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)
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 ($M/\text{SiO}_2$; $M = \text{Ag/Zr, X}$)

Task 2 (ORNL): metal modified Lewis acid zeolite (Cu-Zn-Y/BEA)
 Employ TEA of process based on Cu-Zn-Y/BETA catalyst (ORNL) to evaluate process costs and guide R&D efforts

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

<table>
<thead>
<tr>
<th></th>
<th>FY17</th>
<th>FY18</th>
<th>FY20</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETO Catalyst</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conversion (single pass, %)</td>
<td>100</td>
<td>~99</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>C3+ olefin selectivity (%)</td>
<td>33</td>
<td>87</td>
<td>89</td>
<td>95</td>
</tr>
<tr>
<td>Total olefin selectivity (%)</td>
<td>65</td>
<td>92</td>
<td>98</td>
<td>98</td>
</tr>
<tr>
<td>ETO Catalyst WHSV (h⁻¹)</td>
<td>-</td>
<td>0.5</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Hydrocarbon Yield (GGE/gal ethanol)</td>
<td>0.27</td>
<td>0.54</td>
<td>0.58</td>
<td>0.62</td>
</tr>
</tbody>
</table>

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

TEA sensitivity analysis provides guidance for critical future R&D efforts:
- Optimize C₃+ 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)
Employ TEA of process based on mixed oxide catalyst (PNNL) to set targets and periodically assess state of technology

### Enabling catalyst improvements:

<table>
<thead>
<tr>
<th>Timeframe</th>
<th>Single-pass conversion (%)</th>
<th>n-Butene Selectivity (%)</th>
<th>Total Olefins Selectivity (%)</th>
<th>Distillate yield (GGE/dry ton)</th>
<th>Co-Product (wt. %)</th>
<th>MFSP ($/GGE)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ketonization for C-C coupling produces CO₂</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Start of FY17(^1) (Zn(_x)Zr(_y)O(_z))</td>
<td>99</td>
<td>47</td>
<td>58</td>
<td>41</td>
<td>None</td>
<td>5.90</td>
</tr>
<tr>
<td>FY18-G/NG(^1) (Ag-ZrO(_2)/SiO(_2))</td>
<td>99</td>
<td>58</td>
<td>85</td>
<td>57</td>
<td>None</td>
<td>4.57</td>
</tr>
<tr>
<td><strong>Aldol condensation for C-C coupling produces NO CO₂</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>End of FY20(^2) (X/SiO(_2))</td>
<td>98</td>
<td>62</td>
<td>89</td>
<td>58</td>
<td>None</td>
<td>4.06</td>
</tr>
<tr>
<td>Goal - distillate(^2)</td>
<td>100</td>
<td>65</td>
<td>96</td>
<td>59</td>
<td>None</td>
<td>3.58</td>
</tr>
<tr>
<td>Goal – distillate + co-product(^2)</td>
<td>100</td>
<td>65</td>
<td>96</td>
<td>33</td>
<td>44 wt.% n-butene</td>
<td>3.16</td>
</tr>
</tbody>
</table>

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

- 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](chart)

**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*
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
Project Overview

Program objective
• Develop new upgrading technologies enabling cost-competitive conversion of C₂ 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
### Management: Core Project within the ChemCatBio – FY21

