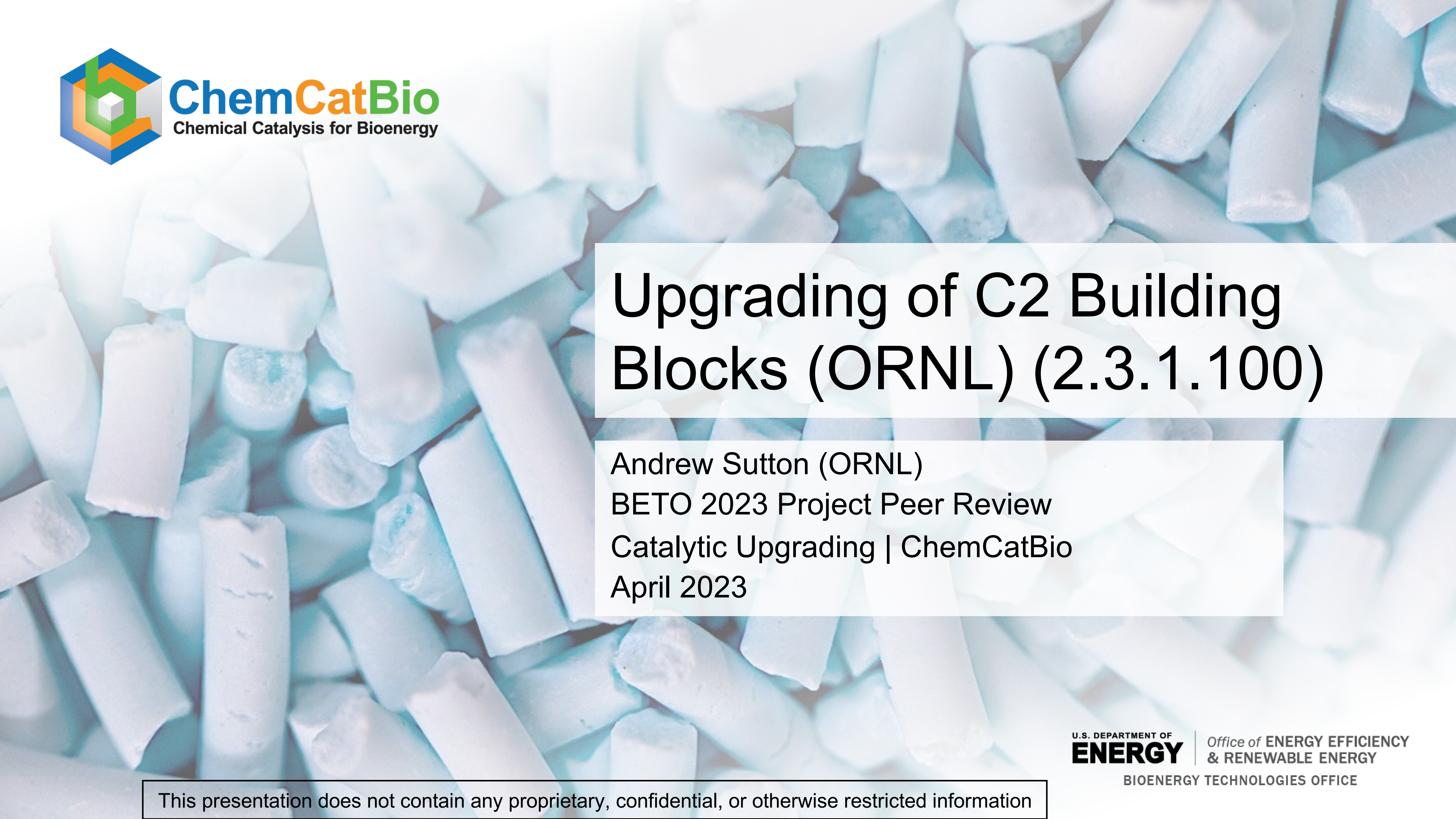
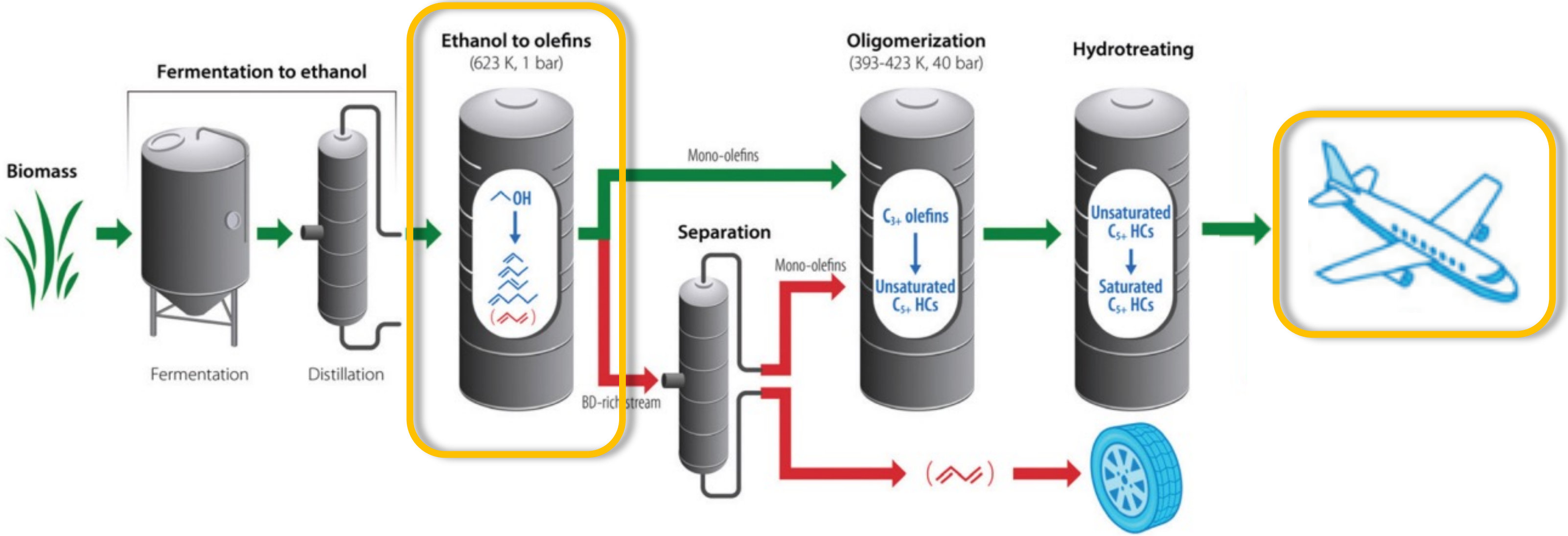


