ChemCatBio
Chemical Catalysis for Bioenergy

Liquid Fuels via Upgrading of Indirect Liquefaction Intermediates

WBS: 2.3.1.100/304/305

U.S. Department of Energy (DOE)
Bioenergy Technologies Office
2019 Project Peer Review

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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)

Goal Statement

Project Goal

Develop a market-responsive biorefinery concept based on indirect liquefaction (IDL) to **enable control** over the gasoline, diesel, jet and co-product **distribution to address shifting gasoline/distillate fuel demand**.

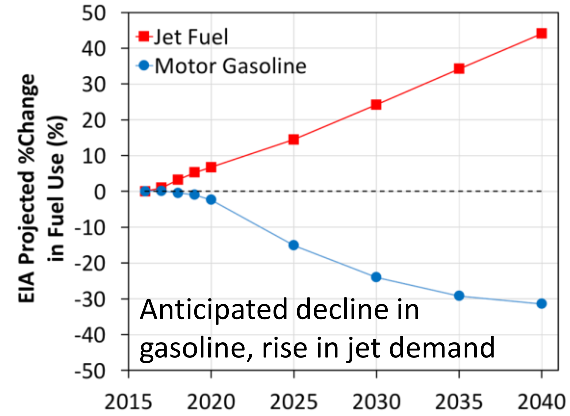
Project Outcome

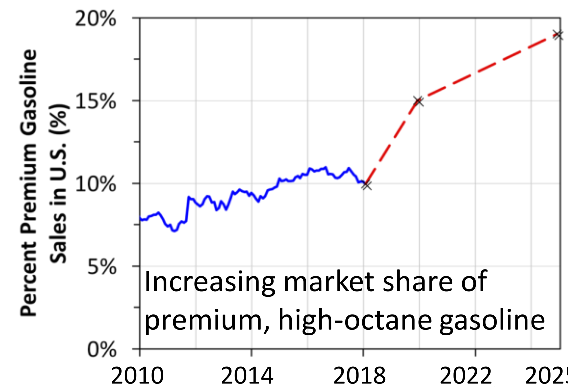
- Develop new IDL processes for **high-octane gasoline and distillate fuels** from methanol and ethanol intermediates
- **Exceed fuel product yields** of benchmark Mobil Olefins to Gasoline and Distillate (MOGD) process with **lower capital cost processes**

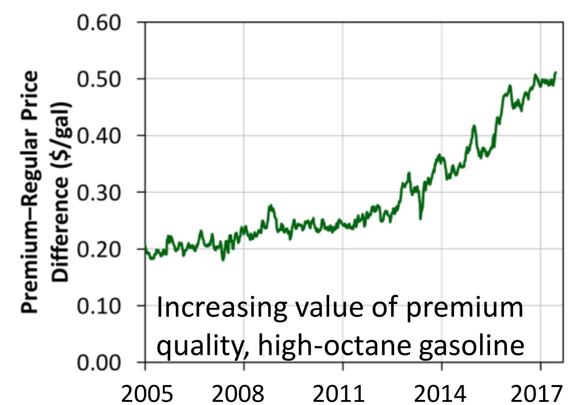
Relevance

- Known **drawbacks for traditional syngas-to-fuels processes** at smaller production scale: High capital and process costs, limited product quality
- Advanced upgrading technologies address these shortcomings by focusing on:

  Mild process conditions, high yield and C efficiency, high-quality (high-value) fuel products







Data from Energy Info. Admin (EIA)

Quad Chart Overview

Timeline
- 10/01/2017
- 09/30/2019
- 83% Complete

	Total Costs Pre FY17**	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded	8.1 M	3.6 M	2.2 M	2.5 M

•Partners: Percentages of project funding from FY 17-18:
- **NREL (56%); PNNL (41%), ORNL (3%)**

Barriers addressed & Actions

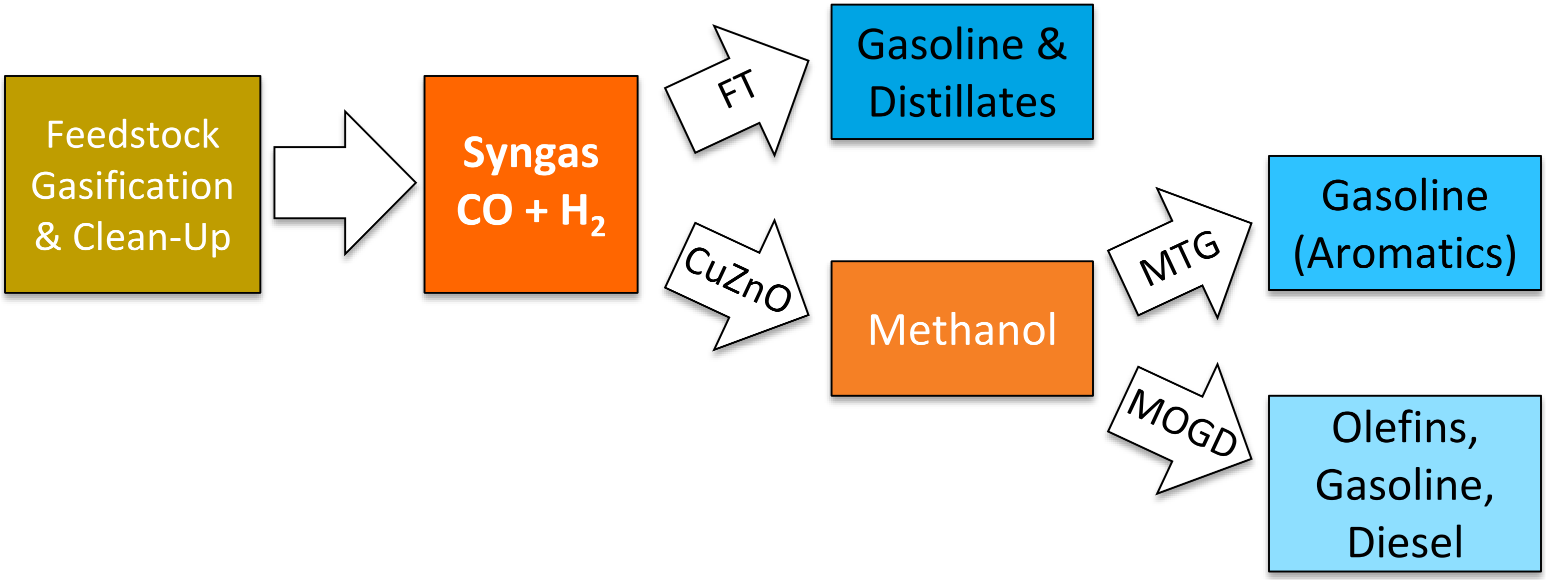
Ct-F: Increasing the Yield from Catalytic Processes
- Developing catalysts that enable processes with higher carbon efficiency and yield
- Understanding catalytic active sites and reaction mechanisms to minimize by-products

Ct-E. Improving Catalyst Lifetime
- Understanding the effects of real biomass impurities
- Exploring deactivation through characterization, and developing regeneration/mitigation strategies

Objective
Establish the regeneration protocol for each oxygenate conversion catalyst at the bench-scale after a minimum of **200 h total time-on-stream with at least 2 regenerations** targeting an activity goal of at least **85% of the original activity**

End of Project Goal
Develop a market-responsive biorefinery concept based on indirect liquefaction (IDL) to **enable control** over the gasoline, diesel, jet and co-product **distribution to address shifting gasoline/distillate fuel demand**

1 - Overview: Traditional Syngas-to-Fuels Processes



Traditional syngas to hydrocarbon fuels have known drawbacks

– Fischer Tropsch (FT): Costly catalytic upgrading to produce quality fuels
– Methanol-to-Gasoline (MTG): Capital intensive, high aromatics content
– Mobil Olefins-to-Gasoline-and-Distillate (MOGD): Capital intensive, high number of process steps