**Integrated and collaborative portfolio of catalytic technologies and enabling capabilities**

<table>
<thead>
<tr>
<th>Catalytic Technologies</th>
<th>Enabling Capabilities</th>
<th>Industry Partnerships (Phase II Directed Funding)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytic Upgrading of Biochemical Intermediates (NREL, PNNL, ORNL)</td>
<td>Advanced Catalyst Synthesis and Characterization (NREL, ANL, ORNL)</td>
<td><strong>Opus12</strong> (NREL)</td>
</tr>
<tr>
<td>Upgrading of C1 Building Blocks (NREL)</td>
<td>Consortium for Computational Physics and Chemistry (ORNL, NREL, PNNL, ANL, NETL)</td>
<td><strong>Visolis</strong> (PNNL)</td>
</tr>
<tr>
<td><strong>Upgrading of C2 Intermediates</strong> (PNNL, ORNL)</td>
<td><strong>Catalyst Deactivation Mitigation for Biomass Conversion</strong> (PNNL)</td>
<td><strong>Sironix</strong> (LANL)</td>
</tr>
<tr>
<td>Catalytic Fast Pyrolysis (NREL, PNNL)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrocatalytic CO₂ Utilization (NREL)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Cross-Cutting Support**

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

<table>
<thead>
<tr>
<th>CDM</th>
<th>CCPC</th>
<th>ACSC</th>
<th>WSU</th>
<th>TEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Task 1 (R. Dagle) Ethanol upgrading: mixed oxide catalysis (PNNL)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Task 2 (Z. Li) Ethanol upgrading: zeolite catalysis (ORNL)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Task 3 (R. Dagle) Olefins to distillate (PNNL)</td>
<td></td>
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</tr>
</tbody>
</table>

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

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

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T (°C)</th>
<th>Conv (%)</th>
<th>Selectivity (mol C%)</th>
<th>Ethylene</th>
<th>n-Butene</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al₂O₃ ZSM-5</td>
<td>350</td>
<td>&gt;95</td>
<td>99</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Ag-ZrO₂/ SiO₂ (this work - FY18)</td>
<td>400</td>
<td>98</td>
<td>26</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>ZnₓZrᵧO₂*</td>
<td>450</td>
<td>99</td>
<td>&lt; 5</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>Ce-HZSM-5</td>
<td>400</td>
<td>100</td>
<td>N/A</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Ni-MCM-41</td>
<td>350</td>
<td>100</td>
<td>N/A</td>
<td>8.1</td>
<td></td>
</tr>
</tbody>
</table>

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

### Ethanol-to-C₃⁺ olefins
- **Poor selectivity** to higher olefins (C₃+) from ethanol reported in literature (and often high in aromatics)
- Single step conversion to jet/diesel from C₃⁺ olefins.

*ACS Catal. 2020, 10, 18, 10602–10613*

* Produces iso-olefins

- Multi-step (PNNL-LanzaTech ATJ) or homogenous processes (SHOP/ Ziegler) required for selective conversion of ethylene to jet/diesel
- Single step conversion of C₃⁺ olefins to jet/diesel demonstrated
- However, selective routes from ethanol to C₃⁺ olefins do not exist
Flexible single-step catalytic process for production of butadiene or butene-rich olefins from ethanol

- Low H₂ partial pressure: butadiene product
- Higher H₂ partial pressure: butene-rich olefins

<table>
<thead>
<tr>
<th>Feed</th>
<th>Conv (%)</th>
<th>Selectivity (C mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C₂⁺</td>
</tr>
<tr>
<td>EtOH in inert</td>
<td>99.0</td>
<td>5.8</td>
</tr>
<tr>
<td>EtOH in reducing environment</td>
<td>93.9</td>
<td>25.7</td>
</tr>
</tbody>
</table>

Best catalyst (FY18 G/NG):

- Butadiene selectivity = 75%, conversion > 90%
- C₂⁺ olefins selectivity = 85% (C₃⁺ 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-ZrO₂/SiO₂).
2 – Approach – Project Objective and Goals

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 C₃⁺ 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

<table>
<thead>
<tr>
<th>Milestone/ G/NG</th>
<th>Brief Description</th>
<th>Due Date</th>
</tr>
</thead>
</table>
| **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) |
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

Technological 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

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

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

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

**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

- Catalytic mechanism verified
- Product flexibility of n-butene/butadiene processing further explored by studying effect of H₂ partial pressure, other process variables
- Systematic evaluation of metal and Lewis acid sites effect on catalytic performance
- New catalytic pathway first published (ACS Catalysis)

