U.S. DEPARTMENT OF
ENERGY

Office of
ENERGY EFFICIENCY &
RENEWABLE ENERGY

DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review
Higher energy-content jet blending components derived from ethanol

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Systems Development and Integration

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Project Overview

Program objective

- Enable selective processing for **cycloalkanes** and understanding their use as a **jet fuel.**

Project outcome

- Develop a commercially viable process to convert an ethanol-derived olefin intermediate into a **jet-range hydrocarbon** with **60 wt.% yield to cycloalkanes** and demonstrate its commercial utility as a jet blendstock via fuel property analysis, ASTM characterization, and techno-economic and life cycle analyses.

1 – Management: Project Partners

Purdue

- Purdue contains specialized expertise with molecular level characterization of complex mixtures of hydrocarbons, including aviation fuels
- Techno-economic and life cycle analysis expertise

Pacific Northwest National Laboratory

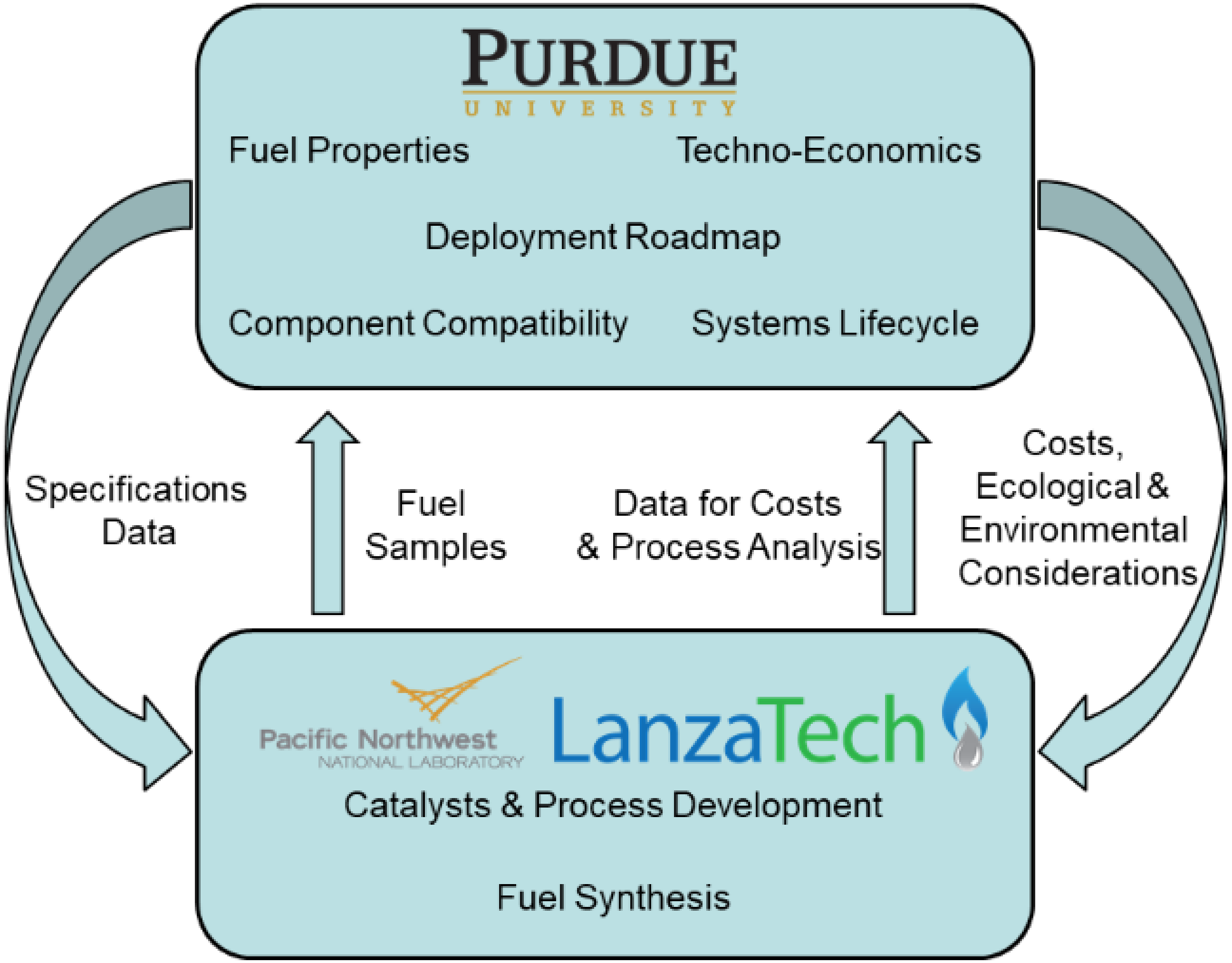
- Developed the Alcohol-to-Jet (ATJ) process that LanzaTech has demonstrated at scale and is now commercializing
- Expertise in catalysis, reaction engineering, and process engineering

