ChemCatBio
Chemical Catalysis for Bioenergy

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle *Since 1965*

LanzaTech
capturing carbon. fueling growth.

DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review

Improved Value of the Gasoline and Fuel Oil Co-Product Fractions w/ LanzaTech

6th March 2019

Catalytic Upgrading

Robert Dagle

Pacific Northwest National Laboratory

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

ChemCatBio Foundation

Integrated and collaborative portfolio of catalytic technologies and enabling capabilities

Catalytic Technologies

- **Catalytic Upgrading of Biochemical Intermediates** (NREL, PNNL, ORNL, LANL, NREL*)
- **Catalytic Upgrading of Indirect Liquefaction Intermediates** (NREL, PNNL, ORNL)
- **Catalytic Fast Pyrolysis** (NREL, PNNL)
- **Electrocatalytic and Thermocatalytic CO_2 Utilization** (NREL, ORNL*)

*FY19 Seed Project

Enabling Capabilities

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

Industry Partnerships (Directed Funding)

- **Gevo** (NREL)
- **ALD Nano/JM** (NREL)
- **Vertimass** (ORNL)
- **Opus12**(NREL)
- **Visolis** (PNNL)
- **Lanzatech** (PNNL) - Fuel
- **Gevo** (LANL)
- **Lanzatech** (PNNL) - TPA
- **Sironix** (LANL)

Cross-Cutting Support

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

Quad Chart Overview

Timeline (2-Year Project)

- Project start date: April 3, 2018
- Project end date: March 31, 2020
- Percent complete: 33%

	Total Costs Pre FY17	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded	0	0	$105K	$495K
Project Cost Share	0	0	$27K	$230K

Partners: PNNL (70%) and LanzaTech (30%)

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

LanzaTech

capturing carbon. fueling growth.

Barriers addressed

- Ct-D. Advanced Bioprocess Development
  Developing more robust and efficient chemical process for converting bio-derived intermediates to valuable co-products (fuel blendstocks and/or lubricant)
- Ct-K. Developing Methods for Bioproduct Production:
  Understanding the properties of the co-product lubricant must be fundamentally understood.

Objective

Increase the value of the current PNNL/LanzaTech alcohol-to-jet process by:

1) Increasing the RON of the lighter-than-jet gasoline fraction above 98, and
2) Creating a synthetic lubricant base oil from the heavier-than-jet fraction.

End of Project Goal

1) Increase RON of lights to 98, and 2) produce synthetic lubricant base oil from heavies, both meeting ASTM standards.

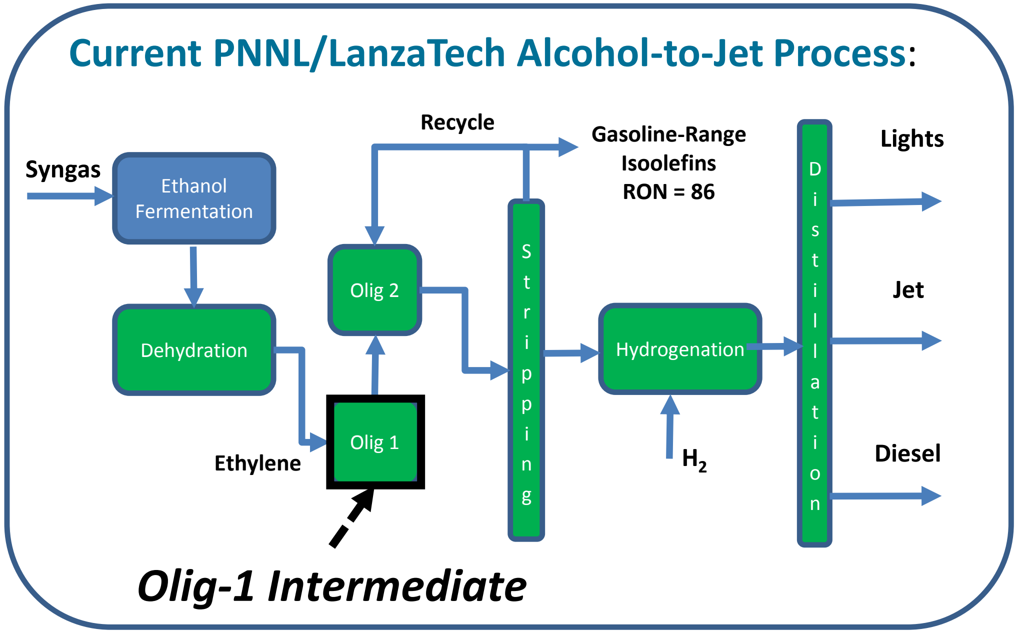
Project Overview

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

LanzaTech capturing carbon. fueling growth.

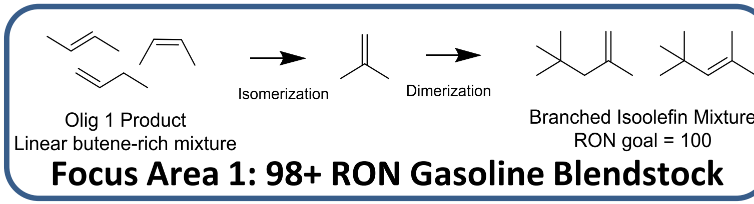
Goal: Increase value of the current PNNL and LanzaTech alcohol-to-jet process by:

1) **Increasing RON** of lighter-than-jet fraction to 98.
2) **Producing synthetic lubricant base oil** from heavier-than-jet fraction.



Approach:

1) **Lights**: skeletal isomerization of Olig-1 intermediate (comprising C_4, C_6, and C_8 mono-olefins), followed by oligomerization and RON verification (ASTM validation)
2) **Heavies:** Fuel oil characterization, hydroisomerization, and evaluate renewable synthetic lube oil property-structure relationships (ASTM validation)



1. Investigate as Group III base oil
2. Hydroisomerization to increase viscosity index

Focus Area 2: Group III Base Oil

Improve Value of the Gasoline and Fuel Oil Co-Product Fractions Generated by the PNNL/LanzaTech Alcohol-to-Jet (ATJ) Process with high octane gasoline and lubricant base oil.

Research Challenges & Approach

- Balancing multiple reactions to selectively produce high octane gasoline from Olig-1 intermediate(C_4-C_{10} olefin mixture)
  - Control isomerization, oligomerization, cracking reactions to maximize both ***RON*** and ***C efficiency***
  - Understand ***catalytic properties*** (e.g., acidity, pore size) that favor desired properties
  - Develop processing conditions (T, P, SV) to maximize high RON product
  - Maximize catalyst ***lifetime*** and develop ***regeneration*** protocols if necessary

- Produce relevant quantities to confirm high-quality fuel/lubricant properties using real fermentation-derived feedstock from LanzaTech
  - IQT characterization to provide DCN and calculated ***RON values***
  - ***Engine testing*** to be performed by LanzaTech to confirm RON values, obtain additional fuel properties
  - Utilize multiple ***ASTM International test methods*** to characterize lubricant properties

Table 1. Physical and Compositional Property Tests for Lubricant Base Oils. Adapted from ASTM D6074.

Property	ASTM Test
Saturates	D2007
Sulfur	D2622
Viscosity Index	D2270
Density (15°C)	D287
Color	D1500

Impact on Bioenergy Industry & Success Factors

Value-Added Co-Products

- Decrease effective cash cost of PNNL/LT process jet fuel by >$1/gal via creation of ***high value gasoline*** and ***synthetic lubricant*** co-products
- Utilize light and heavy cuts for co-products and provide additional markets

Success Factors

- A 98+ RON blendstock has a premium of >25% above gasoline
  - ASTM characterization for RON
- Group III base oils (4 cSt viscosity) valued at \$3.80-\$4.60 (2017), versus diesel spot prices of \$1.40-\$1.70 (2017)
  - ASTM characterization for Group III base oil

Why National Laboratory Capabilities?

Complimentary Expertise and Capabilities

- Capabilities at PNNL represent the best path forward for LanzaTech to quickly develop the proposed catalytic process technology and move it into commercial practice
- LanzaTech utilizes PNNL capabilities and expertise already in place with ***thermocatalytic conversions***:
  - PNNL has the expertise, catalysts, flow reactors and analytical equipment necessary to quickly and efficiently perform this R&D
- Researchers at PNNL also have access to the Environmental Molecular Sciences Laboratory at PNNL for advanced catalyst characterization techniques

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965

LanzaTech capturing carbon. fueling growth.

LanzaTech-PNNL Commercial Success

Co-Developed Alcohol-to-Jet Process (ATJ)

- The demonstration scale LanzaTech ATJ process operating in Georgia utilizes conversion technology licensed from PNNL.

"LanzaTech and PNNL have already co-developed a process to efficiently convert waste gases and other sustainable sources to high performance fuels including a road diesel and jet fuel. We are interested in extending our portfolio of sustainable products to include high octane gasoline and lubricants. ***We have worked closely with research teams at PNNL and they have provided significant technology advances that have supported our commercial efforts****.*

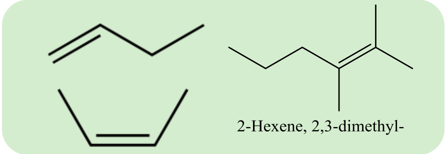
LanzaTech has state of the art facilities to develop and scale-up bio organism based routes to waste gas conversion while PNNL has complementary skills in basic catalysis research that complement our core competencies and allow us to jointly develop new routes to sustainable fuels and products."

- Michelle Kocal, LanzaTech

In October 2018 Virgin Atlantic operated a flight using low-carbon fuel that came from LanzaTech's facility in Georgia using technology co-developed with PNNL.

Low Temperature Oligomerziation of Olig-1 Intermediate

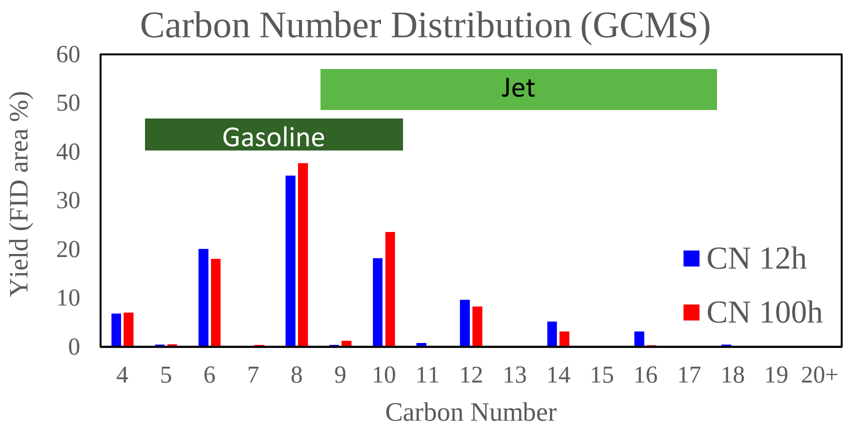
Olig-1 Intermediate (C_4-C_{10} Olefins)



Acid Catalyst
80°C, 250 psig

High Octane Gasoline Blendstock

1-Step

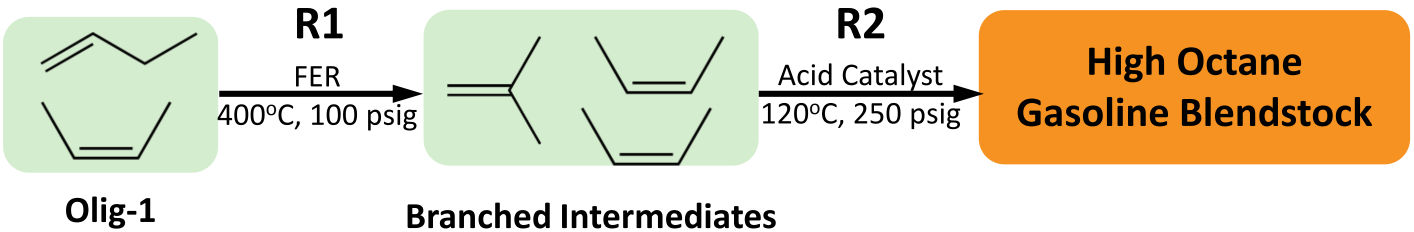


- Zeolites and solid acid resins investigated
- Multi vs monobranched are thermodynamically favored at low temperature; however, dimerization is kinetically favored
- **Few quaternary carbons in product → No skeletal isomerization occurs**

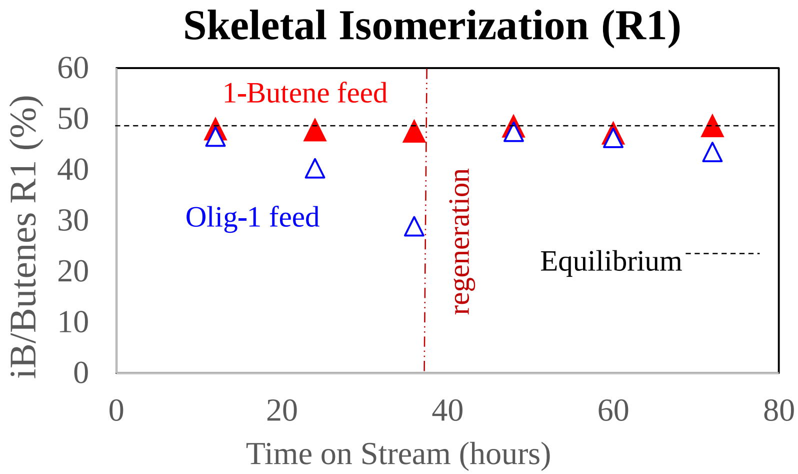
RON_{IQT}= 94 (gasoline fraction)

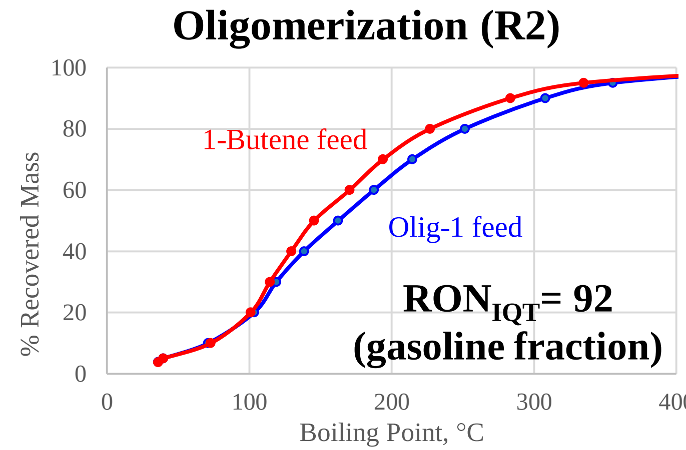
- Low temperature oligomerization of Olig-1 increased RON of the gasoline fraction from 86 to 94; however, further RON enhancement restricted by limited branching.
- To increase branching of oligomerized product, skeletal oligomerization must be carried out at higher temperatures (400°C) followed by controlled oligomerization.

Skeletal Isomerization at 400°C Followed by Oligomerization



2-Step





- Skeletal isomerization (R1) studied using shape selective & non-shape selective catalysts
- Skeletal isomerization (R1) followed by oligomerization (R2) demonstrated for ~ 80 hours using both Olig-1 and 1-butene feed, for comparison purpose; resulting RON ~ 92
- **High quaternary carbon content in product; however, further development of R2 required to further enhance RON**

2-step process developed increasing RON of gasoline fraction from 86 to 92; efforts to further enhance RON underway.

Note: We believe IQT analysis is underreporting RON; engine tests will confirm.

Future Work

High Octane Gasoline

- Additional work is required to further enhance RON and/or potentially exclude C_{6+} olefins from gasoline feedstock
- Optimize the process for carbon efficiency by further reduce cracking products (lower acidity and conversion, increased recycle) and understand long term stability

Lubricant

- Group III base oils (synthetic motor oils) typically consist of isoparaffins w/ 18-40 carbons (b.p. 288 - 566°C)
- Requirements include > 90% saturates, < 0.03 wt.% S, and a viscosity index > 120
- Develop hydroisomerization processing to increase the viscosity index of the lubricant fraction
- Perform ASTM D6074 characterizations on the heavier than jet cut(s) to understand properties relevant to Group III base oils

- High Octane Gasoline: Further develop the 2-step processing and then produce sufficient quantity of product for ***ASTM engine testing*** of the gasoline product.
- Lubricant: Increase viscosity index of the lubricant fraction and evaluate lubricant properties via ***ASTM testing.***

Future Work: Milestones/Deliverables

June 30, 2019 — Sept 30, 2019 — Dec 31, 2019 — March 30, 2020 (End)

High Octane Gasoline:

Determine optimum conditions with a strong acid catalyst for the oligomerization of the isomerized Olig 1 product to generate a high RON fraction. Obtain enough sample for engine testing using real fermentation-derived feedstock.

Measure the RON via ASTM D2699 of the isomerized and dimerized isoolefins generated from LanzaTech-derived Olig 1 intermediate OR from C4 cut.

ASTM characterizations using real feedstock.

Lubricant:

Complete the viscosity index (ASTM D2270), density (D287), and saturates (D2007) measurement of two fractions, one boiling between 290-570°C and the other between 350-570°C, to determine the level of hydroisomerization processing required to ***generate Group III base oil***.

Complete ***initial hydroisomerization processing tests*** with a commercial catalyst (if available) using the best conditions identified in the literature in order to improve the properties of the base oil lubricant.

Measure the properties of a ***hydroisomerized fuel oil fraction*** via ***ASTM standards*** for viscosity index (ASTM D2270), density (D287), and saturates (D2007), and compare with Group III base oil.

Submit a **Final Report** including:
i) processing conditions
ii) lessons learned
iii) TEA modeled costs required to produce 98+ RON gasoline and generate Group III fuel oil.

Summary

Approach & Relevance

- The LanzaTech ATJ process currently being commercialized utilizes conversion technology licensed from PNNL
- The objective of the project is to improve value of the gasoline (light) and fuel oil (heavy) co-product fractions
- Goal: 1) increase RON of lights to 98, and 2) produce a synthetic lubricant base oil from the heavies (meeting ASTM standards)

Technical Accomplishments/Progress

- To produce a high RON from the lighter than jet, linear olefin fraction a process employing skeletal isomerization is being developed
- Enhancement to RON from 86 to 94 has thus far been demonstrated

Future Work

- Additional work is required to further enhance RON and optimize the C efficiency
- Development of a hydroisomerization process is required to increase the viscosity index of the heavies; understand their properties relevant to Group III base oils
- Evaluate fuel/oil properties using ASTM methods and using real waste-derived feedstock obtained from LanzaTech

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle *Since 1965*

LanzaTech
capturing carbon. fueling growth.

Acknowledgements

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Bioenergy Technologies Office

- Andrea Bailey

LanzaTech

capturing carbon fueling growth

- Michelle Kocal

Pacific Northwest NATIONAL LABORATORY

- Johnny Saavedra Lopez
- Alan Cooper
- Evgueni Polikarpov
- Rich Hallen

This research was supported by the DOE Bioenergy Technology Office

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

ChemCatBio Chemical Catalysis for Bioenergy

Energy Materials Network U.S. Department of Energy

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

BIOENERGY TECHNOLOGIES OFFICE

Thank you!

ChemCatBio Team

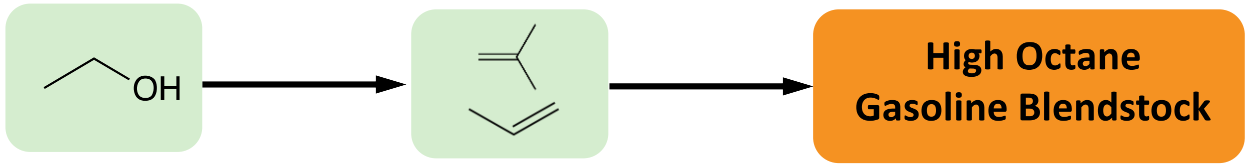
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Bioenergy Technologies Office

Extra Slides

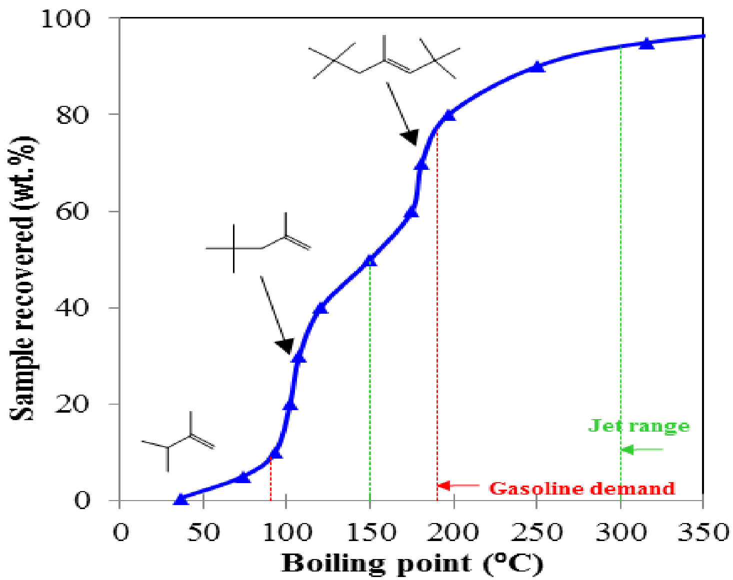
ChemCatBio
Chemical Catalysis for Bioenergy

High Octane Gasoline Produced from Isobutene-Rich Intermediates



Ethanol

Isobutene/
Propene



Simulated distillation profile for the oligomerization product of ethanol-derived isobutene/propene intermediates.

Fuel Properties for Gasoline-Cut

Analysis	Measurement[a]
RON number	103.3[a] (99[b])
MON number	91.4[a]

a. Near-IR Transmission Spectroscopy
b. Ignition Quality Test (IQT)

Catalysis Science & Technology, 2019, DOI: 10.1039/C8CY02297F

A high octane gasoline blendstock can be produced from isobutene intermediates.

RON Enhancement w/ Skeletal Isomerization

Project Start: April 2018

Feed	Approach	RON
Olig-1	90-180°C gasoline fraction after higher temperature oligomerization via Olig-2 **(baseline)**	RON=86
Olig-1	90-150°C cut after lower temperature isomerization/oligomerization **(1-step)**	RON_{IQT}=94
Olig-1	90-150°C cut after skeletal isomerization followed by oligomerization **(2-step)**	RON_{IQT}=92

- 1-step processing provides a RON ~ 94 (sets a baseline)
- 2-step processing still under development has potential for further RON enhancement; thus far provides a RON ~ 92

Note: we believe IQT analysis is underreporting the RON; engine tests will confirm

Enhancement to RON demonstrated with the use of skeletal isomerization followed by oligomerization; efforts to further enhance RON underway.