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

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

ACS Catal. 2020, 10, 18, 10602–10613
Understanding metal and Lewis acid site characteristics on performance

- **Ethanol Conversion**: Correlated to Ag dispersion (not shown)
  - Facilitates initial ethanol dehydrogenation
- **C₄ Selectivity**: Correlated to Lewis acid site concentration
  - Increasing acidity ➔ more dehydration (bad) and less cross condensation (good) side products
  - Optimum Lewis acidity for making C₄ products (butadiene/n-butene)

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

Corelated metal dispersion (Ag) and Lewis Acidity (Zr-SiO₂) to activity and product selectivity, respectively.
Atomic layer deposition (ALD) synthesis of Zr on SiO₂ provides insights into the nature of acid sites on reactivity. Baseline ZrO₂ shows Zr ~3 wt.% Amorphous ZrO₂, while 0.1 M Zr⁴⁺ reveals Zr ~3 wt.% Monodisperse Zr⁴⁺, and 1.0 M Zr⁴⁺ shows Zr ~36 wt.% Monodisperse Zr⁴⁺ (10X Zr).

- 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 C₄ 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 C₄ versus dehydration products.
Catalyst stability – 800 hours test

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)

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

ChemCatChem 2020, 12, 1-11
Improved catalyst (FY20) versus Ag (<FY19) catalyst formulation:

- **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.
4- Progress and Outcomes: Mechanistic Insights & Design Improvements

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

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

- 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%, C₂⁺ olefin sel. = 90%, C₃⁺ 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.

Models for metal nanoparticles supported on ZrO₂/SiO₂ 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.
4 – Progress and Outcomes: Future Work

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)

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### Fuel Properties of jet-range hydrocarbons using C$_3$-C$_4$ olefin intermediates from FY17 SOT catalyst (Zn$_x$Zr$_y$O$_z$)

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

- 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

**Bioenergy Technologies Office**
- Sonia Hammache
- Nichole Fitzgerald
- Trevor Smith
- Ben Simon
- Jeremey Leong

**ORNL Experimental Team (Task 2)**
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- Junyan Zhang
- Shiba Adhikari
- Kinga Unocic

**TEA Team**
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- Lesley Snowden-Swan (PNNL)
- Ling Tao (NREL)

**WSU team**
- Austin Winkelman
- Yong Wang

**CDM (PNNL)**
- Huamin team
- Fan Lin
- Yinlin Wang

**CCPC – Atomic Scale (PNNL)**
- Roger Rousseau
- Vanda Glezakou
- Sneha Akhade
- Simuck Yuk
- Mal-Soon Lee
- Jun Zhang
- Asanga Padmaperuma

**Other Collaborators – ChemCatBio**
- Susan Habas (NREL)
- Josh Schaidle (NREL)
- Jim Parks (ORNL)

**CCPC – Mesoscale (NREL)**
- Peter Ciesielski
- Vivek Bharadwaj
- M. Brennan Pecha
- Lintao Bu
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.

**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

<table>
<thead>
<tr>
<th>DOE Funding</th>
<th>FY20</th>
<th>Active Project</th>
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<td></td>
<td>$750K</td>
<td>$2.25M</td>
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<tr>
<td></td>
<td>(FY20)</td>
<td>(FY20-22)</td>
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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
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 to be 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 be evaluating 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.
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-Tropsch 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:

• "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.
• “Multi-scale simulation of reaction, transport and deactivation in a SBA-16 supported catalyst for the conversion of ethanol to butadiene.” Catalysis Today, 2019, 338, 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:


Commercial Engagement:

FY21-FY23 BETO multi-topic FOA proposal project w/ partners Oregon State University and LanzaTech to scale up ethanol to n-butene catalytic process developed on this project.
Publications, Patents, and Commercial Engagement, continued

Presentations:

Presentations: