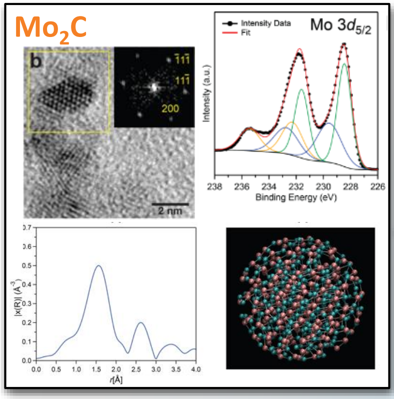
Foundational Science

Enables hypothesis-driven catalyst design

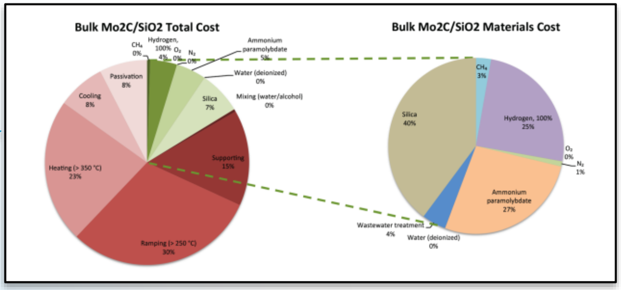
Applied Engineering

Enables evaluation of key process metrics and deactivation

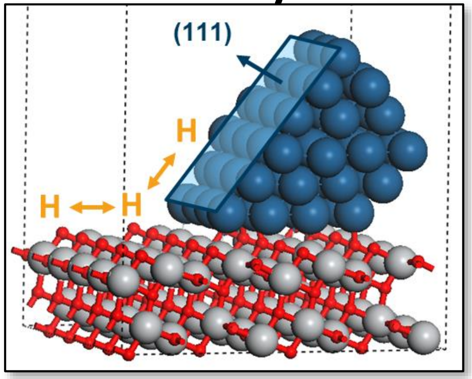
Advanced Synthesis and Characterization



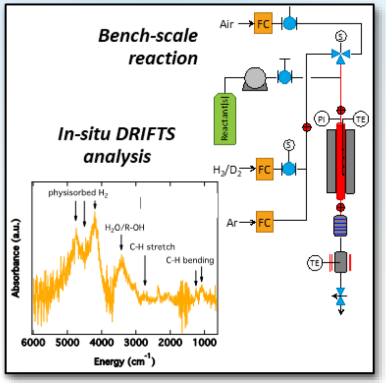
Catalyst Cost Estimation

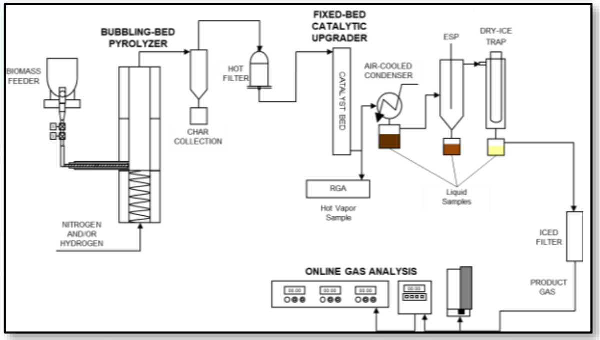


Theory



Performance Evaluation



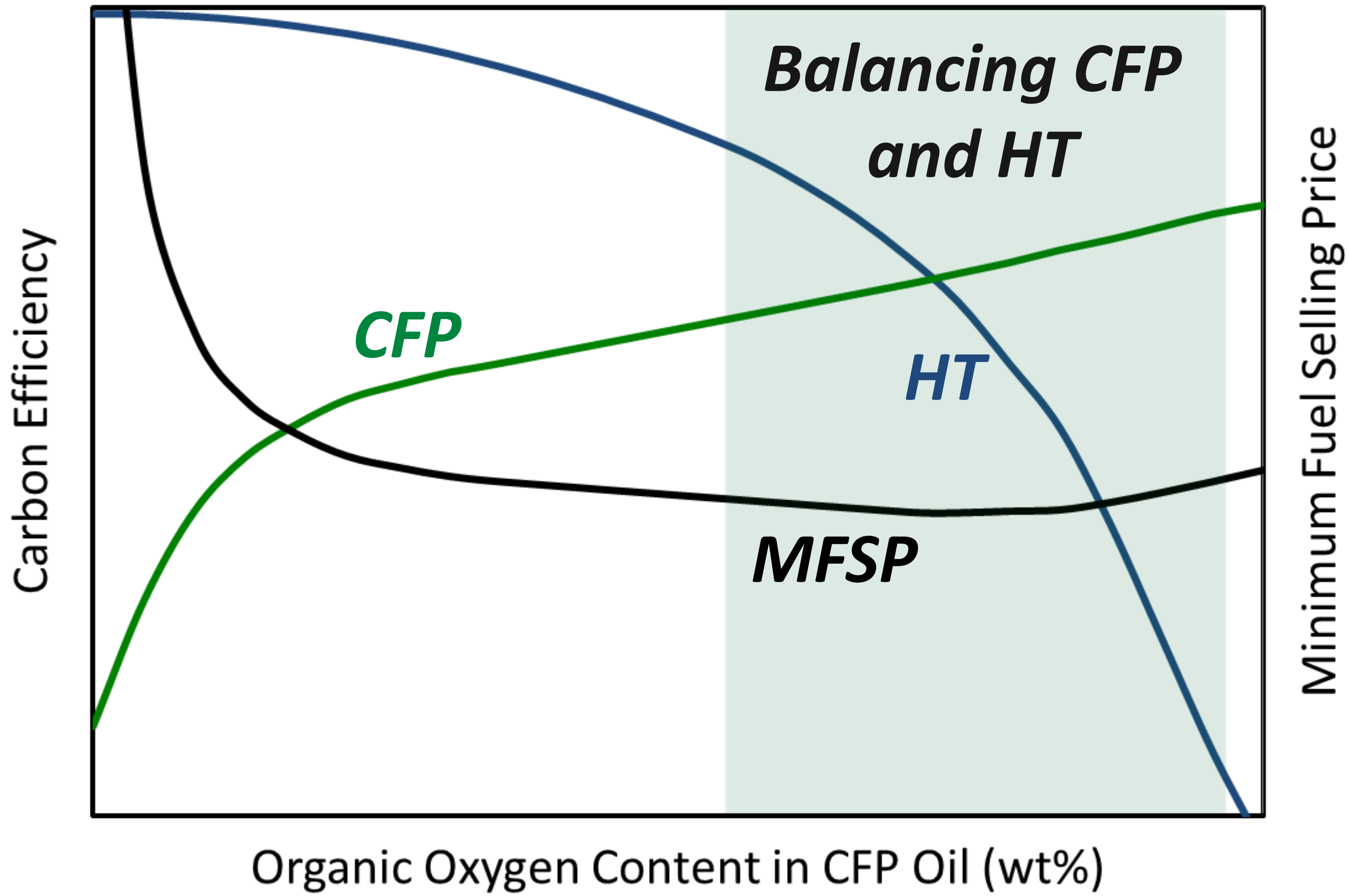


Catalyst Scaling and Integrated Testing

Technical Approach: Balance Process Steps

Challenge: Complex, multi-step process (CFP + HT) linked through quality/properties of bio-oil intermediate

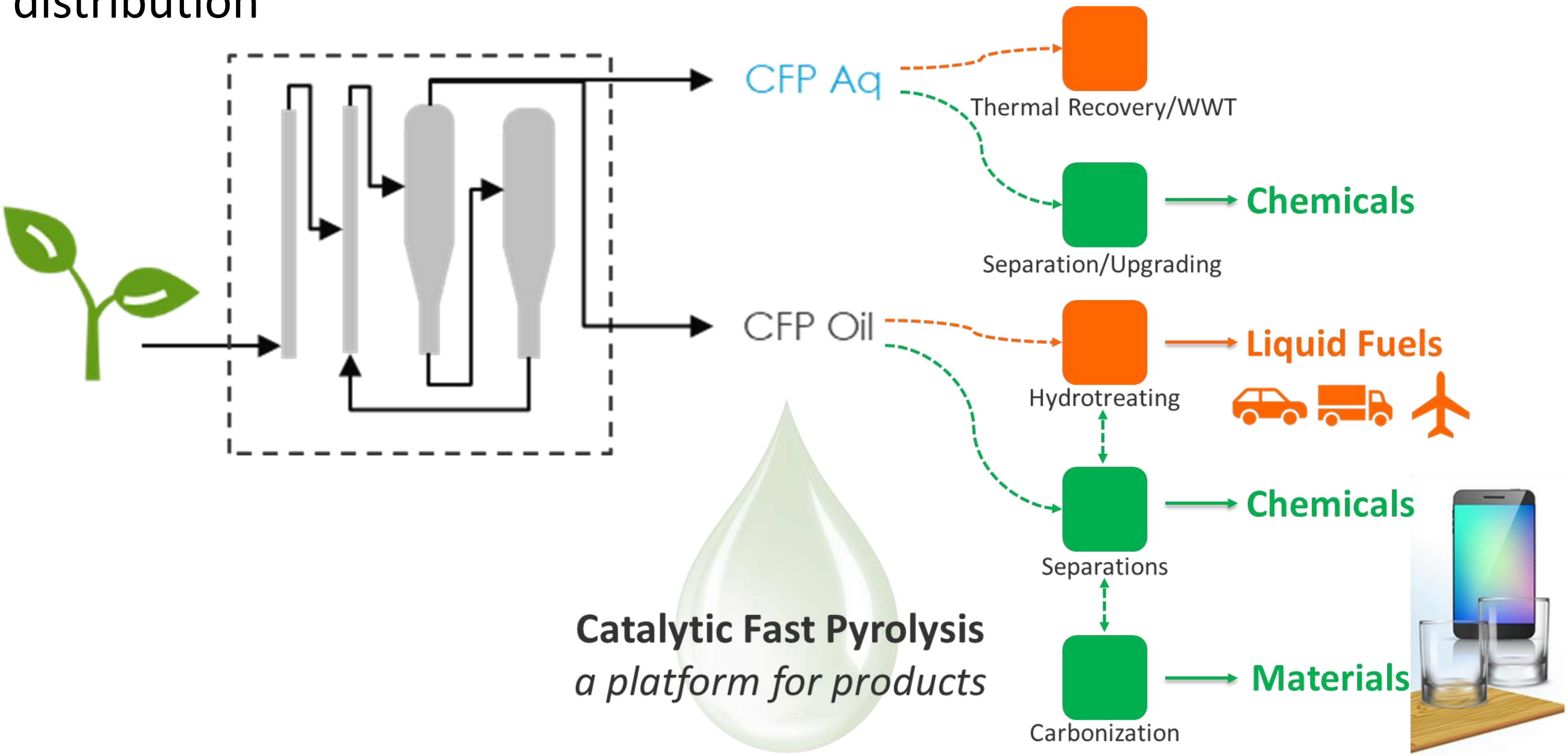
Approach: Improve overall carbon efficiency by balancing CFP and HT



Technical Approach: Product Diversification

Challenge: Heterogeneity of CFP bio-oil limits fuel quality

Approach: Expand product slate by evaluating opportunities for co-products and developing catalysts that provide control over product distribution



Management Approach: Project Structure

Vertically-integrated approach spanning catalyst development to production of fuel blendstocks

Project Structure	Purpose	
Task 1: CFP Catalyst Design and Development **Lead**: Susan Habas	Develop next-generation catalysts with enhanced performance	Vertically-Integrated Approach
Task 2: CFP with Model Compounds **Lead**: Mike Griffin	Provide mechanistic insight for catalyst development	Vertically-Integrated Approach
Task 3: CFP with Biomass Pyrolysis Vapors **Lead**: Calvin Mukarakate	Evaluate catalyst and process performance with integrated systems	Vertically-Integrated Approach
Task 4: CFP with Riser Reactor System (DCR) **Lead**: Kim Magrini	Evaluate catalyst and process performance with integrated systems	Vertically-Integrated Approach
Task 5: Hydrotreating **Leads**: Huamin Wang and Kristiina Iisa	Generate fuel blendstocks for analysis of fuel properties	Vertically-Integrated Approach
Task 6: Light Gas Incorporation **Lead**: Matt Yung	Develop routes to re-incorporate light gases back into CFP oil	Enabling Technologies
Task 7: Co-Product Formation **Lead**: Mark Nimlos	Develop viable routes to co-products	Enabling Technologies

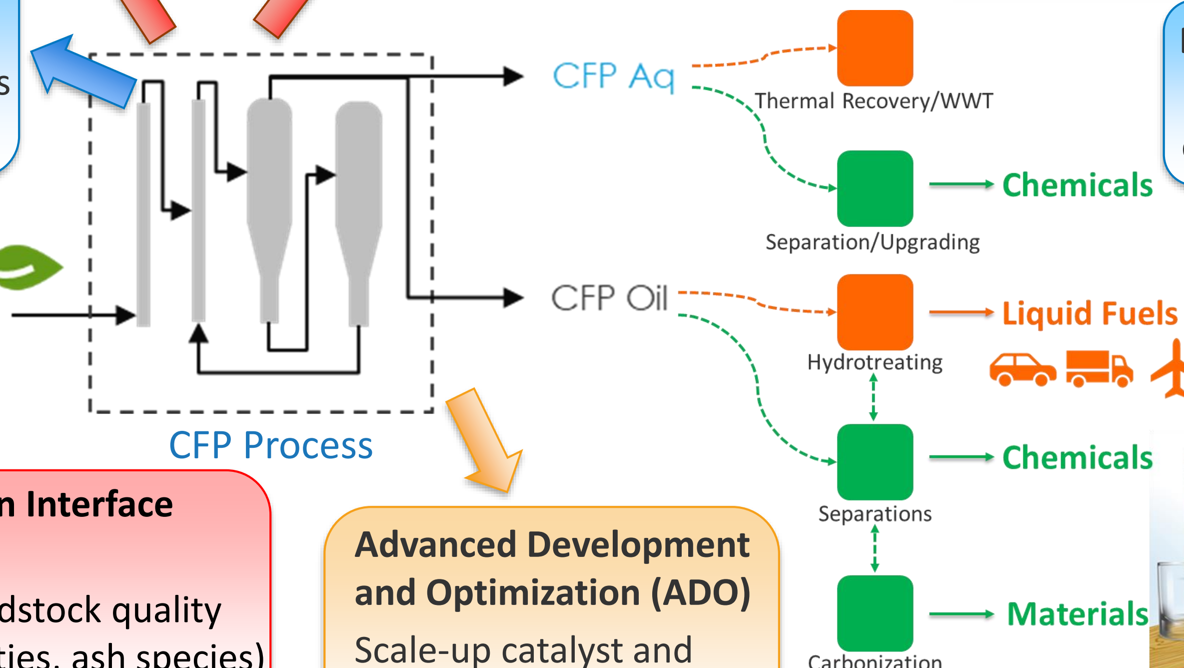
Management Approach: Project Interactions

Separations Consortium
Evaluate and develop hot-gas filtration technologies and bio-oil separation strategies

ChemCatBio Enabling Capabilities
First-principles catalyst design and operando catalyst characterization to understand deactivation modes

Performance-Advantaged Bioproducts
Identify and synthesize performance-advantaged polymers and materials

Johnson-Matthey CRADA
Develop CFP catalysts and processes



ExxonMobil CRADA
Develop routes to chemicals via CFP

Co-Optima
Identify species best suited for fuels vs. chemicals

TCF
Pursue opportunities for bio-derived graphite

Feedstock Conversion Interface Consortium
Evaluate effect of feedstock quality (composition, impurities, ash species) on CFP catalyst performance/lifetime

Advanced Development and Optimization (ADO)
Scale-up catalyst and process for BETO 2022 verification

Cross-Cutting Technoeconomic Analysis

Progress: Evaluation of CFP Process Configurations

Selected *ex-situ* fixed-bed CFP as SOT in 2017 based on our first-of-its-kind, side-by-side comparison of CFP approaches from feedstock to fuel property analysis

- Feedstock: Clean pine provided by INL
- >500mL of CFP oil generated from each process configuration
- ***Single-stage continuous hydrotreating:***
  - Ni-Mo sulfide catalyst, 400°C, 12.8 MPa, 0.2-0.3 h^{-1} LHSV
- Hydrotreated oils fractionated then analyzed for fuel properties

Process	***In-situ* CFP**	***Ex-situ* Riser CFP**	***Ex-situ* Fixed-Bed CFP**
Catalyst (Conditions)	Red Mud (400°C)	ZSM-5 (550°C)	Pt/TiO_2 (400°C, H_2 co-feed)
Reactor	Utah State's Fluidized Bed Pyrolyzer	NREL's 2" Fluidized Bed Pyrolyzer + Catalytic Upgrading	
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***
Product Distribution (% GGE) (Gasoline / Diesel)	37% / 43%	49% / 42%	45% / 39%
Fuel Quality (AKI / Cetane**)	57 / 26	71 / 22	65 / 24

*Normalized carbon efficiencies
**Derived cetane number

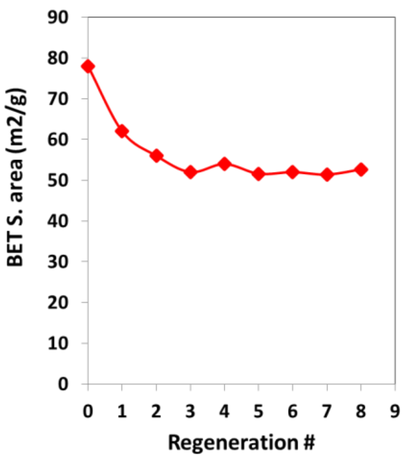
Progress: *In-situ* CFP using Red Mud Catalyst

Demonstrated that a low-cost and robust red mud catalyst can withstand harsh *in-situ* CFP conditions

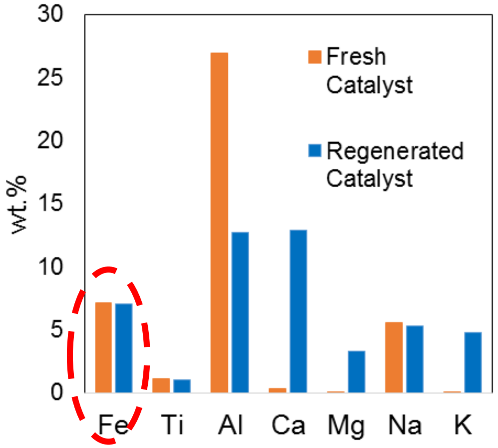
In situ CFP and HT	Pine	Forest Thinning
CFP Carbon Yield (%)	42	42
O in CFP (wt.%, dry)	28	27
HT Carbon Yield (%)	85	87
Overall Carbon Yield (%)	36	37

CFP: 400 °C, red mud catalyst;
Hydrotreating: single stage, 400 °C, 0.20 h^{-1}
*Normalized carbon yields

Maintained surface active sites and acid-base properties



Surface area



Surface composition (XPS)

- Red mud catalyst enabling steady, efficient, and economical *in situ* CFP with single unit CFP configuration
  - Low-cost catalyst from waste materials
  - Robustness and resistance towards mineral deposition
  - Lower pyrolysis temperatures (400 °C)
  - Steady performance for various biomass feedstocks
- MFSP met MYP technical targets ($4.55/GGE FY17, 2014$)

Pacific Northwest NATIONAL LABORATORY
UtahStateUniversity
VTT

Progress: *In-situ* CFP using Red Mud Catalyst

Procured large quantity of red mud catalyst and partnered with VVT to scale-up *in-situ* CFP process to pilot-scale

- Scaled-up production of 300 kg red mud catalyst
- The first pilot-scale testing of *in situ* CFP with red mud catalyst
  - 4-day *in situ* CFP test with 72 hours steady state operation
  - Two feedstocks (stem chips and forest residue) and three CFP temperatures (460-520 ^{o}C)
- Lower bio-oil yield was observed at pilot-scale compared to bench-scale
  - Due to difference in reactor configuration (bubbling vs circulating fluidized bed)

300 kg Red mud catalyst

VTT 20 kg/h CFP unit

Pacific Northwest NATIONAL LABORATORY

VTT

UtahStateUniversity

Closed out and summarized work on *in-situ* CFP

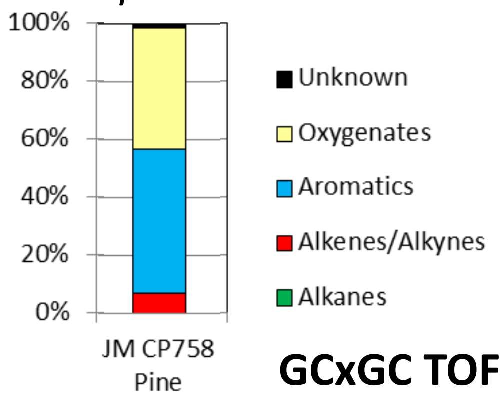
- Further work required to address the *challenges of property variation with source of red mud*
- Further work required to evaluate CFP and HT by larger-scale and longer-term continuous testing and with a wider range of biomass

Progress: *Ex-situ* Entrained Bed CFP

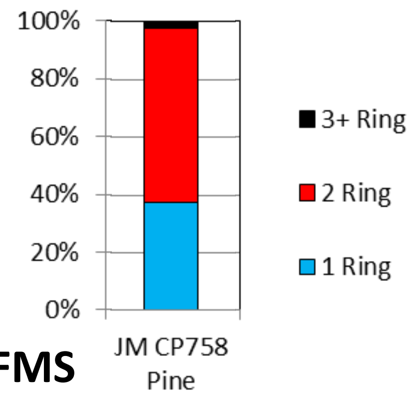
Scaled-up entrained bed CFP to commercially-relevant riser reactor system leveraging commercial zeolite catalysts

- Partnered with Johnson Matthey to evaluate commercial and under-development zeolite catalyst
- Conditions:
  - Pyrolysis: 500°C, 1:1 biomass:N_2 ratio
  - CFP: 550°C, 1 sec residence time in riser
- Similar yields observed to 2" system
- **High selectivity to aromatics in CFP oil, but yield still limited**

Compound Classes



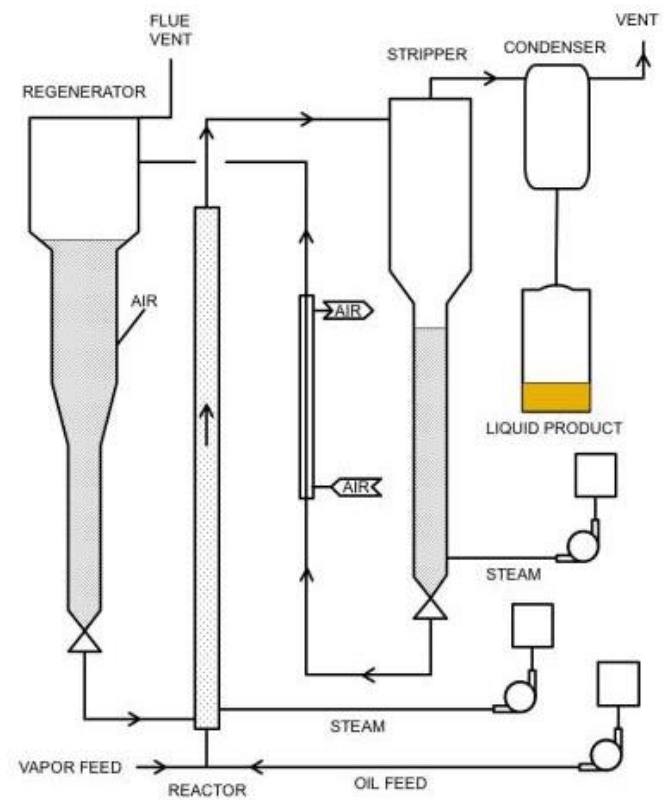
Aromatic Distribution



GCxGC TOFMS

Davison Circulating Riser (DCR)

Analogous to FCC



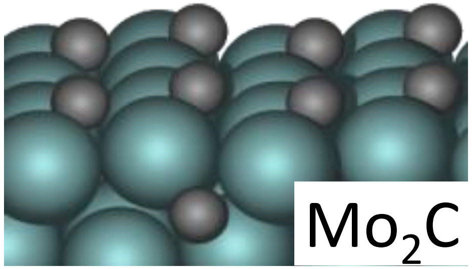
Progress: *Ex-situ* Fixed-Bed CFP
Opportunity to Harness Catalytic Multi-Functionality

To be effective, CFP catalysts need to possess both metallic-like sites for hydrogenation and acidic sites for dehydration

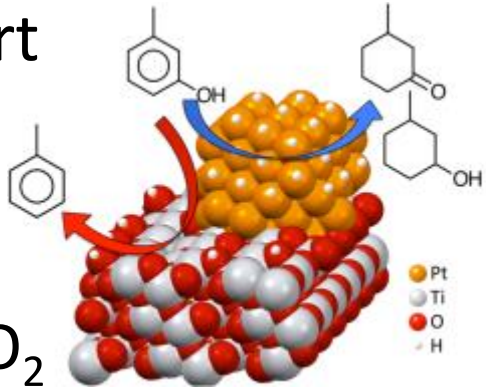
D. Ruddy, et al. *Green Chem* 16 (2014) 454

Classes of Multi-Functional Catalysts

- Single active phase possessing multiple active sites
  - Advantages: Single phase and site proximity
  - Disadvantage: Sites are not optimized



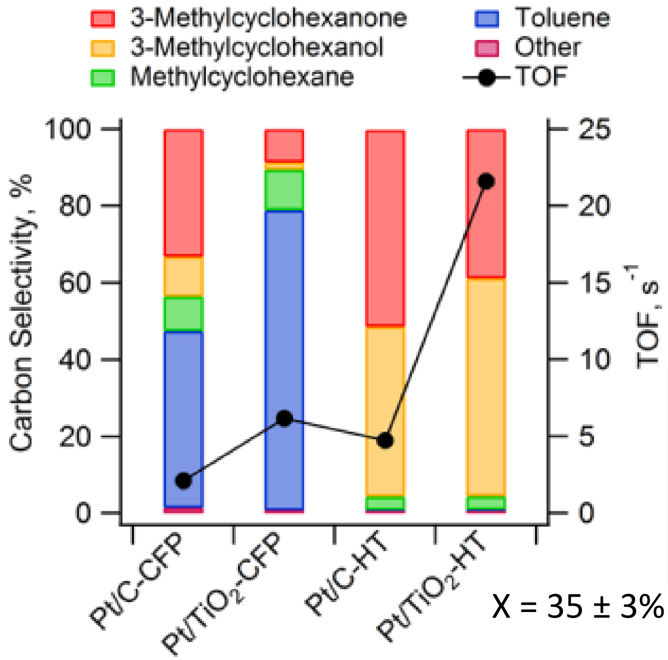
- Active phase dispersed on an active support
  - Advantages: Site optimization/proximity
  - Disadvantage: Particle sintering



Pt/TiO_2

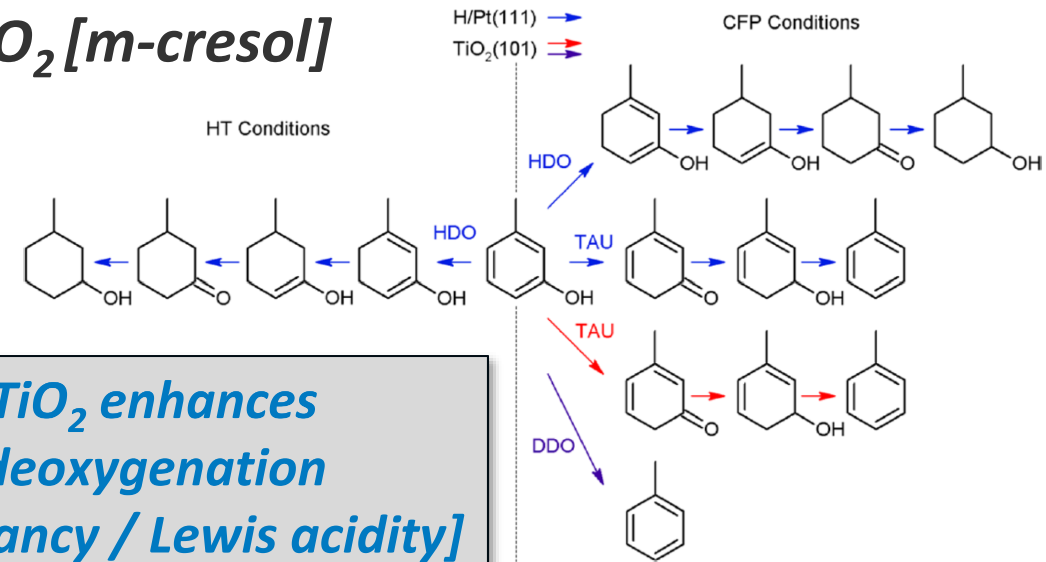
*Catalyst design and development in collaboration with ACSC and CCPC

Progress: *Ex-situ* Fixed-Bed CFP
Probed Multi-Functionality with Model Compounds



*CFP: 350°C, 0.5MPa, HT: 250°C, 2MPa

Pt/TiO_2 [m-cresol]

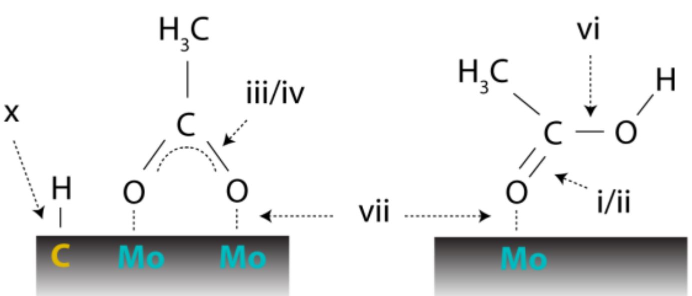


TiO_2 enhances deoxygenation [O vacancy / Lewis acidity]