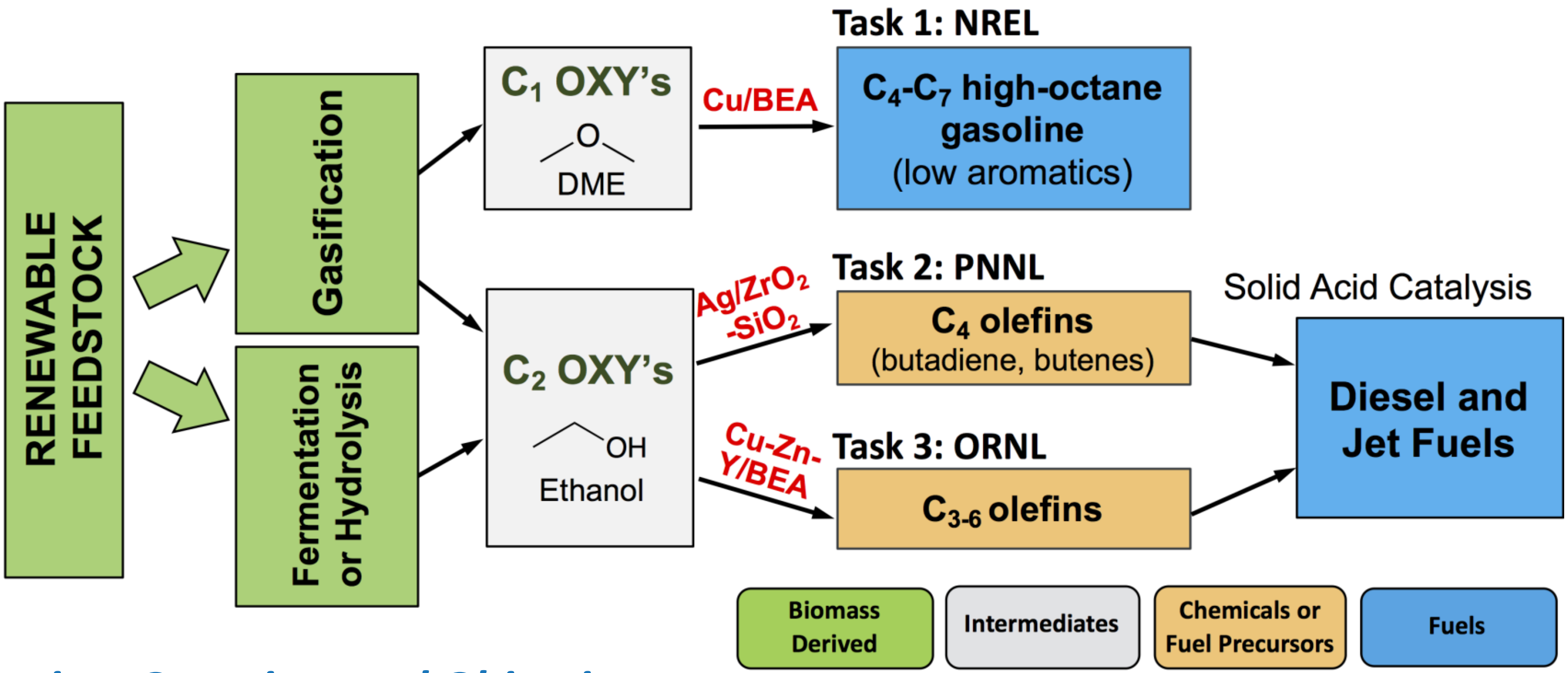
MFSP from biomass (2016 $)

- FT = $3.17/GGE
- MOGD = $4.23/GGE

Advanced upgrading technologies can reduce MFSP through reduced process complexity, reduced separations duty, higher quality fuel products

E. Tan, et al., *Biofuel Bioprod. Bioref*. **2017**, *11*, 41.

1 - Overview: Pathways explored in this Project



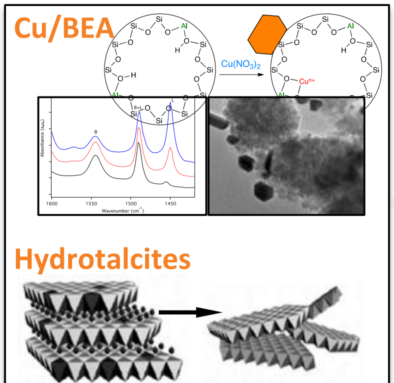
Project Overview and Objectives

- Explore multiple, alternative pathways (tasks) that leverage light oxygenate intermediates
  - Develop new catalysts that **outperform commercial catalysts**
  - **Identify commercial catalysts that can be adapted** to upgrading routes
  - Compare against benchmark processes (e.g., MOGD)
- **Leverages lab-specific strengths** in oxygenate production and conversion
- **Synergize efforts** for olefin coupling to distillates and fuel-property testing across the labs

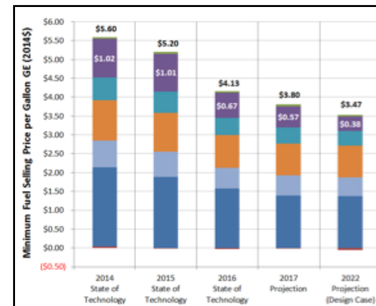
2 - Technical Approach – Dual Research Cycle

- **Hypothesis-driven catalyst development** coupled with sophisticated catalyst synthesis and characterization (with Adv. Catalyst Synthesis & Characterization)
- Develop **structure-function relationships** (with Cons. Comp. Physics & Chemistry)
- **TEA-informed research targets**, experimental data informs process models and TEA

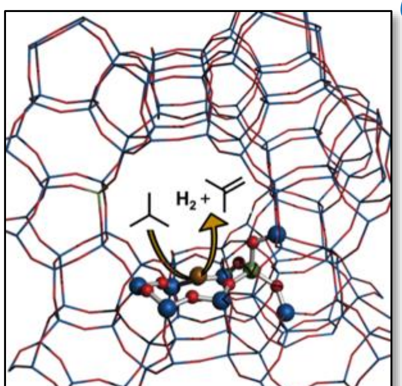
Synthesis & Characterization



Techno-economic Analysis (TEA)



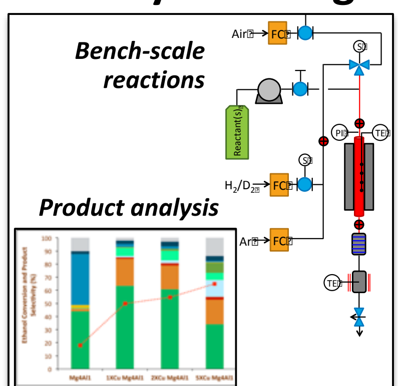
Computation

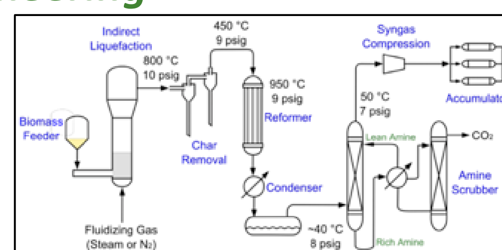


Foundational Catalysis Science

Applied Engineering

Catalyst Testing



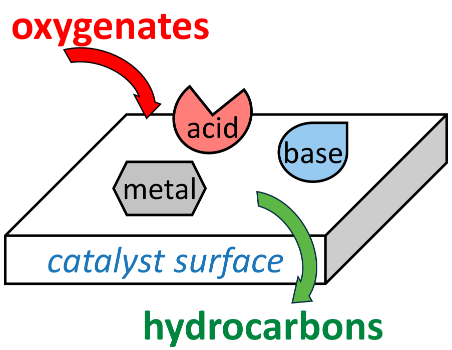


Catalyst Scaling & Process Models

2 - Technical Approach and Success Factors

Research Challenges

- Balancing ***multiple reactions*** under lower severity conditions
- ***Selectively producing fuel-range (C_{5+}) products***
- Maximizing catalyst ***lifetime***
- Generating relevant ***quantity*** to confirm ***high-quality fuel properties*** to compete with mature, conventional fuel-synthesis processes



Critical Success Factors

– Maximize carbon efficiency via ***multi-functional catalysts that perform cascade chemistry***

– ***Recycle by-products*** to higher value fuel products to maximize yield

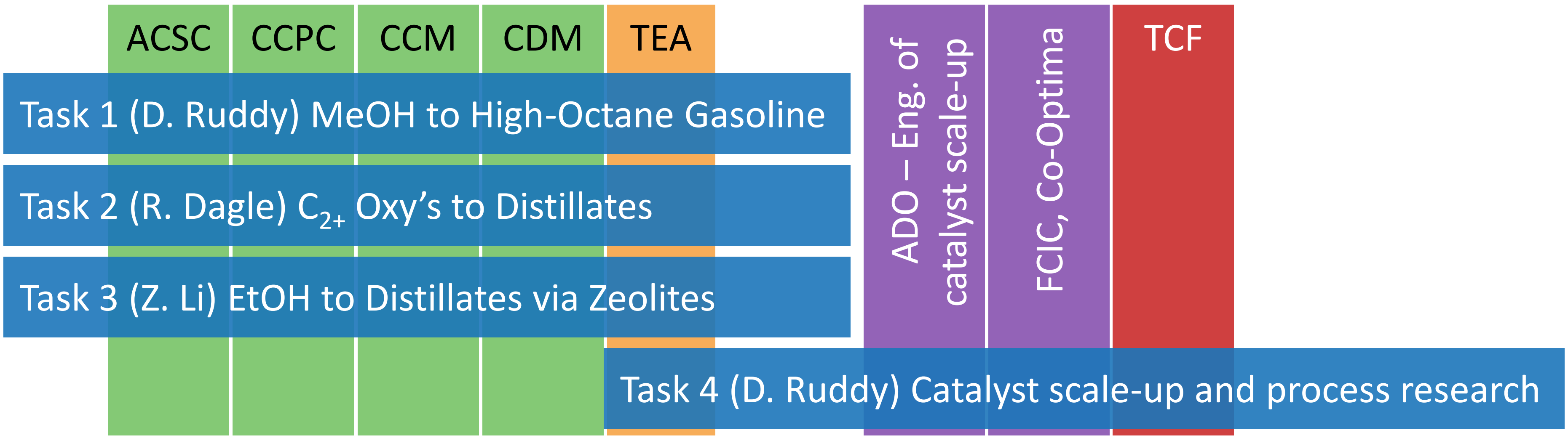
– Collaborate with Enabling Technologies to **understand deactivation, develop regeneration/mitigation approaches** at the bench-scale

– Utilize **multiple ASTM International test methods** with fuel-testing experts

– **Advance technologies** with bioenergy industry partnerships, TCF funding

2 – Management Approach

Task management integrated with CCB enabling technologies and analysis team, other BETO projects and consortia, and technology advancement opportunities



- **"Constant contact" between PIs and Enabling Technology** points-of-contact
- **Cooperative and synergistic research areas** identified
  - Leverages lab-specific strengths in oxygenate production and conversion
  - Olefin coupling and fuel testing between NREL, PNNL, ORNL
- **TEA-informed metrified milestones and Go/No-Go** to relate catalyst improvements to costs
- Utilized the **TEA-informed FY18 Go/No-Go** to re-focus FY19 research

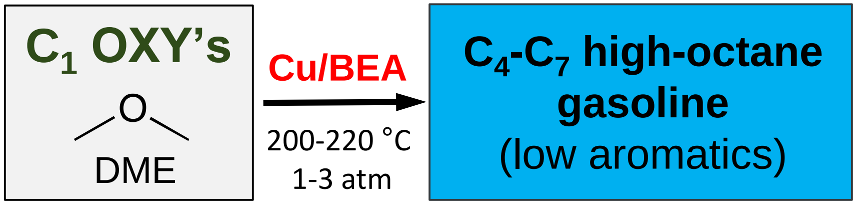
3 – Research Progress: Baseline in FY17

	MOGD Benchmark	Task 1: C_1 to Gasoline	Task 2: C_{2+} to Dist. (Guerbet)#	Task 2: C_{2+} to Dist. (C_4-Olefin)#	Task 3: EtOH to Dist. (C_{3+} Olefins)#
Catalyst	ZSM-5	Cu/BEA	Cu/MgO-Al_2O_3	$ZnZrO_x$	ZSM-5
Severity of Process Conditions	350–400 °C 20 atm *Frequent regen.*	200–220 °C 1–3 atm *Stable >100h*	300-350 °C 1 atm *200 h, aq. EtOH*	400-450 °C 1-3 atm *Aq. EtOH*	400 °C 1 atm
Start of FY17 Metrics	–	19% DME conv. 0.044 $g/g_{cat}/h$	44% EtOH conv. 75% C_{4+} sel.	99% EtOH conv. 47% C_4 sel.	100% EtOH conv. 33% C_{3+} sel.
Fuel Yield* and MFSP	G= 34 GGE/ton D= 27 GGE/ton **$4.23/GGE**	G= 50 GGE/ton **$3.99/GGE**	D= 42 GGE/ton **$4.04/GGE**	D= 41 GGE/ton **$5.90/GGE**	D= 16 GGE/ton **$5.21/GGE**

#Task 2: thermochemically derived C_{2+} alcohols; Task 3: fermentation derived ethanol   *G = gasoline, D= distillate

- FY17 TEA data **sets the stage for catalyst development**
  - TEA-directed research goals to target most impactful metrics
  - Comparison against benchmark MOGD process
  - **Discontinued $ZnZrO_x$ catalyst research** due to high MFSP, low C-efficiency
    - Developing new catalysts for this pathway

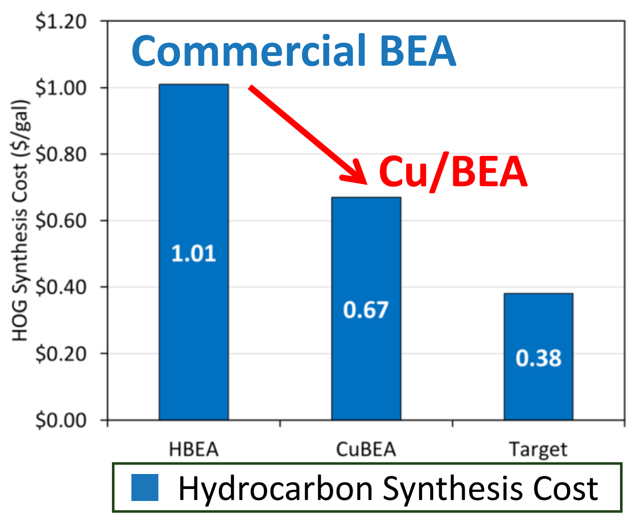
Overview of the pathway

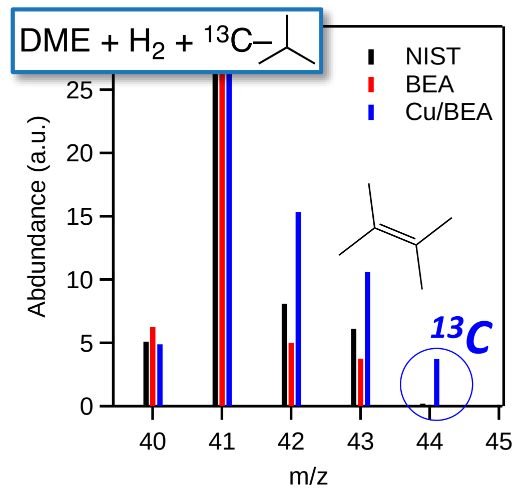


Schaidle et al. *ACS Catal.*, 2015; Tan et al., *Biofpr*, 2016;
Farberow et al., *ACS Catal.* 2017; Ruddy et al., *Nature Catalysis*, *under review*

Differentiators versus MTG

- **Catalyst –** BEA vs MFI
- **Product composition**
  - – Alkylate vs regular-gasoline
- **Higher product RON –** ≥95 vs 92
- **Lower coking rate**
- **Higher yield from biomass –** +18%



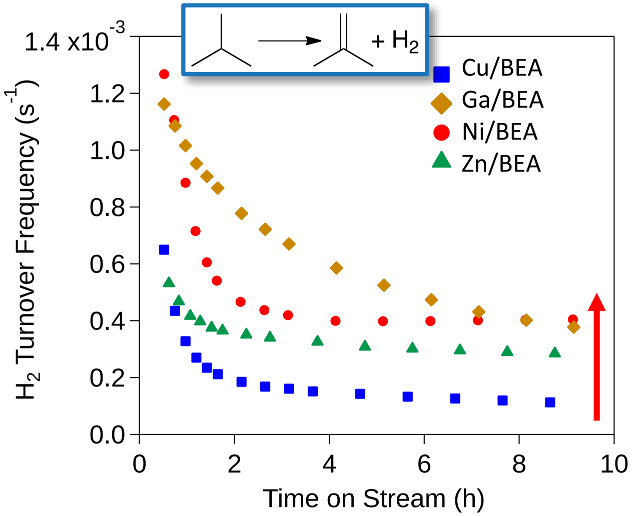


NREL-developed Cu/BEA catalyst reduces MFSP versus commercial BEA by 20%

– Increases gasoline fuel product yield by 38% vs BEA

– Reincorporates non-fuel C_4 alkanes into C_{5+} fuel products at Cu(I) active sites

Goal: Increase C_4 recycle conversion to increase yield, reduce MFSP



- **Computationally predicted ionic Ni, Zn, and Ga** to out-perform Cu(I) for alkane dehydrogenation
  - Lower activation energy
- Motivated bimetallic catalyst development to increase alkane re-activation
- **Experimentally Ni(2+), Zn(2+), Ga(3+) outperform Cu(+)**

Simulated C_4H_{10} Recycle with DME + H_2

Catalyst	C_4H_{10} Recycle Conversion (%) 1 atm	C_4H_{10} Recycle Conversion (%) 3 atm
Cu/BEA	12	22
Zn-Cu/BEA	20	28

- Developed a 2-step method to prepare bimetallic catalysts with targeted structures (with ACSC)
– **Zn-Cu/BEA increased C_4 recycle conversion (27-33% relative) vs Cu/BEA**
– Direct impact to reduce MFSP

Bimetallic catalysts** with predicted and synthetically-controlled active sites **enable increased C_4 recycle conversion

3 - Task 1: DME to High-Octane Gasoline Research Progress

Goal: Control paraffin:olefin (P:O) product ratio to control fuel properties

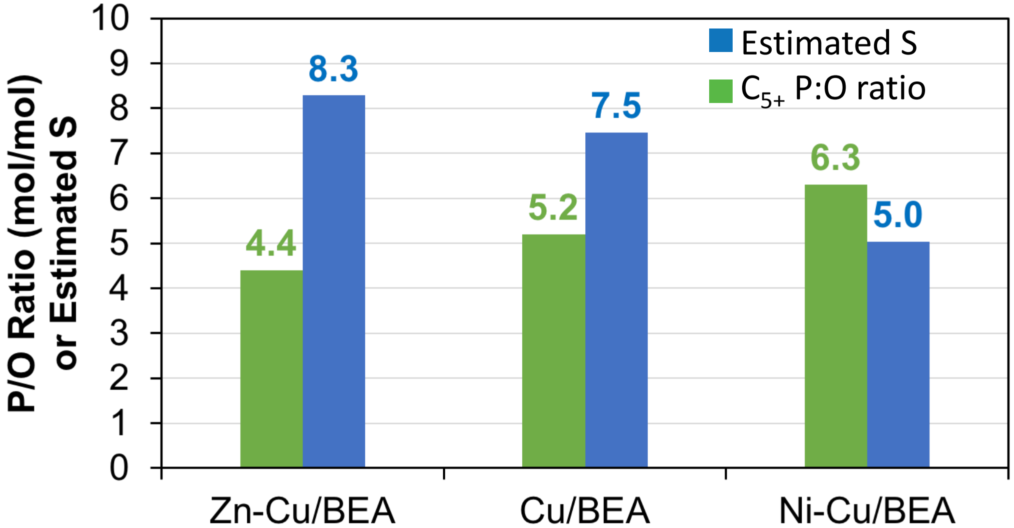
Paraffin Products		Olefin Products	
Compound	**RON/MON**	**Compound**	**RON/MON**
Branched-C_6	99/**94**	Branched-C_6	100/**83**
Branched-C_7	94/**90**	Branched-C_7	90/**78**
Triptane	112/**101**		

Ghosh et al., *Ind. Eng. Chem. Res.* **2006**, *45*, 337.

- **Sensitivity (S = RON – MON)** is a key metric for gasoline applications
  - **Automotive fuel – high S**
  - **Aviation gasoline – low S**
- Co-optima Merit Function favors greater S
- ***+1 S increases efficiency more than +1 RON***

Controlling olefin content enables control of S, directs fuel application

Paraffin:Olefin Product Ratio from DME + H_2



- **Bimetallic catalysts change the product P:O ratio and resulting estimated S**

Bimetallic catalysts** with predicted and synthetically-controlled active sites **enable fuel property tuning

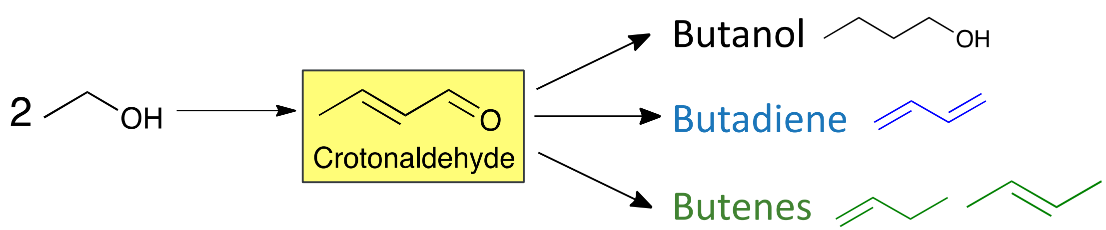
3 - Task 2: Ethanol to Distillates Research Progress

Overview of the pathway

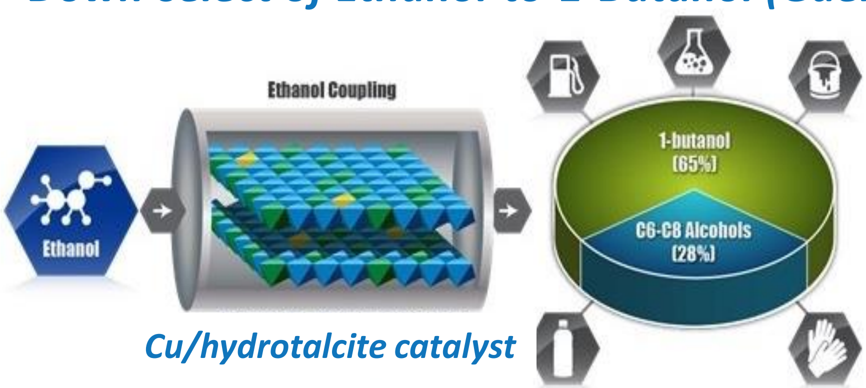
Differentiators versus ATJ

- **Multifunctional catalyst**
- **Eliminates dehydration step**
  - 3 vs 4 unit ops
- **Aqueous ethanol compatible**
- **Decreased CapEx**

- **Metal-acid bifunctionality** produces **crotonaldehyde intermediate**
  - **Branch-point** to give butanol, butadiene, or butenes
- Catalyst design and process conditions can ***direct crotonaldehyde to desired intermediate***



Down-select of Ethanol-to-1-Butanol (Guerbet) at FY18 Go/No-Go

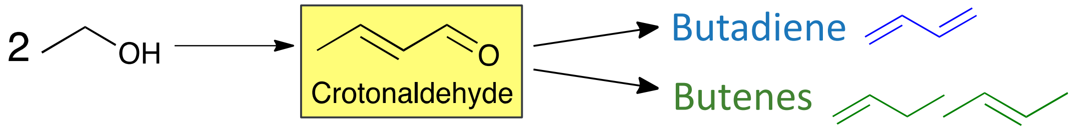


Cu/hydrotalcite catalyst

- **50% yield** to higher alcohols (single pass)
- Stable lifetime **>500 h in plug flow reactor**.
- Cu(I) limits undesired side products
- **De-emphasized at FY18 Go/No-Go**, moved to Co-optima Project evaluating branched alcohols as gasoline blendstocks

3 - Task 2: Ethanol to Distillates Research Progress

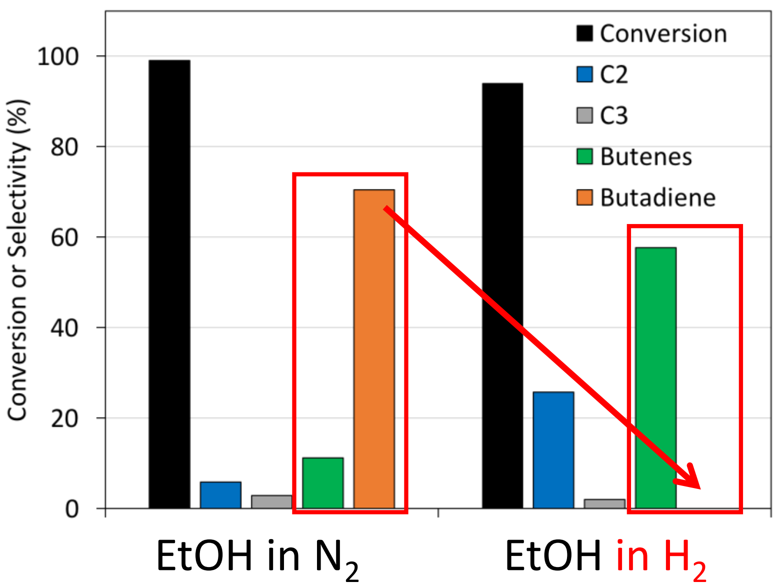
Goal: Control cascade chemistry to increase yield of C_4-olefins



PNNL developed a Ag/ZrO_2-SiO_2 catalyst for high-yield of butadiene

- Achieved **90% conversion, 70% butadiene selectivity**
  - Highest butadiene production rate reported (0.40 $g_{BD}/g_{cat}/h$ vs 0.11 $g_{BD}/g_{cat}/h$)
  - Tailored Lewis acidity with highly dispersed Ag nanoclusters (< 3 nm)

Dagle, V.L. *et al.*, *Appl. Catal. B* **2018**, *236*, 576.
Dai, W. *et al.*, *ACS Catal* **2017**, *7*, 3703.

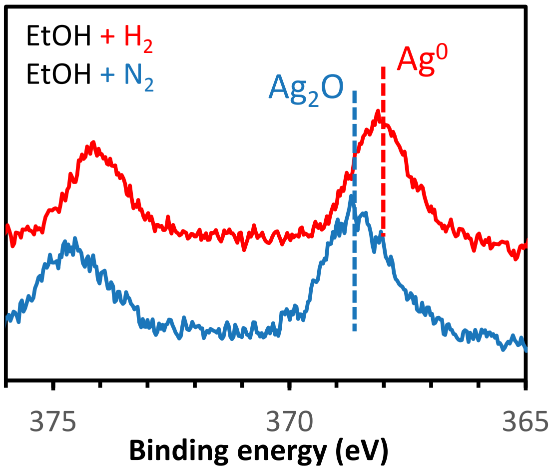


- **Butadiene vs butenes selectivity can be controlled with co-fed N_2 vs H_2**
- Co-fed H_2 directs crotonaldehyde to butenes product
- **No Butadiene observed**

Ag/ZrO_2-SiO_2 catalyst offers product tunability from butadiene to butenes

3 - Task 2: Ethanol to Distillates Research Progress

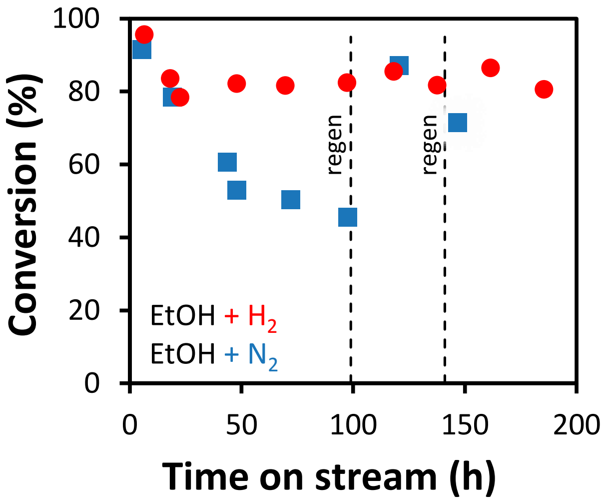
Structure-function relationships explored via in-situ XPS with ACSC



Ag/ZrO_2-SiO_2 catalyst explored under inert versus reducing conditions with flowing ethanol

- **Butadiene** formed over **oxidized Ag** species (N_2 co-feed)
- **Butenes** formed over **reduced Ag** species (H_2 co-feed), mild hydrogenation activity

Lifetime is significantly increased with co-fed H_2 versus N_2



T=325°C, P=100 psig, 24% ethanol

- Activity steadily decreases with co-fed N_2
- Initial decrease in activity **with H_2, then stable for 80 h, and after regenerations**

Co-fed H_2 has multiple impacts: reduces Ag, shifts products to butenes, and improves catalyst lifetime

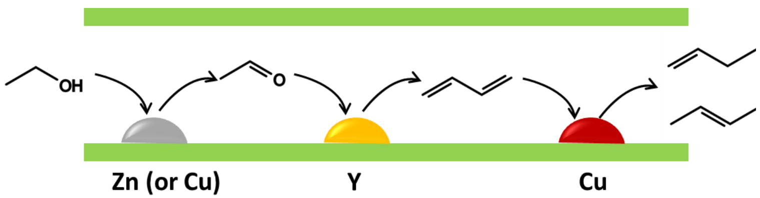
3 - Task 3: Ethanol to Distillates Research Progress