Upgrading of C2 Building Blocks (ORNL) (2.3.1.100)

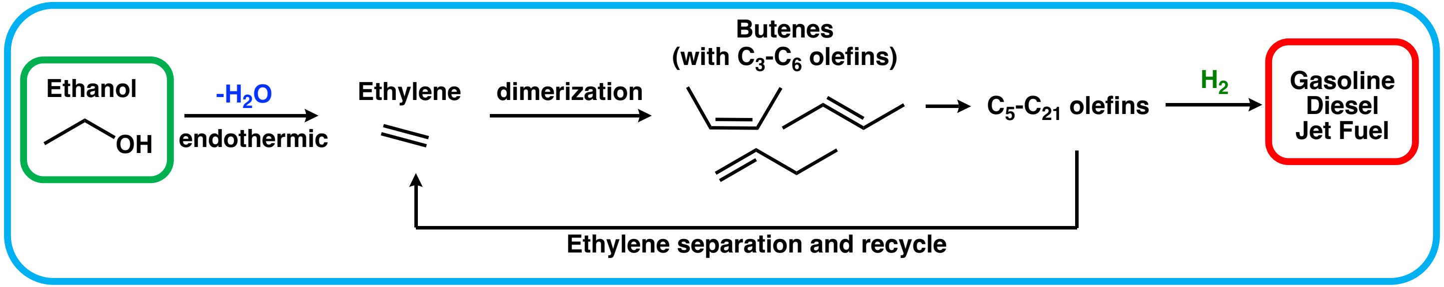
Andrew Sutton (ORNL)
BETO 2023 Project Peer Review
Catalytic Upgrading | ChemCatBio
April 2023

Project Overview

Develop novel catalytic upgrading technologies that enable cost-competitive conversion of **cellulosic ethanol** to **sustainable aviation fuel (SAF)**. We aim to develop a commercially viable process within the concept of an integrated biorefinery that **lowers fuel production costs and carbon intensity** to aid in the transition towards net-zero aviation.



Overview – Current Ethanol-to-Jet (ETJ) Approach

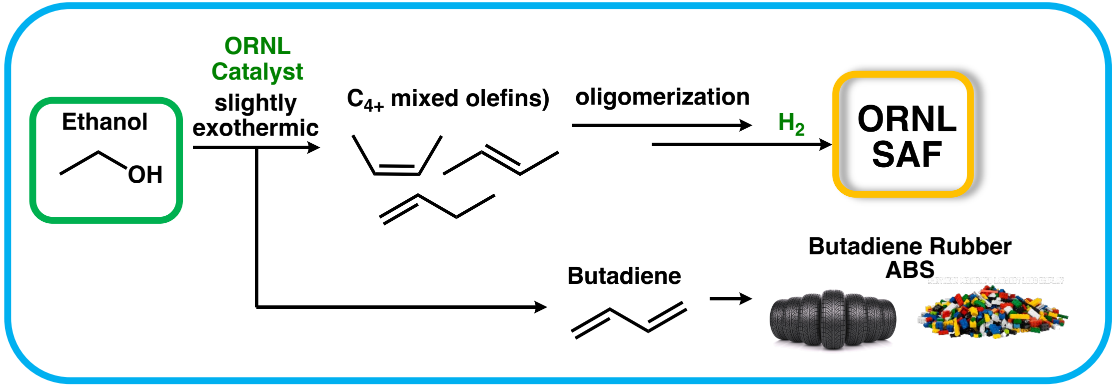


Limitations (based on available literature)

- *Process requires two-steps to produce C_{3+} olefins*
- *Ethanol dehydration is endothermic (requires significant energy input)*
- *Ethylene conversion to C_{3+} olefins typically exhibits low-medium conversion*
- *Multiple steps impacts CapEx and OpEx*
- *Limited co-product opportunities*

Advancing ETJ production technologies via reducing the number of unit operations, energy requirements and heat management demands can positively impact economics and GHG reductions to enable additional ETJ technologies

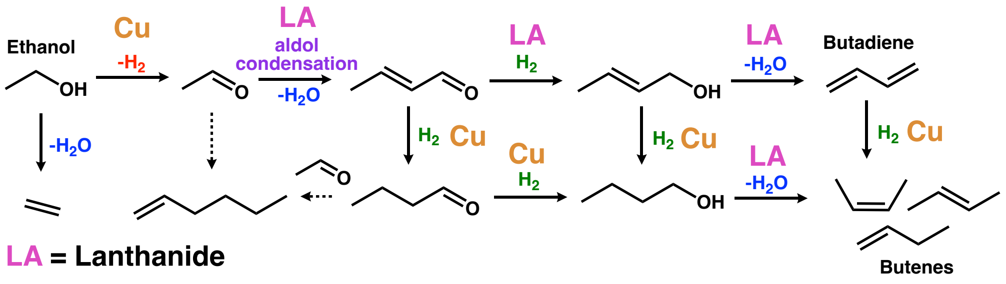
Overview – ORNL Approach



Compared with ethanol to jet industrial SOT:

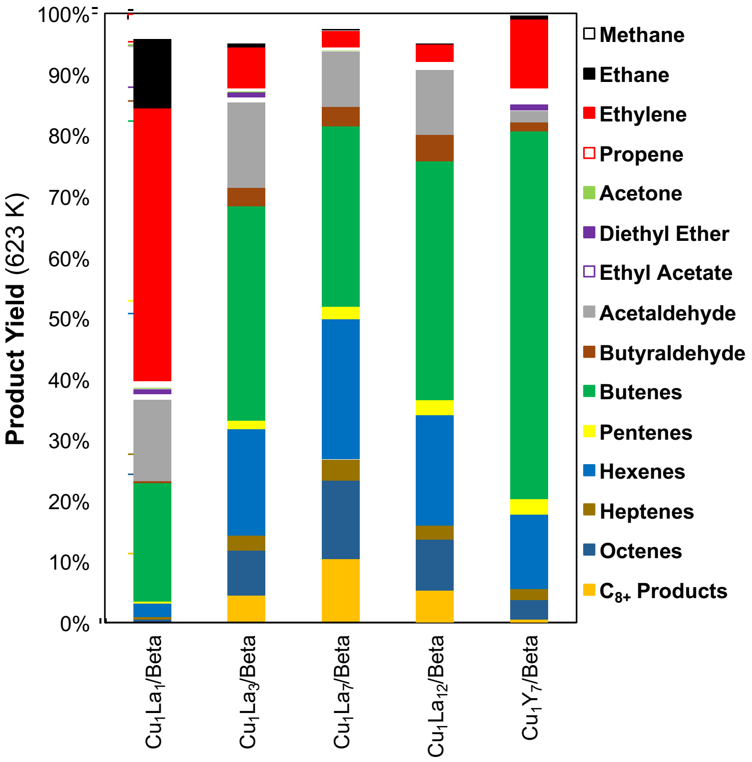
- Bypass the ethylene production step: first step is **slightly exothermic**
- Opportunity to **reduce CapEx and OpEx** through process intensification (3 step)
- Significantly increase the distillate range hydrocarbons (Increase C_{4+} olefin yield)
- Opportunity to produce either **SAF** from simple alcohols
- 1,3-butadiene (co-product): **USD 33.01 Billion by 2020 (globally)**
- **Market responsive**: flexibility to tune the product distribution

Overview – Cost-Effective Metal Lanthanides on Active & Durable Zeolite Support



LA = Lanthanide

- We understand which active site and what type of metal we need for each step
- Copper very effective for (de)hydrogenation
- Lanthanides (LA) effective for dehydration and and Meerwein–Ponndorf–Verley (MPV) reduction
- deAl-beta alone dehydrates ethanol
- LA content allows for product distribution tuning



1. Approach: Collaborative Workflow Accelerates R&D

Joint milestones to tackle challenges associated with catalyst development and deactivation mitigation

Advanced catalyst synthesis and characterization (ACSC)

In situ/operando catalyst characterizations to understand catalyst structures and catalyst deactivation mechanisms

Consortium for Computational Physics and Chemistry (CCPC)

Computational modeling to understand the catalysis and chemistry, and predict new catalyst design

Catalyst deactivation mitigation (CDM)

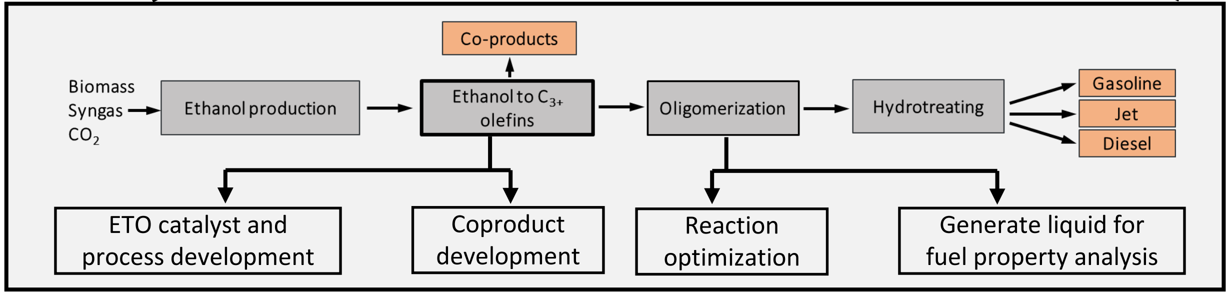
Probe catalyst deactivation mechanism and mitigate catalyst deactivation

BETO peer review

CCB industry advisory board

Industry outreach

Inputs



Biomass
Syngas
CO_2

Ethanol production

Ethanol to C_{3+} olefins

Co-products

Oligomerization

Hydrotreating

Gasoline
Jet
Diesel

ETO catalyst and process development

Coproduct development

Reaction optimization

Generate liquid for fuel property analysis

Publications, conference presentations, webinars, IP, tech transfer

Outputs

End goal is to transfer R&D discoveries to industry and promote US bioeconomy

C_2 upgrading – PNNL

Collaborate on olefin oligomerization and coproduct development

Analysis team (NREL & ANL)

Perform process design, TEA, and LCA

TEA-informed metrified milestones and Go/No-Go to relate catalyst advancement to cost

Technology Licensed by:

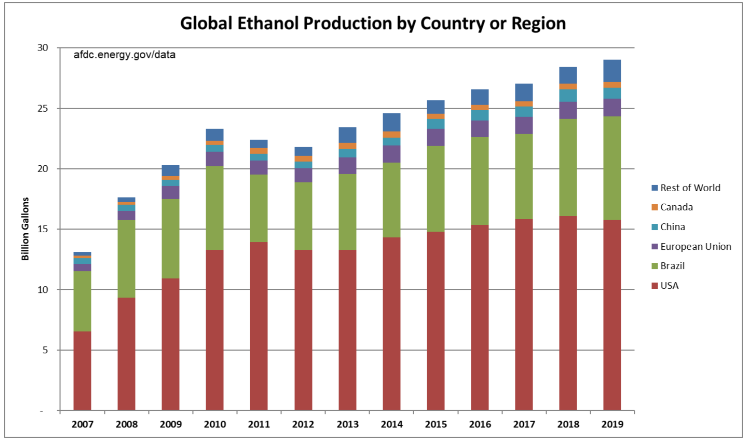
PROMETHEUS

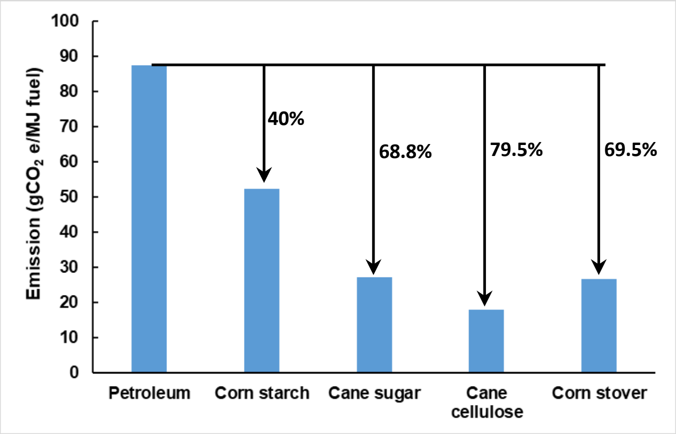
Vertimass
Transformative fungible biofuels.

