ChemCatBio
Chemical Catalysis for Bioenergy

DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

Upgrading of C2 Intermediates - TEA

March 10, 2021
Catalytic Upgrading Session

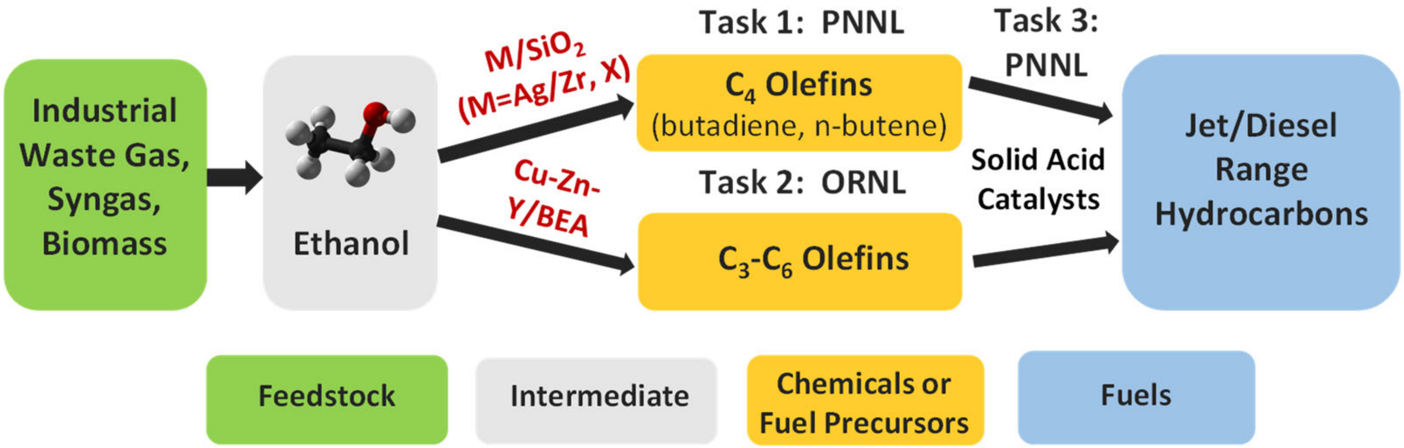
Ling Tao (NREL), Steve Phillips (PNNL)
Presenter: Robert Dagle (PNNL)

TEA Overview: C2 Upgrading

Two new catalyst systems for producing higher olefins (C_{3+}) directly from ethanol, as intermediates for distillate fuels, are being investigated:

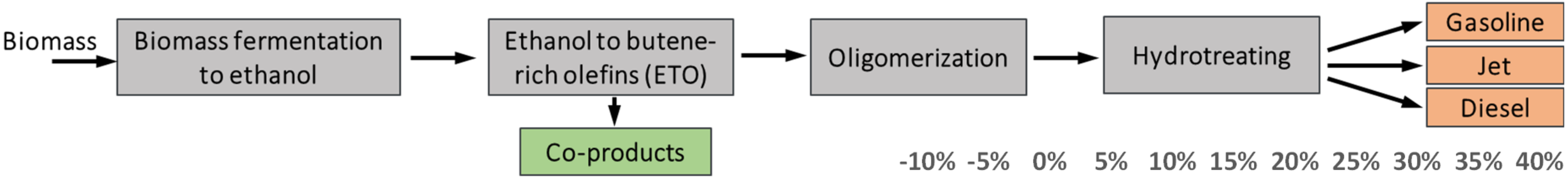
Task 1 (PNNL): mixed oxide-based (M/SiO_2; M = Ag/Zr, X)

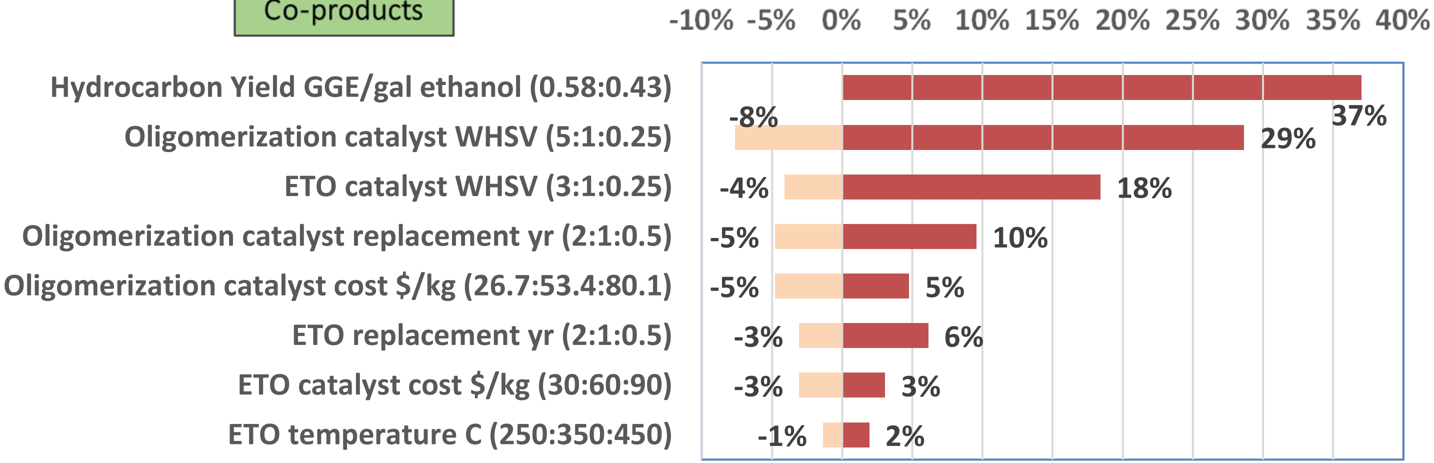
Task 2 (ORNL): metal modified Lewis acid zeolite (Cu-Zn-Y/BEA)



TEA and Process Design: Ethanol to Middle Distillates (ORNL-NREL)

Employ TEA of process based on Cu-Zn-Y/BETA catalyst (ORNL) to evaluate process costs and guide R&D efforts



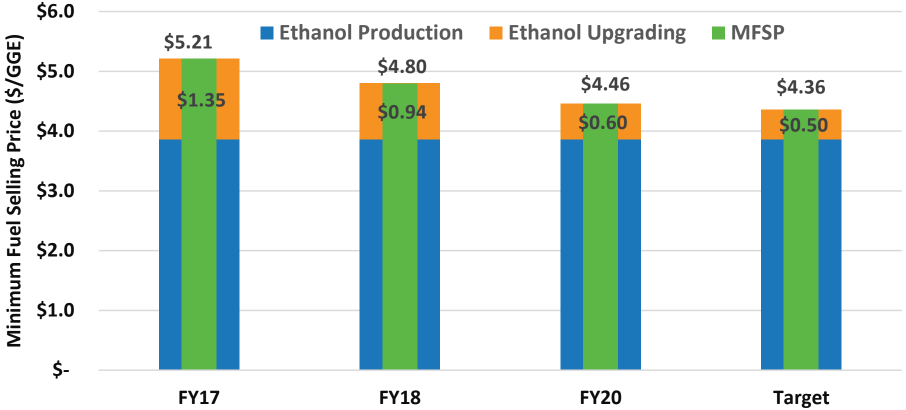


Sensitivity analysis based on ethanol upgrading cost

Process model developed for ethanol to middle distillate technology using ORNL catalyst, with key sensitivities on the processing costs evaluated

TEA Key Findings: Cost Improvements from FY17-FY20 (ORNL-NREL)

State of technology assessments provided annually



	FY17	FY18	FY20	Target
ETO Catalyst	H-ZSM-5	Cu-Zn-Y/Beta	Cu-Zn-Y/Beta	
Conversion (single pass, %)	100	~99	100	100
C3+ olefin selectivity (%)	33	87	89	95
Total olefin selectivity (%)	65	92	98	98
ETO Catalyst WHSV (h^{-1})	-	0.5	1	3
Hydrocarbon Yield (GGE/gal ethanol)	0.27	0.54	0.58	0.62

TEA sensitivity analysis provides guidance for critical future R&D efforts:

- Optimize C_{3+} olefins selectivity
- Improve catalyst space velocity
- Demonstrate and improve catalyst stability
- Critical to get coproducts either from lignin or ethanol

Further TEA guidance in FY21 on the types of coproducts to focus on.

Ethanol source: biochemical processing of corn stover (updated from Humbird 2011 report)

Advances in ethanol to olefin catalyst technology reduce ethanol upgrading cost by $0.75/GGE from FY17 to FY20

TEA and Process Design: Ethanol to Middle Distillates (PNNL)

Employ TEA of process based on mixed oxide catalyst (PNNL) to set targets and periodically assess state of technology

Enabling catalyst improvements:

Ketonization for C-C coupling produces CO_2

Aldol condensation for C-C coupling produces <u>NO</u> CO_2

Timeframe	Single-pass conversion (%)	n-Butene Selectivity (%)	Total Olefins Selectivity (%)	Distillate yield (GGE/dry ton)	Co-Product (wt. %)	MFSP ($/GGE)
Start of FY17[1] ($Zn_xZr_yO_z$)	99	47	58	41	None	**5.90**
FY18-G/NG[1] ($Ag\text{-}ZrO_2/SiO_2$)	99	58	85	57	None	**4.57**
End of FY20[2] (X/SiO_2)	98	62	89	58	None	**4.06**
Goal - distillate[2]	100	65	96	59	None	**3.58**
Goal – distillate + co-product[2]	100	65	96	33	44 wt.% n-butene	**3.16**

1. IDL FY18 G/NG Memo 2. Analysis Q4-FY20 QPM Report

Ethanol feedstock: gasification of forest residue

- Advances in ethanol to higher olefin catalyst technology reduce cost by $1.84/GGE from FY17 to FY20
- C_{3+} olefin selectivity a key driver for economics (carbon efficiency)
- n-Butene co-product enables $3/GGE (and more co-product further lowers MFSP)

TEA Key Findings: Key Sensitivities & Future Direction (PNNL)

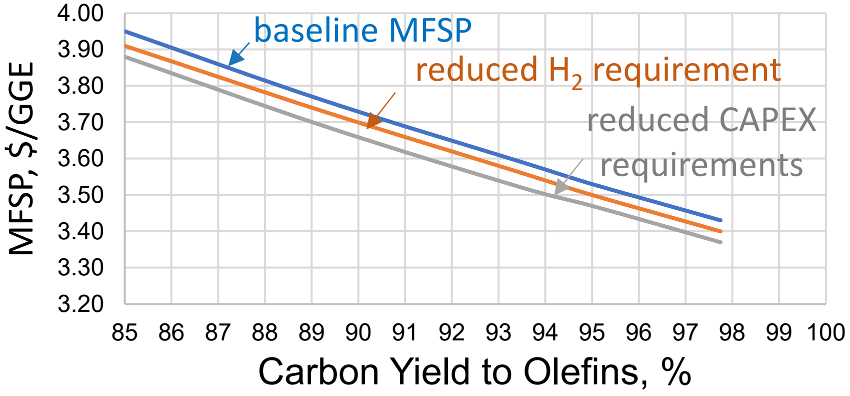
Key sensitivities determined for process model using mixed oxide catalyst (PNNL)

Guidance provided for future R&D efforts:

- Increase C_{3+} olefins selectivity (C efficiency)
- Verify oligomerization to distillates processing assumptions
- Demonstrate and improve catalyst stability/ regenerability
- Critical to get co-products (reduce costs/ product flexibility)

Further TEA guidance in FY21 on the types of coproducts to focus on.

Carbon Yield to Olefin vs. MFSP



Olefin selectivity key cost driver (carbon efficiency)

TEA informing PNNL experimental team on key drivers to reduce processing cost, and key assumptions that need verified

Feedstock: Forest Residues

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DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

Upgrading of C2 Intermediates- PNNL Experimental

March 10, 2021
Catalytic Upgrading Session

Robert Dagle
Pacific Northwest National Laboratory

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

Project Overview

Program objective

- Develop new upgrading technologies enabling cost-competitive conversion of **C_2 oxygenated intermediates** (including ethanol) to desirable **distillate fuels** and valuable **co-products**

Project outcome

- Develop catalytic pathway for **direct ethanol** to **butene-rich olefin** intermediates, recently discovered by our team, providing control over **jet** and **diesel** blendstocks and **co-products**, with the potential to obtain a distillate fuel MFSP of $3.00/GGE

Relevance

- Drawbacks for **current bioenergy conversion** pathways:
  - Smaller production scales
  - High capital and process costs
  - Limited carbon efficiency
  - Poor fuel quality
- **Advanced oxygenate upgrading** technologies address shortcomings by focusing on:
  - Process intensification (catalysis/ process)
  - Producing desirable distillate fuel
  - Co-products (lower cost/ product flexibility)
  - High carbon efficiency

1 – Management: Core Project within the ChemCatBio – FY21

Integrated and collaborative portfolio of catalytic technologies and enabling capabilities

Catalytic Technologies

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

Upgrading of C1 Building Blocks (NREL)

Upgrading of C2 Intermediates (PNNL, ORNL)

Catalytic Fast Pyrolysis (NREL, PNNL)

Electrocatalytic CO_2 Utilization (NREL)

Enabling Capabilities

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

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

Catalyst Deactivation Mitigation for Biomass Conversion (PNNL)

Industry Partnerships (Phase II Directed Funding)

Opus12 (NREL)

Visolis (PNNL)

Sironix (LANL)

Cross-Cutting Support

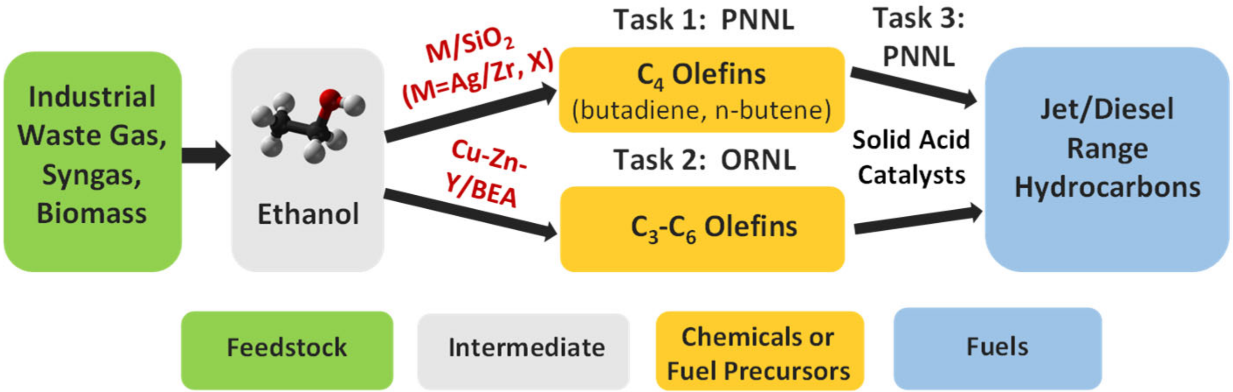
ChemCatBio Lead Team Support (NREL)

ChemCatBio DataHUB (NREL)

1 – Management: Project Overview and Communications

Project overview:

- Explore two different new catalyst systems to convert **ethanol** to **C_{3+} olefins** (PNNL, ORNL)
- Produce **distillate fuels** from olefin intermediates & understand fuel properties/ economics (PNNL)



Integration of enabling projects & communication plan:

- **PNNL** and **ORNL** experimental teams **communicate** on quarterly basis with combined reporting to DOE & ChemCatBio leadership
- **Integrated** with **enabling projects/** collaborations with joint quarterly milestones (& written/ oral reporting)
- **Joint patents, presentations, publications** stem from collaborations

1 – Management: Collaboration Structure

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

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

Washington State University

CDM | CCPC | ACSC | WSU | TEA

Task 1 (R. Dagle) Ethanol upgrading: mixed oxide catalysis (PNNL)

Task 2 (Z. Li) Ethanol upgrading: zeolite catalysis (ORNL)

Task 3(R. Dagle) Olefins to distillate (PNNL)

Higher TRL Project Spinoffs:

Ethanol to n-butene scale-up via microchannels (FY21-23 FOA)

Higher energy-content jet blending components (FY21-23 FOA)

Microchannel Reactive Distillation (FY19 TCF)

Spin out of technologies to higher TRL activities

- **Cooperative** and **synergistic research areas** between PNNL and ORNL leverages strengths in catalysis, oxygenate conversion, and oligomerization
- **Enabling projects** Catalyst Deactivation Mitigation (CDM), Computational Modeling (CCPC), and Advanced Catalyst Synthesis and Characterization (ACSC) projects
- **Washington State University (WSU)** fundamental catalysis understanding, leverages BES catalysis
- **Techno economics analysis (TEA)** target costs, state of technology assessments
- **Spin out** of technologies to higher technology readiness level (TRL) activities