LanzaTech

- Commercializing a process for producing sustainable aviation fuels, through spin-off company LanzaJet, and aims to diversify its product offering to jet blendstocks that offer superior fuel properties to conventional jet fuel

1 – Management: Collaboration Structure

- **Analyze fuel samples** generated from **novel cyclization catalysis** being developed in this project
- **Feedback loop** to fuel manufacturing the set of chemistry-base properties that are proxies for jet fuel performance and operability
- Examination of **economic** and **ecological** impacts associated with deployment of the technology in the U.S.
- Close**ly** tie and integrate **Purdue's fuel property analysis** with **PNNL's process development**, targeting an economically feasible process
- Collaboration with **LanzaTech** across all tasks to ensure **commercial viability** of the resulting fuel and process developed



1 – Management: Communications

- Integration of project tasks and overall project execution will be managed by Purdue
- Activities within PNNL and LanzaTech will be managed on a weekly basis by a co-principal investigator (co-PI)
- Purdue graduate student or post doc will be placed at PNNL to broaden lines of communication between the institutions
- Quarterly reports will be provided to DOE that documents progress
- Experimental and modeling results will be documented in a final report with description of experimental setups, procedures, and data analysis

1 – Management: Risk Management Plan

Risk	Description	Mitigation Plans
Meeting cycloalkane selectivity target	Achieving **60% selectivity to cycloalkanes** in the jet range may be difficult to achieve	**Two different routes** to **cycloalkanes** have been identified: • In **the preferred route** a set of process parameters and catalyst functionalities/ formulations will be evaluated • If the preferred route is not successful, an **alternative pathway** with a higher likelihood to meet the cycloalkane target will be investigated. This pathway introduces additional processing steps; thus, brings added costs to be evaluated by **TEA**
Aromatics production	Production of **aromatics** may be higher than anticipated	Hydroprocessing will be used to reduce the amount of **aromatics. TEA** will be utilized to analyze the effect of additional processing on total costs.
Project coordination	Difficulty coordinating across **multiple organizations**	PNNL and LanzaTech have a strong working history leading to commercialization efforts. Purdue has extensive experience in leading multi-component projects. Purdue graduate student or post doc will be placed at PNNL to broaden lines of communication and technology transfer.

2 – Approach: Sustainable Aviation Fuels

- Bioenergy Technologies Office (BETO) efforts in generating **sustainable aviation fuels (SAF)** have helped establish the production of synthetic isoparaffinic jet fuels with favorable properties, such as high energy density, excellent thermal stability, and favorable cold flow performance

- When blended with **isoparaffins**, **cycloalkanes** carry the potential of further fuel performance improvement with at least a 4% net increase in energy density