1. Approach: Relevance to Bioenergy Industry

New ETJ technology addresses the needs for both ethanol producers and growing markets of middle-distillate fuels

Increasing ethanol production, ethanol ‘blend wall’ and decreasing ethanol price urge for **new applications of ethanol**





ETJ present a great opportunity to expand the ethanol applications, **diversifying the product portfolios** for ethanol producers

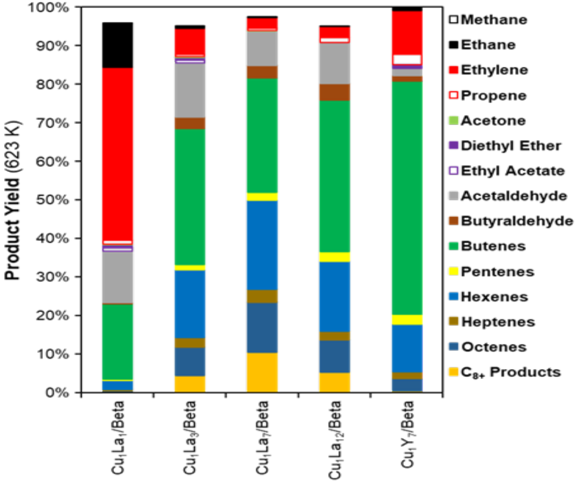
Vertimass ethanol upgrading technology licensed from ORNL shows **significant opportunities for GHG emission reduction** (joint study with Vertimass*)

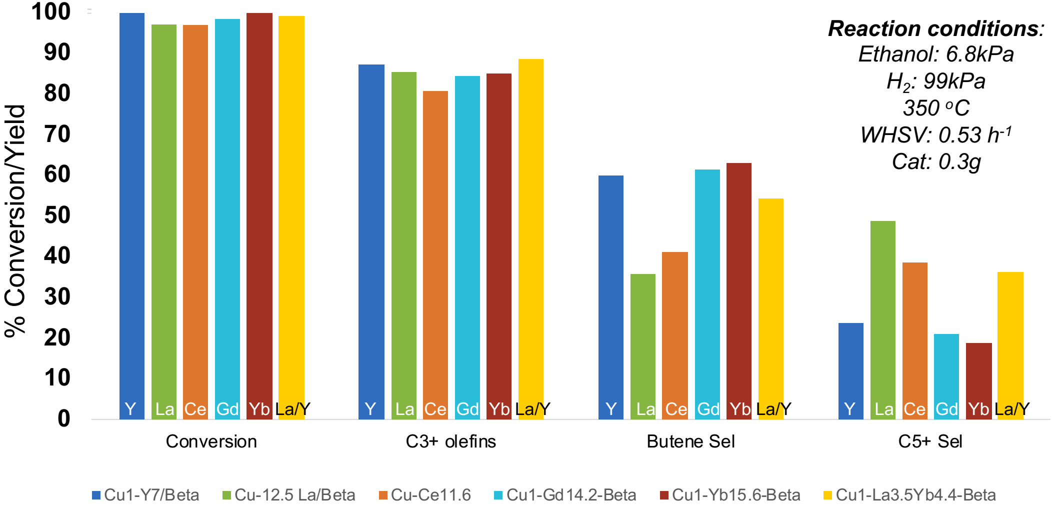
*Hannon et al. *PNAS*. **2020**, 117 (23), 12576-12583.

2. Progress & Outcomes: Olefin Composition Tunability

Goal: New series of catalysts offer the flexibility to tune the fuel product: SAF vs renewable diesel

- Established the structure-function relationship via understanding of catalyst structures via characterization (ACSC) and modeling (CCPC) collaborations



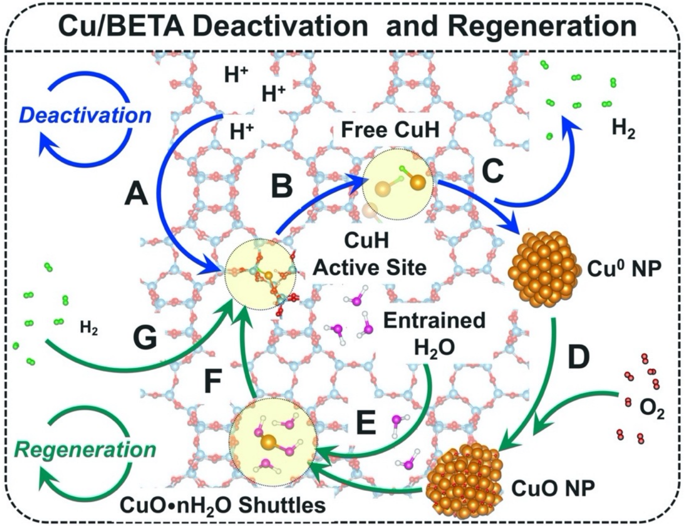


***Reaction conditions*:**
Ethanol: 6.8kPa
H_2: 99kPa
350 °C
WHSV: 0.53 h^{-1}
Cat: 0.3g

- La-based catalysts favor **higher selectivity of C_{5+}** (hexenes, octenes)
- Tune the **ratio of C_4/C_{5+} olefins by varying metal centers** to modify the acid sites
- Offer a **spectrum of olefin** composition to fit for **high yield and/or high-quality SAF production**

