



**ChemCatBio**  
Chemical Catalysis for Bioenergy

# Upgrading of C2 Intermediates - PNNL

April 7, 2023

Catalytic Upgrading Session

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Pacific Northwest National Laboratory



# Project Overview

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## Program objective

- Develop new upgrading technologies enabling cost-competitive conversion of **C<sub>2</sub> oxygenated intermediates** to **distillate fuels** and valuable **co-products**



## Project outcome

- Develop catalytic pathway for **direct ethanol to butene-rich olefin intermediates**, discovered by our team, providing control over jet blendstock and co-products, with the potential to obtain a distillate fuel MFSP of \$3.00/GGE and achieve >70% reduction in GHG emissions.



## Relevance

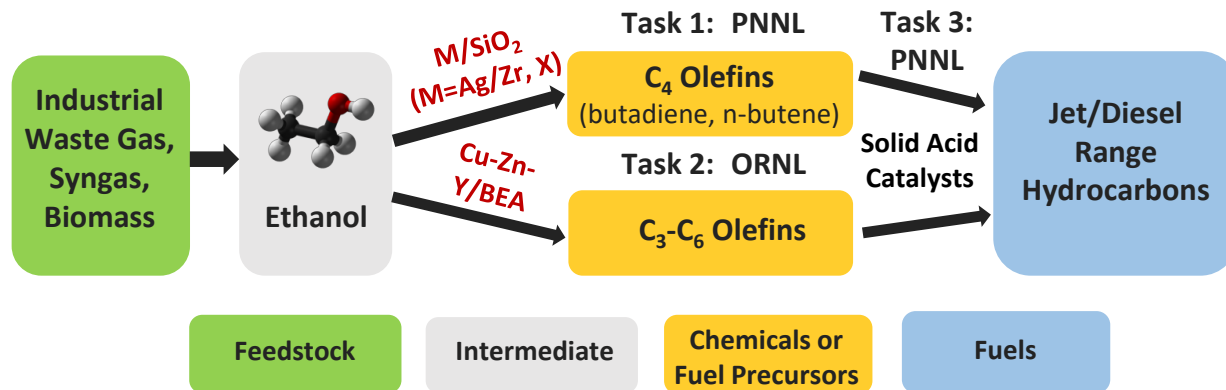
- **Drawbacks** for **current bioenergy conversion** pathways:
  - Smaller production scales
  - High capital and process costs
  - Limited carbon efficiency
  - Poor fuel quality
- **Advanced oxygenate upgrading technologies** address shortcomings by focusing on:
  - Process intensification (catalysis/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



# 1 – Approach: Project Overview

## Project overview:

- Explore two different catalyst systems to convert **ethanol** to **C<sub>3+</sub> olefins** (PNNL, ORNL)
- Produce **distillate fuels** from olefin intermediates & produced fuels with desired properties/ economics (PNNL)



## Collaborative effort within ChemCatBio and other partners

- **PNNL** and **ORNL** experimental teams communicate on quarterly basis with combined reporting
- Collaborate with ChemCatBio **enabling projects**
- Joint patents, presentations, and publications stem from collaborations



## 1 – Approach: Goal (FY23-F25)

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### End Project Goal – FY25

- Improve **direct ethanol to butene-rich olefins catalytic pathway** enabling modeled distillate MFSP of <\$3.00/GGE and >70% GHG reduction, and de-risk for commercial adaption.
- Perform at the bench scale the integrated processing of:
  1. Ethanol-to-butene-rich olefins, and
  2. Olefins-to-SAF-range hydrocarbons
- Demonstrate at least 80% carbon efficiency for ethanol to SAF
- Meet ASTM properties for SAF blendstock



## Project Objectives

### 1. Ethanol-to-butene-rich olefin catalyst development – *continuing*

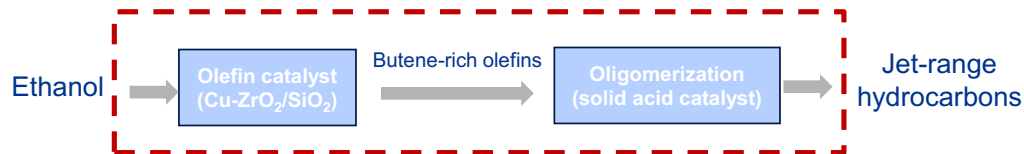
- Leverage catalyst advances made to date to further improve catalytic performance.

### 2. Olefin oligomerization catalyst development – *continuing*

- Develop the one-step oligomerization processing to incorporate all olefinic intermediates into jet-range.

### 3. Integrated process demonstration - *continuing*

- Demonstrate integrated processing of ethanol to SAF blendstock with high carbon efficiency of >80%.



### 4. Kinetics and reactor modeling – *new FY23+*

- Collect kinetic information to develop a kinetic model for reactor modeling.

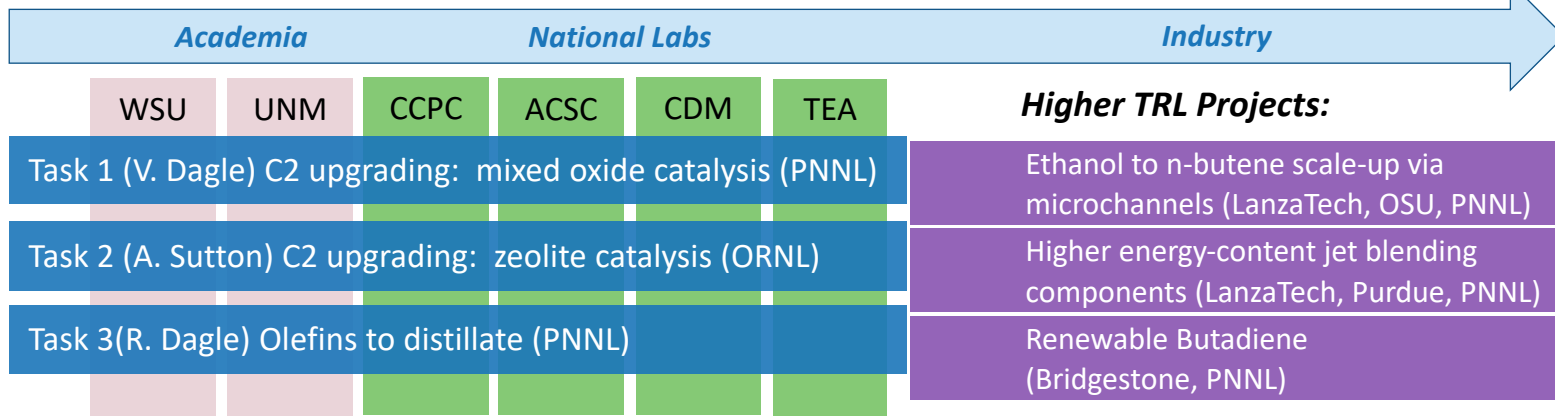
### 5. Engineered catalyst development – *new FY23+*

- Engineered catalysts for scale-up using conventional technology (e.g., extrudates, pellets).