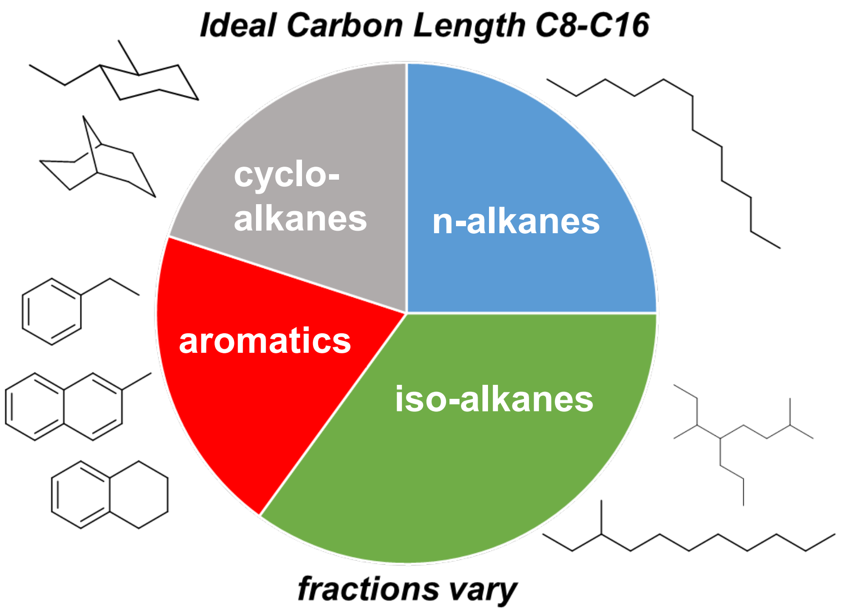
- However, economically feasible cycloalkane production from waste and biomass has historically been challenged by large hydrogen requirements, preferential selectivity to aromatic compounds, and low yields to jet fuel range components

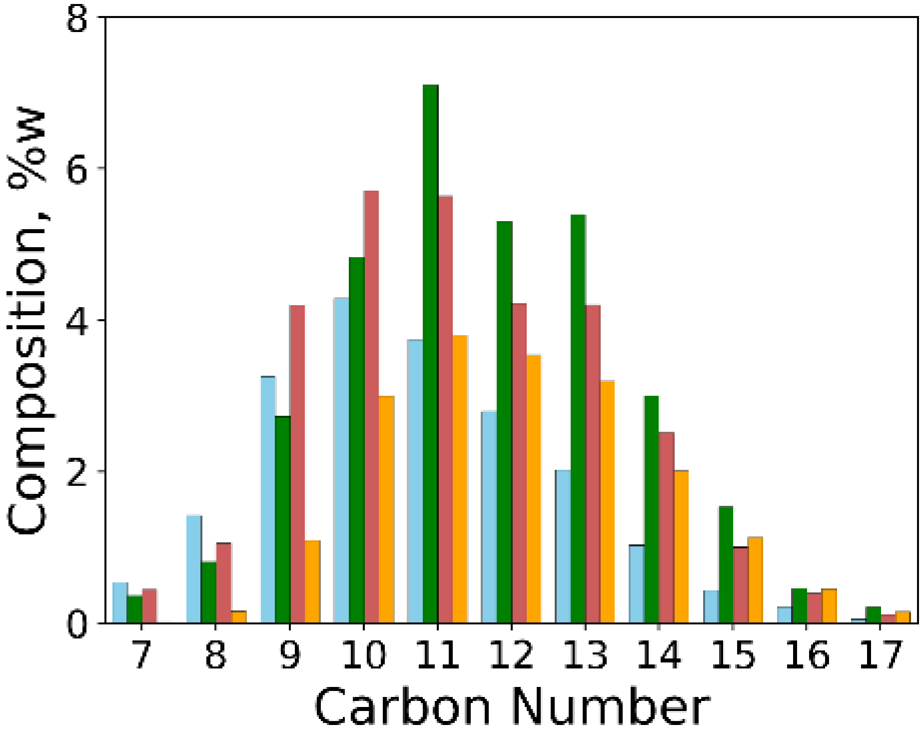
- PNNL and LanzaTech have already demonstrated a sustainable, non-petroleum route to isoparaffins that could be tuned toward producing a jet blendstock with more favorable properties than conventional jet fuel

- This project also addresses current gaps in understanding of properties of cycloalkanes as well as their performance in complex jet fuel mixtures

2 – Approach: Jet Fuel Today

Jet fuel is composed primarily of C8-C16 hydrocarbons





Aromatics are limited to 25vol%
Olefins and heteroatoms are limited (not allowed)

- Olefins (<1%)
- S, N, O containing (limited allowance)

Source: https://www.energy.gov/sites/prod/files/2020/09/f78/beto-sust-aviation-fuel-sep-2020.pdf

