Liquid Fuels via Upgrading of Indirect Liquefaction Intermediates
WBS: 2.3.1.304/305

U.S. Department of Energy (DOE)
Bioenergy Technologies Office (BETO)
2017 Project Peer Review
Thermochemical Conversion
March 7th, 2017

Project Leads:
Daniel Ruddy – NREL
Robert Dagle – PNNL
**ChemCatBio Structure**

### Core Catalysis Projects

- **Catalytic Upgrading of Biochemical Intermediates**  
  (NREL, PNNL, ORNL, LANL)
- **Liquid Fuels via Upgrading of Indirect Liquefaction Intermediates**  
  (NREL, PNNL)
- **Fast Pyrolysis and Upgrading**  
  (PNNL, ORNL)
- **Catalytic Fast Pyrolysis**  
  (NREL, PNNL)
- **Recovering and Upgrading Biogenic Carbon in Aqueous Waste Streams**  
  (PNNL, NREL)

### Enabling Projects

- **Advanced Catalyst Synthesis and Characterization**  
  (NREL, ANL, ORNL)
- **Catalyst Cost Model Development**  
  (NREL, PNNL)
- **Consortium for Computational Physics and Chemistry**  
  (ORNL, NREL, PNNL, ANL, NETL)

**Consortium Integration**

- Core catalysis projects focused on specific *applications*
- *Collaborative* projects leveraging core capabilities across DOE laboratories
- *Cross-fertilization* through discussion groups
Goal Statement

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

Project Outcome
- Develop a new IDL process that maximizes distillate fuel production
- Exceed the distillate fuel product yield of 27.4 GGE/dry ton biomass of the benchmark Mobil Olefins-to-Gasoline-and-Distillates (MOGD) process
  - Target is an increase from 10.3 GGE/dry ton for the DME pathway (FY16 SOT)
  - Verification of distillate product pathway in FY22

Relevance
- Known drawbacks for traditional syngas-to-fuels processes at smaller production scale: High capital and process costs, limited product quality
- Advanced upgrading technologies address these shortcomings by focusing on:
  Mild process conditions, high yield and C efficiency, high-quality fuel products
Quad Chart Overview

**Timeline**
- Project start date: 10/1/2016
- Project end date: 9/30/2019
- Percent complete: 17%

**Barriers addressed & Actions**
- Ct-H: Efficient Catalytic Upgrading of Sugars/Aromatics, Gaseous, and Bio-oil Intermediates to Fuels and Chemicals
  - Developing more robust and efficient chemical processes for converting oxygenate intermediates to hydrocarbons
- Ct-J. Process Integration
  - Understanding the effects of real biomass syngas (e.g., impurities) and the limits of process integration through verification

**Budget**

<table>
<thead>
<tr>
<th></th>
<th>FY15 Costs</th>
<th>FY16 Costs</th>
<th>Total Planned Funding (FY17-Project End Date)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOE Funded</td>
<td>$4.05M</td>
<td>$4.05M</td>
<td>$10.8M</td>
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</table>

*FY17 operating budget reduced to $3.3M

**Partners**
- National Labs
  - NREL (55%)
  - PNNL (45%)
- University
  - Washington State Univ. (SUB)
  - Colorado School of Mines (SUB)
Overview: Industrially Relevant Syngas-to-Fuels Processes

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

MFSP from biomass when maximizing distillate yield (2014 $)
- FT = $3.82/GGE
- MOGD = $4.80/GGE

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

Overview: Roadmap to Fuels and Co-Products

**Project Overview**
- Explore multiple, alternative pathways that leverage light oxygenate intermediates
- Develop new catalysts for high-yield, high-C efficiency processes
- Target gasoline, diesel, and jet fuel products with integrated co-product opportunities
- Synergistic NREL-PNNL olefin coupling to distillates and fuel-property testing
Overview: Comparing New Routes with Benchmarks

<table>
<thead>
<tr>
<th></th>
<th>MOGD Benchmark</th>
<th>DME to High-Octane Gasoline (and Jet Fuel)</th>
<th>Ethanol to High-Octane Gasoline (and Jet Fuel)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Catalyst</strong></td>
<td>ZSM-5</td>
<td>Cu/BEA (H⁺ resin)</td>
<td>ZnZrOₓ (H⁺ resin)</td>
</tr>
<tr>
<td><strong>Product Quality Metrics</strong></td>
<td>Gasoline RON 93 <em>High aromatics</em></td>
<td>Gasoline RON 95-110 <em>Minimal aromatics</em> (Jet passes freeze point, flash point, density)</td>
<td>Gasoline RON 103 <em>Minimal aromatics</em> (Jet passes freeze point, flash point, density)</td>
</tr>
<tr>
<td><strong>Fuel Yield</strong></td>
<td>55–65 GGE/ton</td>
<td>60–65 GGE/ton</td>
<td>66 GGE/ton</td>
</tr>
</tbody>
</table>

**Project Objectives**

- Develop new catalytic pathways to hydrocarbon fuels with **low-severity conditions, high C efficiency, and high-quality products**
  - Leverage previously developed syngas-to-oxygenates conversion
  - Inform TEA models, define state of technology, incorporate TEA-defined metrics
- Develop catalysts that **outperform commercial catalysts**, and **identify commercial catalysts that can be adapted** to upgrading routes
Approach—Management

- Monthly PI teleconferences, quarterly team teleconferences
- Yearly updates to TEA models (SOT) to relate catalyst improvements to costs
- Cooperative olefin coupling and fuel testing between NREL and PNNL
- Utilize the TEA-informed Go/No-Go to direct FY22 verification
Technical Approach: Cross-Cutting Research

- Hypothesis-driven catalyst development coupled with sophisticated catalyst synthesis and characterization (with ACSC)
- Catalytic mechanisms investigated to develop structure-function relationships (with CCPC)
- Verification (FY22) integrates biomass gasification and clean up strategies with the conversion technology selected in FY18 Go/No-Go
Technical Approach and Success Factors

Research Challenges

– Balancing multiple reactions under lower severity conditions to **selectively produce fuel-range (C$_5^+$) products**
  • Control C–C, C–H bond making and C–O bond breaking to **maximize C efficiency**
  • Perform cascade chemistry without separations
  • **Recycle by-products** to higher value fuel products versus lower value co-products to maximize yield

– Maximizing catalyst **lifetime** and developing **regeneration** protocols
  • Determine with bench-scale experiments prior to verification
  • Confirm with real biomass syngas in verification

– Generating relevant **quantity** to confirm **high-quality fuel properties** to compete with mature, conventional fuel-synthesis processes
  Utilize multiple ASTM International test methods with fuel-testing experts at NREL and PNNL
Task 1: TEA Motivation to Recycle C₄ Product

**Improve Fuel Yield Through C₄ Re-Incorporation and Lower MFSP**

Feed Handling & Processing → Gasification & Clean-Up → Syngas CO + H₂ → Methanol and DME → High-Octane Gasoline

*Recycle enabled by moving from HBEA to Cu/BEA*

**Yield and Cost Impact with Successful C₄ Recycle**

- **Graph a):** Methanol-Free Carbon Selectivity vs. Carbon Number
- **Graph b):** Conversion Cost per Gallon GE (2014$)

Recycle, reactivate, and reincorporate in chain-growth cycle for higher C₅+ yield in lower synthesis cost
Goal: Employ simulated isobutane recycle to evaluate catalyst performance

**Isobutane Dehydrogenation**

- **Identified ionic Cu(I) as the active site** with ACSC and CCPC
- **Simulated recycle** – DME + H₂ + ^13^C-C₄H₁₀ – confirms ^13^C reincorporation into C₅⁺ products

**Simulated C₄ Recycle**

- Achieved FY16 target MFSP $4.13/GGE
- 20.6% reduction from FY15 ($1.07/GGE absolute)
- Requires high-productivity Cu/BEA and C₄ reactivation at Cu⁺ sites (not HBEA)
- Recall MOGD at $4.80/GGE for gasoline and distillate from biomass
Task 2: Ethanol-to-Isobutylene Research Progress

- **Complex reaction network** requiring tailored acidic and basic sites for selectivity control.
- **Feedstock flexibility**—ethanol, acetaldehyde, acetic acid, acetone, and ethyl acetate upgrading demonstrated.
- **Propanol** and **butanol** form C₆ and C₈ olefins.
- **Yield to C₃+ olefins ~ 60%**.

**Oligomerization of Olefins Produce C₈–C₁₆ Range Product**

- ~75% of liquid product in the 150–300°C boiling point range (jet-range) reported in Green Chemistry Paper.
- Optimization of the olefin oligomerization has recently improved yield to jet range HC’s to ~90%.

_Demonstrated syngas-to-jet via Rh-derived mixed oxygenates and isobutylene oligomerization_

**Alternative Ethanol Coupling Routes**

**FY16 Go/No-Go:** Zn$_{x}$Zr$_y$O$_z$ reliance on ketonization in the reaction mechanism produces significant CO$_2$ byproduct, and a minimum projected MFSP of $3.70/GGE
- Not realistic as a primary fuels pathway
- Shift focus to chemistry that does not rely on CO$_2$ production

*Reaction Scheme at Low Temperature*

- **Goal is to facilitate 1-butanol or 1,3-butadiene route (projected MFSP at or below $3.00/GGE)**
- **Leverage alcohol/olefin coupling already developed**
Two Routes for Ethanol Conversion

### Guerbet Coupling

**Feed:** Ethanol; **Catalyst:** Cu-MgO-Al\(_2\)O\(_3\); **T:** 300-350°C; **WHSV:** 0.1-0.2h\(^{-1}\)

- 90% selectivity to C\(_4\)-C\(_6\) alcohols
- Produced higher alcohols can then be dehydrated and oligomerized to distillates
- Catalyst stable for > 200 h time-on-stream

### Butadiene

**Feed:** 50% Ethanol/N\(_2\); **Catalyst:** Ag/ZrO\(_2\)-SiO\(_2\); **T:** 325°C, **P:** 1atm; **WHSV:** 0.3-0.47 h\(^{-1}\)

- PNNL catalyst provides higher yield and 2.5X productivity (g/g\(_{cat}\)/h)
- In process of patent application(s)
- Currently developing oligomerization of butadiene-rich olefins

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**Table:**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>BD Selectivity (%)</th>
<th>BD Yield (%)</th>
<th>C2-C4 Olefin Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>State of the Art Ag/4ZrO(_2)-SiO(_2)</td>
<td>55</td>
<td>71</td>
<td>39</td>
<td>45</td>
</tr>
<tr>
<td>PNNL formulation</td>
<td>98</td>
<td>73</td>
<td>72</td>
<td>87</td>
</tr>
</tbody>
</table>
Project Technological Achievements (FY15–16)

- Cu/BEA catalyst exhibits **2 to 3 times rate improvement** for high-octane gasoline production; **olefin oligomerization** yields distillate-range product with jet-fuel properties.
- Ethanol coupling pathways through C₄ olefin or alcohol intermediates, **selective conversion to distillate fuels** and provide **co-product** opportunities.
- Bimetallic catalyst for direct syngas conversion exhibits **high selectivity to olefins** for coupling to distillates (**no wax**).
Relevance

*Developing a market-responsive biorefinery concept based on IDL to enable control over the biomass-derived gasoline, diesel, and jet product distribution.*

Directly supports BETO’s **mission** “to develop and demonstrate transformative and revolutionary bioenergy technologies for a sustainable nation,” and its **goal** “to develop commercially viable bioenergy and bioproduct technologies.”

Project metrics and technical targets are **driven by TEA with yearly updates to SOT.** Project research is **highly collaborative with BETO enabling technologies.**

Technology developed here was awarded a **Technology Commercialization Fund $740k investment by DOE + $750k cost-share investment from Enerkem**

- Demonstrate DME homologation with Enerkem at the pilot scale
- 1,000 times larger than FY17 verification scale, will provide complementary data
- Researchers at NREL selected for LabCorps to explore commercialization
- Additional TCF proposals in preparation with LanzaTech and ZeaChem
Developing a market-responsive biorefinery concept based on IDL to enable control over the biomass-derived gasoline, diesel, and jet product distribution.

Gasoline products developed in FY15–16 from DME and Ethanol represent **premium fuels (RON 95-110)**. Unlike ethanol, hydrocarbon product has no blend limit.

**Entry points for the bioenergy industry to compete**
- Racecar fuel—100 octane, $13.66/gal; wholesale blended $6/gal to $8/gal
- Unleaded aviation gasoline—100 octane, $4.70/gal
  - 175 M gal/yr market for avgas
  - Smaller markets that value (and pay for) a premium product

*Project now shifts focus to jet/diesel production and promising initial results meet both commercial and military-grade specifications.*
Future Work—Next 18 Months

**Catalyst and Process Development Research**

**Task 1**  Further develop dehydrogenation to control paraffin-to-olefin ratio to increase jet-range product yield.

**Task 2**  Establish the new state of the art for EtOH-to-BD, develop oligomerization. Demonstrate full process of EtOH-to-butanol-to-distillates set the SOT with TEA models for both.

**Task 3**  Demonstrate the complete pathway for syngas-to-olefins-to-fuels.

**Task 4**  Verify integrated biomass-to-hydrocarbons process (annual milestone) Joint Q2 milestone with Feedstock Interface Project to select optimal feedstock Perform 300 h verification of biomass to high-octane gasoline at 1-2 kg\(_{\text{biomass}}/h\)

**FY18 Go/No-Go:** Down-select syngas upgrading pathway for verification in FY22

Each will be assessed for ability to exceed the benchmarks of FT and MOGD for distillate product yield and MFSP
Summary

Leveraging syngas-derived light oxygenates to develop new, low-severity catalytic upgrading technologies to high-quality fuels and high-value coproducts

- Developing **multifunctional catalysts** to perform selective, cascade reactions, leading to low operating costs and high C efficiency

- Interdisciplinary, **collaborative approach** within ChemCatBio leveraging enabling technologies

- Successful **isobutane reactivation enabled a $1.07 reduction in MFSP** for DME to gasoline over Cu/BEA ($4.13/GGE is less than the $4.80/GGE MOGD benchmark)

- **Setting the state of the art in ethanol coupling** with high-yield, high C efficiency processes for distillate fuel production and coproduct opportunities

- Demonstrated **technology transfer with the bioenergy industry (e.g., TCF)**—publish results in top-tier peer-reviewed journals

- Integrated **verifications** in FY17 (gasoline) and FY22 (distillate) to reduce the risk toward commercialization for processes developed in this project
Acknowledgements

**NREL Catalyst Development Team**
Connor Nash Carriee Farberow
Jesse Hensley Joshua Schaidle
Seonah Kim Singfoong Cheah
Matthew Yung Susan Habas
Anh To Terry O’Neill

**PNNL Catalyst Development Team**
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Matt Flake Heather Brown
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Mond Guo Carlos Alvarez-Vasco

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Eric Nelson Gary Grim

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Eric Tan (NREL)
Steven Phillips (PNNL)
Lesley Snowden-Swan (PNNL)
Sue Jones (PNNL)

**Collaborators**
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Jeffrey Miller (ANL)
Earl Christensen (NREL)
Yong Wang (WSU)
Liquid Fuels via Upgrading of Indirect Liquefaction Intermediates
(WBS 2.3.1.304-5)

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Response to FY15 Peer Review Comments—NREL

1. **Comment:** The scientific work is good. A better justification of why this particular approach offers more potential than other would be useful. The project team needs to read the literature. There are inherent limitations to triptane due to back cracking. Why not use FT, hydrocrack, hydrosisom? All of this is known technology

**Response:** The presentation contains many citations to the literature pertaining to this project, which we have reviewed extensively. We have also discussed challenges and catalyst limitations with several of the researchers who published that literature. In previous years, NREL (with PNNL) has considered the MTG and FT processes with biomass syngas. In both cases, yield loss was problematic, and this was due to the higher-severity operating conditions, higher losses to coke, and large number of process steps. As process size becomes smaller (as with biofuels), yield losses tend to have a larger impact on economics. Using FT as an example, it has been demonstrated that massive scale is required to turn profits, even with inexpensive (or free) feedstock. The pathway we are studying holds promise in that it uses lower-severity conditions, has a smaller number of process steps, and has the potential for higher yield.

2. **Comment:** Only by removing small amounts of products with a large recycle will the process work, and this will be costly. It would be better to target isobutane and send it to an alkylation unit to produce a high octane gasoline.

-This project has potential to produce distillate or high octane gasoline if the C4 fraction can be converted to higher hydrocarbons.

**Response:** The process models (developed in a complementary project) suggest that the separation of product from recycle is straightforward and, because the process is not operated at high pressures, the OPEX/CAPEX associated with C4 recycle is not prohibitive. It is acknowledged that additional experiments with simulated and then actual recycle will be required to verify those Aspen models (planned for FY16). Depending on the customer (refiner vs. blending terminal), we agree that optimization to isobutene production could be valuable. Our process models do not suggest, however, that an alkylation unit (instead of C4 recycle) is more attractive. We will certainly continue to explore that possibility as our research and the process models evolve. Finally, we agree with the reviewers that C4 conversion to larger hydrocarbons is critical to project success. We will focus our attention on this challenge and continue to couple our work with the thermochemical analysis project to ensure that we are spending our time and resources on the most impactful research and data.

3. **Comment:** High octane gasoline can be achieved with ethanol. And gasoline is in decline. Why not work to maximize high cetane diesel which enjoys a price premium due to high demand?

**Response:** While ethanol provides octane boost it lowers energy density and has incompatibilities with engines at concentrations above 10-15%. This was one of the critiques of alcohol fuels and a driver of moving toward biomass-derived hydrocarbon fuels. It is correct that demand for kerosene fuels is going up relative to gasoline (or gasoline demand going down relative to kerosene) and this is why we’re exploring conversion to distillates as well. Our fuel analyses suggest that high cetane will not be achieved by our route, although some of the product may still be suitable in diesel blends. We also note that a significant demand for high cetane diesel has come from hydrofracturing activity, which is in decline due to the presently low price of oil, so we assert that given this volatility it isn’t practical for a 5-10 year research program to be in lockstep with (often unpredictable) changes in the petrochemical markets. It is nearly certain that demand for gasoline, diesel, and jet will remain for decades, and prices and supply will fluctuate. This project covers two of those three.
1. **Comments** around techno economic analysis and need for performance targets:
   - The project was clearly explained, but measurable targets for success were not obvious.
   - Project objective should quantify such things as production targets, type of experimental data that are current gaps, how TEA and LCA will feed back to inform process development (the optimization approach).
   - Goal fits with BETO object of producing jet, diesel and gasoline. But this project badly needs a TEA done.
   - Includes TEA and continuing to develop catalysts. Need some scoping economics done now.

**Response:** Models for each of the pathways were developed and preliminary results for each were unfortunately not included in this particular presentation. “Goal case” techno economic targets were developed that assume best case catalyst performance given future catalyst advances. “State of technology” economics are then obtained using the best experimental results. A joint NREL-PNNL analysis was completed in Q4 FY15 (and published FY16) and this helped to eliminate the oxygenate to distillates pathway via isobutene intermediates (Tan et al, 2016). This TEA analysis directly supported the FY16 Go/No-Go decisions for the experimental team to focus on the most impactful catalyst research areas. **It was found that $3/GGE distillate from oxygenates is achievable from both the Guerbet and butadiene pathways when co-products are utilized (alcohols or butadiene).** These projected targets are driving the experimental research. Sue Jones is providing more detail in her analysis presentation. Furthermore, these processes are also being compared against conventional fuel synthesis approaches such as FT and MOGD that also produce distillate fuels.

2. **Comment:** Need to consider catalyst life.

**Response:** We have indeed evaluated stability (unfortunately we did not fully address this point in our presentation). For the mixed oxides catalyst useful for isobutene production we have illustrated how gradual deactivation of the catalyst does occur. However, complete catalytic regeneration was demonstrated after mild oxidative treatment and we have demonstration multiple regeneration cycles resulting in a catalyst time-on-stream of greater than 200 hours with no signs of irreversible deactivation. For the Guerbet process catalyst stability was demonstrated for greater than 1000 hours resulting in constant ethanol conversion and butanol yield without any need for catalyst regeneration. We certainly agree that catalyst lifetime is very important to consider and we will continue to address this issue.

3. **Comment:** This project seems to be about syngas conversion, not conversion of biomass to syngas. It is therefore relevant to natural gas and coal conversion to liquids as well. Not sure why DOE is doing this research as others probably are.

**Response:** We are evaluating conversion options that would be relevant both solely to biomass (e.g., upgrading of fermentation products) as well as those applicable to syngas, the latter certainly being relevant to waste fume gas, municipal solid waste, natural gas, and coal in addition to biomass. Due to the high costs and complexity associated with conventional synthetic fuel processes (e.g., FT, MTG), the production cost of finished fuel cannot currently compete with petroleum-derived fuel, particularly at the scale of biomass. To incorporate the smaller scale desirable for biomass, novel processes must be developed with reduced capital costs, and secondary processing of products (e.g., hydrocracking/hydrosomerization of FTS waxes) must be minimized. Yield and selectivity are also critical cost factors and must be maximized in biomass conversion processes. Thus, syngas conversion processes that can selectively produce a more desirable high octane gasoline, jet, and/or diesel fuel with high yield, and at a reduced cost to conventional synthesis approaches would be highly advantageous for the biomass industry.
Publications


Selected Presentations

17. C. Farberow, S. Kim, D. Ruddy, S. Cheah, J. Hensley, J. Schaidle, AIChE Fall National Meeting, Salt Lake City, UT 2015.