1 – Management: Risk Management Plan

Risk	Mitigation Plans Aided by Partnering	
Carbon efficiency • High carbon efficiency critical to enable cost goals	Development of selective catalyst(s): • **Computational modeling team (CCPC):** mechanistic understanding and catalyst design improvements	• **Washington State University (WSU):** new catalyst synthesis/ improved structure-function understandings.
Catalyst durability, regeneration • Robust/ regenerable catalysts required for commercial adaption	Catalyst durability and regeneration studies: • **Catalyst Deactivation Mitigation (CDM):** advanced characterizations for durability/ regenerability studies	• **Techno-Economic Analysis (TEA):** process cost of regeneration schemes to guide feasibility
Process economics • Achieving $3/GGE distillate fuel is challenging for bioenergy	Technoeconomic analysis (TEA): • **Establish performance targets, sensitivity analysis** to identify largest cost reduction parameters and experimental verification needs	• Evaluation of **co-product** strategies to **reduce MFSP**, suitable for distillates

2 – Approach: Benchmarking Ethanol-to-Olefin Catalysis

Catalyst	T (°C)	Conv (%)	Selectivity (mol C%)	
			Ethylene	n-Butene
γ-Al_2O_3 ZSM-5	350	>95	99	0
Ag-ZrO_2/SiO_2 *(this work - FY18)*	**400**	**98**	**26**	**58**
$Zn_xZr_yO_z$*	450	99	< 5	42
Ce-HZSM-5	400	100	N/A	20
Ni-MCM-41	350	100	N/A	8.1

ACS Catal. 2020, 10, 18, 10602–10613

* *Produces iso-olefins*

Ethanol-to-Ethylene

- **High selectivity** to ethylene from ethanol
- However, multiple steps required to selectively convert to distillate fuels

Ethanol-to-C_{3+} olefins

- **Poor selectivity** to higher olefins (C_{3+}) from ethanol reported in literature (and often high in aromatics)
- Single step conversion to jet/ diesel from C_{3+} olefins.

- Multi-step (PNNL-LanzaTech ATJ) or homogenous processes (SHOP/ Ziegler) required for selective conversion of **ethylene** to **jet/ diesel**
- Single step conversion of **C_{3+} olefins** to **jet/ diesel** demonstrated
- However, selective routes from **ethanol** to **C_{3+} olefins** do not exist

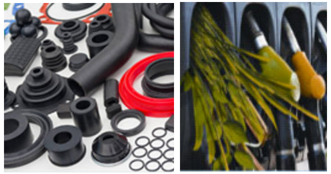
2 – Approach: Baseline Status ($Ag\text{-}ZrO_2/SiO_2$)

Technological achievement coming into FY19

Applied Catalysis B 2018, *236*, 576–587
ACS Catal. 2020, 10, 18, 10602–10613

Flexible **single-step** catalytic process for production of **butadiene** or **butene-rich olefins** from **ethanol**

- Low H_2 partial pressure: butadiene product
- Higher H_2 partial pressure: butene-rich olefins



n-Butene Uses
(fuel precursor/ co-product)

Butadiene Uses

US Patent 10,647,625, issued May 2020
US Patent 10,647,622, issued May 2020

Feed	Conv (%)	Selectivity (C mol %)		
		$C_2^=$	$C_4^=$	Butadiene
EtOH in inert	99.0	5.8	11.2	**70.5**
EtOH in reducing environment	93.9	25.7	**57.7**	0.0

Best catalyst (FY18 G/NG):

- Butadiene selectivity = 75%, conversion > 90%
- C_{2+} olefins selectivity = 85% (C_{3+} olefins selectivity = 60%), conversion > 90%

FY17-FY18 discovery of new metal promoted Lewis acid catalyst system offering tunability for producing either butadiene or n-butene ($Ag\text{-}ZrO_2/SiO_2$).

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Project objective:

- Develop **ethanol** to **butene-rich olefins** process using **new catalyst technology** developed by our team, providing control over jet, diesel, and co-products, with ability to obtain a **distillate MFSP** of **$3.00/GGE**
  - > 20% cost reduction over state of technology at FY18 G/NG
  - Performance improvements & co-product option(s) required

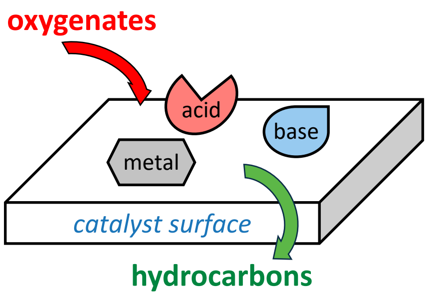
Project goals:

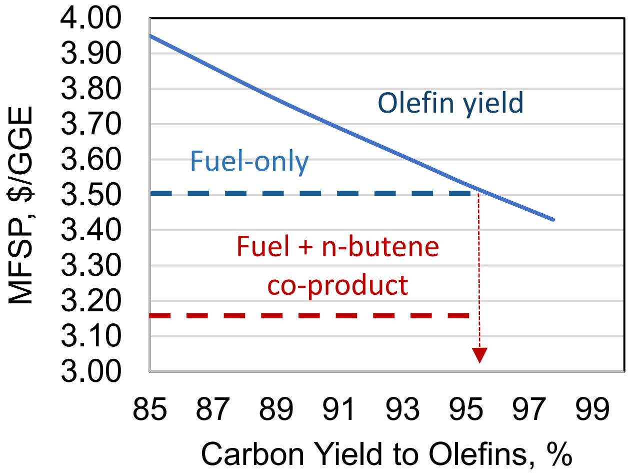
- Increase selectivity to **C_{3+} olefins**, enhance **catalyst stability**, and **develop regeneration protocols**.
- Control product slate to **diesel, jet,** and **co-products** through produced olefin intermediates.
- Investigate **co-product options** (e.g., n-butene, butadiene) with co-production appropriate for distillate production and with the potential to reduce distillate MFSP.
- Leverage and expand process models, **TEAs**, and sensitivity developed for ethanol pathways.

2 – Approach: Research Challenges & Cost Drivers

Research challenges:

- Balancing **sequence of reactions** and selectively produce C_{3+} olefins directly from ethanol using **multifunctional catalyst**
- Catalyst selectivity (carbon efficiency)
- Catalyst durability





Major cost drivers:

- Increasing **olefin selectivity** & developing **co-product option(s)** are critical to reducing processing costs
- Distillate MFSP cost target; assuming **95% carbon yield to olefins** achieved:
  - **$3.58 - Distillate-only**
  - **$3.16 - Distillate** + n-butene **co-product** (44 wt.%)

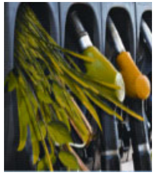
2 – Approach: Major Deliverable Schedule for FY20-22

Milestone/ G/NG	Brief Description	Due Date
PNNL, ORNL Milestone Yr 1.5	**Ethanol-to-olefins intermediate performance target** • Experimentally *achieve* 65% C_{4+} olefin selectivity, 90% C_{2+} olefin selectivity, and 90% conversion from ethanol	Q2-FY21 (3/31/2021) ✓
Go/No-Go	**Evaluation of overall pathway to meet FY22 cost targets** • Given performance results to-date assess feasibility for achieving $3/GGE distillates MFSP via TEA modeling. Develop co-product strategi(es) enabling cost target be met, informing experimental next steps	FY21 (5/31/2021)
PNNL Milestone Yr 2	**Ethanol-to-distillates process evaluation** • Experimentally evaluate 2-step processing & understand carbon/ process efficiency and fuel properties	FY21 (9/30/2021)
PNNL, ORNL Milestone Yr 3	**End Project Outcome:** • Set state of technology with experimental catalyst/ process demonstration at bench scale, assess ASTM properties of fuel and ability to obtain $3/GGE distillate process from ethanol	FY22 (9/30/2022)

3 – Impact: Ethanol Feedstock & Technology Value Proposition

Ethanol – an attractive feedstock:

- Ethanol commercially produced from renewable biomass & waste sources
- Ethanol prices 5-yr avg $1.25 - 1.80 /gal with 17 billion gallon/yr U.S. (from corn)[1]
- Factors expected to reduce ethanol prices:
  - Ethanol "blendwall"
  - Advancement in production efficiency
  - Feedstock diversification

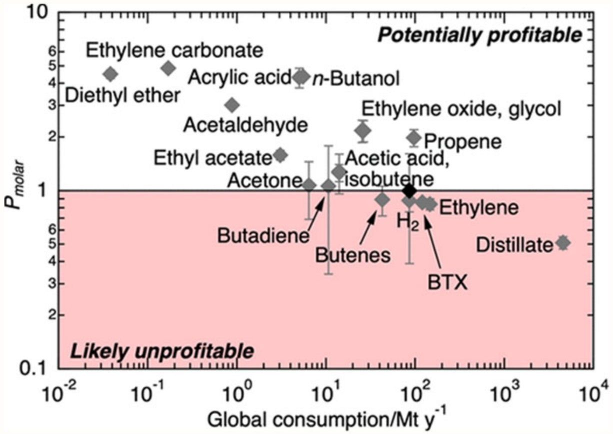
n-Butene Uses
- fuel precursor/
co-product

Butadiene Uses



1. https://markets.businessinsider.com/commodities/ethanol-price

Ethanol as a Renewable Building Block for Fuels & Chemicals



Approximate indicator of operating costs. P_{molar} = ratio of the price of a product divided by the cost of the stoichiometric quantity of ethanol required to produce it.