2 – Approach: Performance-Enhanced Jet Fuel Possible

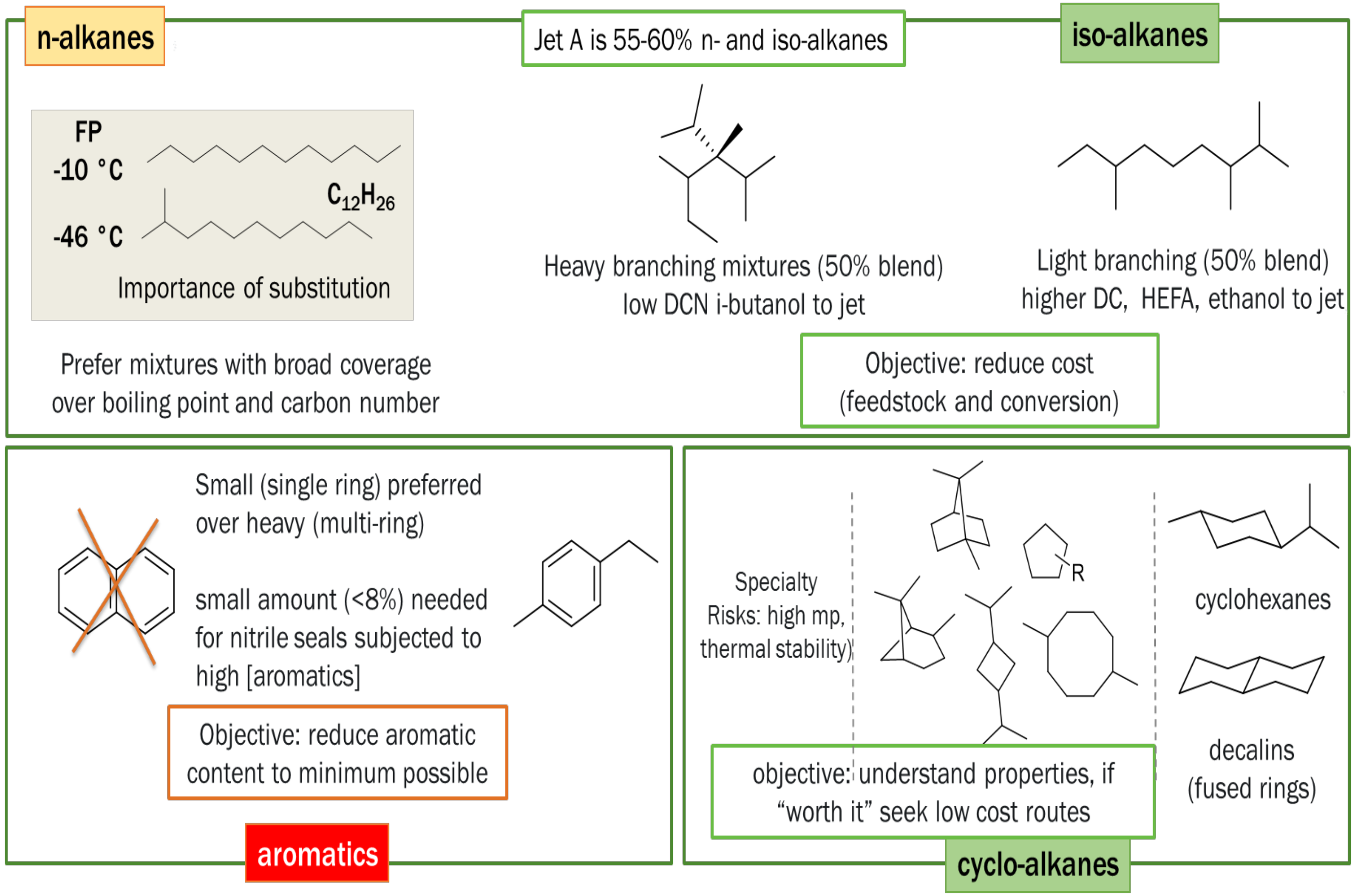
Biojet does not need to mimic the composition of petroleum…but could have more favorable fuel properties and still needs to be low cost

Goal 1

Develop new platform(s) to reduce cost of iso- and cyclo-alkanes

Goal 2

Understand properties of current and new cycloalkanes

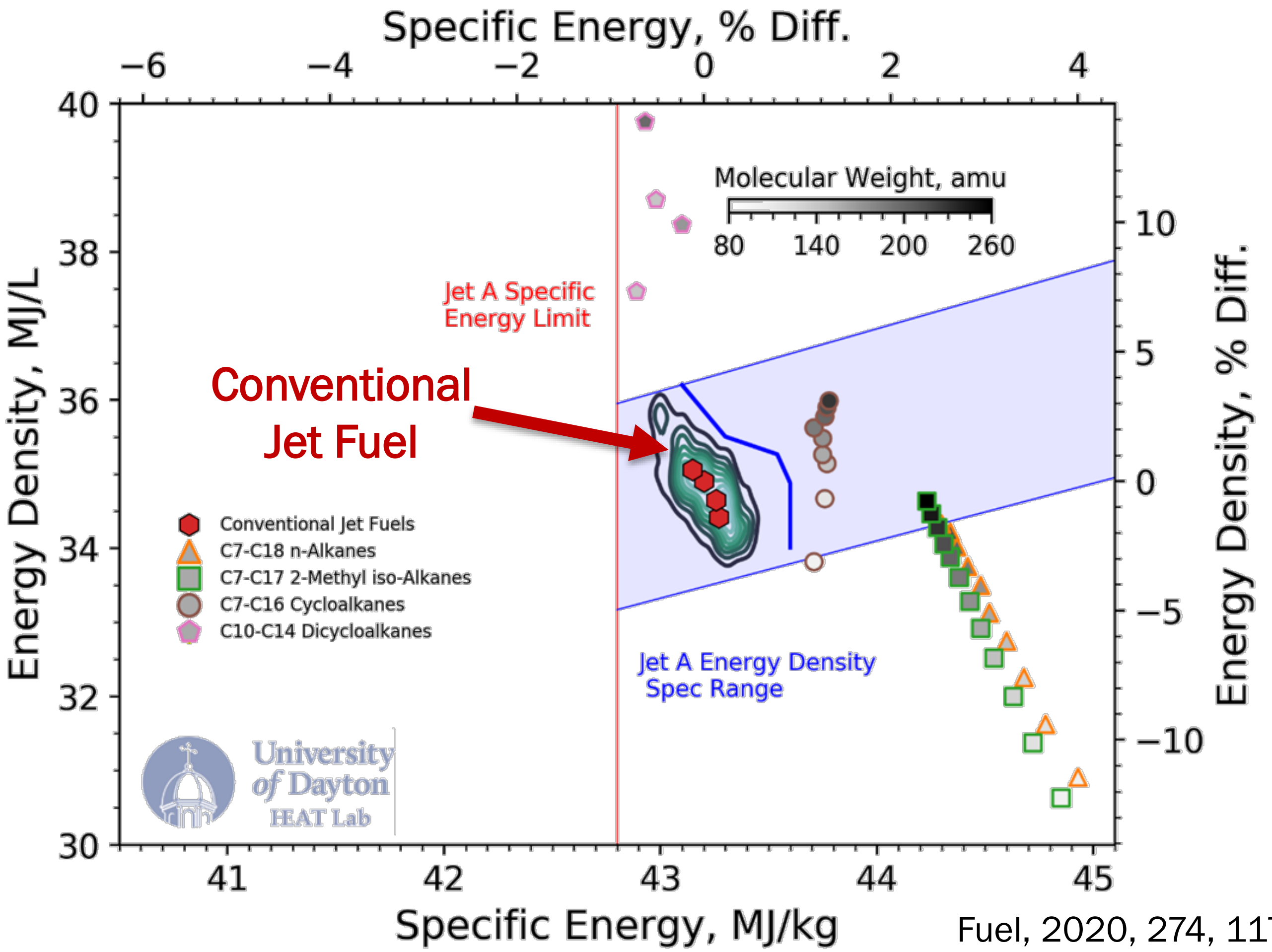


2 – Approach: Motivation for Cycloalkanes

Project leverages PNNL-LanzaTech alcohol-to-jet process for making isoparaffinic-rich hydrocarbon with new processing for cyclolalkanes

By making fuels without aromatics, performance enhancement over conventional jet:

- Higher specific energy
- Retain energy density
- Cleaner burning



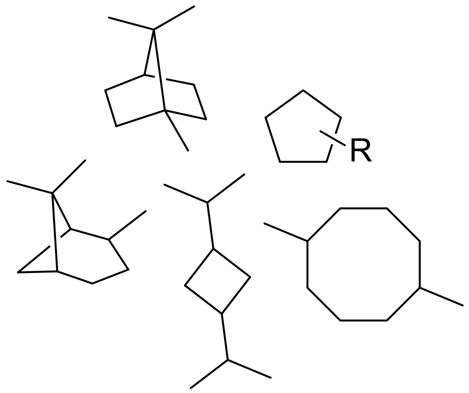
Fuel, 2020, 274, 117832

2 – Approach: Project Objectives

Develop a commercially viable process to convert an olefin intermediate into a cyclic-rich jet-range hydrocarbon with 60% selectivity to cycloalkane:

- This process enables production of a tunable iso-alkane/cycloalkane jet fuel with optimized fuel properties
- Cycloalkanes provide the potential for improved fuel density and combustion characteristics over paraffinic and aromatic hydrocarbons
- Technology enhances the value proposition of PNNL/LanzaTech's Alcohol-to-Jet process funded by the DOE, by improving the fuel properties and subsequent value
- Varies blend ratios of produced alkane/ cycloalkane streams will be analyzed to infer fuel properties
- Developed technology will enable the conversion of waste streams to tunable cycloalkane streams

Risks: high mp, thermal stability

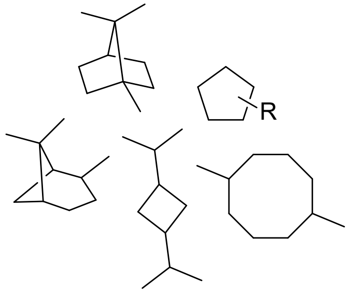


objective: understand properties and seek low cost route

2 – Approach: Project Goals

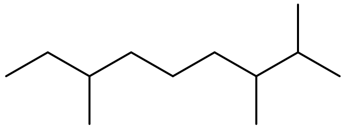
To accomplish this objective there are 5 primary goals:

1. Develop design criteria for catalysts for selective cyclization of olefins
2. Achieve >60% selectivity towards cycloalkanes through catalyst development, and process optimization
3. Produce a minimum of 2 gallons of fuel blend-stock to facilitate ASTM fuel tests
4. Deliver the optimum blend ratio of our product stream (cycloalkanes/ paraffins) with conventional jet fuel that satisfy all ‘drop-in’ requirements
5. Quantify the economic basis: develop the flow sheeting, conceptual design, and estimated costs for a 50 million gallon/yr commercial scale process
   – Close integration of TEA and LCA with process development will facilitate understanding of areas to reduce overall processing costs



Cycloalkanes

+

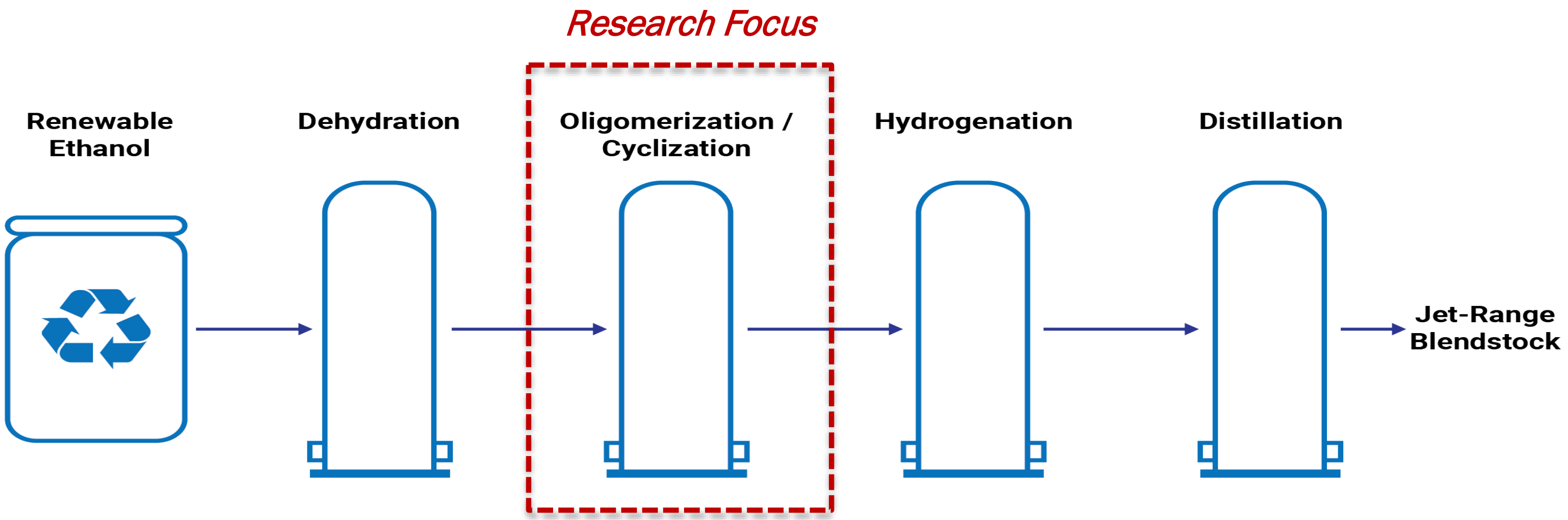


Isoparaffins

2 – Approach: Catalyst Development

Develop oligomerization/cyclization catalysis step to favor cycloalkanes

- Current olefin oligomerization process relies on solid acid/ base surface reactivity to selectively produce a jet-range hydrogen rich in isoparaffins
- Catalyst properties such as structure, reactivity, and adsorption/ desorption rates can be tuned to favor cycloalkanes
- Processing parameters also need tuned to maximize selectivity



2 – Approach: Fuel Property Analysis

Properties of the produced fuels will be characterized in order to determine suitability for jet blendstock, including:

- Energy density (mass & volumetric)
- Freezing and flash points
- Density
- Distillation curve
- Viscosity
- Chemical composition (e.g., olefin, cyclooparaffins, sulfur, aromatics, trace metals, N_2 and H_2O concentrations)

Property	Units	Description
Specific energy	[MJ/kg]	Enables fuel efficiency by lowering take-off weight, critical for mass-limited missions
Energy density*	[MJ/L]	Most important metric for volume-limited missions or military operations involving refueling
Thermal stability		Ability of fuel to sustain elevated temperatures in the engine and fuel injector
Emissions	Variable	Particulate emissions

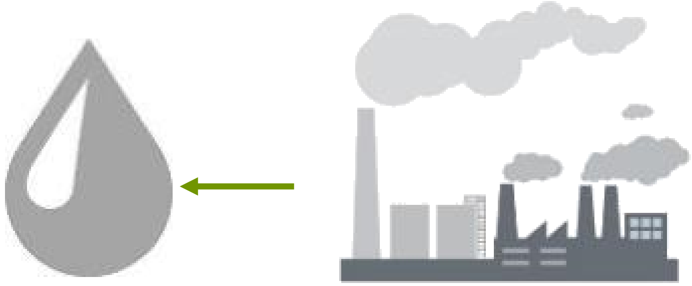
2 – Approach: ASTM Specification

- ASTM D7566 Annex A5 describes approved pathways for manufacturing synthesized hydrocarbons for ATJ synthetic paraffinic kerosene (ATJ-SPK) contained in Aviation Turbine Fuel
- Sufficient volume of sample will be produced to obtain ASTM characterizations

Property	Units	SPK + Jet A Blend ASTM D7566 Table 1	Description
Viscosity	mm^2/s	8 max (D445)	Flow performance especially at cold temperatures
Density	kg/m^3	775-840 (D4052)	Fuel tank volumes
Freeze Point	°C	-40 max (D5972)	Critical at high altitude
Flash Point	°C	38 min (D56)	Flammability
Distillation Temp	°C	range 150-300(D86)	Ability to vaporize

3 – Impact: LanzaTech ATJ Commercialization

LanzaTech successfully extended alcohol to jet to include ethanol and increased the blend to 50%