# 1 – Approach: Collaboration Structure

## Project integration with CCB enabling and analysis projects and partners



- **Cooperative 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/ Characterization (ACSC)
- **Techno economics analysis (TEA)/ Life Cycle Analysis (LCA)** provide targets, state of technology assessments
- **Washington State University (WSU) and University of New Mexico (UNM)** fundamental catalysis, leverages BES catalysis
- **Addressing DEI:** Assisted UNM – a **Minority Serving Institute** – in winning BETO project and will partner with them in applying their unique catalysis capabilities toward project goals (deactivation mitigation)
- **Transition technologies** to higher TRL activities and commercial engagement



# 1 – Approach: Risks & Mitigation

## Project risks addressed in scope with partner assistance

Risk	Mitigation	Partnering
<b>Carbon efficiency</b> <ul style="list-style-type: none"><li>High carbon efficiency critical to enable cost goals</li><li>Oligomerization needs improved for oligomerization step</li></ul>	<b>Development of more selective catalysts</b>	<ul style="list-style-type: none"><li><b>Techno-Economic Analysis (TEA)</b> process modeling to inform catalyst performance goals and evaluate co-product options</li><li><b>Computational atomic scale modeling team (CCPC)</b> mechanistic understanding and catalyst design improvements</li></ul>
<b>Catalyst durability, regeneration</b> <ul style="list-style-type: none"><li>Robust/ regenerable catalysts required for commercial adaption</li></ul>	<b>Catalyst durability and regeneration studies:</b>	<ul style="list-style-type: none"><li><b>Catalyst Deactivation Mitigation (CDM)</b> advanced characterizations for durability/ regenerability studies</li><li><b>University of New Mexico</b> new catalyst catalysis and advanced characterizations for new concepts for improving stability</li></ul>
<b>Engineering catalysts</b> <ul style="list-style-type: none"><li>Structured substrates and binders can impact catalyst performance</li></ul>	<b>Optimize binder/ composition formulations</b>	<ul style="list-style-type: none"><li><b>Advanced Catalyst Synthesis and Characterization (ACSC)</b> of metallic site distribution/ coking in catalyst particles</li><li><b>Computational reactor scale modeling team (CCPC)</b> kinetic modeling and reactor modeling for scale-up using conventional approaches (e.g., extrudates)</li></ul>



# 1 – Approach: Major Deliverable Schedule

## Milestones and G/NG leading to process demonstration in FY25

Milestone/ G/NG	Name	Description	Due Date
End Project Outcome (FY20-22)	<b>Projection for overall pathway to meet cost targets</b>	<ul style="list-style-type: none"> <li>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.</li> </ul>	FY22 (9/30/2022)
Go/No-Go	<b>Carbon Efficiency of Oligomerization Processing Step Demonstrated to Meet Economic Target</b>	<ul style="list-style-type: none"> <li>Achieve &gt; 80% carbon efficiency for single step oligomerization of produced olefins to SAF range hydrocarbons.</li> <li>If unsuccessful evaluate use of more complex multi-step oligomerization technology.</li> </ul>	FY24 (5/31/2024)
End Project Outcome (FY23-25)	<b>Demonstrate improvements to meet cost targets</b>	<ul style="list-style-type: none"> <li>Enable modeled distillate MFSP of &lt;\$3.00/GGE and &gt;70% GHG reduction versus petroleum fuels.</li> <li><b>Perform at the bench scale the integrated processing of ethanol to SAF-range hydrocarbons and demonstrate &gt;80% carbon efficiency.</b></li> <li><b>Meet at least 5 key ASTM properties for SAF blendstock.</b></li> </ul>	FY25 (9/30/2025)





# 1 – Approach: Ethanol-to-Olefin Catalysis – Background

## What options exist for producing olefins?

### • Ethanol to ethylene

- Highly selective, however, ethylene difficult to selectively oligomerize into jet in one step
- Ethylene to jet can selectively be performed with two-step process (PNNL/LanzaTech) or with homogeneous processing (SHOP/ Ziegler)

### • Ethanol to C3+ olefins

- Poor selectivity reported in literature (and often aromatic-rich)
- However, single step conversion of C3+ olefins to jet/ diesel exists

Catalyst Comparison from Literature

Catalyst	T (°C)	Conv (%)	Selectivity (mol C%)	
			Ethylene	n-Butene
g-Al <sub>2</sub> O <sub>3</sub> ZSM-5	350	>95	99	0
Ag-ZrO <sub>2</sub> /SiO <sub>2</sub> (this work - FY18)	400	98	26	58
Zn <sub>x</sub> Zr <sub>y</sub> O <sub>z</sub> *	450	99	< 5	42
Ce-HZSM-5	400	100	N/A	20
Ni-MCM-41	350	100	N/A	8.1

\* Produces iso-olefins

Dagle et al, ACS Catal. 2020, 10, 18, 10602–10613

**Our approach:** Here we are developing efficient route for **direct ethanol to C3+ olefin conversion** (which does not currently exist).

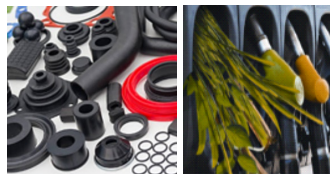


## 2 – Progress and Outcomes: Ethanol-to-Butene Catalysis Baseline

### Prior Accomplishments (FY20)

Flexible single-step catalytic process developed for producing either **butadiene** or **n-butene**:

- **Low H<sub>2</sub>** partial pressure: butadiene
- **Higher H<sub>2</sub>** partial pressure: butene



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

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

**Butadiene Uses**



Feed	Conv (%)	Selectivity (C mol %)		
		C <sub>2</sub> =	C <sub>4</sub> =	Butadiene
EtOH in inert	99.0	5.8	11.2	<b>70.5</b>
<b>EtOH in H<sub>2</sub></b>	93.9	25.7	<b>57.7</b>	0.0

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

**Prior accomplishment:** Discovery of new metal promoted Lewis acid catalyst system offering **tunability** for producing either **butadiene** or **n-butene** from ethanol (Ag-ZrO<sub>2</sub>/SiO<sub>2</sub>).

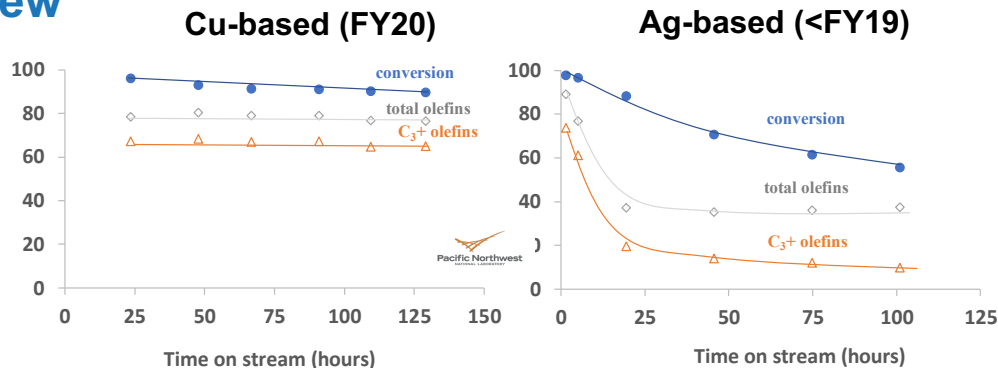
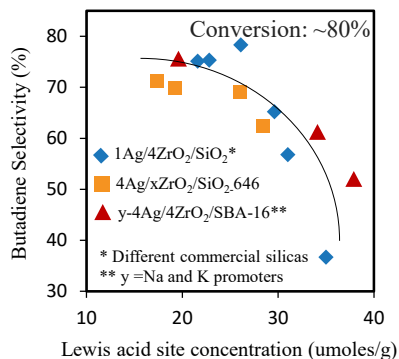


## 2 – Progress and Outcomes: Ethanol-to-Butene Catalysis Baseline, continued

### Technical baseline at FY21 peer review

- Replacing **Ag** with **Cu** improves catalyst stability over prior Ag-based baseline (3X less coke)
- Improved stability attributed to **change in mechanism**, avoiding butadiene intermediate

#### Effect of Lewis Acidity on Selectivity



- Catalytic factors found to influence reactivity:
  - ✓ **Metal dispersion** controls ethanol dehydrogenation and **conversion** (not shown)
  - ✓ **Lewis acidity** controls ethanol dehydration and aldol condensation and **selectivity** (see figure)

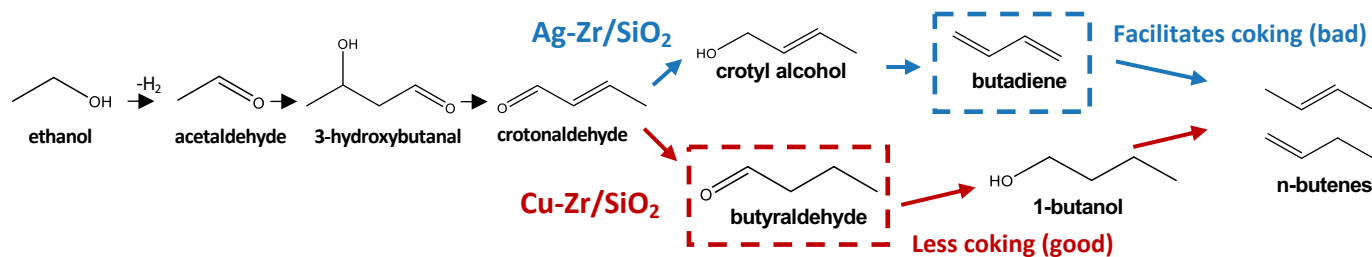
**Prior accomplishment:** Discovered how **metal** and **Lewis acid sites** of Cu or Ag supported by ZrO<sub>2</sub>/SiO<sub>2</sub> can be tuned to control activity and selectivity to **butadiene** or **n-butene**.



## 2 – Progress and Outcomes – NMR & Atomic Scale Modeling

Consortium for Computational Physics and Chemistry (CCPC) Collaboration

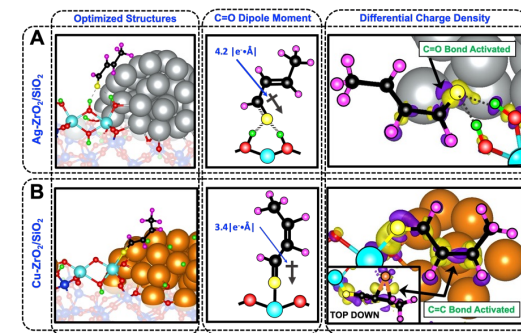
### Bifurcation in mechanism verified by NMR



Manuscript in Review

### Atomic scale modeling for improve design

- **H\*** more enriched on Cu than Ag nanoparticles, with the Ag catalyst H\* prefers to spillover to ZrO<sub>2</sub> and SiO<sub>2</sub>
- **Crotonaldehyde** binds preferentially to **ZrO<sub>2</sub>**:
  - **C=O** over Ag-ZrO<sub>2</sub>/SiO<sub>2</sub>, reduction to crotyl alcohol (*undesired*)
  - **C=C** over Cu-ZrO<sub>2</sub>/SiO<sub>2</sub>, reduction and butyraldehyde formation (*desired*)



**Accomplishment:** Favorable mechanism identified - close proximity of **small Cu nanoparticles** and **ZrO<sub>2</sub> interfaces** found to facilitate the desired route via **butyraldehyde** intermediate.