Overview of the pathway

Differentiators versus ATJ

- **Multifunctional catalyst**
- **Eliminates dehydration step**
  - 3 vs 4 unit ops
- **Aqueous ethanol compatible**
- **Decreased CapEx**

Goal: Control cascade chemistry to mixed olefins from ethanol

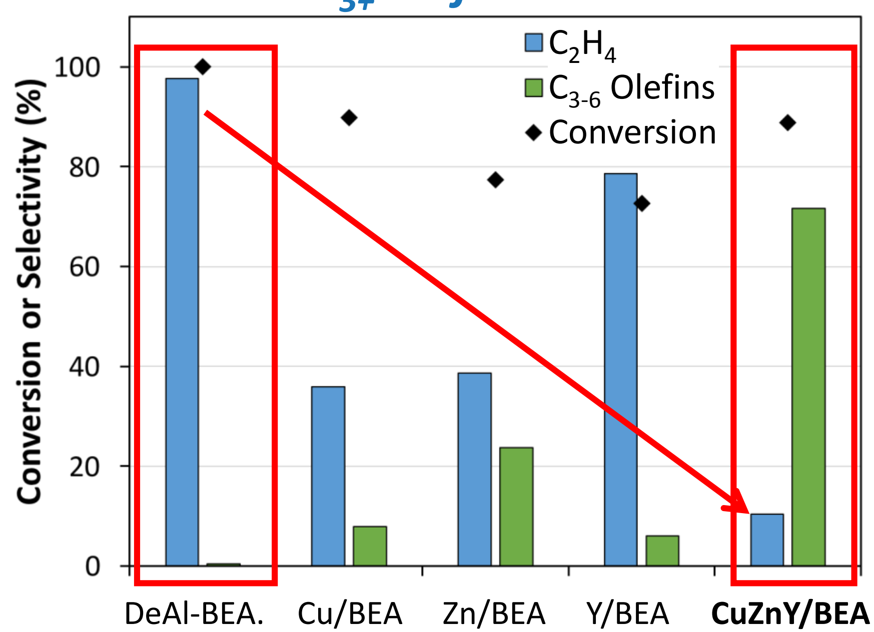


- **Zeolite provides a scaffold to introduce well-defined active sites**
- **No H^+ sites required**
- **Achieved 99% conversion and 87% selectivity of C_3-C_6 olefins**

Cu-Zn-Y/BEA catalyst enables a step-change in selectivity

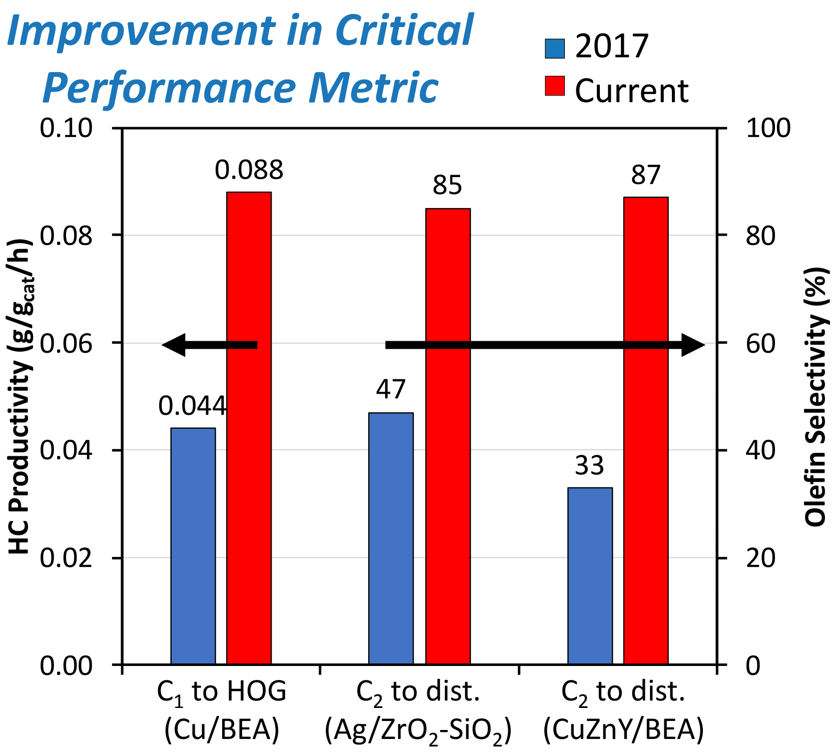
Sets the state-of-the-technology for further development

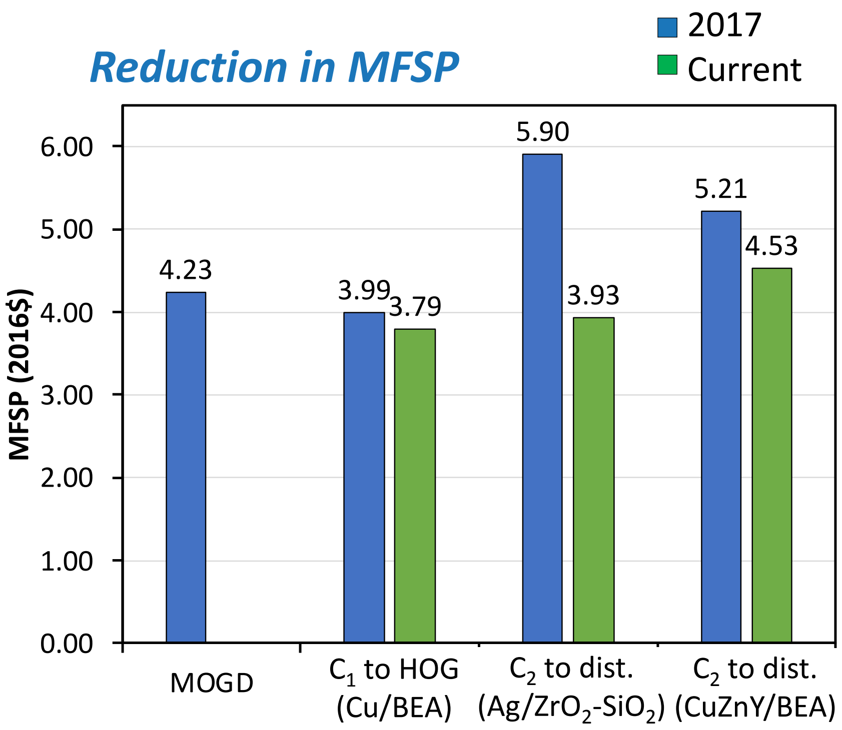
Selectivity shift from C_2H_4 to C_{3+} olefins



330°C, 1 atm H_2, WHSV= 0.62 h^{-1} and ethanol conc. 13%

3 - Research Progress Summary





Project Technological Achievements (FY17–18)

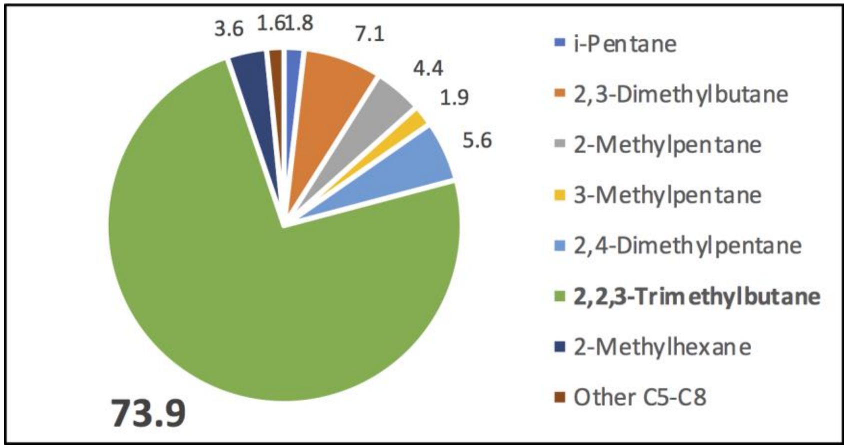
- Significant **increases in critical performance metrics and reductions in MFSP**
- ***Lifetime and regeneration*** studies are on-going, including with known biomass impurities

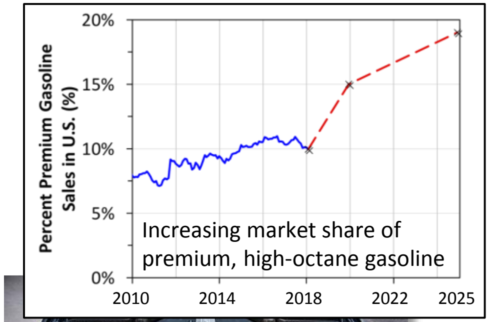
4 - Relevance to Bioenergy Industry

High-octane Gasoline technology awarded a ***Technology Commercialization Fund - $740k investment by DOE + $750k cost-share from Enerkem***

- Demonstrated high-octane gasoline production at the **pilot scale** (20-kg_{cat}) with ***MSW-derived methanol for 500 h time-on-stream***
- Produced ***20 L of high-octane gasoline***, sent to ***refinery industry partners***

High Octane Product
73.9% Triptane
RON = 108
MON = 97





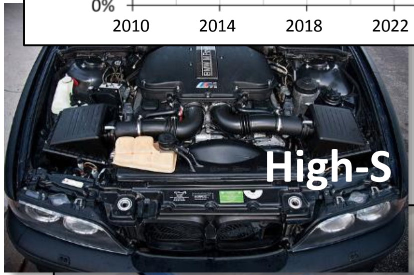
HOG product targets ***growing premium gasoline fuel demand***

– Unlike ethanol, **gasoline product has no blend limit**.

– Control over fuel properties (S =RON – MON) enables **automotive and aviation gasoline target markets**

  – Automotive – synthetic alkylate blendstock

  – Aviation – high-MON blendstock



4 - Relevance to Bioenergy Industry

Jet-range hydrocarbon from ethanol-derived C_4 olefins met 4 key ASTM standards for jet fuel

Property		Jet-Range Hydrocarbons	Blendstock Requirements (ASTM D7566)
Yield (b.p. 150 to 300 °C, wt. %)		86.9 (75 single pass)	
Aviation Fuel Properties	Freezing point (°C)	–74	–40 max (D5972)
	Flash point (°C)	51.5	38 min (D445)
	Viscosity (mm^2/s)	2.0	8 max (D93)
	Density (kg/m^3)	780	775 to 840 (D4052)

Properties for C_4-olefin derived oligomerization products after distillation and hydrotreatment.

Catalysis Science & Technology **2019**,
DOI: 10.1039/C8CY02297F.

Tasks 2 and 3 target ***growing distillate fuel demand***

– Utilize **ethanol beyond the "blend wall"**

– Ethanol is now an approved feedstock and the **blend ratio limit for ATJ-SPK fuels has been raised to 50%**

– Oligomerization of C_4 olefins can be tailored to **jet and/or diesel target markets**

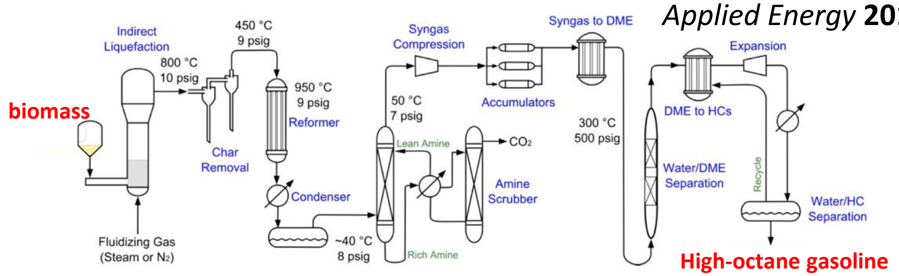
4 - Relevance to BETO

Research goals directly address BETO **conversion barriers** *to increase yield in catalytic processes* and *to improve catalyst lifetimes*

- Enabled by cross-cutting foundational science and applied engineering approach
- Include **impurities** associated with **real feeds and non-ideal conditions**
- Investigate **catalyst performance and regeneration** at longer times on stream

FY17 Demonstration: biomass gasification and DME-to-HOG with scaled-up Cu/BEA catalyst

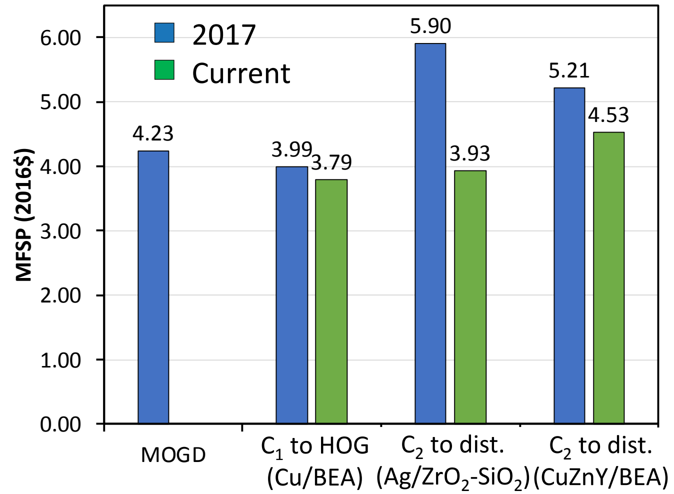
Applied Energy **2019**, *in press.*



- **Feedstock flexibility and blend linearity** with 5 feeds
  - Collaborative with Feedstock-Conv. Interface Con.
- **Multiple conditions and regenerations**, and **TOS >250 h**

- Identified the key challenges and **supported pilot-scale TCF project** with Enerkem
- ***Lessons learned*** informed new-start ADO Engineering of Catalyst Scale-Up Project

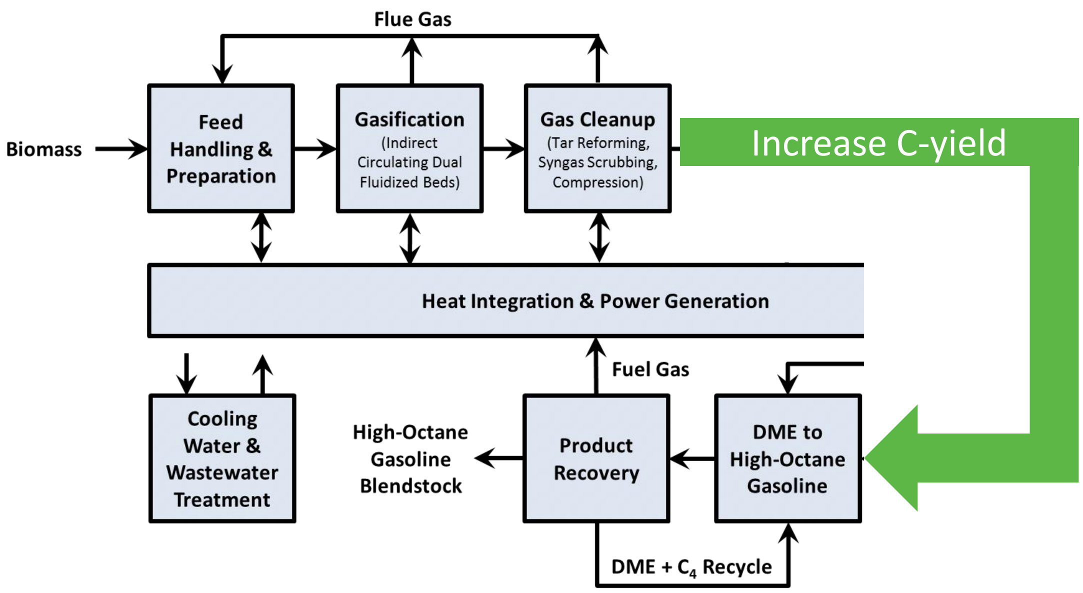
Cost reductions across each conversion pathway



5 - Future Work

Tasks 1 and 4: DME to High-Octane Gasoline

- **Increase carbon yield**
  - Q1 - Explore process model and TEA to direct **CO_2 to high-octane gasoline**
  - Q4 - Improve ***C4 recycle conversion*** by balancing **relative dehydrogenation vs hydrogenation rates** with highly-defined active site structures (with ACSC and CCPC)
- **Control fuel properties/quality**
  - Q4 - Develop catalyst formulations to **maximize and minimize S value of fuel product**



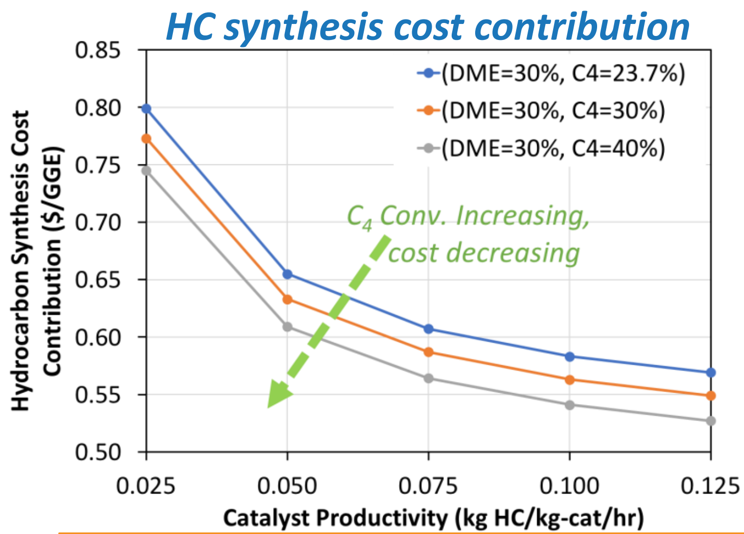
Utilize **CO_2-rich syngas** for DME:
Increase fuel yield 50% with 10% MFSP reduction (large H_2 import)

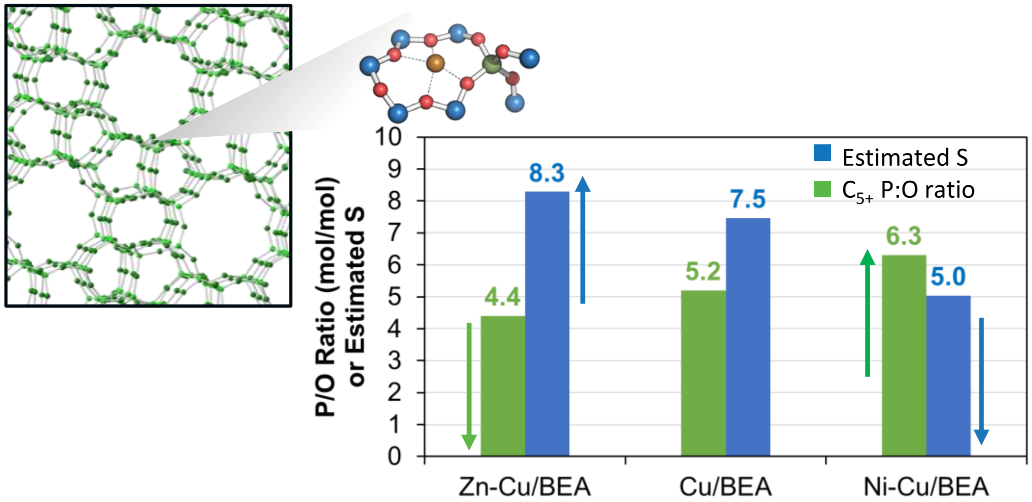
Catalyst development and process intensificaiton for **direct syngas-to-high-octane gasoline:**
Increase fuel yield 3% with 3% MFSP reduction (low H_2 import)
modest catalyst performance metrics used in model