M. Griffin, et al., *ACS Catalysis*, **2016**, 6, 2715

Mo_2C [acetic acid]

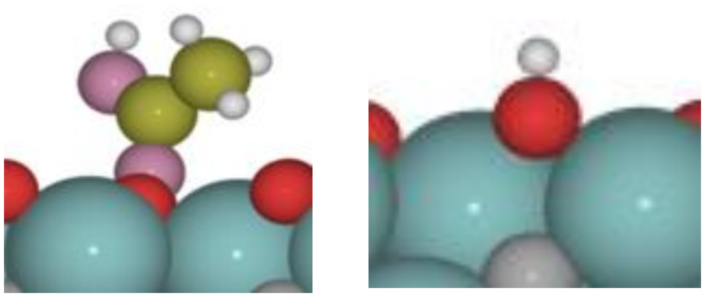
In-situ DRIFTS



Bidentate/Bridged

Monodentate Acid

Computational Modeling



0.75ML O/Mo-$Mo_2C(001)$

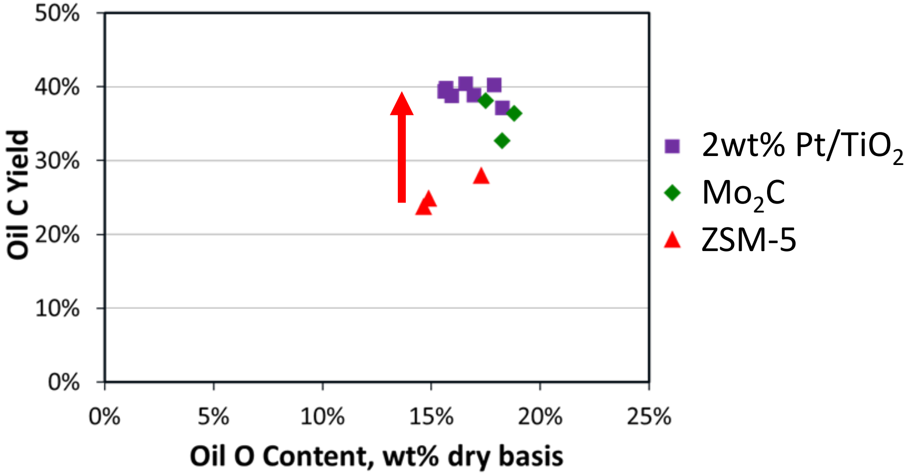
Mo_2C possesses Mo, C, and acidic hydroxyl sites under CFP conditions

J. Schaidle, et al. *ACS Catalysis*, **2016**, 6, 1181

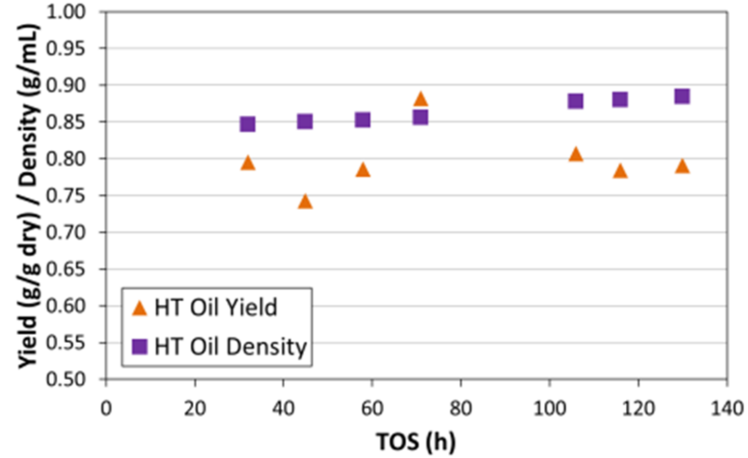
Progress: *Ex-situ* Fixed-Bed CFP 2017 State-of-Technology

Demonstrated high carbon yield and catalyst regenerability, yielding a CFP oil that can be hydrotreated in a single-stage unit to <1wt% O

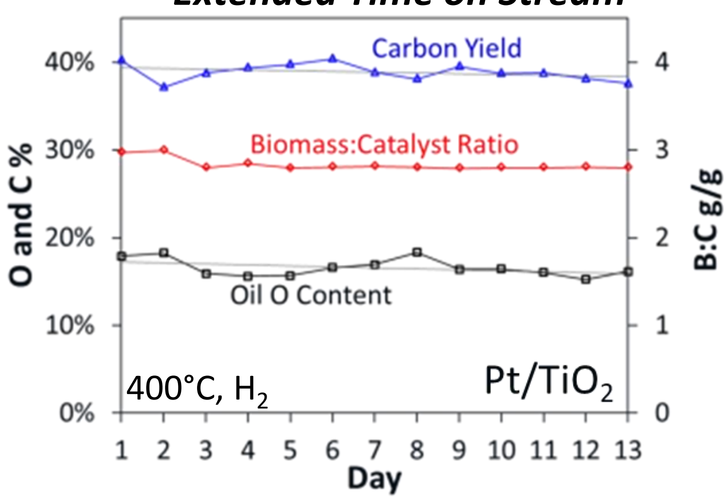
High C Yield during CFP



Single-Stage Hydrotreating at High C Yield

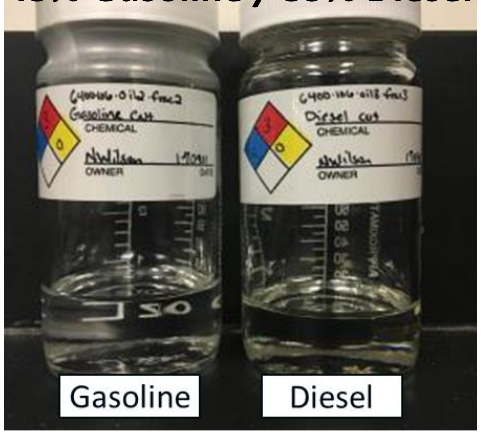


Extended Time on Stream



Fuel Production:

45% Gasoline / 39% Diesel

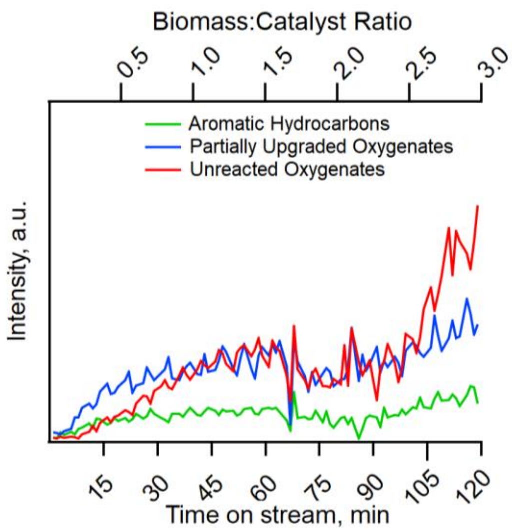


M. Griffin, et al., *Energy Environ. Sci.*, 2018, 11, 2904-2918

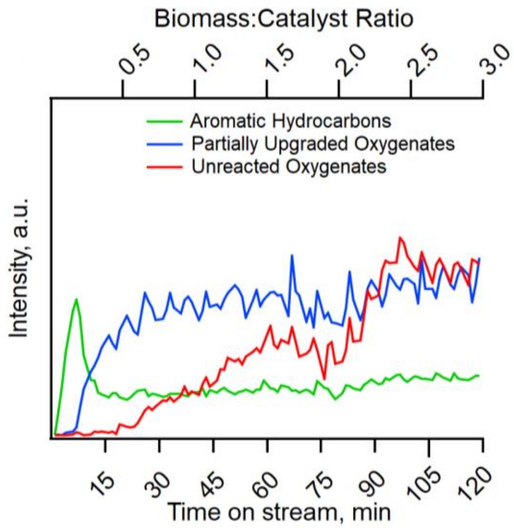
Progress: *Ex-situ* Fixed-Bed CFP
Established Role of Pt/TiO_2 Bifunctionality

Although the catalyst deactivates, the presence of Pt enhanced activity and/or reduced the rate of deactivation of TiO_2 active sites

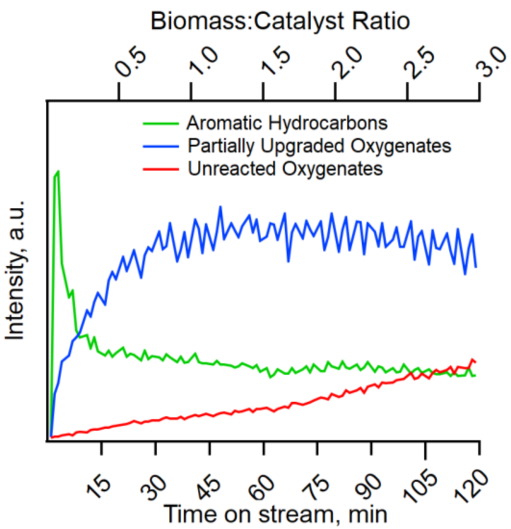
TiO_2 in N_2



TiO_2 in H_2/N_2



Pt/TiO_2 in H_2/N_2

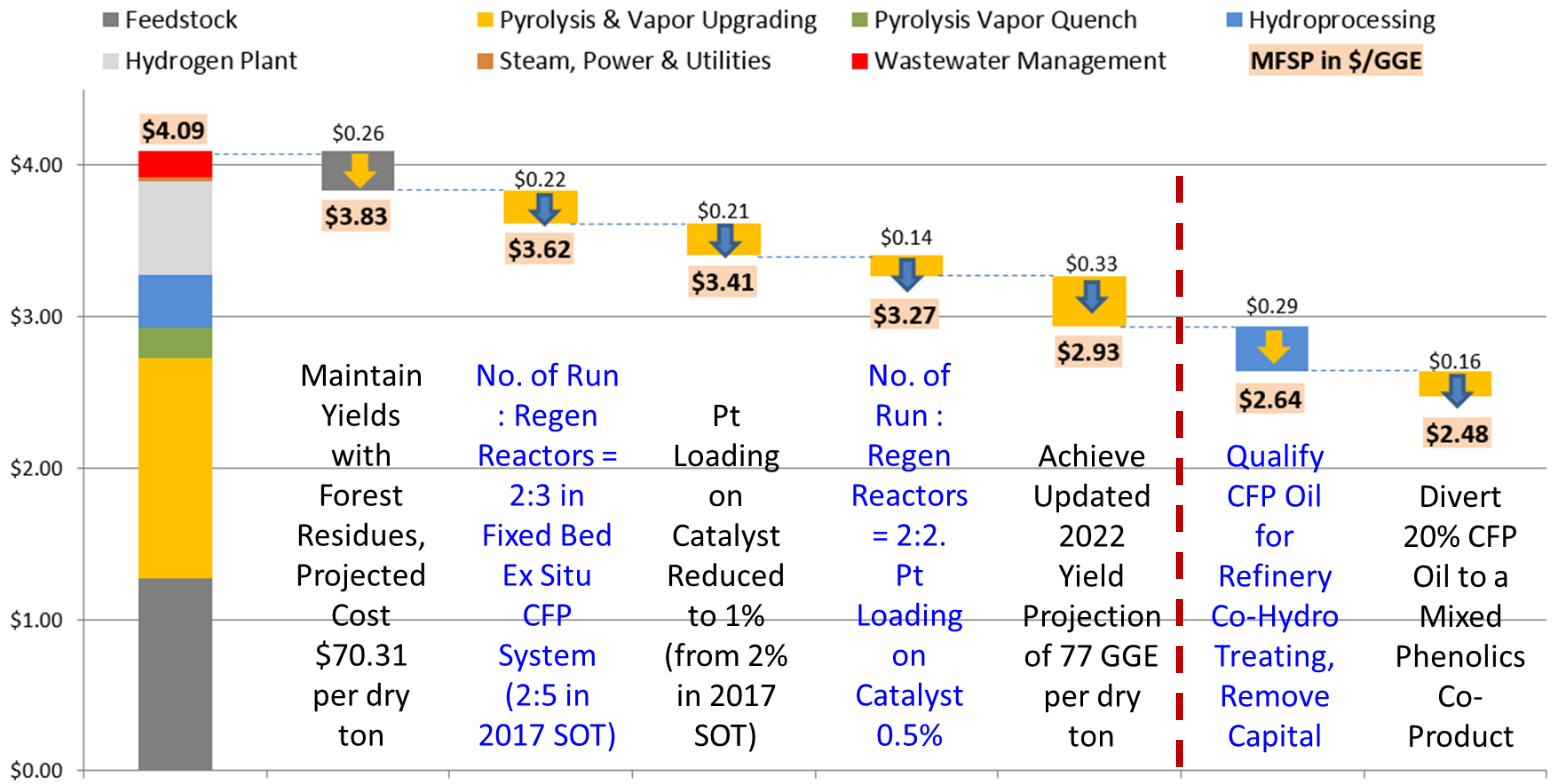


- Hydrogen spillover from Pt sites may (re)generate oxygen vacancies on TiO_2, which are capable of aryl-OH bond scission
- Pt may also prolong lifetime by facilitating the removal of coke precursors
- Hydrogenation activity is lost rapidly during early B:C ratios, which may be associated with the blocking of metallic Pt sites

M. Griffin, et al., *Energy Environ. Sci.*, **2018**, 11, 2904

Progress: *Ex-situ* Fixed-Bed CFP Routes to $2.5/GGE

Working in collaboration with our analysis team, we identified a viable route and associated technical targets to reach $2.5/GGE