2. Progress & Outcomes: Ethanol-to-Olefins (ETO) Catalyst Regeneration

- **Goal:** Understand ETO catalyst deactivation mechanisms and develop a regeneration protocol to mitigate.
  - with ACSC, CCPC, CDM

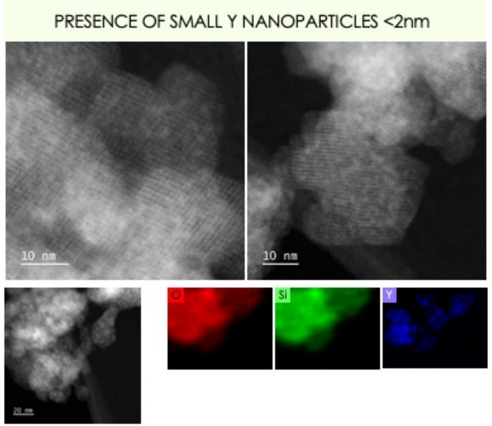


- ***DRUV-vis of ETO catalyst identifies deactivation mechanisms***
- **Cu redispersion mechanism determined experimentally and in collaboration with CCPC**
- **Full recovery of initial activity after regeneration**

- Multi technique characterization identified coking and copper sintering as deactivation mechanisms
- Oxidative regeneration **fully recovers** initial catalytic activity

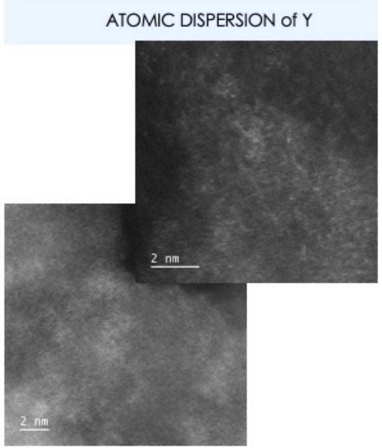
2. Progress & Outcomes: Hydrothermal aging of ETO catalyst

- **Goal:** Evaluate impact of steaming on catalyst activity and product yield.
  - with ACSC, CCPC, CDM


PRESENCE OF SMALL Y NANOPARTICLES <2nm

No major changes to catalyst structure

Impact of steaming on yields are minor


ATOMIC DISPERSION of Y

Product	Product yields (%)		
	Fresh	Steamed	difference
Ethylene	5.7	6.9	+1.2
Total C_2	6.5	10.4	+3.9
Diethyl ether	3.7	2.8	-0.9
C_{3+}	87.7	83.4	-4.3
Butenes	65.4	58.4	-7.0
C_{5+}	17.3	23.1	+5.8
Total olefin	93.5	90.4	-3.1

Steaming conditions: 20 vol% H_2O in air, 450°C, 24 h.

- Impact of steaming on catalyst structure and performance are minor

2. Progress & Outcomes: Catalyst Synthesis Scale-Up

- **Goal:** Scale-up catalyst synthesis to ensure activity is maintained at scale
  - Transition from research powders to extrudates while decreasing synthesis cost

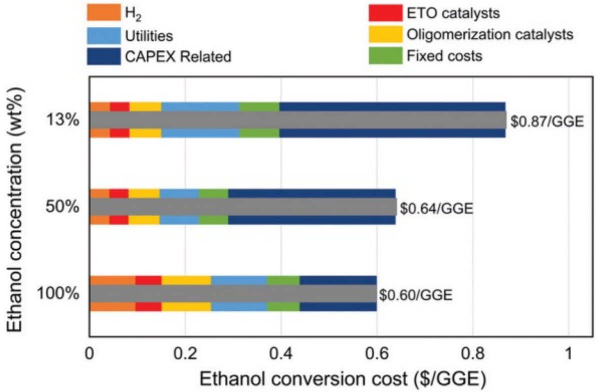
	FY18	FY21	FY23	Target
Dealumination scale (batch)	4.5g	9-10g	90-100g	450-500g
Metal loading scale (batch)	*1g*	*1g*	*10g*	*100g*
Wastewater generation (L/g)	0.9	0.4	0.09	0.02
Nitric acid use (mL/g zeolite)	25	12.5	5	3
Hours per synthesis (hr)	20	20	32	8
Hours per synthesis (hr/g)	4.4	2	0.3	0.1
C_{3+} Olefin Selectivity	87%	89%	89%	89%

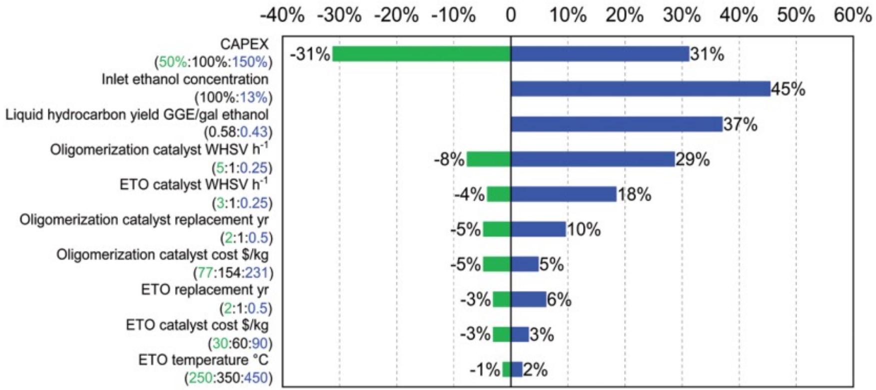
Initial formulation started Q2 FY23 in collaboration with ACSC and a major catalyst manufacturer

Targeted decreasing HNO_3 use and wastewater generation to decrease catalyst cost

- Catalyst can be synthesized reproducibly without performance loss at scale necessary for formulation

2. Progress & Outcomes: Techno-Economic Analysis (TEA)





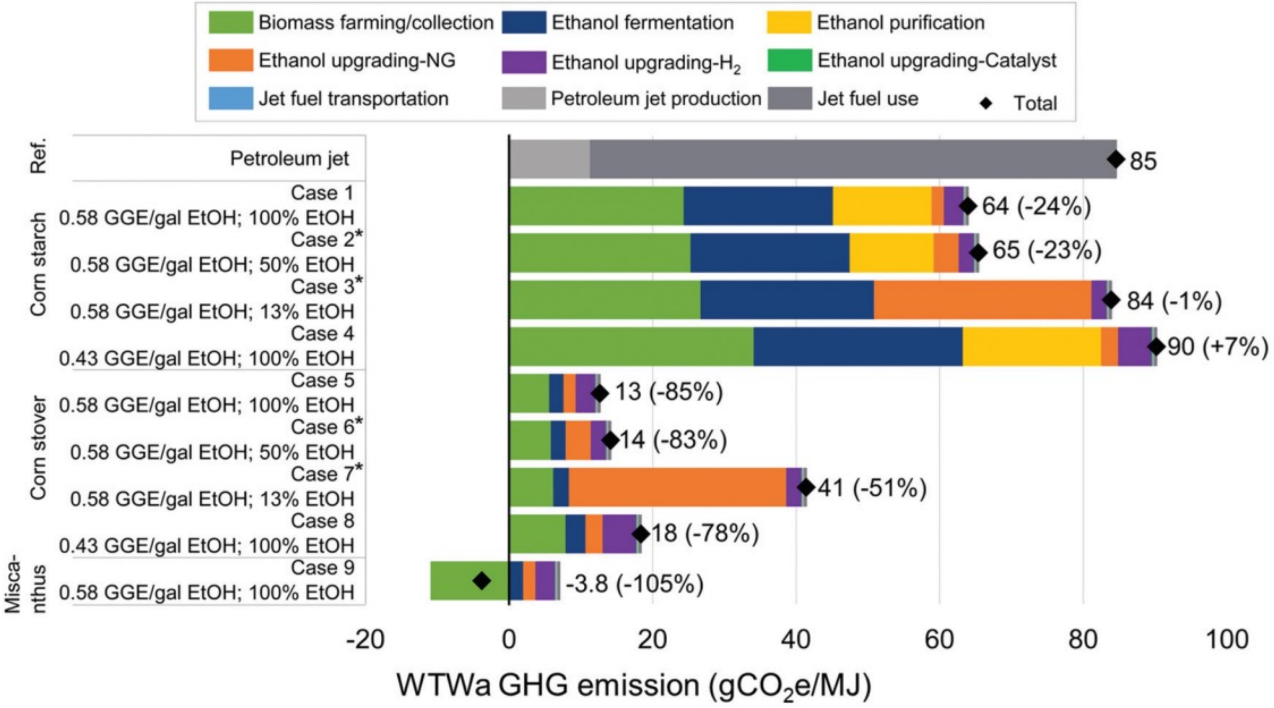
Higher ethanol concentration reduces upgrading cost

Feedstock	Case	Ethanol Prices ($/gal)	Ethanol upgrading technology	Upgrading Costs ($/GGE)	MFSP ($/GGE)	Average jet fuel price ($/GGE)[1]	High jet fuel price ($/GGE)[1]	Blenders Tax Credit	BTC Price ($/GGE)
Petroleum	Benchmark					$2.00	$2.97		
Corn starch	Current	$1.80[2]	Baseline	$0.60	$3.70			0	0
	Projected	$1.41[3]	Projected[4]	$0.53	$2.78			0	0
	BD coproduction[5]	$1.41	BD coproduction	----	$1.64			0	0
Corn stover	Current	$2.54[6]	Baseline	$0.60	$4.98			$1.60	**$3.38**
	Projected	$1.55[7]	Projected	$0.53	$3.02			$1.60	**$1.42**
	BD coproduction[5]	$1.55	BD coproduction	----	$2.23			$1.60	**$0.63**

[1] Average and high U.S. Gulf Coast Kerosene-Type spot price of petroleum jet fuel in 2010-2020[42]. [2] 2010-2020 10-year average corn ethanol price is used. [3] 2015-2020 5-year average corn ethanol price is used. [4] The projected ethanol upgrading technology assumes 95% of the theoretical maximum liquid hydrocarbon yield. [5] BD coproduction case considers 44% carbon from ethanol goes to butadiene with butadiene selling price of $0.8/lb. [6] Ethanol selling price for current case with corn stover is calculated from NREL 2011 model[40] after adjusting the cost to 2016$. [7] Ethanol selling price for the projected case with corn stover is based on future cellulosic ethanol technology.

Green Chem, 2021, 23, 9534

2. Progress & Outcomes: Life-Cycle Analysis (LCA)



Up to 85% reduction in GHG emissions possible with corn stover relative to petroleum jet fuel

Green Chem, 2021, 23, 9534

2. Progress & Outcomes: Improvements

	FY18	**FY21**	**FY23**	**Target**
Catalyst	Cu-Zn-Y/Beta	Cu-Zn-Y/Beta	Cu-Zn-Y/Beta	Improved Design
Process Conditions	*350 °C* *1 atm* *Regenerated /40h*	*350 °C* *1 atm*	*350 °C* *1 atm* H_2 *100 kPa*	*350 °C* *1 atm* ***H_2 50 kPa***
ETO Single-pass EtOH Conversion	~98%	100%	100%	100%
EtOH Feed	Pure EtOH	Pure EtOH Aq EtOH (up to 60 wt.% water)	**Mixed alcohols Simulated Fermentation Grade EtOH**	**Fermentation Grade EtOH**
C_{3+} Olefin Selectivity	87%	89%	**~ 92%**	**95%**
Catalyst Synthesis Scale	*< 1g, research powder*	~5g *research powder*	**100g research powder & formed catalyst particles**	**Exclusively formed catalyst particles**
GHG & MFSP	$4.20 GGE Corn Mill $6.14 Corn Stover	$3.02 GGE Corn Stover	**Corn Starch: $1.64 GGE** **Corn Stover: $2.23 GGE** **($0.64 GGE w/BTC)** **-85% GHG**	***TBD***