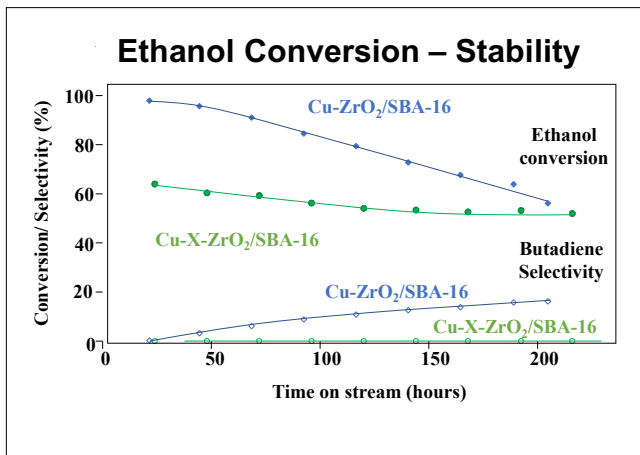
## 2 – Progress and Outcomes: Olefin Catalyst Design Improvements

Catalyst Deactivation Mitigation (CDM) Collaboration

### New catalyst design strategies evaluated for improved catalytic performance

- Different metal oxides investigated for adjusting acidity
- Dopants to  $\text{Cu-ZrO}_2/\text{SiO}_2$  evaluated for modulating metal/ acidic sites
- Promoted catalysts evaluated for resistance to Cu sintering
- New synthesis strategies for spatial arrangement of catalytic functions

Example:  
catalyst  
promoter X



### Spent catalyst analysis

Sample		Baseline Catalyst (Cu)	New Catalyst (Cu-X)
Fresh	Cu size (nm)	1-3	1-3
Spent	Cu size (nm)	5.6	3.7
	Coke(wt.%)	20.0	3.7

- **Catalyst promoter** markedly enhances stability by **reducing Cu sintering** by ~30%.
- However, selectivity needs improved (only 45% olefins).

**Accomplishment:** Multiple catalyst design strategies investigated leading to catalyst providing **>95% ethanol conversion, 92% C<sub>2</sub>+ olefin selectivity, and 75% C<sub>3</sub>+ olefin selectivity.**



## 2 – Progress and Outcomes – TEA and LCA Sets Targets

PNNL Analysis Project Collaboration

### FY22 state of technology assessment – ethanol to olefin catalyst performance meets cost goal

- **Carbon efficiency** and **ethanol cost** key cost drivers – improvements made to C efficiency in program
- **\$3.00/GGE** distillate fuel feasible (with n-butene co-product)
- LCA projects **84% GHG emission reduction** for corn stover to ethanol to jet pathway

*Manuscript in Preparation*

	Timeframe	Single-pass conversion (%)	n-Butene Selectivity (%)	Total Olefins Selectivity (%)	Distillate yield (GGE/dry ton)	Co-Product (wt. %)	MFSP (\$/GGE)
<i>Ketonization</i> for C-C coupling produces CO <sub>2</sub>	Start of FY17 <sup>1</sup> (Zn <sub>x</sub> Zr <sub>y</sub> O <sub>2</sub> )	99	47	58	41	None	<b>5.90</b>
<i>Aldol condensation</i> for C-C coupling produces <u>no</u> CO <sub>2</sub>	FY22 - fuel <sup>2</sup>	100	65	90	59	None	<b>3.58</b>
	FY22 – fuel + co-product <sup>2</sup>	100	65	90	31	46 wt.% n-butene	<b>3.08</b>

1. IDL FY18 G/NG Memo 2. Analysis Q2-FY22 QPM Report

Ethanol feedstock: gasification of forest residue

**Accomplishment:** Catalyst selectivity and activity (initial) achieved \$3/GGE model TEA target in FY22. Therefore, improving catalyst stability is currently a focus moving forward.



## 2 – Progress and Outcomes: Impact of Real Feedstocks on Stability

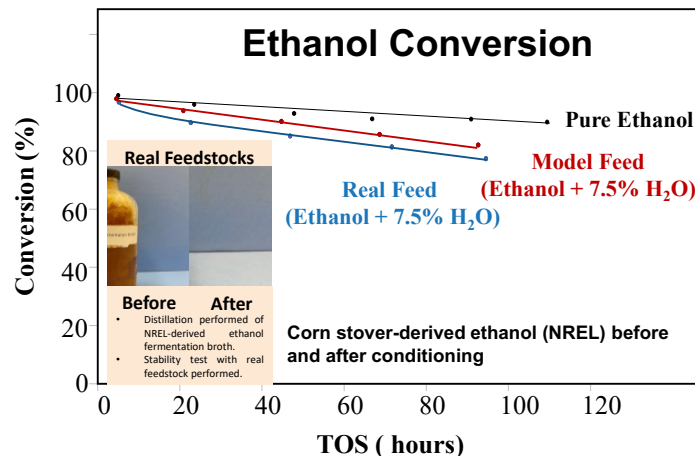
Catalyst Deactivation Mitigation (CDM) Collaboration

### Water in real feed adversely affects catalyst stability

- Sugars and inorganics removed from real feedstock after conditioning (below detection limits)
- Deactivation profile similar for both **real feed** and **model feed** with same water content
- Water in feedstock (7.5 wt.%) found to adversely impact catalyst stability

### Spent catalyst characterization

Method	Fresh Catalyst	Spent Catalyst -Model feed		Spent catalyst – Real Feed
		EtOH	EtOH + H <sub>2</sub> O	
Surface Cu dispersion (% N <sub>2</sub> O titration)	41.4	35.6	20.4	15.4
Cu particle size (nm, TEM)	n.d.	2.8 ± 1.6	5.1 ± 1.5	4.2 ± 1.5
Carbon content (wt. %)	0.22	2.2 ± 0.1	3.5	3.6
BET surface area (m <sup>2</sup> /g)	527	497	N/A	479

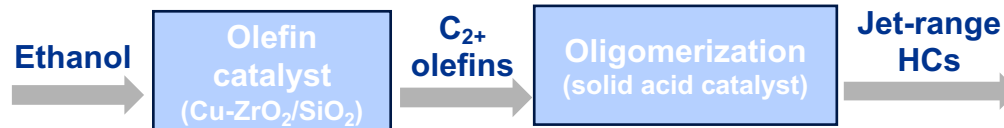


- **Carbon deposits** – on both metal and Lewis acid sites
  - **Cu sintering** – and enhanced in presence of H<sub>2</sub>O
  - **Silica support remains intact** – even under hydrothermal conditions (400°C, up to 35% H<sub>2</sub>O generated in reaction)
- Manuscript in Preparation*

**Accomplishment:** Conditioning process of real feedstock effective, however, water adversely impacts catalytic stability.



## 2 – Progress and Outcomes: Integrated Process Demonstration (Partial) Success



- **Successful olefin production:**

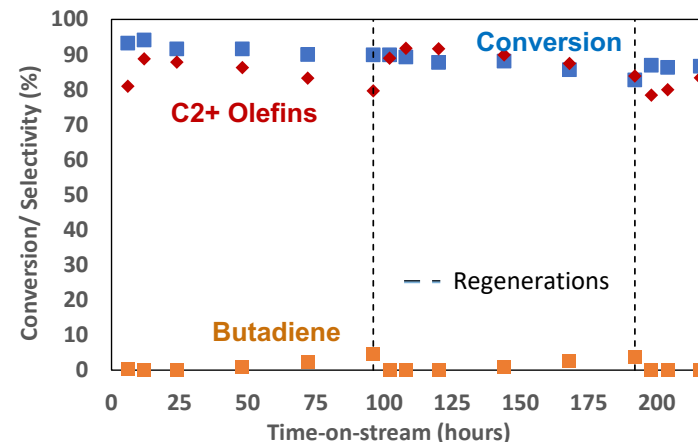
- Ethanol conversion > 90% for 300+ hours duration
- 90% C2+ olefin sel., 75% C3+ olefin sel. (before deactivation)
- Catalyst regenerable (with initial step change)

- **Favorable fuel production:**

- Liquid product 91% jet-range (w/ recycle)
- Fuel properties met key ASTM standards

- However, issues with **oligomerization** processing identified that are being improved upon for future demonstration.

### Ethanol Conversion



**Accomplishment:** Process demonstrated with partial success but improvements needed for oligomerization processing identified:

- Improved interstage separation & regeneration schemes
- Better incorporation of ethylene (5-20% ethylene) into liquid product





## 2 – Progress and Outcomes: Single-Step Oligomerization Catalyst Development

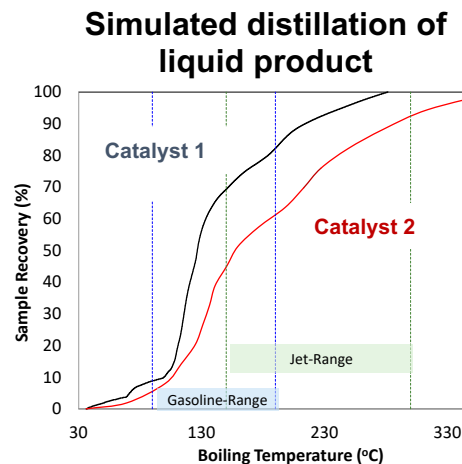
### Catalytic system for single step oligomerization identified

- **Ethylene** difficult to selectively convert into SAF in one step with current technology
- Ethylene in mixture found to favorably **co-oligomerize** with higher olefins
- **Catalyst improvements** led to >70% conversion (single pass) while still maintaining high olefin content

	Feed	Ethene Conv. (%)	Butene Conv. (%)	Alkane/Olefin (mol/ mol)
<b>Catalyst 1</b>	Ethene	6.1	---	0.93
	Ethene + Butene	25.3	52.3	0.03
<b>Catalyst 2</b>	Ethene + Butene	77.6	73.0	0.02

>70% single pass conversion (good)

Low alkane content (good)



*Patent application*

**Accomplishment:** Multi-functional **oligomerization catalyst developed** enabling high conversion and olefin selectivity of produced C2-C4 olefin intermediates into SAF-range olefins in one step.



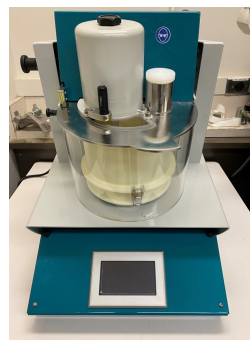
## 2 – Progress and Outcomes: Future Work

- Further develop the catalysis (two catalysts) and demonstrate  $> 80\%$  carbon efficiency at the bench scale the **two-step integrated processing** for:
  - Ethanol-to-butene-rich olefins
  - Olefins-to-SAF-range hydrocarbons
- **Engineered catalyst development, kinetics, and reactor modeling** – *initiated FY23*

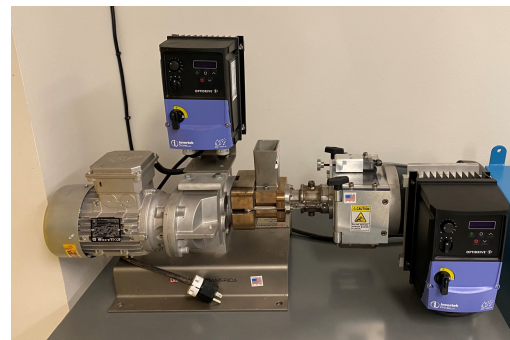
Commercial Support Extrudates



In-House Extrudate Capability Purchases



Mixer



Extruder

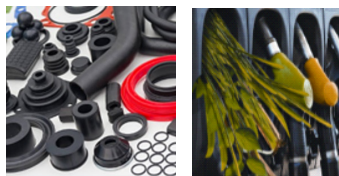
**Accomplishment:** Moving towards integrated process demonstration, and engineered catalyst development (e.g., extrudates) to accelerate follow-on reactor scale-up effort.



### 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)<sup>1</sup>
- Factors expected to reduce ethanol prices:
  - Ethanol “blendwall”
  - Advancement in production efficiency
  - Feedstock diversification



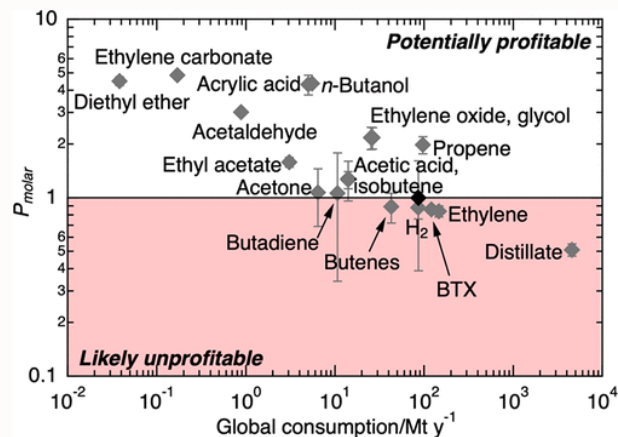
**n-Butene Uses**  
- fuel precursor/  
co-product

#### 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.

Dagle et al., *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**



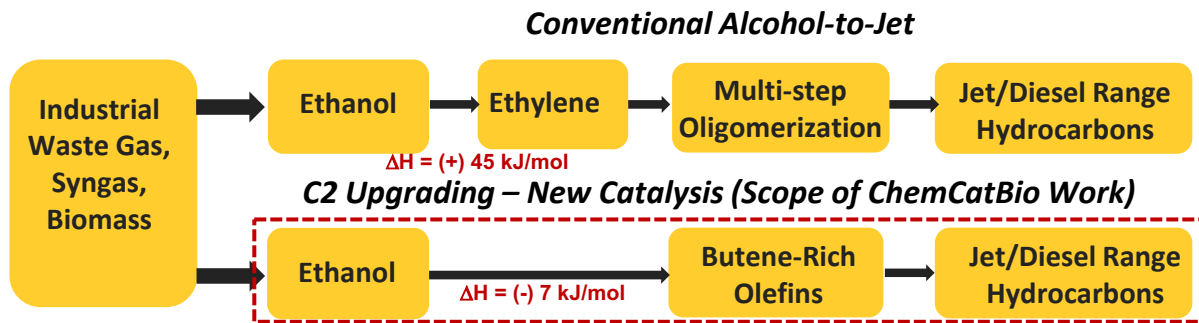
### 3 – Impact: Improvement to State-of-the-Art

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

- DOE-BETO goal to enable SAF production of 35 billion gallons per year by 2050.
- ATJ is regarded as one of the most promising technologies for scaled production of SAF.
- LanzaTech/ LanzaJet is commercializing earlier ATJ process technology developed at PNNL.

## Differentiators versus current ATJ:

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



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



### 3 – Impact: Transition of Technology to Higher TRL Projects

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

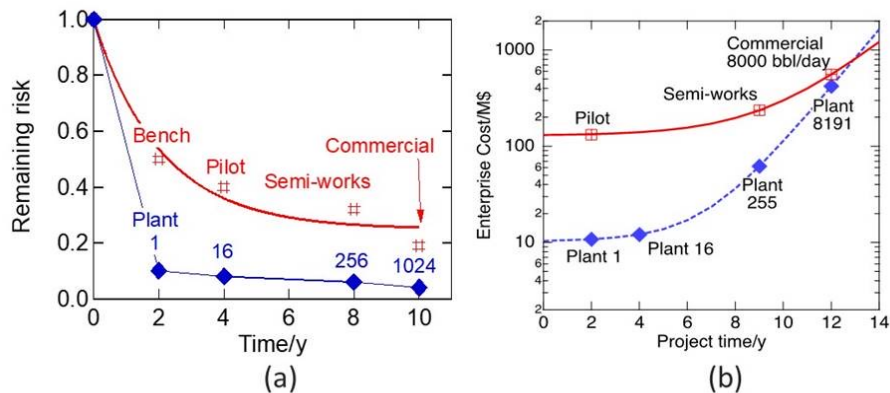
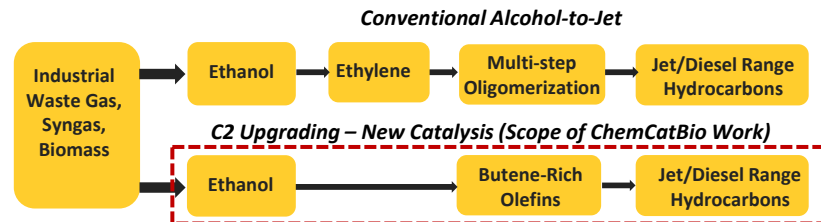


Figure: (a) risk-reduction, and (b) enterprise cost models for numbering up and conventional scaling

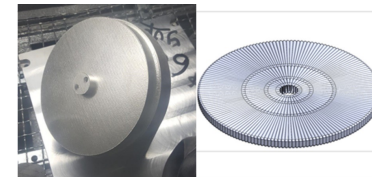


US Patent 10,647,625  
US Patent 10,647,622

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

- 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*





# Summary

## Project Goal:

- Develop catalytic pathway for **direct ethanol to n-butene-rich olefins** to enable distillate MFSP of \$3.00/GGE and >70% GHG emission reduction.
- Demonstrate integrated processing of **ethanol to SAF** blendstock with > 80% carbon efficiency.
- Meet key ASTM specifications for jet blendstock

## Approach

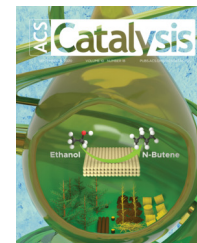
- Collaborative approach within ChemCatBio leveraging expertise targeting key challenges around catalyst performance, durability, and scale-up
- **Multifunctional catalysts** employing tandem reactions leading to high C efficiency
- Setting state-of-the-art ethanol conversion for **process intensification & high carbon efficiency**
- **Co-products** reduce costs, diversity product offerings

## Progress and Outcomes

- Ethanol to butene catalyst developed with improved stability and selectivity versus prior formulations.
- Use of **real feedstocks** demonstrated effective cleanup however water in feed found to adversely impact stability.
- Integrated processing of **ethanol to SAF** identified improvements needed for oligomerization processing
- **Oligomerization catalyst** system identified for effective single-step conversion of produced olefin intermediates into SAF-range hydrocarbons.

## Impact

- Cost advantage potential to current state of technology
- Tech transfer with industry (CRADA projects with LanzaTech, Bridgestone)
- Multiple patents/ application and published results in top-tier peer-reviewed journals.



ACS Catal. 2020, 10, 18, 10602–10613





# Acknowledgements

## *PNNL Experimental Team (Task 1, 3)*

Robert Dagle (PM)	Vanessa Dagle (PI)
Johnny Saavedra-Lopez	Martin Affandy
Libor Kovarik	Jennifer Jocz

## *ORNL Experimental Team (Task 2)*

Andy Sutton	Stephen Purdy
Shiba Adhikari	Kinga Unocic

## *Washington State University*

Austin Winkelman	Yong Wang
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## *CDM (PNNL)*

Huamin Wang	Fan Lin
Yinlin Wang	

## *Other Collaborators – ChemCatBio*

Susan Habas (NREL)	Josh Schaidle (NREL)
Jim Parks (ORNL)	

## *Bioenergy Technologies Office*

Sonia Hammache	Trevor Smith
Ben Simon	

## *TEA Team*

Steven Phillips (PNNL)
Lesley Snowden-Swan (PNNL)
Ling Tao (NREL)

## *CCPC - Atomic Scale (PNNL)*

Roger Rousseau	Vanda Glezakou
Sneha Akhade	Simuck Yuk
Mal-Soon Lee	Jun Zhang
Greg Collinge	

## *University of New Mexico*

Abhaya Datye





# Quad Chart Overview

## Timeline

- Project start date: 10/1/2022
- Project end date: 9/30/2025

	FY22 Costed	Total Award
<b>DOE Funding</b>	\$750 K	\$2250K (FY23-25)

TRL at Project Start: 3

TRL at Project End: 3-4

## Project Partners

- Within ChemCatBio Consortium
  - C2 Upgrading – ORNL
  - CDM
  - ACSC
  - CCPC
  - Analysis (TEA/LCA)
- Washington State University (FY20-22), and University of New Mexico (FY23-25)

## Project Goal

Further develop and de-risk for commercial offtake the process under development at PNNL and ORNL for two-step conversion of ethanol to jet-range hydrocarbons.

## End of Project Milestone

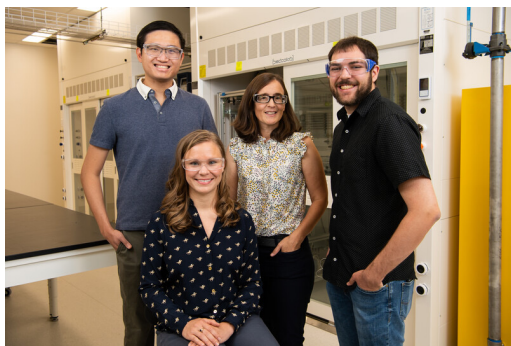
Deliver improvements to the direct ethanol to butene-rich olefins pathway providing control over maximizing the available jet fraction, with the ability to obtain a modeled distillate MFSP of < \$3.00/GGE and >70% GHG reduction versus petroleum fuels.

Perform at the bench scale the integrated processing of ethanol to SAF and demonstrate the ability to produce a jet-range hydrocarbon with at least 80% carbon efficiency and meeting at least 5 key ASTM properties for SAF (e.g., flash, freeze, density, viscosity, and simulated distillation).

## Funding Mechanism

- FY22 BETO Lab Call
- Annual operating plan
- Chemical Catalysis for Biomass (ChemCatBio) Consortium





*This work was performed in collaboration with the Chemical Catalysis for Bioenergy Consortium (ChemCatBio, CCB), a member of the Energy Materials Network (EMN)*

# Thank you!

## Q&A

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[chemcatbio.org](http://chemcatbio.org)

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# Acronyms and abbreviations

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<b>ACSC</b>	Advanced Catalyst Synthesis and Characterization project
<b>BETO</b>	Bioenergy Technologies Office
<b>C2 upgrading</b>	Catalytic Upgrading of C2 Intermediates project
<b>ChemCatBio</b>	Chemical Catalysis for Bioenergy Consortium; ChemCatBio consortium
<b>CCM</b>	Catalyst Cost Model project
<b>CCPC</b>	Consortium for Computational Physics and Chemistry project
<b>CDM</b>	Catalyst Deactivation Mitigation for Biomass Conversion project
<b>CUBI</b>	Catalytic Upgrading of Biochemical Intermediates project
<b>IAB</b>	Industrial Advisory Board
<b>PNNL</b>	Pacific Northwest National Laboratory
<b>TOS</b>	Time on stream
<b>TRL</b>	Technology Readiness Level



# Additional Slides

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## Complimentary remarks

- Overall, comments very favorable to management, approach, impact, and progress on catalyst development.
- Reviewers also reinforced how **co-products** can assist in the economics, and how tuning the catalysis for producing co-products is valid.
- **We agree that co-products and products can be an essential component to future commercial adaption of an ethanol platform.** The use of co-products such as n-butene (and earlier, 1,3-butadiene) is something that we have in fact explored further. A manuscript detailing the process modeling and FY22 state of technology TEA for this process is in preparation. In this report we have evaluated different co-product schemes.
- **We also note that by developing cost-effective routes to bioproducts (but not fuel) would also facilitate market adaption of biofuels.** By using the same feedstock that can also produce jet and diesel fuel (ethanol) this will further incentivize companies to reduce processing costs for ethanol production, thus providing additional market pull for both bioproducts and biofuels. Further, ethanol can be converted into commodity chemicals such as olefins/ aromatics that produce multiple end products (plastic monomers, etc.). In our 2020 paper in *Ind. Eng. Chem. Res.*\* we describe which and how different chemicals can be produced from ethanol, along with a high-level economic analysis for producing them.

\* Dagle et al., *Ind. Eng. Chem. Res.* 2020 59 (11), 4843-4853



## Responses to Previous Reviewer's Comments, continued

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### Suggestion and questions

Three questions were raised around the 1) catalyst targets, 2) TEA, and with the 3) more fundamental catalysis being performed by our academic partner Washington State University. These points are addressed here:

#### 1. Catalyst performance target

- **Comment:** Catalyst improvement targets were not quantitatively mentioned.
- **Response:** Actually, on the Approach slide 16 (FY21 peer review slides) we showed how, according to our model, the MSFP cost target could be met assuming 95% carbon selectivity to the olefins can be achieved, and assuming n-butene co-product was taken. This is our end of project target. We also had a mid-project catalyst performance target milestone of 90% total olefin and 65% C3+ olefin selectivity, which was recently met as shown in the Approach slide 17.
- Regardless, moving forward, as discussed in this peer review, believe the initial catalytic performance for ethanol to butene-rich olefins have now been met, for meeting the cost goals as determined by our process modeling and TEA. Thus, we are now more focused on further advancing the TRL of the two catalysts (for ethanol conversion and oligomerization), for example, with improving catalyst stability. We are also now focused more on further developing the processing for the two-step conversion of ethanol to SAF-range hydrocarbons.



# Responses to Previous Reviewer's Comments, continued

## Suggestion and questions, continued

### 2. TEA

- **Comment:** Confusion between the PNNL (thermochem model) and ORNL (biochem model) TEA that was reported.
- **Response:** This confusion was because there were two separate process models and analysis assumptions – one for PNNL's mixed oxide catalyst (Task 1) and one for ORNL's zeolite-based catalyst (Task 2). For the PNNL catalyst the process model assumes thermochemical conversion of forest residues to ethanol with the most updated biomass feedstock price. The model for the ORNL catalyst was developed based on biochemical processing of corn stover (alternative conversion pathway and feedstock). There are two different process models because the PNNL and ORNL catalyst programs originated from different sections of the BETO program. In recent years these programs were combined due to their similar goals around ethanol upgrading but the same models were kept for consistency.

### 3. ALD catalyst synthesis

- **Comment:** One reviewer suggested that atomic layer deposition (ALD) as a means to obtain monodispersed Zr<sup>4+</sup> was interesting. However, the origin of its improved performance was not clear and the feasibility for long term retention of monodispersed Zr during regeneration was in question.
- **Response:** The synthesis of well-ordered Zr sites may well ultimately contribute to favorable selectivity performance. **Regardless, shortly after the peer review we decided to wrap up this lower TRL study and instead pivot to a different, perhaps more applicable approach.** Here we studied the effect of alkali dopant on the reaction, and this more study was recently published in *Catalysis Science & Technology*. However, we note that our philosophy moving forward is to continue to evaluate promising, albeit more exploratory approaches, with our academic partners as they could lead to new advances.



# Publications, patents, and commercial engagement

## Publications:

- Winkelman A.D., V. Dagle, T.L. Lemmon, L. Kovarik, Y. Wang, and R.A. Dagle. 2022. "Effect of Alkali Metal Addition on Catalytic Performance of Ag/ZrO<sub>2</sub>/SBA-16 Catalyst for Single-Step Conversion of Ethanol to Butadiene." *Catalysis Science & Technology*, first published 12/13/22, advance article, doi:10.1039/D2CY01722a.
- V. Dagle et al. "Single-step conversion of ethanol into n-butene-rich olefins over metal catalysts supported on ZrO<sub>2</sub>-SiO<sub>2</sub> mixed oxides", in review at *Applied Catalysis B*
- "Single-Step Conversion of Ethanol to n-Butenes-rich Olefins over Ag/ZrO<sub>2</sub>/SiO<sub>2</sub> Catalysts." *ACS Catal.* 2020, 10, 18, 10602–10613.
- "Understanding the Deactivation of Ag–ZrO<sub>2</sub>/SiO<sub>2</sub> 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-ZrO<sub>2</sub>/SiO<sub>2</sub> catalysts." *Journal of Catalysis*, 2020, 286, 30-38.

## 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.
- Dagle et al., "CATALYTIC CONVERSION OF ETHANOL TO 1-/2-BUTENES", US Patent # 11,046,623, issued June 2021.

## Commercial Engagement:

- Ongoing separate FOA proposal project w/ partners **Oregon State University** and **LanzaTech** to scale up ethanol to n-butene catalyst formulation developed on this project using advanced microchannel reactor platform.
- Ongoing separate direct funded work with partner **Bridgestone** developing a commercial process for renewable butadiene



# Presentations

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## Presentations:

- Dagle V., A.D. Winkelman, L. Kovarik, M.H. Engelhard, N.R. Jaegers, Y. Wang, and R.A. Dagle, et al. 2022. "Single-Step Conversion of Ethanol to n-Butene-rich Olefins or Butadiene over Metal supported on ZrO<sub>2</sub>/SiO<sub>2</sub> Catalysts with Tailored Metal and Lewis-Acid Sites." Invited presented by Austin Winkelman, 28th Organic Reactions Catalysis Society (ORCS) Meeting, Jacksonville, FL, October 19, 2022.
- Dagle V., R.A. Dagle, A.D. Winkelman, et al. 03/20/2022. "Tailored metal and Lewis-acid sites for the single-step conversion of ethanol to n-butene rich olefins or butadiene over metal supported ZrO<sub>2</sub>/SiO<sub>2</sub> catalysts." Presented by Austin Winkelman at the Spring 2022 ACS National Meeting, Virtual, San Diego, CA.
- Lin, F., H. Wang, V. Dagle, R.A. Dagle, et al. 03/20/2022. "Impact of water in catalytic conversion of oxygenates: reactivity inhibition and catalyst deactivation." Presented by Fan Lin at the Spring 2022 ACS National Meeting, Virtual, San Diego, CA.
- Dagle V., A.D. Winkelman, L. Kovarik, M.H. Engelhard, N.R. Jaegers, J. Hu, and Y. Wang, et al. 05/23/2022. "Single-Step Conversion of Ethanol to n-Butene-rich Olefins or Butadiene over Metal supported on ZrO<sub>2</sub>/SiO<sub>2</sub> Catalysts with Tailored Metal and Lewis-Acid Sites." Presented by A.D. Winkelman at 2022 NACS North American Meeting, New York, New York.
- Dagle V., A.D. Winkelman, J. Saavedra Lopez, L. Kovarik, M. Engelhard, N.R. Jaegers, and J. Hu, et al. 04/05/2021. "Single-Step Conversion of Ethanol to n-Butene-rich Olefins or Butadiene over Metal supported on ZrO<sub>2</sub>/SiO<sub>2</sub> Catalysts with Tailored Metal and Lewis-Acid Sites." Presented at the Spring 2021 ACS National Meeting, Virtual, Washington.