5 - Future Work

Tasks 1 and 4: DME to High-Octane Gasoline

- **Increase carbon yield**
  - Q1 - Explore process model and TEA to direct **CO_2 to high-octane gasoline**
  - Q4 - Improve ***C4 recycle conversion*** by balancing **relative dehydrogenation vs hydrogenation rates** with highly-defined active site structures (with ACSC and CCPC)
- **Control fuel properties/quality**
  - Q4 - Develop catalyst formulations to **maximize and minimize S value of fuel product**



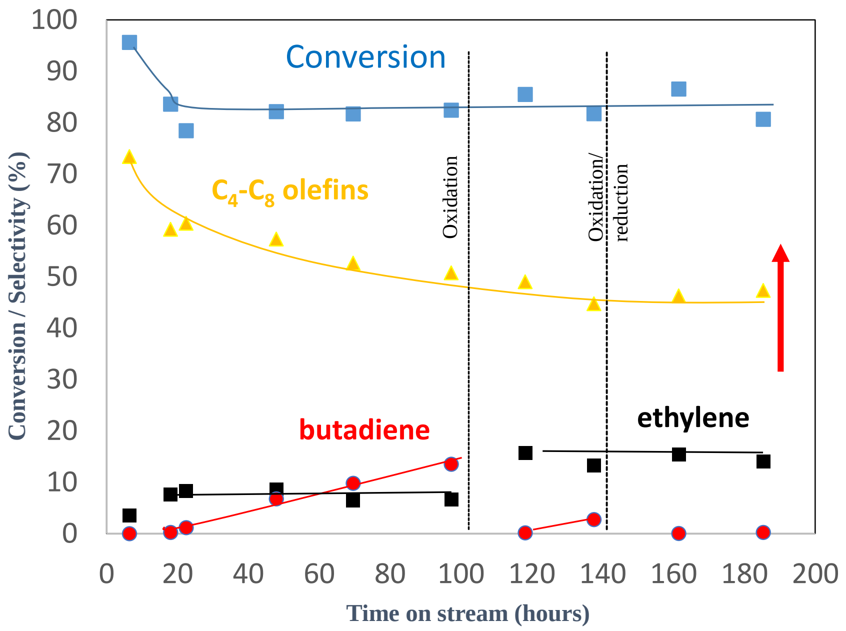


Structure-function relationships for C_4 activation directly link to process cost reductions and fuel quality metrics

5 - Future Work

Task 2: C_{2+} Oxygenates to Distillates via C_4-olefins

- **Increase carbon yield and stability**
  - Q3 - Understand the role of ZrO_2 and Ag to favor butenes and limit byproducts
  - Q4 - Identify and quantify the surface species that lead to deactivation



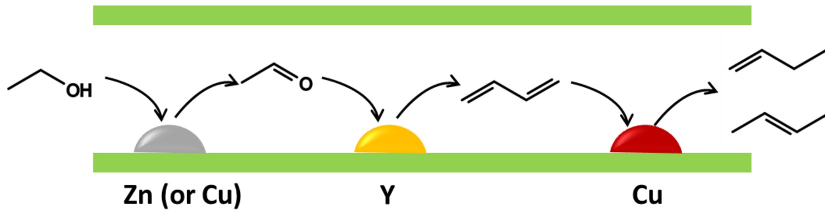
- Understand evolution of **catalyst structure** and **surface properties**
  - with ACSC)
- **Enhance butene selectivity** and **mitigate temporal changes**:
  - process conditions (H_2/H_2O ratio)
  - Ag particle size, dopants to stabilize Ag oxidation state

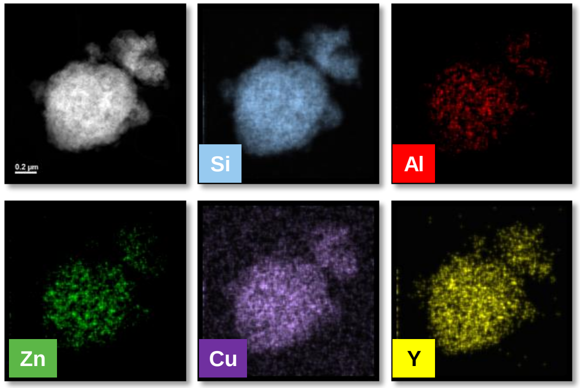
Modifying Ag catalyst structure and properties to increase C_4-olefin selectivity and limit byproduct formation

5 - Future Work

Task 3: EtOH to Distillates via Mixed-Olefins

- Understand catalyst active sites
  - Q2 - Establish the initial **structure-function relationships for Cu-Zn-Y/BEA** (with ACSC)





- Dispersed metals **without Cu, Zn, or Y metal clusters**/particles (XAS and STEM)
- Distinct **Lewis acid sites from Y** to perform the C-C coupling

Direct next-generation catalyst development to maximize olefin selectivity

- ***All Tasks 1-4: FY19 Q4 Annual Milestone (9/30/2019)***
  - Understand **deactivation and develop regeneration/mitigation protocols** to restore **≥85% of original activity** after at least 200 h time-on-stream

Summary

Project Goal

Leveraging syngas-derived light oxygenates to develop new, low-severity catalytic upgrading technologies to high-value fuels that address the shifting gasoline/distillate demand

Approach

- Developing **multifunctional catalysts** to perform selective, cascade reactions, leading to low operating costs and high C efficiency
- Interdisciplinary, **collaborative approach** within ChemCatBio leveraging enabling technologies

Research progress

- Bimetallic M-Cu/BEA catalysts for DME to high-octane gasoline **increase C_4 recycle conversion** and enable **product fuel property control**
- **Setting the state of the art in ethanol coupling** with high-yield, high C efficiency processes for distillate fuel production
- Significant **increases in yield and reductions in MFSP** demonstrated at FY18 Go/No-Go

Relevance

- Demonstration in FY17 (high-octane gasoline) **reduced the risk toward commercialization** for processes developed in this project
- Demonstrated **technology transfer with the bioenergy industry (e.g., TCF with Enerkem)**
- Patented intellectual property, and published results in top-tier peer-reviewed journals

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NREL Catalyst Development Team

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Liquid Fuels via Upgrading of Indirect Liquefaction Intermediates

WBS: 2.3.1.100/304/305

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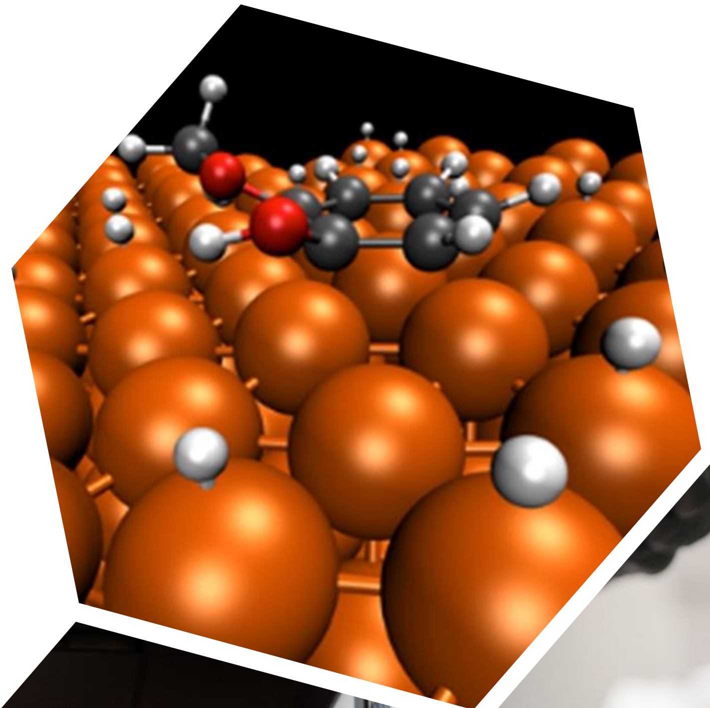
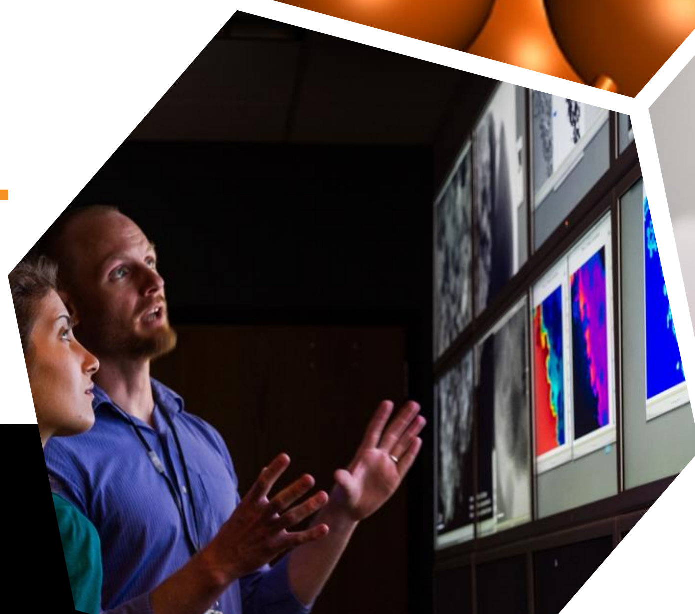
2019 Project Peer Review





Daniel Ruddy – NREL
Robert Dagle – PNNL
Zhenglong Li – ORNL

Responses to Previous Reviewers' Comments

1. **Comment:** Team results are impressive and commendable. The team has well-planned approaches and excellent organizational structure to maximize results, from modeling to catalyst development to improvements since last review. One question I may have not seen an answer to is carbon efficiency for the various processes. I did see gge cost clearly identified and highlighted for Task 1. Is this in progress for Task 2?

Response: We appreciate the reviewers' positive remarks about the project results, approach to target high-value fuels, organizational structure, and incorporation of enabling technologies and researchers with fuel property expertise. We did not highlight carbon efficiency for the processes during the presentation, but rather, focused on the technical accomplishments that feed into that calculation and the resulting MFSP versus mature industry comparisons (e.g., Fischer-Tropsch, Mobil olefin-to-gasoline/distillate). Techno-economics using recent data are being fed into models for determining overall performance and cost assessments, including for Task 2.

2. Comment: It may be difficult to select between the alternative processes in the time available.

- Catalyst life, regenerability, and process complexity should be factors in the selection process.
- It is important for the project team to stay focused and not get distracted by the multiple options for fuel flexibility and co-products. Co-products in a biorefinery may add value, but they also add complexity, as well as uncertainties for the future profitability if the co-product value decreases.

Response: FY18 Go/No-Go has been updated to reflect comments around staying focused and not getting distracted by multiple options. G/NG compares research progress against MOGD benchmark, and can be re-focused to stay on-track towards project goals.

- Catalyst life, regenerability, and complexity are part of the decision. Cu/BEA and Cu/MgO-Al_2O_3 catalysts already evaluated for lifetime >300 h, and regenerability

3. Comment: The Ni-Co catalysts are being developed by a number of groups as the next wave of Fischer-Tropsch catalysts. Showing that this type of catalyst and process conditions can be adjusted to produce olefins from real biomass would be a major leap forward

Response: Our techno-economic analysis of this pathway identified it as high-risk-high-reward. Reduced project funding resulted in discontinuation of this pathway. Catalyst development from the project has been reported in manuscripts

4. Comment: Fewer separations, less H_2 utilization, and close work with the fuel/engine teams is a recipe for success that will support commercial relevance

Response: Continued interaction with fuel property teams, and more in-depth discussions with co-optima team are underway (e.g., efficiency merit function for HOG product)

Publications

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- V.S. Bharadwaj, B. Pecha, L. Bu, R.A. Dagle, V. Dagle, P. Ciesielski, 2018. "Multi-scale simulation of reaction, transport and deactivation in SBA-16 supported catalysts for the conversion of ethanol to butadiene" *Catalysis Today*, **2018**, in review.

Patents

- J. E. Hensley, D. A. Ruddy, J. A. Schaidle, M. Behl, US Patent 9,714,387 B2 “Catalysts and methods for converting carbonaceous materials to fuels”, July 25, 2017.
- J. E. Hensley, D. A. Ruddy, J. A. Schaidle, M. Behl, US Patent 9,796,931 B1 “Catalysts and methods for converting carbonaceous materials to fuels”, October 24, 2017.
- J. E. Hensley, D. A. Ruddy, J. A. Schaidle, M. Behl, US Patent 9,803,142 B1 “Catalysts and methods for converting carbonaceous materials to fuels”, October 31, 2017.
- “Catalysts and systems for the production of liquid fuels and chemicals” US Patent Application 62/482,315, April 6, 2017.
- “Catalysts and systems for the production of liquid fuels and chemicals” US Patent Application 62/515,087, June 5, 2017.
- “SINGLE STEP CONVERSION OF ETHANOL TO BUTADIENE”, US Patent Application 15-837,382, Filed December, 2017.
- “SINGLE-REACTOR CONVERSION OF ETHANOL TO 1-/2-BUTENES”, US Patent Application, Filed May, 2018.
- Zhenglong Li, “ZEOLITIC CATALYTIC CONVERSION OF ALCOHOLS TO OLEFINS” Filed August, 2018.

Selected Presentations

- D.A. Ruddy, “Linking Catalyst and Process Development with Techno-Economic Analysis in the Conversion of Biomass to High-Octane Gasoline” ChemCatBio Webinar Series, March 7, 2018. Available at: https://www.chemcatbio.org/webinars.html
- R.A. Dagle, V. Dagle, J. Saavedra Lopez, “Conversion of Ethanol to 1,3-Butadiene over Ag-ZrO_2/Al_2O_3” ACS National Meeting, New Orleans, LA, March 20, 2018.
- K. Ramasamy, “MgO-Al_2O_3 Supported Copper Pseudo Single Atom Catalysts for Guerbet Ethanol Conversion” ACS National Meeting, New Orleans, LA, March 20, 2018.
- D.A. Ruddy, C. Nash, J. Hensley, C. Farberow, J. Schaidle, “Activation of isobutane over a Cu/BEA catalyst and re-incorporation into the chain growth cycle of DME homologation” ACS National Meeting, New Orleans, LA, March 20, 2018.
- S.C. Marie-Rose, “Renewable and recycled carbon for high octane low carbon gasoline (HOLCG) production at pilot scale” ACS National Meeting, New Orleans, LA, March 20, 2018.
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- Z. Li, J. Zhang, M. Salazar, A. Lepore, C.K. Narula, B. Davison, “Catalytic Conversion of Fermentation Derived Ethanol to Advanced Hydrocarbon Fuels and Valuable Chemicals” ACS National Meeting, New Orleans, LA, March 20, 2018.
- Ramasamy K., M. Guo, M.J. Gray, S. Subramaniam, V. Murugesan, and S. Thevuthasan. "In Operando Analysis Of Ethanol Conversion In Hydrotalcite Based Catalysts." MRS Spring Meeting 2018, Phoenix, Arizona, April 3, 2018.
- Ramasamy K., M.F. Guo, S. Subramaniam, and M.J. Gray. "Ethanol to Infrastructure Compatible (Jet) Fuels via Ethanol Coupling Reactions." 2018 AIChE, Orlando, Florida, April 24, 2018.
- Phillips S.D., R.A. Dagle, M.J. Gray, S.B. Jones, V. Dagle, K. K. Ramasamy, and L.J. Snowden-Swan. "Comparison of Several Indirect Liquefaction Pathways to Fuels and Co-Products via Biomass Gasification and Synthesis." 2018 AIChE Meeting, Orlando, Florida, April 23, 2018.
- D.A. Ruddy, “Research towards biomass-derived high-octane gasoline and jet fuel” Presented to Clariant, Palo Alto, CA, September 22, 2017.
- J.E. Hensley, D.A. Ruddy, J.A. Schaidle, “Production of High-Octane Alkylate from Methanol” Presented at Argus Methanol Forum, Houston, TX, September 11, 2017.
- Saavedra Lopez J, Davidson S D, Dagle V, Flake M, Dagle R A. 2017. "Conversion of C2+ Oxygenates to Jet Fuel via ZnxZryOz Mixed Oxide Catalyst." Oral Presentation at TCBiomass, September 19, 2017, Chicago, IL.

Selected Presentations, continued

- Dagle V, Saavedra Lopez J, Davidson S D, Dagle R A. 2017. "Single-Step Conversion of Ethanol to 1,3-Butadiene over Ag/ZrO2/SiO2." Oral Presentation at TCBiomass, September 19, 2017, Chicago, IL.
- K. K. Ramasamy. 2017. “Chemical Intermediates from Bio-Ethanol.” Poster Presentation at Commercializing Industrial Biotechnology, September 18-19, 2017, San Diego, CA.
- K.K. Ramasamy, M. Gray, M. Guo. 2017. “Guerbet ethanol coupling over a stable Cu-MgO-Al2O3 catalyst.” ACS National Meeting, August 20-24, 2017, Washington D.C.
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- S.Cheah, C.A. Farberow, S. Kim, J. Hensley, J. Schaidle, J.T. Miller, D.A. Ruddy, "Exploring Low-Temperature Dehydrogenation at Ionic Cu Sites in Beta Zeolite To Enable Alkane Recycle in Dimethyl Ether Homologation" Presented at NAM25, June 4-9, 2017, Denver, CO.
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- J Saavedra Lopez, Dagle V, and RA Dagle. 2016. " Insights into Ethanol to Fuels Process: catalyst selection for olefin oligomerization." North American Catalysis Meeting, June 4-9, 2017, Denver, CO

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- K. K. Ramasamy, M. Gray C. Alvarez-Vasco, "Ethanol conversion to n-butanol via the guerbet chemistry: Role of mixed oxide catalysts" Presented at AIChE Fall National Meeting, San Francisco, 2016.
- M. Guo, M. Gray, V. Murugesan, K. K. Ramasamy, "Characteristics and activity of steamed zeolites for butanol upgrading to higher olefins" Presented at AIChE Fall National Meeting, San Francisco, 2016.
- M. J. Gray, C. Alvarez-Vasco, M. Guo, K. K. Ramasamy, "Distillate generation via Guerbet alcohol coupling from biomass" Presented at TCS 2016, Chapel Hill, 2016.
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