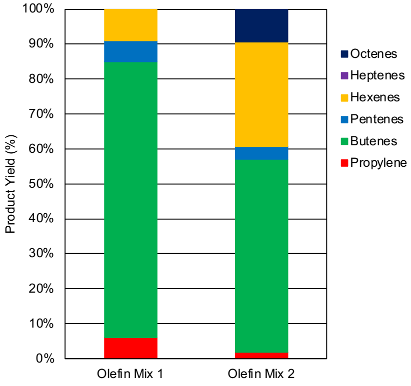
2. Progress & Outcomes: Future R&D

- **Develop the use of engineered catalysts (e.g. extrudates and pellets) (with ACSC)**
- **Improve catalyst selectivity and stability for C_{4+} rich olefin streams (with CDM)**
- **Reactor scale modeling and kinetics for future scale-up (with CCPC)**
- **Demonstrate integrated processing of ethanol to SAF with at least 80% C efficiency**

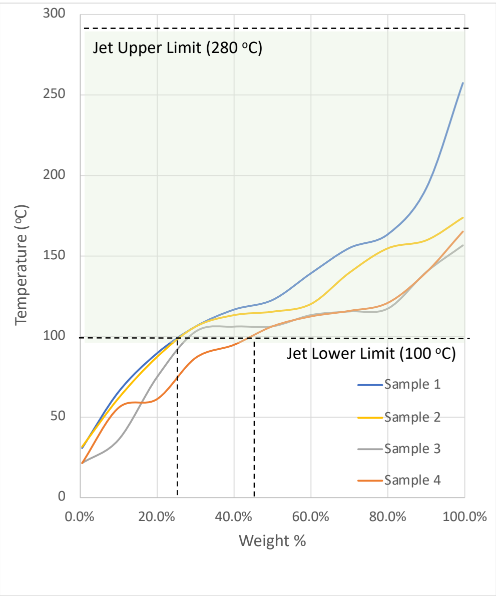
- **FY23-Q2:** Formulate trimetallic zeolite catalyst into extrudates and understand performance changes relative to powdered catalyst
  - Transitions our catalyst work to include binders and additives to provide industrially relevant data
  - De-risks catalyst performance in a fully formed and formulated catalyst pellet
- **FY23-Q4:** Determine process conditions for improved jet yield of C_{3+} olefin oligomerization.
  - Improve oligomerization of C_{3+} to > 80% selectivity to jet range hydrocarbons using industrial catalysts to produce samples ready for full Tier-β fuel property testing.
- **FY24 Go/No-go:** Carbon Efficiency of Oligomerization Processing Step to Meet Economic Targets
  - Achieve at least 80% carbon efficiency for single step oligomerization to produce olefins to SAF range hydrocarbons. Refine current process model and TEA/LCA.
- **End of Project Goal (FY25):** Improve ORNL catalyst technology for ATJ to enabling a new, market-responsive biorefinery pathway through C_{2+} oxygenates to exceed <\$3.00/GGE and > 70% GHG reduction relative to petroleum jet fuel without a loss in performance.

- **New BETO FOA FY22 Waste Feedstocks and Conversion R&D Project** in collaboration with University of Alabama. Topic Area 3: Robust Catalytic Process for Ethanol to Jet.

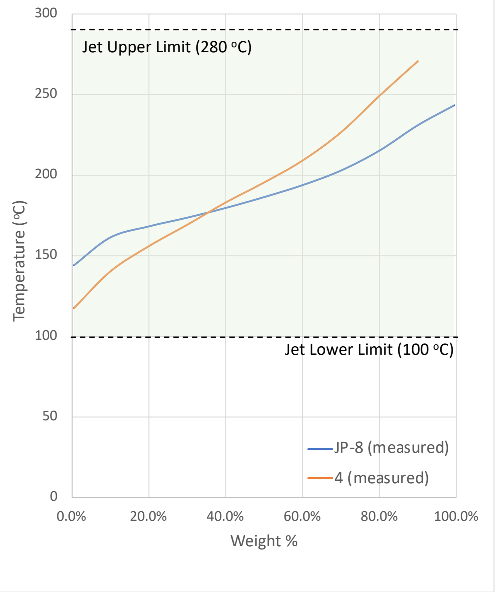
3. Impact: Product Chemistry Well Suited for SAF



ASTM D2887 simulated distillation curves of hydrogenated oligomerization products



ASTM D86 measured distillation curves of JP-8 and the 100 – 280 °C cut of Sample 4



	Sample	Catalyst	Temp (°C)	Time (h)	Scale (g)	Carbon Balance (%)
Olefin Mix 1	1	Amberlyst-36	150	11	70	98.5
	2	ZSM-5	200	11	35	70.0
	3	Beta Zeolite	200	11	35	66.5
Olefin Mix 2	4	Amberlyst-36	150	11	30	85.0

- Olefin surrogate mixtures oligomerized and hydrogenated in batch reactors
- Near quantitative conversion to isoalkanes
- Complete conversion of C3's
- Excellent jet conversion
- 100% with recycle of lights

Fuel Type	Freezing Point (°C)	Flash Point (°C)	Viscosity @ -20 °C (mm$_2$/s)	Cloud Point (°C)	Density @ 15 °C (g/cm^3)	Energy Density (MJ/L)	Specific Energy (MJ/kg)
ORNL SAF (D766-37-1 Distilled)	**< -65**	**32.5**	**4.778**	**< -65**	**0.7743**	**46.5**	**36.0**
Jet-A	< -40	>38	< 8	-	0.775-0.840	42.7	34.0

Summary

Project Goal

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

Approach

- **Enhance stability and selectivity of current catalyst technology while transitioning to industrially relevant catalyst formulations to produce synthetic jet fuel blending components**
- Leverage CCB enabling technologies, process models, techno-economic and life-cycle analyses

Impact

- Licensed technology to Prometheus Biofuels
- In advanced stage negotiations to license our next-gen catalyst technology
- Several patents have been filed and results published in high impact factor journals

Research Progress & Outcomes

- Improved GHG reduction (up to -85% wrt Jet-A) and economics ($1.64 GGE w/o BTC)
- Catalysts exhibit no adverse effects with common ethanol impurities
- Catalyst synthesis increased 100x with comparable performance
- Formed catalyst studies have begun

Quad Chart Overview

Timeline

- *10/01/2022*
- *09/30/2025*

	FY22 Costed	Total Award
DOE Funding	*$600k*	*$600k for FY23* *$1800k for FY23-25*

TRL at Project Start: *2*
TRL at Project End: *4*

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

Improve existing 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.