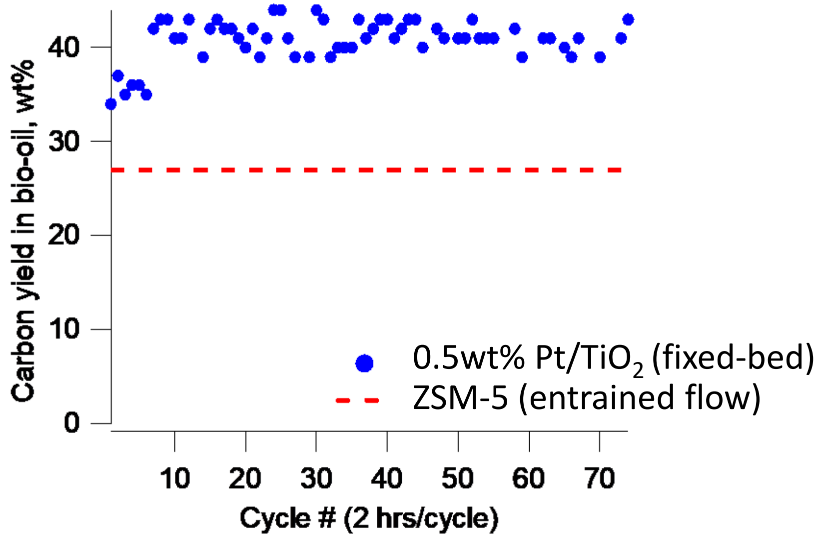


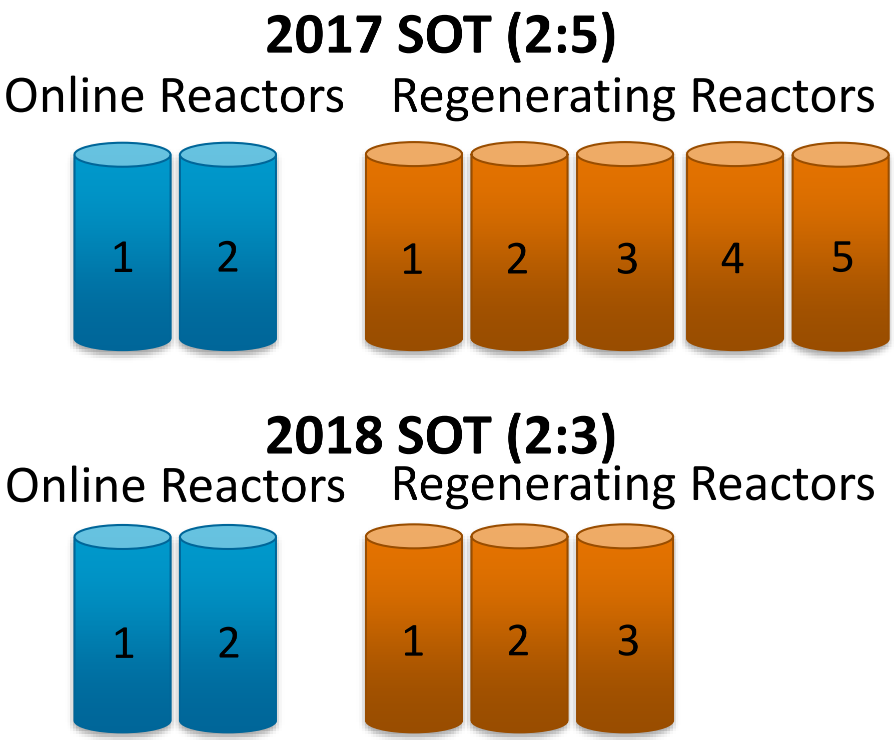
Future R&D efforts should be targeted at ***(1) improving yield, (2) reducing catalyst cost, (3) increasing time-on-stream before regeneration***, (4) maintaining performance with forest residues, (5) generating a co-product stream, and (6) evaluating refinery co-hydrotreating

Progress: *Ex-situ* Fixed-Bed CFP Technical Achievements toward 2018 SOT

Guided by TEA, we demonstrated improved yield and shorter regeneration time with a lower-loading Pt catalyst

Catalyst	Pt Disp.	Metal Sites	Acid Sites	Acid:Metal Site Ratio
2wt% Pt/TiO_2	33%	40 µmol/g	220 µmol/g	5.5
0.5wt% Pt/TiO_2	73%	38 µmol/g	190 µmol/g	4.9



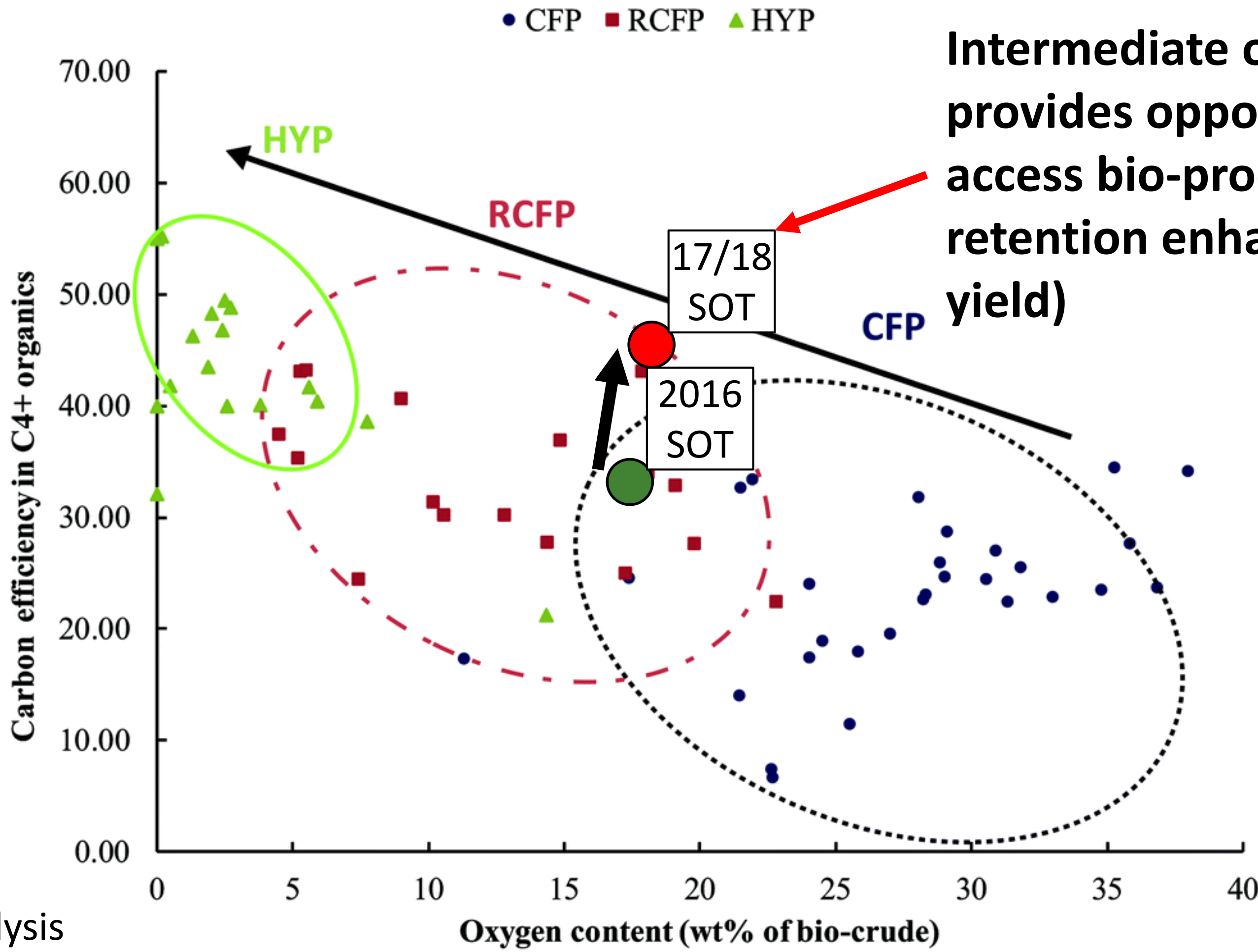


Technical Advancements:

- Reduced Pt loading from 2wt% to 0.5wt%, while achieving a similar ratio of metallic sites to acidic sites *[Informed by CatCost]*
- Increased yield from 69 GGE/dry ton (38.1% overall C efficiency) to 72 GGE/dry ton (39.7% overall C efficiency) and demonstrated extended operations
- Reduced regeneration time, resulting in fewer spare reactors (lower capex)

Progress: *Ex-situ* Fixed-Bed CFP Comparison to Literature

Pt/TiO_2 fixed-bed system achieves carbon efficiencies at the upper limit of those reported in literature



Intermediate oxygen content provides opportunity to access bio-products (oxygen retention enhances mass yield)

HYP: Hydropyrolysis

RCFP: CFP with co-feed of atmospheric P H_2

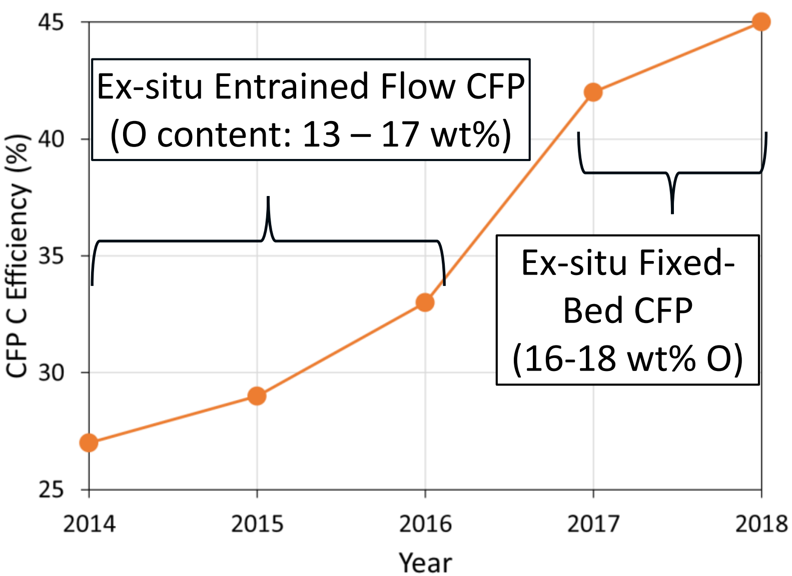
CFP: No H_2 co-feed

K. Wang, et al., *Green Chem.* 19 (2017) 3243

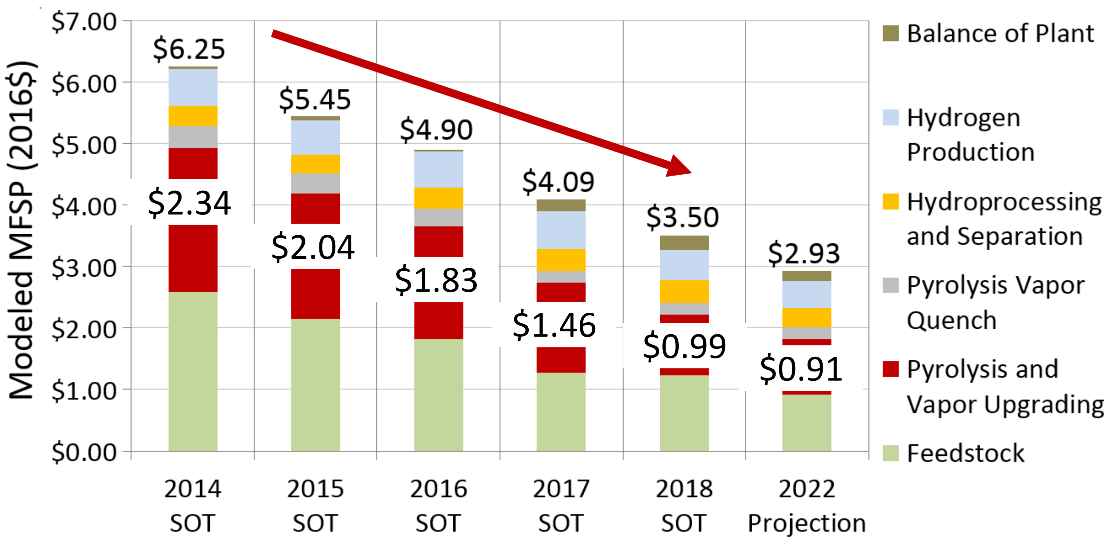
Progress: *Ex-situ* Fixed-Bed CFP Reducing Bio-fuel Production Costs

Reduced conversion costs by $0.8/GGE since 2016 by achieving high carbon efficiency in a fixed-bed system using a lower-loading Pt catalyst

CFP Carbon Efficiency



Biofuel Production Cost

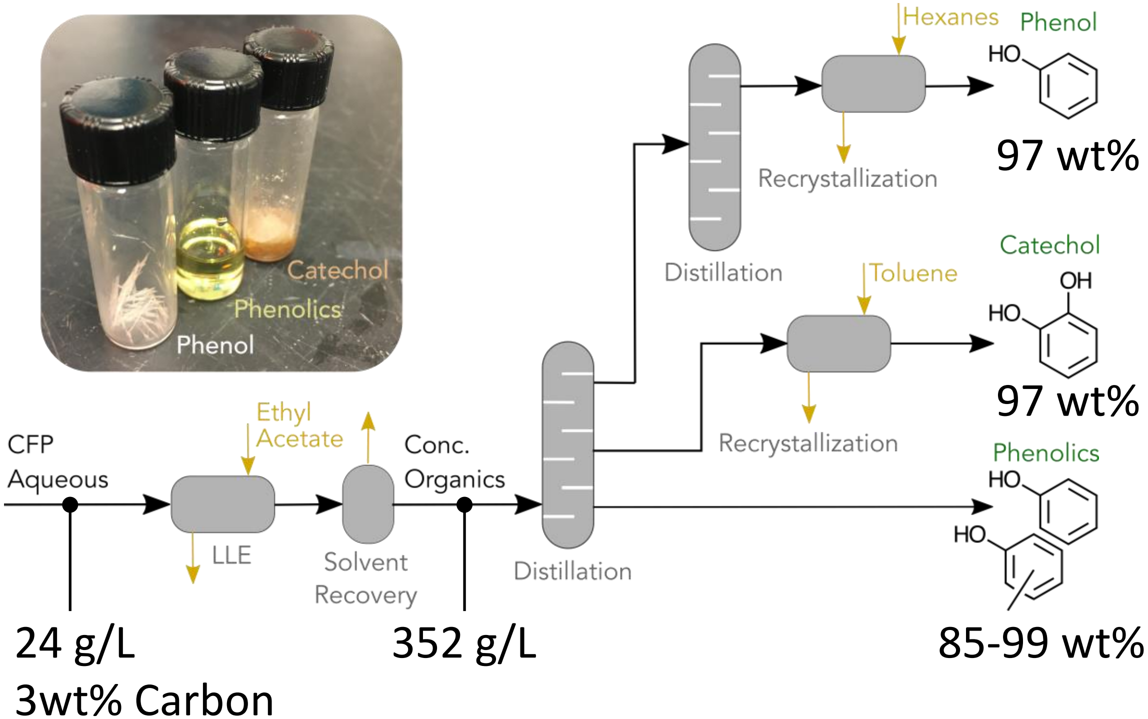


- CFP carbon efficiency increased from 42% to 45% from 2017 to 2018, but bio-oil oxygen content increased to 18.5wt% from 16.5wt%
  - *Cost reduction achieved by balancing CFP and hydrotreating*
- Achieves ~75% reduction in GHG emissions compared to conventional gasoline

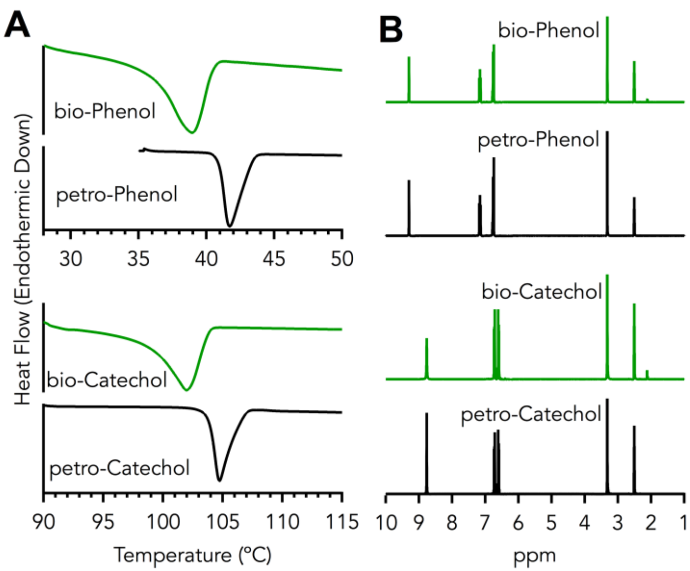
Progress: Co-Product Formation

Demonstrated the separation and purification of phenol, catechol, and mixed phenolics from the CFP aqueous stream