Price ranges were estimated from the ranges of prices over 2015–2019. Does not consider RINs.

Ind. Eng. Chem. Res. **2020** *59* (11), 4843-4853

Technology value proposition:

- Enable existing ethanol producers to overcome stagnating light-duty fuel market by diversifying their product streams toward **middle-distillate fuels** and **renewable chemicals**

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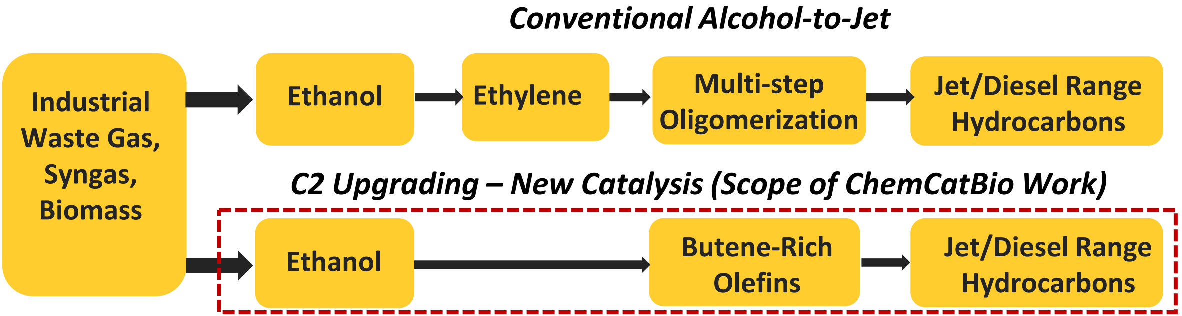
LanzaTech capturing carbon. fueling growth.

PNNL co-developed Alcohol-to-Jet Process (ATJ)

- Demonstration scale LanzaTech ATJ process operating in Georgia utilizes conversion technology licensed from PNNL

October 2018 Virgin Atlantic flight using low-carbon fuel from LanzaTech's biorefinery in Georgia using technology co-developed with PNNL.



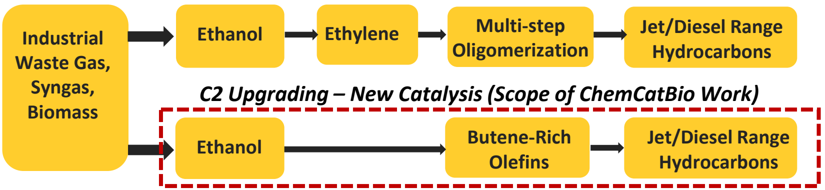
Differentiators versus current Alcohol-to-Jet:

- **Capital savings**: eliminates dehydration step
- **Energy savings:** combines endothermic and exothermic reactions
- Potential for **co-products** from ethanol enabled with new multifunctional catalysts

3 - Impact: One Step Closer to Commercialization

Progression to higher TRL opportunities

- BETO FOA project w/ partners Oregon State University and LanzaTech to **scale-up** the **catalyst technology** developed from this project
- Scale-up also using **microchannel reactors,** enabling further **process intensification** and **modularity**



US Patent 10,647,625
US Patent 10,647,622

ACS Catal. 2020, 10, 18, 10602–10613
ChemCatChem 2020, 12, 1-11

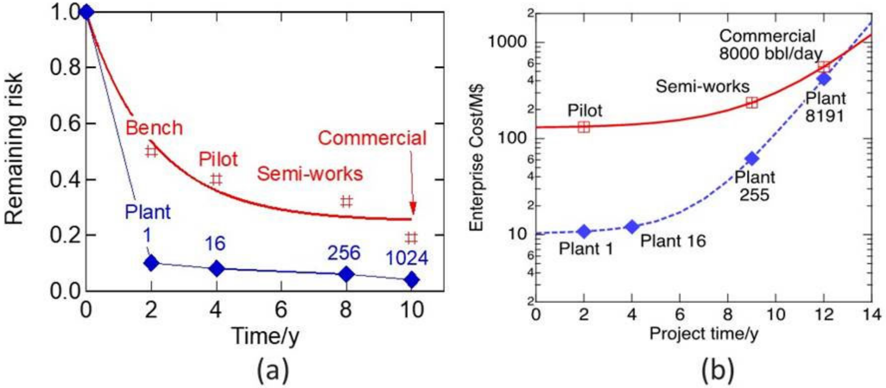
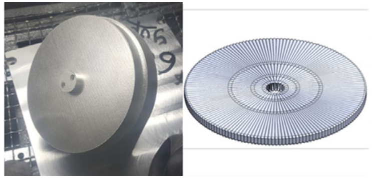


Figure: (a) risk-reduction, and (b) enterprise cost models for numbering up and conventional scaling

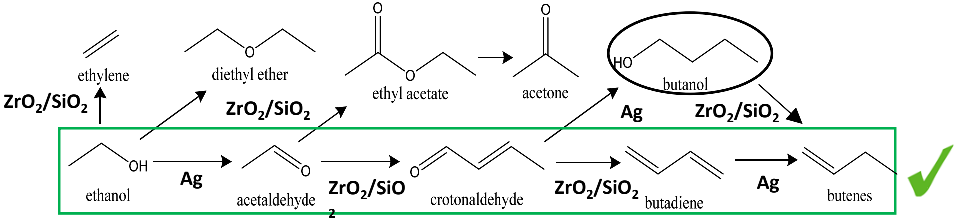
- **Scale up by numbering up**, quickening time to market and reducing risk
- Leverages recent advances in **additive manufacturing**

Microchannel reactors increase efficiency and reduce cost of biofuel/ chemical production; amendable at the scale of biomass

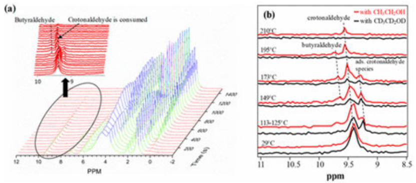


New metal promoted Lewis acid catalyzed system further explored

Cascading sequence of reactions

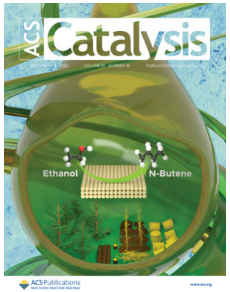


Mechanism Verification
(in situ NMR)



- Catalytic **mechanism** verified
- Product flexibility of n-butene/ butadiene processing further explored by studying effect of **H_2 partial pressure**, other **process variables**
- Systematic evaluation of **metal** and **Lewis acid sites** effect on catalytic performance
- New catalytic pathway first published (ACS Catalysis)

Published New Catalysis



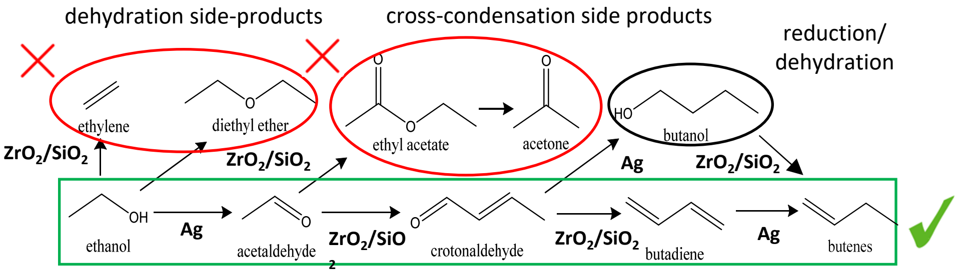
ACS Catal. 2020, 10, 18, 10602–10613

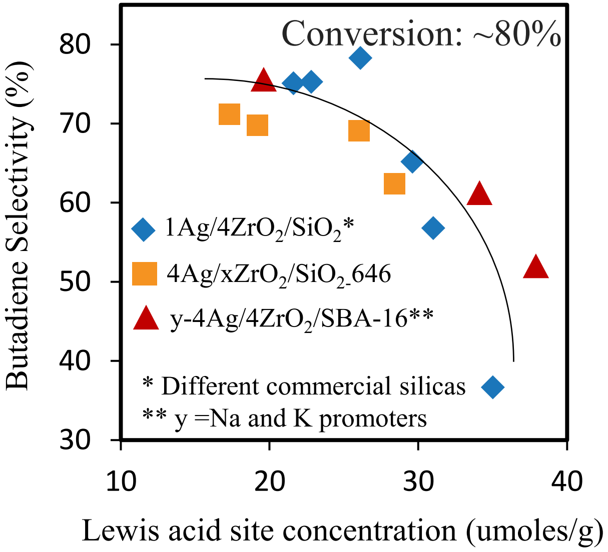
US Patents 10,647,625 and 10,647,622, issued May 2020

Established **catalytic mechanism** and evaluated effect of key **catalyst properties** and **processing variables** on catalytic performance, patented and published findings.