Funding Mechanism

AOP LabCall 2023 - ChemCatBio

Project Partners*

University of Alabama – James Harris

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Ted Krause
Susan Habas
Canan Karakaya
Roger Rousseau
Gregg Collinge
Rajeev Assary
Mingxia Zhou
Vanessa Dagle
Dan Ruddy

Academic Collaborators

Jamie Harris (University of Alabama)
Jeff Miller (Purdue University)
Dongxia Liu (University of Maryland)

Q&A: 10 minutes

chemcatbio.org

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

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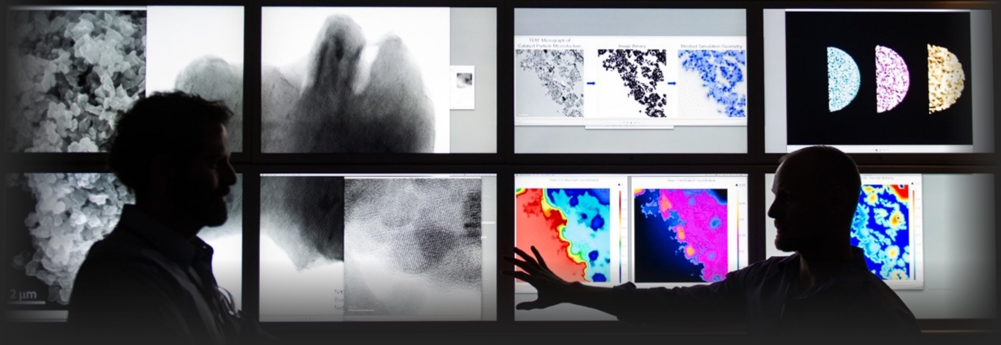
Supplementary Slides



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BIOENERGY TECHNOLOGIES OFFICE

Publications, Presentations and Patents

Publications

1. J. Zhang, E. Yoo, B.H. Davison, D. Liu, J.A. Schaidle, L. Tao*, Z. Li*, Towards cost-competitive middle distillate fuels from ethanol within a market-flexible biorefinery concept. Green Chemistry, 2021,23, 9534-9548
2. M.J. Cordon, J. Zhang, N.R. Samad, J.W. Harris, K.A. Unocic, M. Li, D. Liu, Z. Li*, Ethanol Conversion to C4+ Olefins over Bimetallic Copper- And Lanthanum-Containing Beta Zeolite Catalysts, ACS Sustainable Chemistry & Engineering, 2022, 10 (18), 5702-5707.
3. M.J. Cordon, J. Zhang, Z. Li*, et al. Selective Butene Formation in Direct Ethanol-to-C3+-Olefin Valorization over Zn–Y/Beta and Single-Atom Alloy Composite Catalysts Using In Situ-Generated Hydrogen, ACS Catalysis, 2021, 11 (12), 7193-7209.
4. M. Li*, S. Purdy, J. Zhang, M.J. Cordon, Z. Li, Z. Wu, B. Davison, A. Sutton* , Tailoring Olefin Distribution via Tuning Lanthanide Metals in Beta-Zeolite Catalysts for Ethanol Upgrading. In prep.

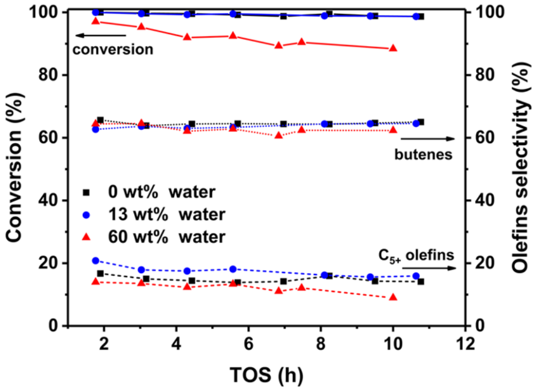
Patents

1. Z. Li, M. Li, “Metal-zeolite comparisons prepared by mechanochemical synthesis, and methods of use” United States Patent Application No. 18/078,195 filed on Dec. 9, 2022
2. Z. Li., B. H. Davison, J. Zhang, “Direct catalytic conversion of alcohols to olefins of higher carbon number with reduced ethylene production” United States Patent Application No. 17/584,651 filed on Jan. 26, 2022
3. Z. Li, “Method for alcohol upgrading to jet, diesel, gasoline, and valuable co-products” United States Patent Application No. 17/083,437 filed on October 29, 2020, issued on April 5, 2022

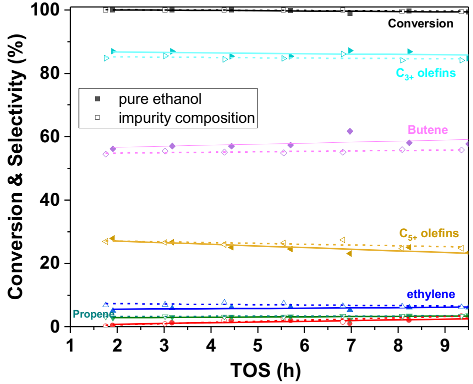
2. Progress & Outcomes: Feedstock flexibility

Goal: Expand into different applications (fermentation-derived, CO_2-derived, syngas-derived mixed alcohols)

Durability to H2O Content Variability



Durability to Impurity Variability



- Water and other impurities **do not** show significant impact on ethanol conversion and product selectivity
  - 0.5% methanol
  - 0.5% acetic acid
  - 0.15% isopropanol
  - 1% acetaldehyde
  - 0.15% butanol

- Offer potential to utilize **pure alcohols, aqueous ethanol, mixed alcohols and impurity ethanol**
- Reduce upstream alcohol separations burden **to cut overall cost**