Separations Approach



Product Characterization



N. Wilson, et al., *in preparation*

Relevance: Bioenergy Industry

Reducing commercialization risk by developing a versatile catalytic fast pyrolysis technology platform that achieves high yields to biofuels and bioproducts

- This project ***addresses critical technical challenges*** limiting commercialization of CFP technologies: carbon efficiency and product diversity/quality
- This project engages in ***collaborative R&D with industrial partners through CRADAs*** to advance the CFP platform

ExxonMobil
Energy lives here™
Chemical Production via CFP

JM Johnson Matthey
Inspiring science, enhancing life
CFP Process and Catalyst Development

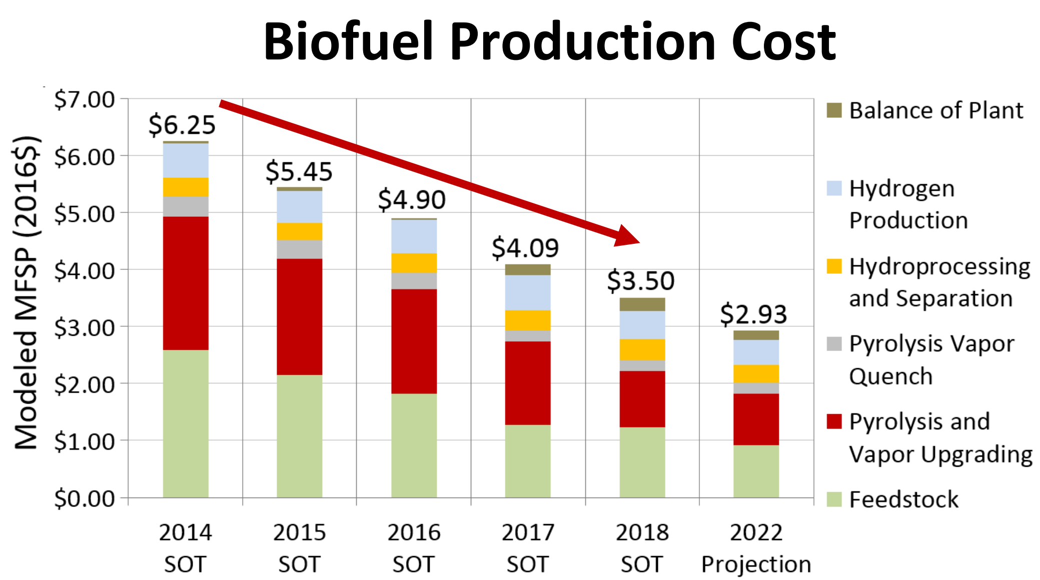
- CFP technologies being pursued commercially for both fuel and chemical production, moving to demonstration scale

Anellotech

Relevance: Reducing Biofuel Production Costs

Improving carbon efficiency and expanding product slate for CFP technology platform to enable cost reductions

- BETO Performance Goals (2018 MYP):
  - By 2022, verify hydrocarbon biofuel technologies that achieve at least 50% reduction in emissions relative to petroleum-derived fuels at **$3/GGE MFSP**
  - By 2030, verify hydrocarbon biofuel technologies that achieve at least 50% reduction in emissions relative to petroleum-derived fuels at **$2.5/GGE MFSP**
- *This project supports these performance goals by:*
  - Providing ***early-stage R&D*** to enable engineering-scale verification
  - Combining catalyst and process development to ***demonstrate fuel production at $3/GGE MFSP*** in 2019
  - ***Identifying viable routes to $2.5/GGE*** through co-products and co-processing

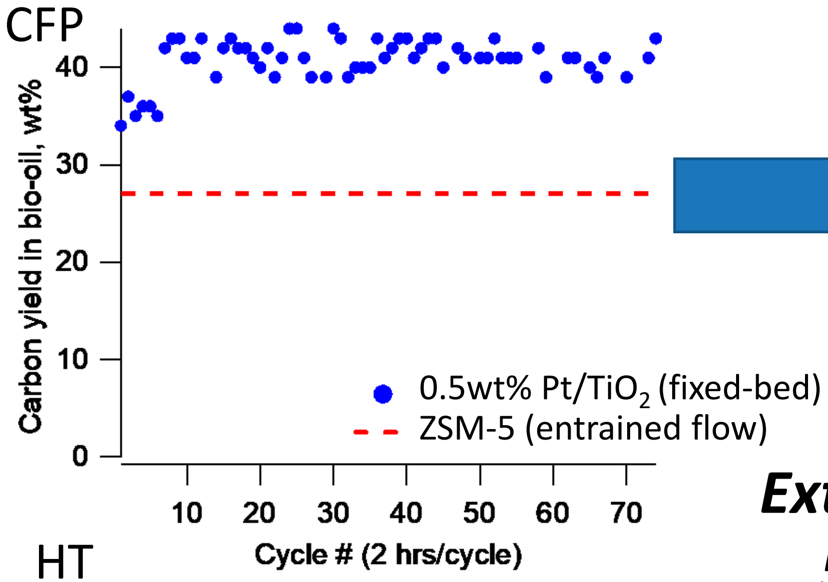


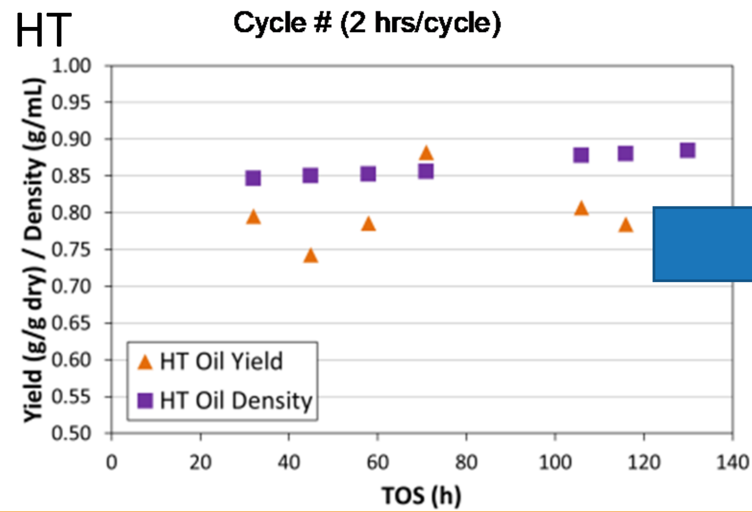
Future Work: Extended Operations

Demonstrate 500h of continuous operation for CFP and HT to evaluate long-term catalyst and process performance

Objectives:

- Evaluate impact of feedstock components (i.e., ash) on catalyst deactivation and lifetime
- Assess CFP and HT oil composition as a function of time on stream
- Identify operability challenges/limitations
- Provide guidance to ADO for engineering-scale verification and meet target MFSP of \$3/GGE



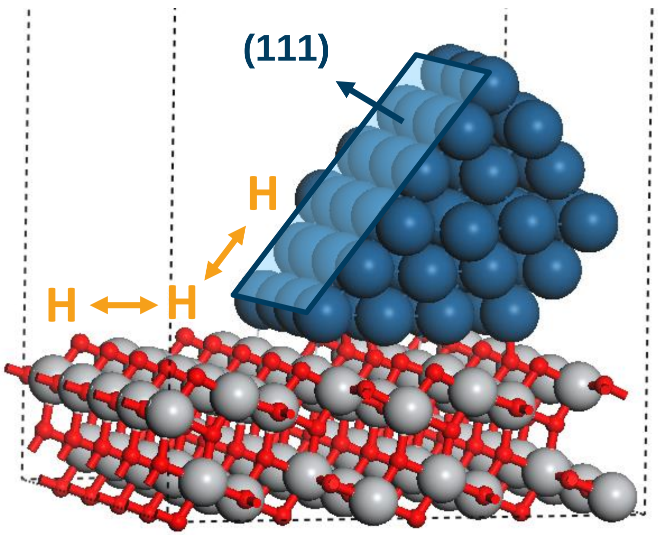


Extend to 500h

Future Work: Foundational Catalyst Insight

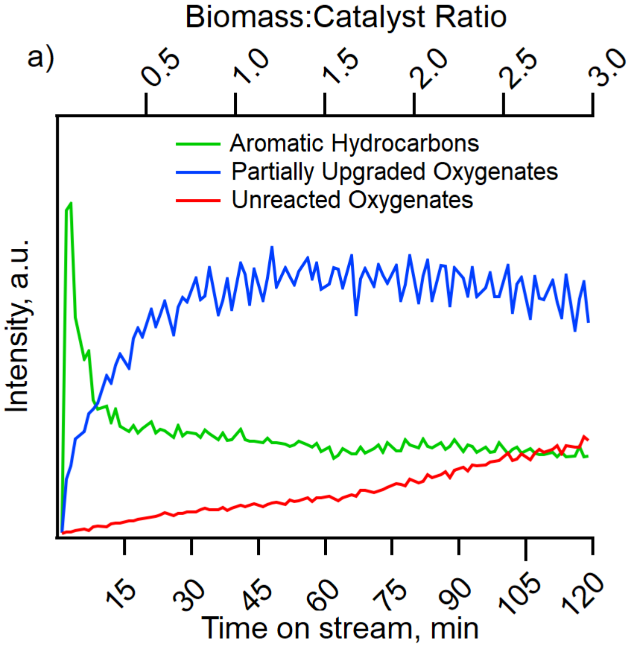
Leverage ChemCatBio enabling capabilities (ACSC, CCPC, CDM) to address TEA-guided targets for yield improvement and extend fixed-bed CFP cycle time

Provide Control over Critical Catalyst Properties
(acid:metal site ratio)



Evaluate Pt-TiO_2 interface effects with CCPC

Understand Deactivation Mechanisms

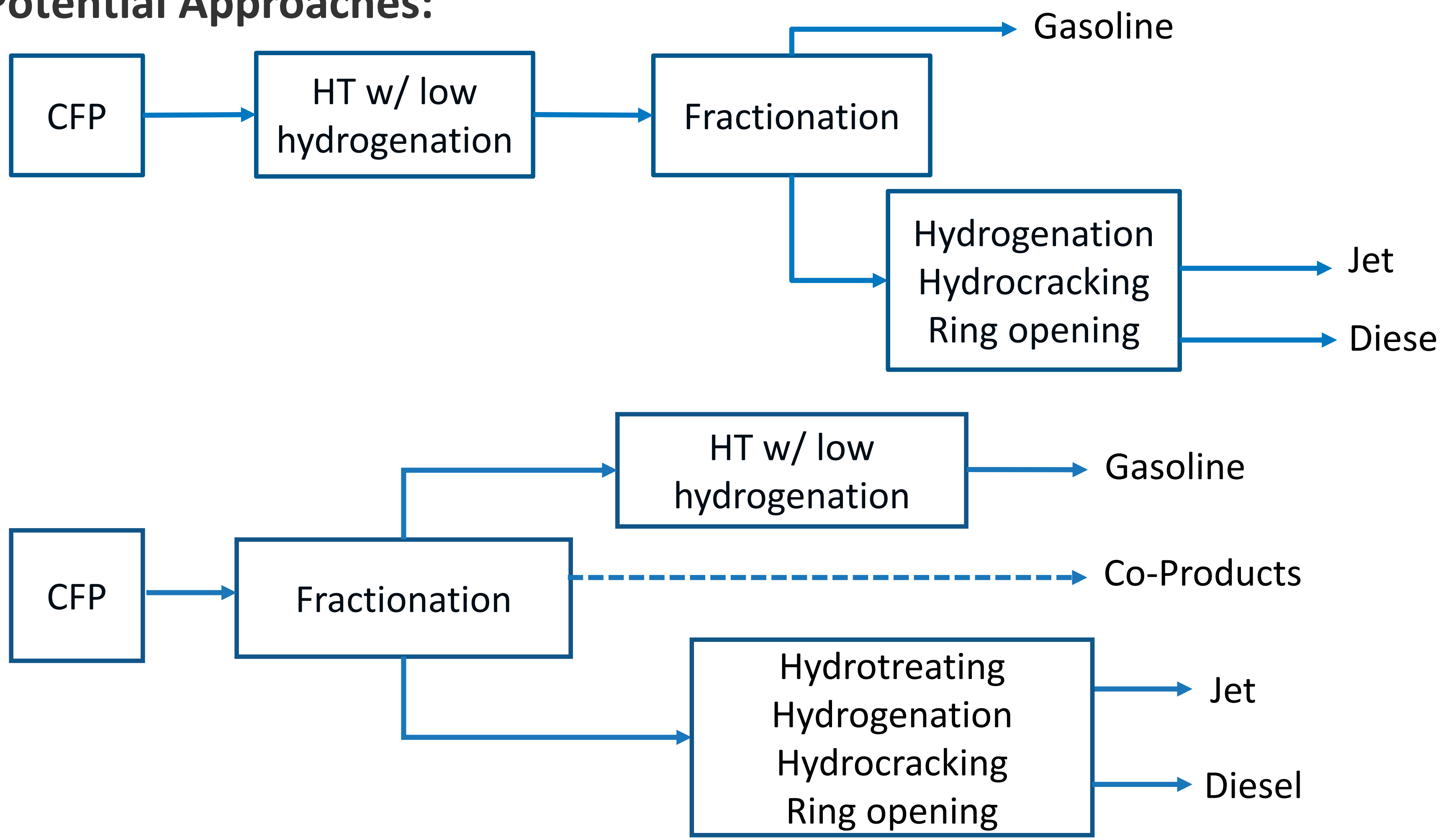


In-situ/in-operando characterization with ACSC

Future Work: Improve Fuel Properties

Develop and implement strategies to improve fuel properties of gasoline, diesel, and jet fractions

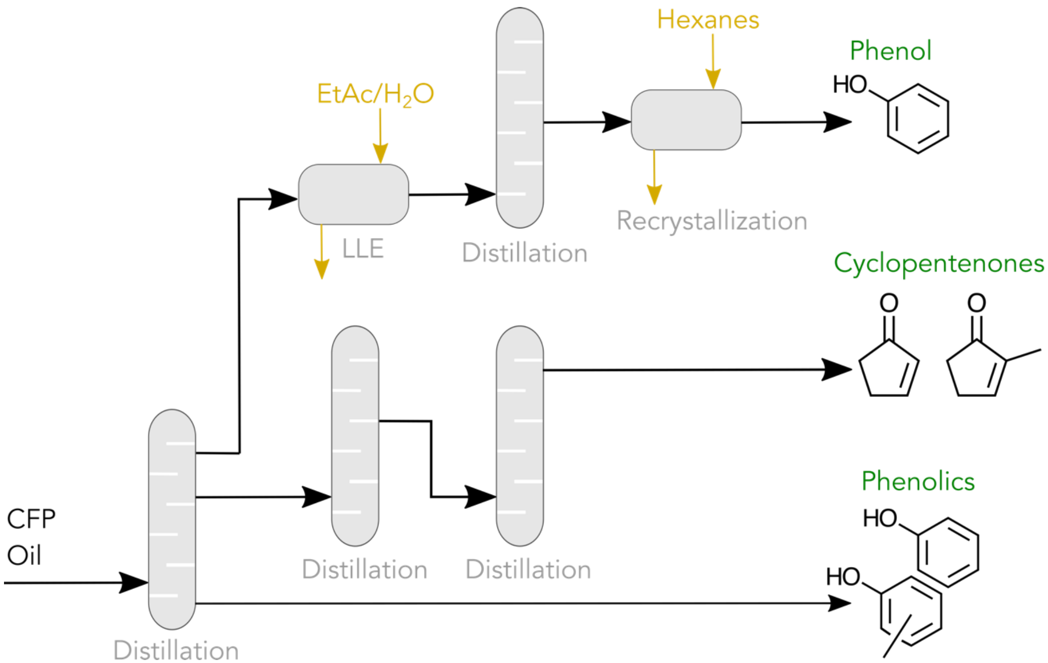
Potential Approaches:



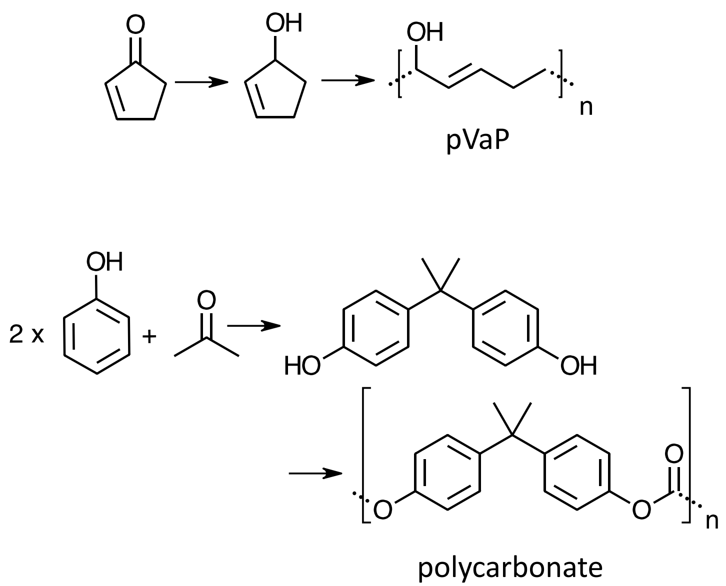
Future Work: Expand Co-Product Opportunities

Develop CFP bio-oil separation strategies to access chemical precursors and demonstrate polymer synthesis

Potential Separation Strategy



Bio-polymer Synthesis



In collaboration with performance advantaged bioproducts

Summary

Goal: Develop a ***CFP technology platform***, which is capable of producing both ***cost-competitive biofuels*** at greater than 75 gasoline gallon equivalent (GGE)/dry ton of biomass and ***high-value co-products***, and can be market-responsive by controlling the product distribution to meet market demand

Approach and Progress: Vertically-integrated, collaborative approach spanning from catalyst design to integrated bench-scale CFP with downstream HT, ***resulting in $1.4/GGE cost reduction since 2016***

Outcome: ***Demonstrate production of fuel blendstocks at $3.0/GGE*** MFSP and develop strategies to reduce MFSP to $2.5/GGE

Relevance to Bioenergy Industry: Addressing ***critical technical challenges*** limiting commercialization of CFP technologies: carbon efficiency and product diversity/quality

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Chemical Catalysis for Bioenergy

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ChemCatBio
Chemical Catalysis for Bioenergy

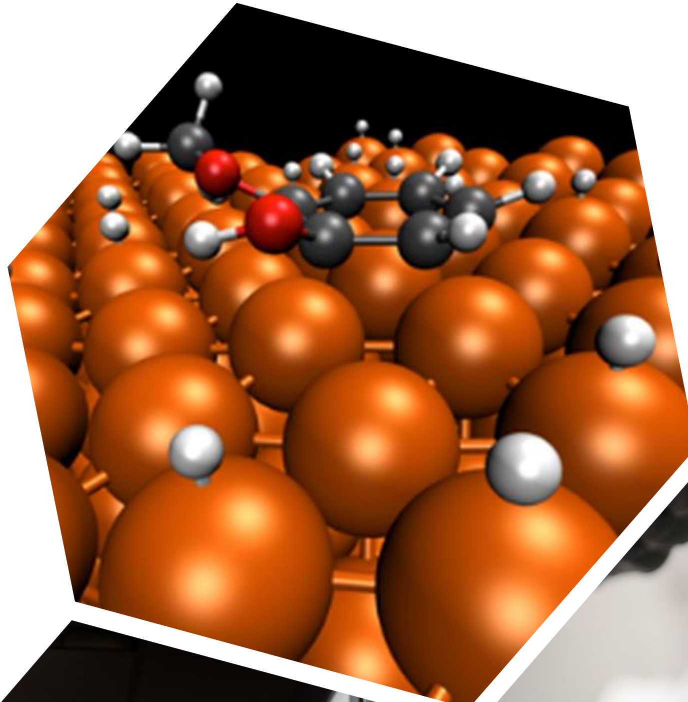
DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review

Catalytic Upgrading of Pyrolysis Products

Josh Schaidle, Kim Magrini, and Huamin Wang

Catalytic Upgrading

March 2019



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

Acronyms

- ACSC – Advanced Catalyst Synthesis and Characterization (enabling project within ChemCatBio)
- ADO – Advanced Development and Optimization Program (BETO)
- AKI – Anti-Knock Index
- CapEx – Capital Investment/Expense
- CCPC – Consortium for Computational Physics and Chemistry
- CDM – Catalyst Deactivation Mitigation (new enabling project within ChemCatBio, started in FY19)
- CFP – Catalytic Fast Pyrolysis
- CRADA – Cooperative Research and Development Agreement
- DCR – Davison Circulating Riser
- FCC – Fluid Catalytic Cracking
- GCxGC TOFMS – 2-Dimensional Gas Chromatography with Time-of-Flight Mass Spectrometry
- GGE – Gasoline Gallon Equivalent
- GHG – Greenhouse Gas
- HGF – Hot Gas Filter
- HT – Hydrotreating
- HYP – Hydropyrolysis
- IRR – Internal Rate of Return
- LLE – Liquid-Liquid Extraction
- MFSP – Minimum Fuel Selling Price
- MYP – Multi-Year Plan (BETO)
- RCFP – Reactive Catalytic Fast Pyrolysis
- SOT – State of Technology
- TCF – Technology Commercialization Fund
- TEA – Technoeconomic Analysis
- TOS – Time on Stream
- WWT – Wastewater Treatment
- XPS – X-ray Photoelectron Spectroscopy

Responses to Previous Reviewers' Comments (FY17)

We thank the reviewers for their support of our accomplishments, team, and management. We acknowledge that catalytic fast pyrolysis (CFP) is a complex and challenging process, but it has many distinct advantages. CFP allows for utilization of the entire plant matter and produces a narrower product slate as compared to fast pyrolysis. We greatly appreciate the reviewers' constructive feedback and guidance on how to best advance the state of technology towards commercialization, especially in regards to innovative process configurations, alternative downstream processing, evaluation of off-the-shell catalysts, reductions in catalyst cost, integration with modeling, and utilization of refined or fractionated feedstocks. The reviewers also raised a number of valid concerns and we have addressed specific comments below.

Feedstock properties definitely affect CFP performance. These effects are currently being evaluated in the Thermochemical Feedstock Interface project, a joint effort between NREL, PNNL, and INL, and will be further evaluated in the future as part of the Feedstock Conversion Interface Consortium. We have evaluated various biomass fractions and feedstocks for CFP in small-scale experiments (py-GCMS/py-MBMS) to target specific product distributions, and will evaluate CFP of these fractions/residues at a larger scale in 2018 using our 2" fluidized bed reactor system. We plan to use these experiments to guide feedstock selection (and feedstock engineering).

We agree that the high catalyst replacement rate for *in-situ* CFP is a major challenge for that approach. The red mud catalyst under development within this project was identified because of its low cost, resistance to deactivation, regenerability, and comparable catalytic performance to HZSM-5. However, we agree that the red mud composition and properties will not be consistent as it is not deliberately produced as a catalytic material. To address this concern, our research is and will continue to be focused on determining the composition-performance relationship of red mud and also on assessing red mud variability based on the source. Using this information, we can evaluate the commercial feasibility of using red mud as a catalyst for *in-situ* CFP and can identify strategies to produce similar low cost materials, but with consistent properties.

We agree with the reviewers that processing lignin and cellulose together through CFP is challenging; however, we believe that significant improvements can still be made in this area through design of bi(multi)-functional catalysts and implementation of new process configurations (e.g., fixed-bed, catalytic hot gas filtration. or dual fixed-bed systems) that enable strategic upgrading based on targeted reaction chemistry.

We also agree that catalyst cost needs to be reduced, and we are currently pursuing two main avenues for cost reduction: (1) reduce/minimize the use of noble metals and (2) increase catalyst lifetime by limiting coke formation and removing other impurities (e.g., tar, aerosols, ash, char) from the pyrolysis vapors through hot gas filtration (or catalytic hot gas filtration).

As a starting point, this project focused on hydrotreating because (1) it is a fairly mature and straightforward approach to upgrade bio-oil to produce hydrocarbon fuel blendstocks and (2) CFP enables single-stage hydrotreating. Moving forward, we are also evaluating chemical co-product opportunities and refinery integration, in conjunction with the BETO-funded Strategies for Co-Processing in Refineries project.

Beyond being cost-competitive, commercialization is driven by product-market fit. As the reviewers suggested, we are pursuing additional industrial partnerships and are in the process of establishing a CRADA with a large petrochemical company this year to identify and target chemicals of interest that can be produced from CFP.

Go/No-Go Review Highlights (March 2018)

- ***Go/No-Go:*** Feasibility Assessment of Fixed-Bed CFP System
- ***Description:*** Based on TEA and bench-scale performance, determine whether ex-situ CFP fixed bed systems are a viable option for meeting our FY22 targets ($3.0/GGE) and have a viable route to $2.5/GGE (FY30)
- ***Criteria:*** The decision criteria are (1) MFSP (fixed-bed systems must demonstrate a MFSP at or below that of fluidized bed systems), (2) FY18 technical targets (fixed-bed systems must demonstrate that they can meet or exceed the FY18 CFP targets for C efficiency, H/C molar ratio, oxygen content, and selectivity to diesel/jet range products), and (3) identification of viable routes to $2.5/GGE.
- ***Outcome:*** Based on our first-of-its-kind, side-by-side comparison of CFP approaches, the fixed bed system achieved a MFSP value of $4.34/GGE (2014$), which was lower than both the ex-situ entrained flow CFP system ($4.55/GGE) and the in-situ CFP system ($4.55/GGE). The fixed-bed system using a Pt/TiO_2 catalyst also achieved carbon efficiency values (42% CFP, 38% overall) that significantly exceeded 2018 targets (36% CFP, 33% overall). Working with the Thermochemical Platform Analysis project (2.1.0.302), we identified a viable route to $2.5/GGE using the ex-situ fixed bed CFP system, which leverages refinery integration (reduced capex) and co-product opportunities (increased revenue).

Publications (1 of 3)

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A. Wang, D. Austin, A. Kamakar, G.M. Bernard, V.L. Michaelis, M.M. Yung, H. Zeng, and H. Song, “Methane Upgrading of Acetic Acid as a Model Compound for a Biomass-Derived Liquid over a Modified Zeolite Catalyst,” ACS Catalysis, 2017, 7 (5), 3681–3692. DOI: 10.1021/acscatal.7b00296

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Presentations (1 of 7)

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Braden Peterson, Chaiwat Engtrakul, Nolan Wilson, Stefano Dell’Orco, Jessica Olstad, Yves Parent, Kim Magrini, “Conditioning of Pyrolysis Vapors via Catalytic Hot-Gas Filtration for Enhancement of the Ex-Situ Catalytic Fast-Pyrolysis Process”, TCS 2018, October 8-10, 2018, Auburn, AL.

Presentation at the AIChE National Meeting, Pittsburgh (October 31, 2018) “Renewable Materials from Catalytic Fast Pyrolysis”, Mark R. Nimlos, A. Nolan Wilson, Christopher M. Kinchin and Calvin Mukarakate

TCS-Biomass, Auburn, (October 9, 2018) “Separation and Utilization of Catalytic Fast Pyrolysis Co-Products”, A. Nolan Wilson, Calvin Mukarakate, Abhijit Dutta & Mark Nimlos

TCS-Biomass, Auburn, (October 9, 2018) “Carbon from Thermochemical Conversion Processes for Use in Advanced Energy Storage Devices”, Mark R. Nimlos, A. Nolan Wilson, Chunmei Ban, Bryon S. Donohoe, Peter N. Ciesielski, Michael Griffin and Robert M. Baldwin

Presentation at the ACS National Meeting for Storch Award Symposium “Catalytic Fast Pyrolysis for Chemicals and Materials”, Mark R. Nimlos, A. Nolan Wilson, Christopher M. Kinchin and Calvin Mukarakate

Kristiina Iisa, Alexander R. Stanton, Rachel Minor, Calvin Mukarakate, Mark J. Nimlos, Role of cellulose and lignin in catalyst deactivation during catalytic fast pyrolysis over HZSM-5, Presentation at 256th ACS National Meeting, Boston, MA, August 19-23.

F. Baddour, D. Ruddy, C. Nash, S. Habas, J. A. Schaidle, “A Molecular Approach to the Design and Synthesis of Metal Carbide Catalysts for Biomass Upgrading”, 256th ACS National Meeting, Boston, MA, August 20, 2018.

Presentations (2 of 7)

S. Habas, "High-Throughput Synthesis of Nanostructured Catalysts for Biomass Conversion Processes", 256th ACS National Meeting, Boston, MA, August 20, 2018.

K. Magrini, J. Olstad, M. Jarvis. Y. Parent, S. Deutch, B. Peterson, K. Iisa, "Upgrading Biomass Pyrolysis Vapors to Hydrocarbon Fuels", presented at the 2018 Renewable Energy Sources - Research and Business (RESRB), June 18-20, 2018, Brussels, Belgium.

Mark R. Nimlos, A. Nolan Wilson, Christopher M. Kinchin, and Calvin Mukarakate, "Catalytic Fast Pyrolysis for Chemicals and Materials", ACS National Meeting for Storch Award Symposium, New Orleans, LA, March 2018.

Huamin Wang, Daniel M. Santosa, Douglas C. Elliott, Foster Agblevor, In Situ Catalytic Fast Pyrolysis and Hydrotreating to Convert Biomass to Hydrocarbon Fuel Blendstock. Presented at 2018 ACS Spring Meeting, New Orleans, LA, March 20, 2018

Calvin Mukarakate, Kristiina Iisa, Michael Griffin, Connor Nash, Mengze Xu and Josh Schaidle. CFP of Biomass using Mo2C Unravels Promise and Challenges with HDO Catalysts. Spring 2018 255th ACS Meeting, New Orleans, Invited Talk.

C. Farberow, "On the Role of Surface Adsorbed Oxygen in Ethanol Reaction Pathways on Mo2C", Oral Presentation, ACS Annual Meeting, New Orleans

J. Hensley, "Transitioning Rationally Designed Catalytic Materials to Real "Working" Catalysts at Commercial Scale: Nanoparticle Materials", Oral Presentation, ACS Annual Meeting, New Orleans

M. Griffin, "Ex-Situ Catalytic Fast Pyrolysis over Pt/TiO2: Fixed Bed Hydrodeoxygenation Followed By Hydrotreating to Produce Fuel Blendstocks", Oral Presentation, ACS Annual Meeting, New Orleans

S. Habas, F. Baddour, D. Ruddy, J. Schaidle, "Advances in Nanoscale Metal Carbide and Phosphide Catalysts for Biomass Conversion Processes", Invited Presentation, 255th American Chemical Society National Meeting and Exposition, New Orleans, LA, March 21, 2018.

S. Habas, "Advances in Nanoscale Catalysts for Conversion of Biomass to Renewable Fuels", University of Southern California Department of Chemistry Seminar, Los Angeles, CA, March 27, 2018.

Huamin Wang, Daniel M. Santosa, Douglas C. Elliott, Foster Agblevor, Upgrading of In Situ Catalytic Fast Pyrolysis Bio-oil to Hydrocarbon Fuel Blendstock. Presented at 2017 AIChE Annual Meeting, Minneapolis, MN, November 1, 2017.

Presentations (3 of 7)

S. Habas, "Advances in Nanoscale Metal Phosphide and Carbide Catalysts for Biomass Conversion Applications", University of Kansas Department of Chemical and Petroleum Engineering Seminar, Lawrence, KS, November 16, 2017.

J. Schaidle, "The Chemical Catalysis for Bioenergy Consortium: Enabling Production of Biofuels and Bioproducts through Catalysis", Advanced Bioeconomy Leadership Conference Next 2017. San Francisco, CA. October 17th, 2017.

Huamin Wang, Daniel M. Santosa, Douglas C. Elliott, Foster Agblevor F, In Situ Catalytic Fast Pyrolysis (CFP) using Robust and Low-cost Red Mud Catalyst. Presented at Bioeconomy 2017, Washington DC, DC, July 10, 2017.

Huamin Wang, Daniel M. Santosa, Suh-Jane Lee, Mariefel V. Olarte, John G. Frye, Douglas C. Elliott, Alan H. Zacher, Foster Agblevor. Hydrotreating of Bio-oil with Improved Quality: In Situ Catalytic Fast Pyrolysis and Bio-oil Stabilization. Presented at 254th ACS National Meeting & Exposition, Washington DC, DC, August 21, 2017.

J. Schaidle, "Enabling Production of Biofuels and Biochemicals through Catalysis: NREL's Thermochemical Biomass Conversion Platform", Invited Seminar, University of California Santa Barbara. August 25th, 2017. (Invited Talk)

Huamin Wang, Daniel M. Santosa, Douglas C. Elliott, Foster Agblevor, In Situ Catalytic Fast Pyrolysis (CFP) using Robust and Low-cost Red Mud Catalyst. Presented at Commercializing Industrial Biotechnology 2017, San Diego, CA, September 18, 2017.

Foster A Agblevor, Oleksandr Hietsoi, G. Smith, Huamin Wang, Deposition of inorganic elements on red mud catalyst and their effect on catalyst activity. Presented at TCBiomass 2017, Chicago, IL, September 20, 2017.

Huamin Wang, Daniel M. Santosa, Douglas C. Elliott, Foster Agblevor, Balakrishna Maddi, In Situ Catalytic Fast Pyrolysis (CFP) using Robust and Low-cost Red Mud Catalyst. Presented at TCBiomass 2017, Chicago, IL, September 20, 2017.

J. Schaidle, "Enabling Production of Biofuels and Bioproducts through Catalysis: NREL's Thermochemical Biomass Conversion Platform", Invited Seminar, Karlsruhe Institute of Technology, Karlsruhe, Germany. June 19th, 2017. (Invited Talk)

C. Mukarakate, M. Xu, M. Griffin, C. Nash, E. White, K. Iisa, M. Nimlos, D. Ruddy, J. Schaidle, "Alternatives to Zeolites for Catalytic Fast Pyrolysis of Biomass: Mo2C and Pt/TiO2", European Biomass Conference and Exhibition, Stockholm, Sweden. June 12th, 2017.

Presentations (4 of 7)

S. Habas, E. Roberts, L. Wang, D. Ruddy, E. White, F. Baddour, M. Griffin, J. Schaidle, N. Malmstadt, R. Brutchey "High-Throughput Continuous Flow Synthesis of Nickel Nanoparticles for the Catalytic Hydrodeoxygenation of Guaiacol" North American Catalysis Society Meeting, Denver, CO, June 7, 2017.

M. Griffin, et al., "Ex-Situ Catalytic Fast Pyrolysis of Biomass over Pt/TiO2: Multiscale Analysis of Model Compound and Whole Vapor Deoxygenation", North American Catalysis Society meeting in Denver, CO. June 2017.

C. Farberow, "Ethanol Dehydrogenation and Dehydration: Fundamental Insights into Deoxygenation Reactions on Mo2C", North American Catalysis Society meeting in Denver, CO. June, 2017.

C. Mukarakate, M Xu, K McKinney, K Iisa. C. Nash, D. Ruddy, M. Nimlos and J. Schaidle. "Biomass Pyrolysis Vapor Deoxygenation over Mo2C to Produces Paraffinic and Aromatic Molecules", North American Catalysis Meeting (NAM) 2017 in Denver CO.

M. Nimlos, et al., "Catalytic Fast Pyrolysis for Renewable Fuels and Products from Biomass" Shandong Academy of Science, Jinan, China.

M. Nimlos, et al., "Catalytic Fast Pyrolysis for Renewable Fuels and Products from Biomass", Southwest Forestry University, Kunming, China.

M. Xu, C. Mukarakate, R. Richards, and M. Nimlos, "Enhanced Aromatic Production from Lignocellulosic Biomass Upgrading Over In-framework Ga-ZSM5 Catalysts via a Systematic Study." North American Catalysis Meeting (NAM) 2017 in Denver CO.

M.M. Yung, A. Starace, C. Mukarakate, and K.A. Magrini, "Enhanced Stability and Aromatic Hydrocarbon Production during Biomass Pyrolysis Vapor Upgrading on Ni-modified ZSM-5," North American Catalysis Society NAM 25, Denver, CO, June 2017.

C. Sievers, C. Okolie, G.S. Foo, M. Rodrigues, M.M. Yung, and L. Martins, "Deactivation of Pt/HBEA during Hydrodeoxygenation By Formation of Chemisorbed Surface Species," North American Catalysis Society NAM 25, Denver, CO, June 2017.

Huamin Wang, Daniel M. Santosa, Suh-Jane Lee, Mariefel V. Olarte, John G. Frye, Douglas Elliott, Alan H. Zacher, Foster A. Agblevor, Stable Bio-oil for Upgrading to Biofuel: Bio-oil Stabilization and Catalytic Fast Pyrolysis. Presented at NAM25, North American Catalysis Society Meeting 2017, Denver, CO, June 4-9, 2017.

Presentations (5 of 7)

S. Paleg, C. Nash, J. Schaidle, L. Thompson, "Tuning the Selectivity in Upgrading Reactions of Bio-Oil Model Compounds with Alkali Promotion of Molybdenum Carbide", North American Catalysis Society Meeting, Denver, CO. June 2017.

M.M. Yung and K.A. Magrini, "Synthetic Fuel Production from Biomass and Catalysis Research at NREL," Department of Chemical Engineering Guest Lecture, University of South Florida, Tampa, FL, April 2017.

M.M. Yung, A. Starace, C. Mukarakate, and K.A. Magrini, "Biofuel production by catalytic pyrolysis vapor upgrading: Effects of nickel loading and pretreatment on modified ZSM-5," 253rd American Chemical Society National Meeting, San Francisco, CA, April 2017.

K. Magrini, M. Jarvis, J. Olstad, Y. Parent, M. Yung, S. Deutch, K. Iisa, M. Sprague, G. Powell, "Upgrading Biomass Pyrolysis Vapors to Fungible Hydrocarbon Intermediates", 253rd American Chemical Society National Meeting, San Francisco, CA, April 2017.

Mark Jarvis, Jessica Olstad, Yves Parent, Kim Magrini, " Biomass fast pyrolysis with Catalytic Hot Gas Filtration", 253rd American Chemical Society National Meeting, San Francisco, CA, April 2017.

C. Okolie, G. Foo, M.V. Rodriues, M. Yung, and C. Sievers, "Deactivation paths during hydrodeoxygenation of aromatic oxygenates of Pt/HBEA," 253rd American Chemical Society National Meeting, San Francisco, CA, April 2017.C. Mukarakate*, M. Xu, K. Iisa, M. Nimlos, D. Ruddy, and J. Schaidle, "Biomass Vapor Upgrading to Produce Hydrocarbon Fuels", Spring ACS Meeting, San Francisco, CA. April 2017.*Invited presentation

M. Xu*, C. Mukarakate, R. Richards, and M. Nimlos, "Enhanced Aromatic Production from Lignocellulosic Biomass Upgrading Over In-framework Ga-ZSM5 Catalysts Via A Systematic Study", Spring ACS Meeting, San Francisco, CA. April 2017.

Matthew M. Yung*, Anne K. Starace, Calvin Mukarakate, and Kimberly A. Magrini, "Biofuel production by catalytic pyrolysis vapor upgrading: Effects of nickel loading and pretreatment on modified ZSM-5", Spring ACS Meeting, San Francisco, CA. April 2017.

M. Griffin*, G. Ferguson, C. Mukarakate, M. Biddy, D. Ruddy, R. French, F. Baddour, G. Beckham, J. Schaidle, "Ex-situ Catalytic Fast Pyrolysis of Lignocellulosic Biomass over Pt/TiO2: Fundamental Insight to Large Bench Scale Evaluation", Spring ACS Meeting, San Francisco, CA. April 2017.

Presentations (6 of 7)

J. Schaidle*, "Biomass Utilization: Opportunities and Challenges", National Association of State Foresters Joint Committee Meeting, Washington, DC. February 8th, 2017. *Invited presentation

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/TiO2 Catalysts", AIChE Annual Meeting, San Francisco, CA. November 17th, 2016.

C. Farberow*, C. Nash, J. Schaidle, "Mechanistic Insights into Carbon-Oxygen Bond-Breaking on Mo2C Catalysts: Ethanol Dehydration", AIChE Annual Meeting, San Francisco, CA. November 17th, 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.

Kristiina Iisa, Kellene Orton, Richard French, Abhijit Dutta, Joshua Schaidle, "Optimizing Catalytic Fast Pyrolysis and Hydrotreating for the Production of Biofuels," 2016 AIChE Annual Meeting, November 13-18, 2016, San Francisco, CA.

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.

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.

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.

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.

D. Santosa, F. Agblevor, H. Wang, S.-J. Lee, C. Drennan, D. Elliott, B. Roberts, C. Lukins, I. Kutnyakov. "Upgrading Forest Thinning to Fuels: In-situ Catalytic Fast Pyrolysis (CFP) with Red Mud (RM) and Subsequent Catalytic Hydrotreating (HT)", TCS 2016, Chapel Hill, NC, November 1-3, 2016.

Presentations (7 of 7)

C. Mukarakate, M. Xu, C. Nash, K. Iisa, M. Nimlos, D. Ruddy, and J. Schaidle. Biomass "Pyrolysis Vapor Deoxygenation over Mo2C Produces Paraffinic and Aromatic Molecules: The Deactivation and Reactivation of Mo2C", TCS 2016, Chapel Hill, NC, November 1-3, 2016.

M. Xu, C. Mukarakate, R. Richards, and M. Nimlos. "Deactivation Over Multilamellar MFI Nanosheet Zeolite during Upgrading Biomass Pyrolysis Vapors", TCS 2016, Chapel Hill, NC, November 1-3, 2016.

R. French, K. Iisa, K. Orton and J. Schaidle. "Metal-Modified Zeolites for Upgrading of Pyrolysis Vapors", TCS 2016, Chapel Hill, NC, November 1-3, 2016.

Kristiina Iisa, Richard J. French, Kellene A. Orton, Joshua A. Schaidle, "Metal-modified zeolites in the upgrading of pyrolysis vapors," poster presented at TCS Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products, November 1-4, 2016, Chapel Hill, NC.

Richard French, Kristiina Iisa, Kellene Orton, Joshua Schaidle, "Hydrodeoxygenation of model and real vapor-phase-upgraded pyrolysis oils," poster presented at TCS Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products, November 1-4, 2016, Chapel Hill, NC.

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.

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.

J. Schaidle, "Biomass Utilization: Opportunities and Challenges", American Chemical Society Colorado Section Meeting, Golden, CO. October 20th, 2016.

Patents

Full Patent Application: K. Magrini, Y. Parent, J. Olstad, M. Jarvis "Systems and Methods for Producing Fuel Intermediates", USPTO 15/952,857, April 13, 2018.

J. Schaidle, D. Ruddy, C. Mukarakate, A. Dutta, F. Baddour, S. Habas, "Catalysts and Methods for Converting Biomass to Liquid Fuels", US Patent Application 15/794,235. Filed for non-provisional patent on October 26th, 2017.

S. E. Habas, J. Wang, D. A. Ruddy, F. R. G. Baddour, J. A. Schaidle, "Metal Phosphide Catalysts and Methods for Making the Same and Uses Thereof" US Patent 9,636,664 B1, 2017.

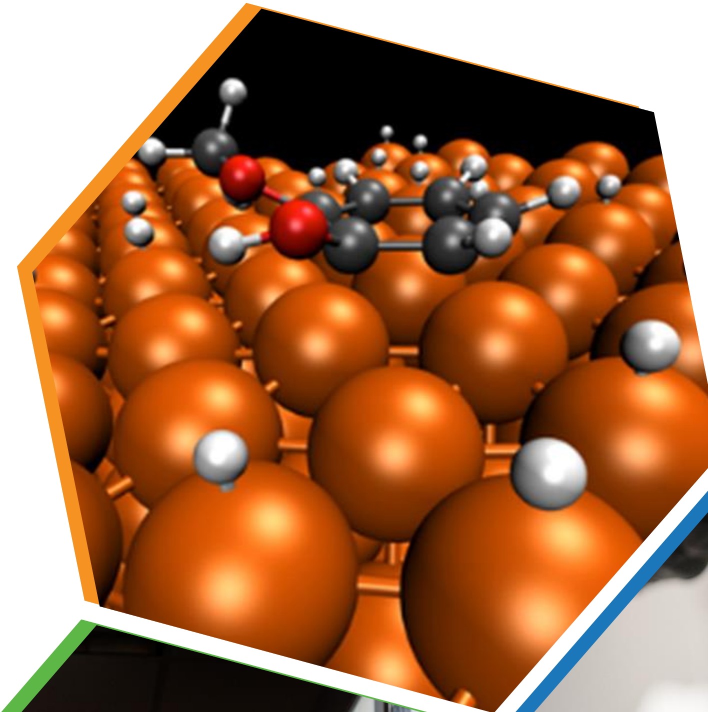
S. E. Habas, J. Wang, D. A. Ruddy, F. R. G. Baddour, J. A. Schaidle, "Metal Phosphide Catalysts and Methods for Making the Same and Uses Thereof" US Patent Application 2017/0197200 Al, 2017.

Awards

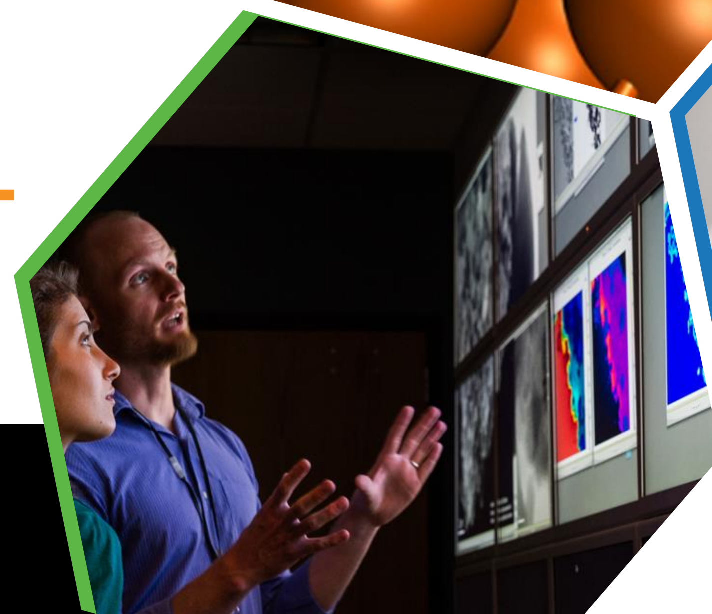
Our recent article in Energy and Environmental Science (impact factor = 30) was selected by the editors as a HOT article in 2018:

M. Griffin, K. Iisa, H. Wang, A. Dutta, K. Orton, R. French, D. Santosa, N. Wilson, E. Christensen, C. Nash, K. Van Allsburg, F. Baddour, D. Ruddy, C. Mukarakate, J. Schaidle, "Driving towards cost-competitive biofuels through catalytic fast pyrolysis by rethinking catalyst selection and reactor configuration", *Energy and Environmental Science*, 2018, 11, 2904-2918.

ChemCatBio
Chemical Catalysis for Bioenergy



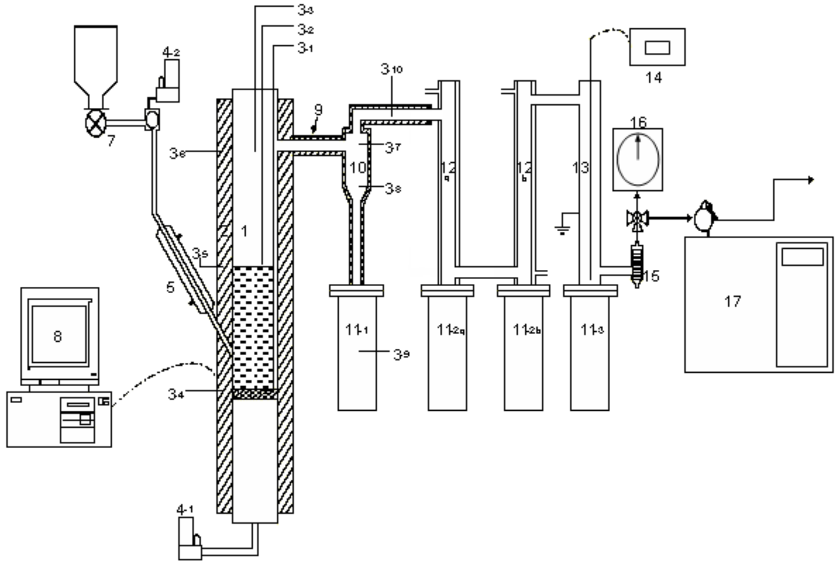
Reactor Systems



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

In-Situ CFP: Utah State University CFP System

1 kg/h Bubbling Fluidized Bed Reactor



Parameter	
Temperature	400-500°C
Pressure	1 atm
WHSV	1-1.5 h^{-1}
Catalyst	ZSM-5 or Redmud
TOS	~5 h

USU reactor system leveraged to:

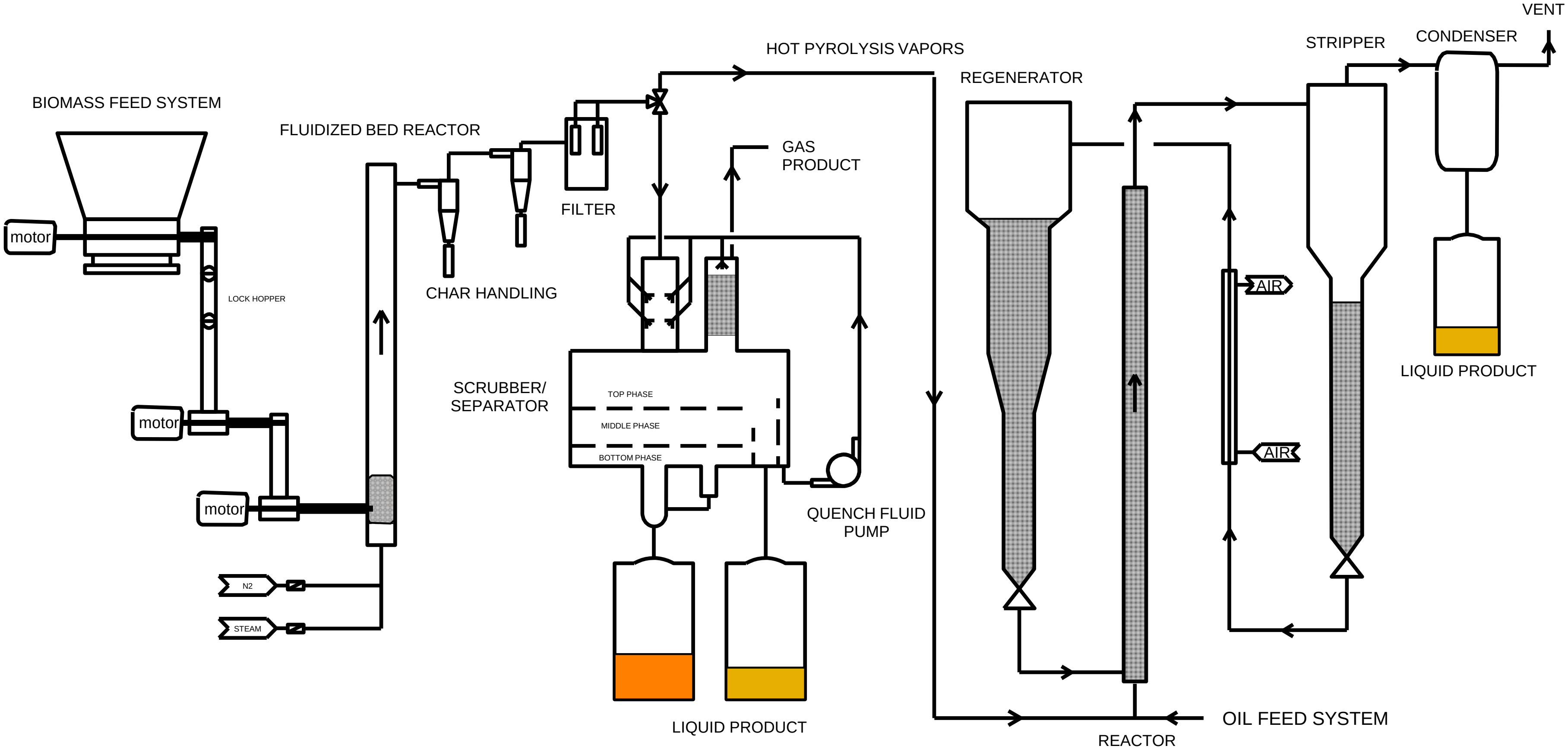
- Evaluate catalyst performance
- Optimize *in-situ* CFP process conditions
- Assess catalyst regenerability
- Produce CFP oil for hydrotreating

Ex-situ Entrained-Flow CFP: NREL's Davison Circulating Riser

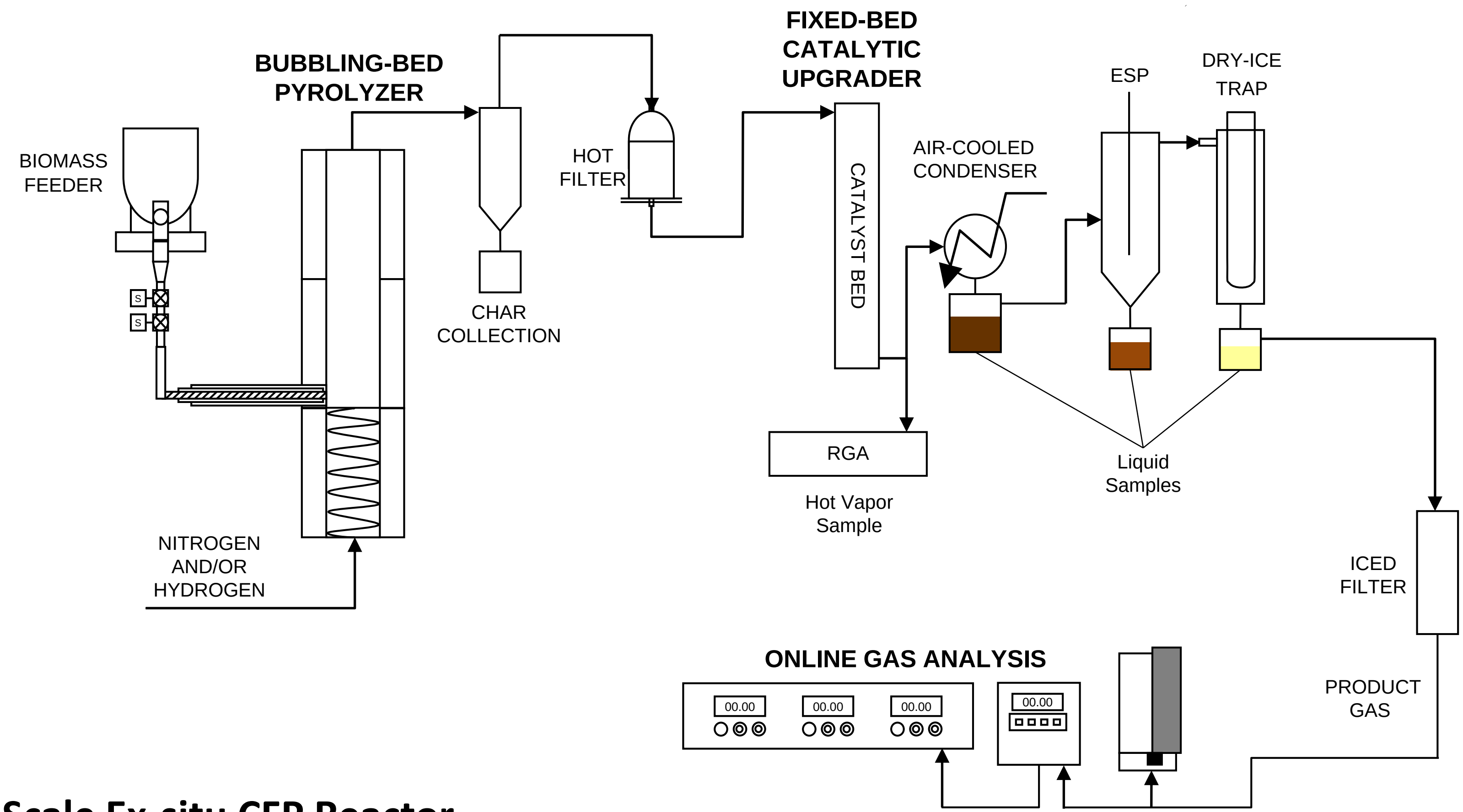
Pyrolyzer
1-3 kg/hr biomass feed
Fast Pyrolysis: 500°C, 1-2s
Pyrolysis oil: 1-2 gal
Analytics: NDIR, MBMS, on line GC (FY17), Total C detector (FY17)

Vapor Handling
Char removal – cyclones and HGF
Condensation System - spray tower, hot vapor slipstream to DCR

Davison Circulating Riser (DCR)
Pyrolysis vapor feed (reduced contaminants)
~2 kg catalyst
8 hr – 2 mass balance runs
Upgraded oil (design): 1 liter
Analytics: on line GC, NDIR, O_2 analysis, MBMS
Continuous coke removal



Ex-situ Fixed-Bed CFP: NREL's 2" CFP System

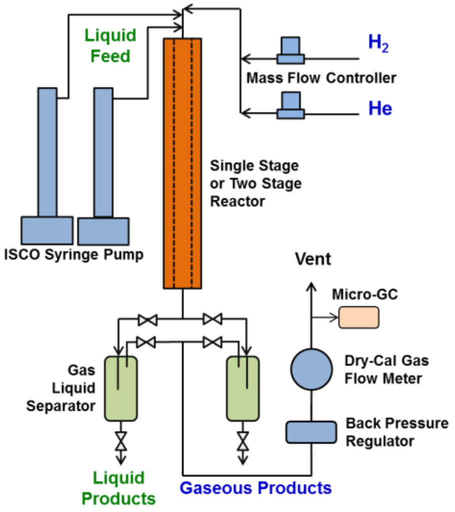


Bench Scale Ex-situ CFP Reactor

- Continuous upgrading of pine pyrolysis vapors
- 100-200 g/h biomass feed rate
- 85 g of catalyst
- Pt/TiO_2: 400 °C, 0.08 MPa H_2

***Hydrotreating*: PNNL's 40mL Continuous System**

▶ 40 ml Lab-Scale Hydrotreater (PNNL)



Parameter	
Temperature	400 ^oC
Pressure	1780 psig
LHSV	0.1-0.3 h^{-1}
Catalyst	Commercial CoMo / NiMo catalyst
TOS	60-300 h

▶ Bio-oil Analysis

CHNOS
Density, Viscosity
Water content
Carbonyl titration
Acid titration
^{13}C NMR
^{31}P NMR
GC-MS

With 2.5.2.302 Bio-oil Analysis Standardization project