Understanding metal and Lewis acid site characteristics on performance

Cascading sequence of reactions





Applied Catalysis B 2018, *236*, 576–587

- **Ethanol Conversion:** Correlated to **Ag dispersion** (not shown)
  - Facilitates initial ethanol dehydrogenation
- **C_4 Selectivity:** Correlated to **Lewis acid site concentration**
  - Increasing acidity ➔ more dehydration (bad) and less cross condensation (good) side products
  - Optimum Lewis acidity for making C_4 products (butadiene/n-butene)

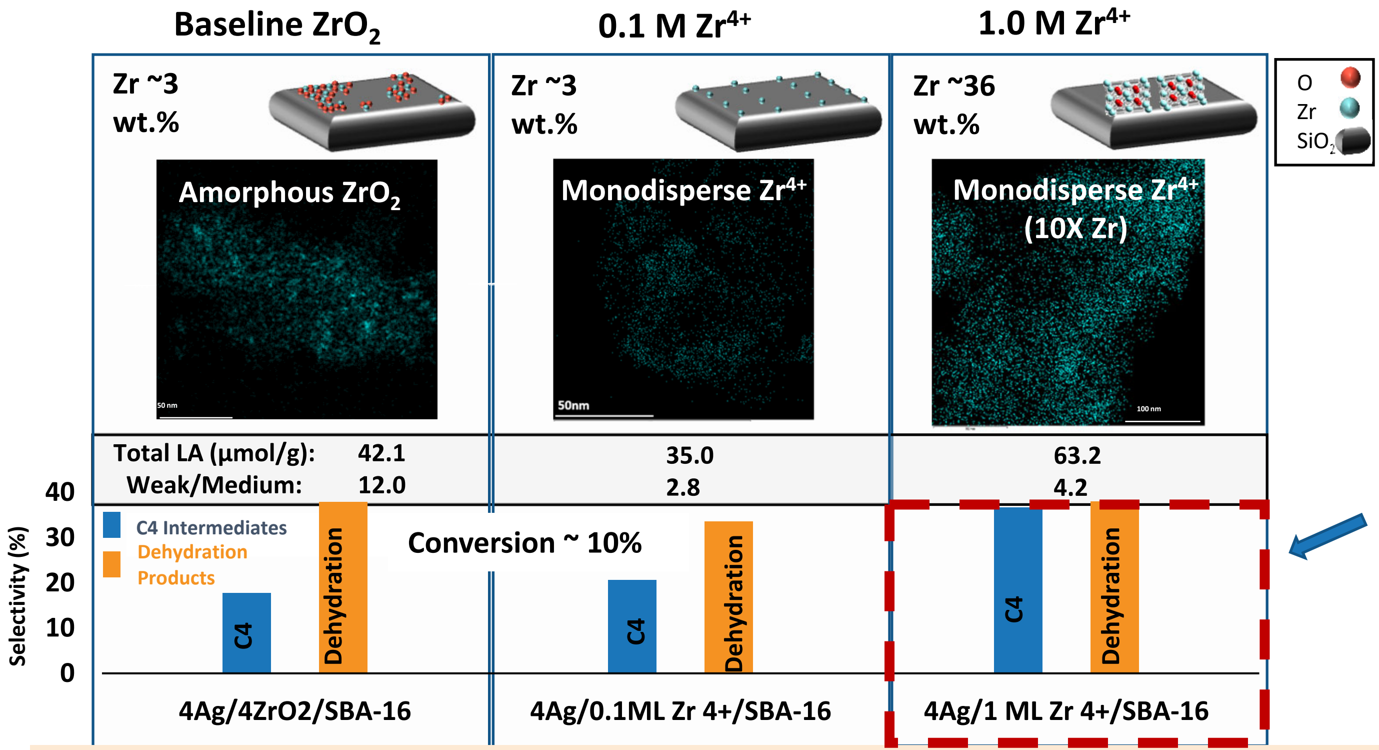
Consistent trends found across silica supports, Zr loading, and dopants (Na, K) investigated.

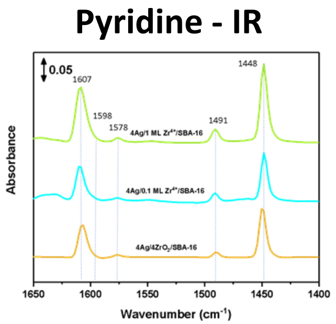
325°C, 1 atm, varied WHSV

Corelated metal dispersion (Ag) and Lewis Acidity (Zr-SiO_2) to activity and product selectivity, respectively.

WASHINGTON STATE UNIVERSITY

Atomic layer deposition (ALD) synthesis of Zr on SiO_2 provides insights into nature of acid sites on reactivity



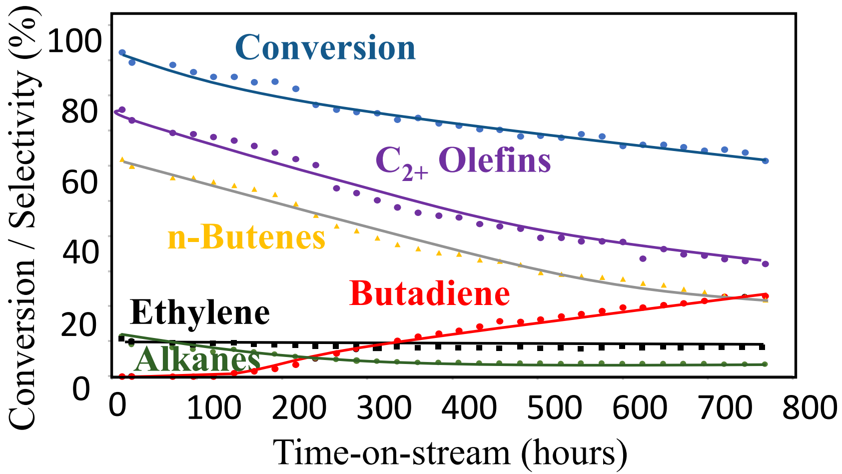


- Grafted Zr reveal differences in **nature of Lewis acidity** versus baseline incipient wetness.
- Increased grafted Zr loadings result in increased *total* **Lewis acid concentration**
- However, decreased **weak/ medium acid site ratios** lead to increasing C_4 formation *without* increase in dehydration products

Developed fundamental understanding for how unique synthesis of catalysts with **tailored Lewis acid strength characteristics** can more selectively favor C_4 versus dehydration products.

325°C, 8.0 hr^{-1}, 1 atm; 10 mol % EtOH in N_2.

Catalyst stability – 800 hours test



ChemCatChem 2020, 12, 1-11

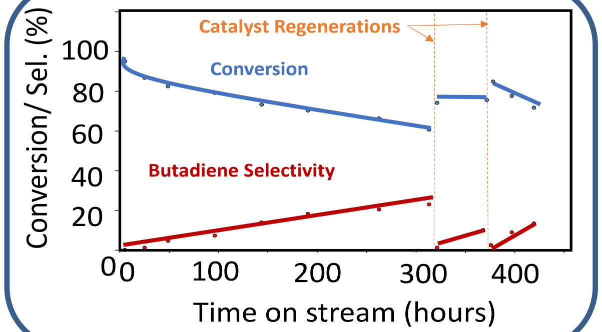
325 ℃, 100 psig, 0.23 hr[-1]

- Deactivation mechanisms identified for Ag catalyst.
- Catalyst regeneration demonstrated; step change in deactivation attributed to irreversible Ag particle sintering.

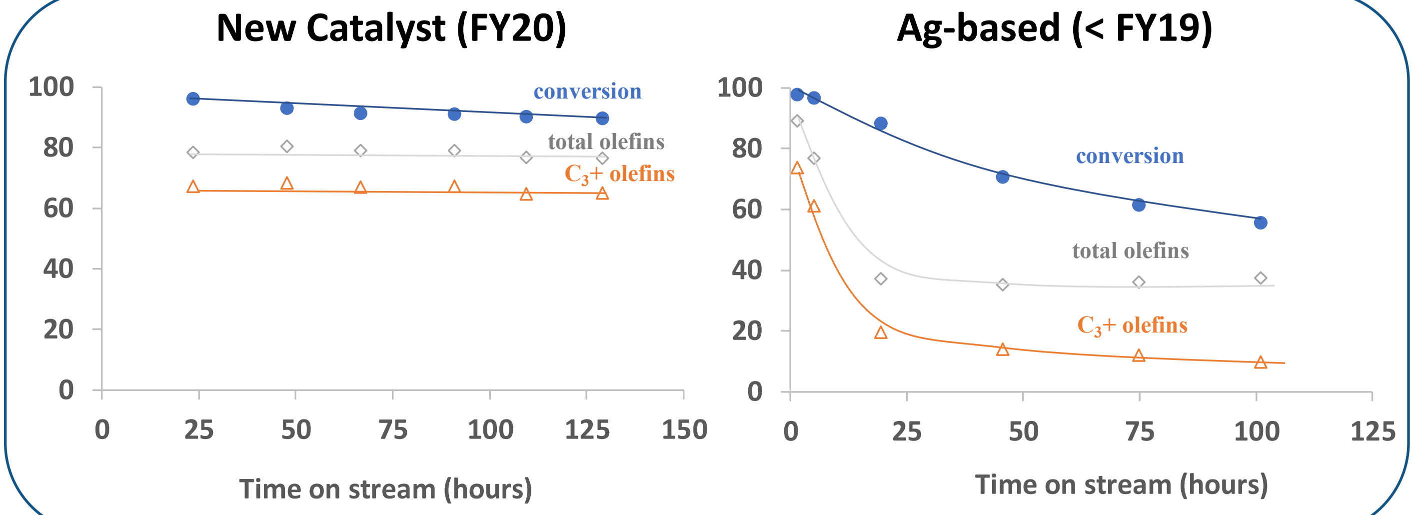
Parameters contributing to deactivation:

- **Change in Ag oxidation state**
  - XPS reveals metallic Ag partially oxidized (reversible)
- **Coking**
  - TCA and TGA reveals carbon deposition (reversible)
- **Sintering of Ag particles**
  - TEM reveals Ag particle sintering from ~2.8 to 4.0 nm (irreversible)

Catalyst Regeneration



Improved catalyst (FY20) versus Ag (<FY19) catalyst formulation:



Parameters contributing to Ag deactivation:
- Change of Ag oxidation state
- Coking
- Sintering of Ag particles

Parameters contributing to new catalyst stability:
- Remains metallic
- Less coke (mechanistic difference)
- ~ 2.5 nm metal particles

ChemCatChem 2020, 12, 1-11

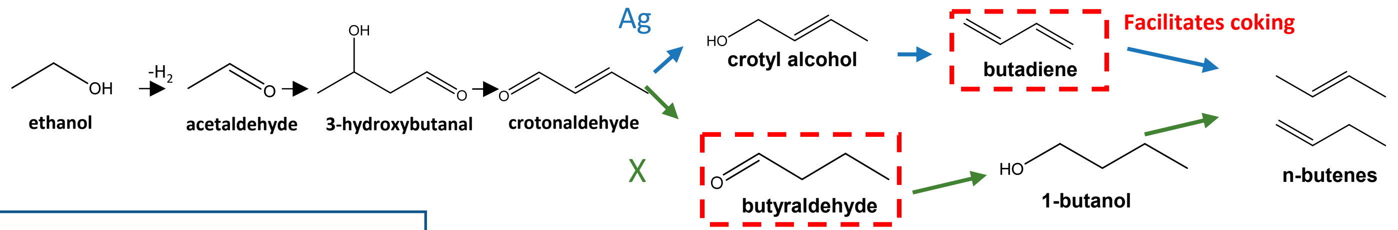
ACS Catal. 2020, 10, *236*, 10602-10613

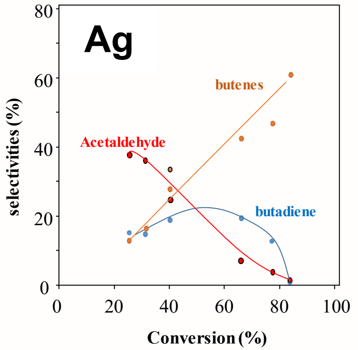
- **Higher stability:** 3X less coke formation with new versus prior Ag baseline catalyst
- **Higher activity:** 8X more activity enabled with higher operating temperature (400 versus 325°C)

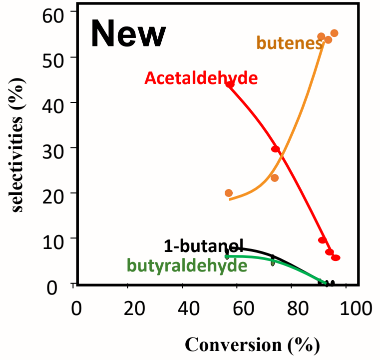
Improved catalyst formulation drastically improves stability over prior Ag-based baseline catalyst.

Unraveling & exploiting mechanistic differences between new catalyst (FY20) and Ag (<FY19)

Favorable Bifurcation in Mechanism Enabled with New Catalyst – to be verified via NMR







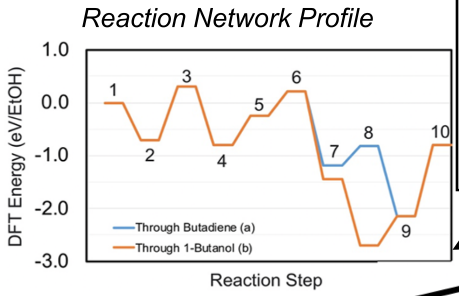
- Butadiene intermediate – coking precursor

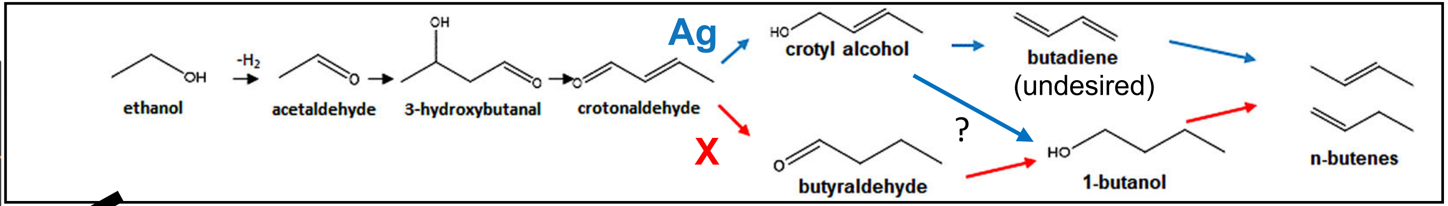
- Butadiene not observed
- Butyraldehyde/ butanol intermediates

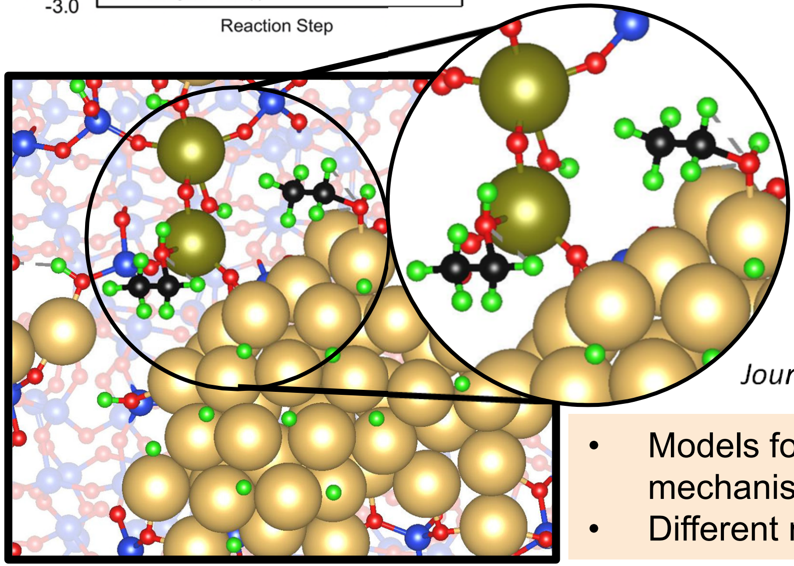
- Improved durability of new catalyst attributed to change in **mechanism**, avoiding butadiene intermediate
- Further **tuning of catalyst parameters** resulted in best catalyst performance to-date:
  - EtOH conv. = 98%, C_{2+} olefin sel. = 90%, C_{3+} olefin sel. = 85%,
- Reducing modelled distillate MFSP from **$4.57/GGE** (FY18-G/NG) to **$4.06/GGE** (end-FY20)

Discerned different mechanism for new catalyst and made additional catalyst design improvements lowering modeled MFSP cost of distillate by $0.51/GGE in ~ 3 years.

Computational models developed to rationalize catalytic mechanism(s) & provide catalyst design inputs

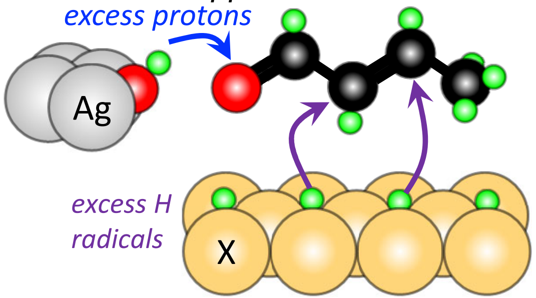






Mechanistic switch explained: Current hypothesis that higher concentration of **H radicals** on X NP vs Ag NP leads to preferential saturation of C=C bonds over protonation of C=O bonds thus avoiding butadiene. Higher concentration of **protons** at Ag NP interface has opposite effect.

Ethanol molecules bind in proximity to each other: one to the Lewis acid promoter, the other to the NP at the interface



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- Models for metal nanoparticles supported on ZrO_2/SiO_2 developed to rationalize mechanisms and role of metal and Lewis acid sites on influencing performance.
- Different metal oxides/ promoters being investigated to inform catalyst design.

Major challenges and risks being addressed moving forward

- Increase **C_{3+} olefin selectivity** (carbon efficiency)
- Understand/ improve **catalyst stability**, develop **regeneration protocols**, and evaluate performance using **real feedstocks** (underway)
- Develop/ demonstrate **oligomerization** processing of produced olefin intermediates to **jet-/ diesel-range hydrocarbons**
- Evaluate additional **co-product** options (reduce cost/ product flexibility)

Real Feedstocks

Before **After**

- Distillation performed of NREL-derived ethanol fermentation broth.
- Stability test with real feedstock performed.

Fuel Properties of jet-range hydrocarbons using C_3-C_4 olefin intermediates from FY17 SOT catalyst ($Zn_xZr_yO_z$)

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)

- Prior fuel product slate met 4 key **ASTM standards** for jet fuel (2018)
- Fuels produced via olefin intermediates from new catalyst need evaluated

Catalysis Science & Technology 2019, 9, 1117

Acknowledgements

PNNL Experimental Team (Task 1, 3)

Robert Dagle, Vanessa Lebarbier Dagle, Johnny Saavedra-Lopez, Matt Flake, Libor Kovarik, Mark Bowden

ORNL Experimental Team (Task 2)

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WSU team

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TEA Team

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CCPC - Atomic Scale (PNNL)

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CCPC – Mesoscale (NREL)

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Energy Materials Network U.S. Department of Energy

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

WASHINGTON STATE UNIVERSITY

EMSL

Summary

Project Goal:

- New catalytic pathway for direct ethanol conversion to **n-butene-rich olefins**, providing control over **jet** and **diesel** blendstocks and **co-products**, to enable distillate MFSP of $3.00/GGE

Management

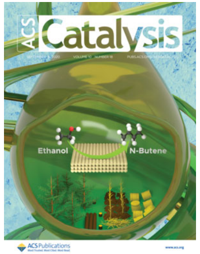
- **Multifunctional catalysts** employing tandem reactions leading to high C efficiency
- **Collaborative approach** within ChemCatBio leveraging expertise targeting **key challenges** around catalyst selectivity and durability

Approach

- Setting **state-of-the-art ethanol catalysis** enabling process intensification and **high C efficiency**
- **Co-products** reduce costs & diversity product offerings

Impact

- **Reduced costs** versus **current state of technology**
- **Tech transfer** with industry (CRADA projects with LanzaTech)
- Patented **intellectual property** (2), and **published results** (6 papers) in top-tier peer-reviewed journals.



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Progress and Outcomes

- Established catalytic mechanisms and effect of key catalyst properties and processing variables
- Better catalyst with **improved activity** (8X productivity) and **stability** (3X less coke formation) versus prior Ag formulation
- Reduced modelled distillate MFSP from **$4.57/GGE** (FY18-G/NG) to **$4.06/GGE** (end-FY20)

Quad Chart Overview

Timeline

- Project start date: October 1, 2019
- Project end date: September 30, 2022

	FY20	Active Project
DOE Funding	$750K (FY20)	$2.25M (FY20-22)

Project Partners

- ORNL – C2 Upgrading WBS 2.3.1.100
- Within ChemCatBio Consortium:
  - CCPC - Atomic Scale Modeling Team
  - CDM Project
- TEA Analysis Task
- WSU – Sub-contract (Experimental Catalysis)

Barriers addressed

Ct-F: Increasing the Yield from Catalytic Processes

Ct-E. Improving Catalyst Lifetime

Project Goal

By FY22 demonstrate improvements to the direct ethanol to butene-rich olefins catalyst technology thereby enabling a new, market-responsive biorefinery pathway through C2+ oxygenates providing control over gasoline, diesel, jet, and co-products, with potential to achieve a modeled distillate MFSP of $3.00/GGE

End of Project Milestone

Obtaining a $3/GGE MFSP for distillates represents a > 20% cost reduction over the state of technology reported from the FY18 GNG. The baseline FY18 model as reported in the FY18 G/NG projected a distillates MFSP cost of $4.57/GGE. If $3.00/GGE were achieved this would represent a 34% reduction in MFSP. This will be achieved by improving the catalyst formulation to enhance selectivity to n-butene and validating the TEA model regarding catalyst durability. The olefin catalyst will be evaluated for at least 100 hours' time-on-stream and the effectiveness of regeneration will be evaluated for at least two regeneration cycles. New co-product options (e.g., para-xylene, n-butene) will also be investigated via TEA starting in Year 2, with co-production appropriate for distillate production and with the potential to reduce distillate MFSP to enable cost target.

Funding Mechanism

CCB Merit Review AOP for FY20-22

Additional Slides

Responses to FY19 Peer Reviewers' Comments

1. **Comment: "**The team should stay vigilant and not trivialize the oligomerization chemistry required to drive the C-C bond formation to distillation range."

Response: We agree completely The upstream oxygenate-to-olefin catalysis has certainly been prioritized because this is where we believe the primary advances need made to achieve major improvement to the state-of-the-art. Most conventional routes to jet/ diesel from ethanol – at least those that do not also produce aromatics - rely on ethanol dehydration to produce ethylene. Controlling the selectivity to distillate-range hydrocarbons from ethylene is where much of the innovation has historically been made, versus direct oxygenate conversion to higher olefin pathways. Further, we have prior experience already with the oligomerization of n-butene to jet-range hydrocarbons. However, when mixtures of olefins, particularly lighter olefins, are present in the oligomerization tradeoffs in the processing are made to incorporate these lighter feedstocks in the oligomerized product. These tradeoffs can affect the product distribution and fuel properties. **In 2019 we published a paper in *Catalysis Science & Technology* that demonstrates these tradeoffs, entitled, "Oligomerization of ethanol-derived C3 and C4 alkenes to transportation fuels: catalyst and process considerations".** We do note that in FY21 we will being to evaluate the oligomerization processing for the olefin mixture produced by our most recent olefin catalyst. Selective oligomerization to the desired product slate is indeed a critical element.

2. **Comment:** "The butadiene product produced and other intermediate olefins are more valuable than fuel and should be considered as the main product."

Response: Yes. Per DOE mandate the primary objective of this project is to produce high quality distillate fuel(s) with high carbon efficiency. Producing valuable co-products is nominally one way to drive down the cost of the fuel. We also realize that converting more valuable intermediates (e.g., higher olefins) to fuels versus chemicals may not be rational from an economic perspective. **However, one of our aims of this development program is to better understand and develop pathways for light oxygenate conversion, and these scientific discoveries are expected to be applicable to both fuel and chemicals.** We have talked before about a biorefinery concept where different fuels or products could be produced given varying market conditions. Further, while this project is at least currently focused on distillate production, we envision spinning out different project(s) focused on producing specific products such as butadiene. We note that we have received significant interest from industry for making butadiene from ethanol, however, we have not yet been successful in obtaining funding from DOE for this.

Responses to FY19 Peer Reviewers' Comments, cont.

3. **Comment:** "Scaling is an important consideration on this project. It would be beneficial to evaluate modular processes as well and evaluate how synthetic catalysts work on large scale processes."

Response: Yes, we couldn't agree more! **As reported in this presentation the project team was recently awarded a FOA project to scale up the catalyst technology developed on this project – for ethanol to n-butene – and this scale up will be performed using new microchannel reactor technology.** The heat and mass transfer reductions enabled by microchannel reactors enable modularity and therefore scale up by numbering up. For over two decades our group at PNNL has played a leadership role in the development of microchannel reactor technology. PNNL has spun out two companies engaged in the commercialization of microchannel technology (Velocys for Fischer-Tropcsch technology, and more recently STARS LLS for solar-aided steam methane reforming). Further, recent advances made by our group at PNNL in additive manufacturing – funded by the DOE Advanced Manufacturing Office - have resulted in major cost reductions to the fabrication of microchannel reactors. This new scale-up activity will include Oregon State University and commercial partner LanzaTech.

4. **Comment:** "How does some of the catalysts compare with the ones in the literature or commercially available – benchmarking?

Response: **In the Approach section we provided a benchmark of currently known ethanol to olefins catalysis.** We also describe how ethylene today can be selectively produced from ethanol however multiple steps are required to produce jet/ diesel range hydrocarbons from ethylene. Also note that there are no true commercial process to baseline the ethanol-to-jet technology with. In this presentation we show how the technology under development represents the potential for major improvement to the alcohol-to-jet process developed by PNNL and being commercialized by LanzaTech that we believe to represent the state-of-the-art. However, this performance data has not been published due to proprietary concerns. Other relevant industrial processes that could be used for ethanol-to-jet include well known homogenous catalyzed system to convert ethanol-derived ethylene to distillate (e.g., Shell's SHOP, Ziegler Processes). However, faster, larger scale production is typically better realized when using heterogenous catalyzed systems. Other ethanol to *higher olefin catalysts* have been reported in the literature and these results are quite poor (as shown). Finally, since our TEA model uses gasification of forest residue as its source of feedstock, route to distillate from methanol could be produced as benchmark. Thus, using a methanol-to-olefins-to-distillate process would be relevant as a commercial benchmark. For baseline MOGD we reported a MFSP of $4.80/GGE at the FY18 G/NG.

Publications, Patents, and Commercial Engagement

Publications:

- "Single-Step Conversion of Ethanol to n-Butenes-rich Olefins over Ag/ZrO2/SiO2 Catalysts." *ACS Catal*. 2020, 10, 18, 10602–10613.
- "Understanding the Deactivation of Ag–ZrO2/SiO2 Catalysts for the Single-step Conversion of Ethanol to Butenes." ChemCatChem 2020, 12, 1-11.
- "Ethanol as a renewable building block to value-added fuels and chemicals." *Industrial and Engineering Chemistry Research,* 2020, 59, 4843-4853.
- "Influence of Ag metal dispersion on the thermal conversion of ethanol to butadiene over Ag-ZrO2/SiO2 catalysts." *Journal of Catalysis,* 2020, 286, 30-38.
- "Oligomerization of ethanol-derived C3 and C4 alkenes to transportation fuels: cat. and process considerations." *Catal. Sci. Technol.,* 2019, 9, 1117-1131.
- "Multi-scale simulation of reaction, transport and deactivation in a SBA-16 supported catalyst for the conversion of ethanol to butadiene." *Catalysis Today,* 338, 2019, 141-151.
- "Effect of the SiO2 support on the catalytic performance of Ag/ZrO2/SiO2 catalysts for the single-bed production of butadiene from ethanol" *Applied Catalysis B: Environmental,* 2018, 236, 576–587.

U.S. Patents:

- Dagle et al., "SINGLE STEP CONVERSION OF ETHANOL TO BUTADIENE", US Patent # 10,647,625, issued May 2020.
- Dagle et al., "SINGLE-REACTOR CONVERSION OF ETHANOL TO 1-/2-BUTENES", US Patent #10,647,622, issued May 2020.

Commercial Engagement:

FY21-FY23 BETO multi-topic FOA proposal project w/ partners **Oregon State Univ**ersity and **LanzaTech** to scale up ethanol to n-butene catalytic process developed on this project.

Presentations:

- Dagle R.A., V. Dagle, and R.S. Weber. 7/9/19. "Single-Step Conversion of Ethanol to n-Butenes and Butadiene over Mixed Oxide Catalysts." Presented by R.S. Weber at Bio World Congress on Industrial Biotechnology 2019, Des Moines, Iowa.
- Dagle R.A., V. Dagle, and Z. Li. "Single-Step Catalytic Conversion of Ethanol to n-Butene-Rich Olefins and 1,3-Butadiene Chemical Coproduct." Presented by Robert Dagle, Vanessa Dagle, and Zhenglong Li at ChemCatBio Webinar Presentation (Online), July 31, 2019.
- Dagle V., A.D. Winkelman, S.A. Akhade, J. Saavedra Lopez, S.F. Yuk, V. Glezakou, and R.J. Rousseau, et al. 10/07/2019. "Single-Step Conversion of Ethanol to Butadiene and Butenes over Ag/ZrO2/SBA-16 Catalysts." Presented by R.A. Dagle at Tcbiomassplus2019, Rosemont, Illinois.
- Davidson S.D., J.A. Lopez-Ruiz, V. Dagle, K.O. Albrecht, and R.A. Dagle. 06/27/2019. "Production of Olefins from Biomass Liquefaction Derived Aqueous Phase over ZnxZryOz Catalyst." Presented by S.D. Davidson at NAM-26, Chicago, Illinois.
- Dagle V., A.D. Winkelman, J. Saavedra Lopez, and R.A. Dagle. 04/04/2019. "Single-Step Conversion of Ethanol to Butadiene and butenes over Ag/ZrO2/SiO2Catalysts." Presented by A.D. Winkelman at American Chemical Society, Orlando, Florida.
- Dagle V., A.D. Winkelman, L. Kovarik, M. Engelhard, N.R. Jaegers, H. Wang, and J.Z. Hu, et al. 10/05/2020. "Single-Step Conversion of Ethanol to n-Butenes-rich Olefins or Butadiene over metal supported on ZrO2/SiO2 Catalysts." Presented by A.D. Winkelman at 2020 Thermal & Catalytic Sciences Virtual Symposium, Richland, Washington.
- Winkelman A.D., V. Dagle, S.A. Akhade, J. Saavedra Lopez, V. Glezakou, R.J. Rousseau, and N.R. Jaegers, et al. 08/02/2019. "Single-Step Conversion of Ethanol to Butadiene and Butenes over Ag/ZrO2/SBA-16 Catalysts." Presented by Austin Winkelman at PNNL's Gold Experience Symposium, Richland, Washington.

Presentations:

- Dagle R.A., K. Kallupalayam Ramasamy, and R.S. Weber. 04/02/2020. "Process intensification facilitates producing renewable building block chemicals from ethanol." Presented by R.S. Weber at Spring ACS 2020 National Meeting, Virtual, United States.
- Saavedra Lopez J., R.A. Dagle, and V. Dagle. 06/24/2019. "Producing Jet and High Octane Gasoline Blendstocks from Ethanol-derived C3 and C4 Olefins Intermediates." Presented by J. Saavedra Lopez at North American Catalysis Society Meeting 2019, Chicago, Illinois.
- Winkelman A.D., V. Dagle, S.A. Akhade, L. Kovarik, S.F. Yuk, M. Lee, and J. Zhang, et al. 08/17/2020. "Identification of Structure-Activity Relationships and Optimization of the Ag-ZrO2/SiO2 Catalyst System for the Single-Step Conversion of Ethanol to Butadiene." Presented by Austin Winkelman at the Fall ACS 2020 National Meeting, Virtual, United States.
- Winkelman A.D., S.A. Akhade, L. Kovarik, R.J. Rousseau, V. Glezakou, Y. Wang, and V. Dagle, et al. 06/26/2019. "Effect of Ag Metal Promoter Dispersion on the Single Step Conversion of Ethanol to Butadiene over Ag/ZrO2/SiO2 Catalysts." Presented by A.D. Winkelman at North American Catalysis Society National Meeting 2019, Chicago, Illinois.
- Winkelman A.D., V. Dagle, S.A. Akhade, L. Kovarik, S.F. Yuk, M. Lee, and J. Zhang, et al. 10/05/2020. "Identification of Structure-Activity Relationships and Optimization of Ag-ZrO2/SiO2 Catalysts for the Single-Step Conversion of Bioethanol to Butadiene." Presented by A.D. Winkelman at 2020 Thermal & Catalytic Sciences Virtual Symposium, Richland, Washington.