Ethanol ← Industrial waste gas

Industrial waste gas provides a low-cost route to ethanol

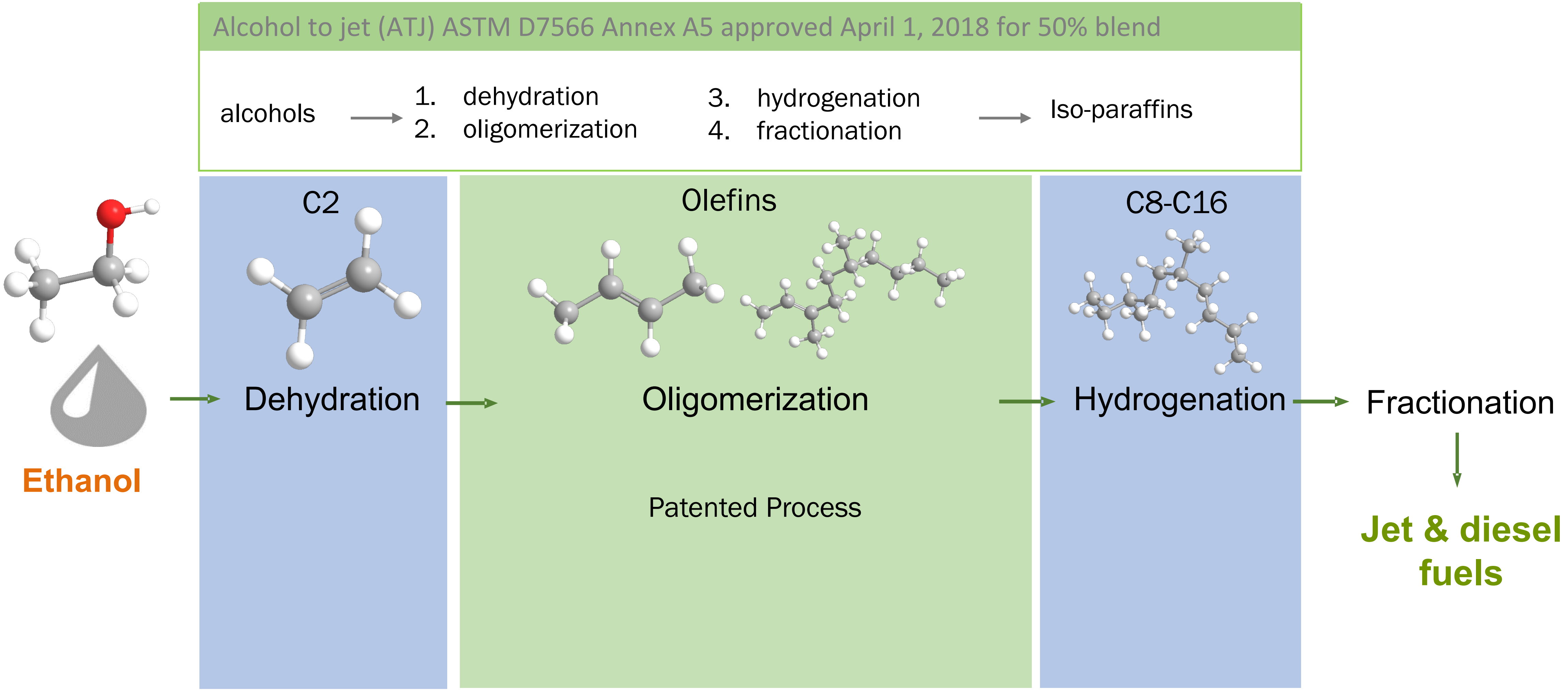
Ethanol → Dehydration → Oligomerization → Hydrogenation → Fractionation → **Synthetic paraffinic kerosene (ATJ-SPK)**

LanzaTech | 首钢朗泽 Shougang LanzaTech | virgin atlantic | BOEING | HSBC | GE | Pacific Northwest National Laboratory | U.S. Department of Energy – Energy Efficiency & Renewable Energy

Source: LanzaTech

3 – Impact: Leverage Alcohol-to-Jet Process Developed

PNNL developed the catalyst technology for converting alcohols to targeted fuel molecules



3 – Impact: Product Flexibility

Fuel is exceptionally high in quality AND the technology is flexible to product output

Ethanol to Jet

- Highly energy dense
- Safe to handle
- Low Freeze Point

Ethanol to Diesel

- High Cetane
- Excellent Cold Flow properties

✓ Isoalkane-rich

3 – Impact: Performance-Enhanced Jet Fuel

Biojet can burn cleaner and have higher energy content than petroleum commensurate

To reduce soot

- Limit aromatic content (and S)

To increase energy content

- Increase iso-alkanes (specific energy)
- Increase cycloalkanes (energy density)

To maintain low temperature fluidity

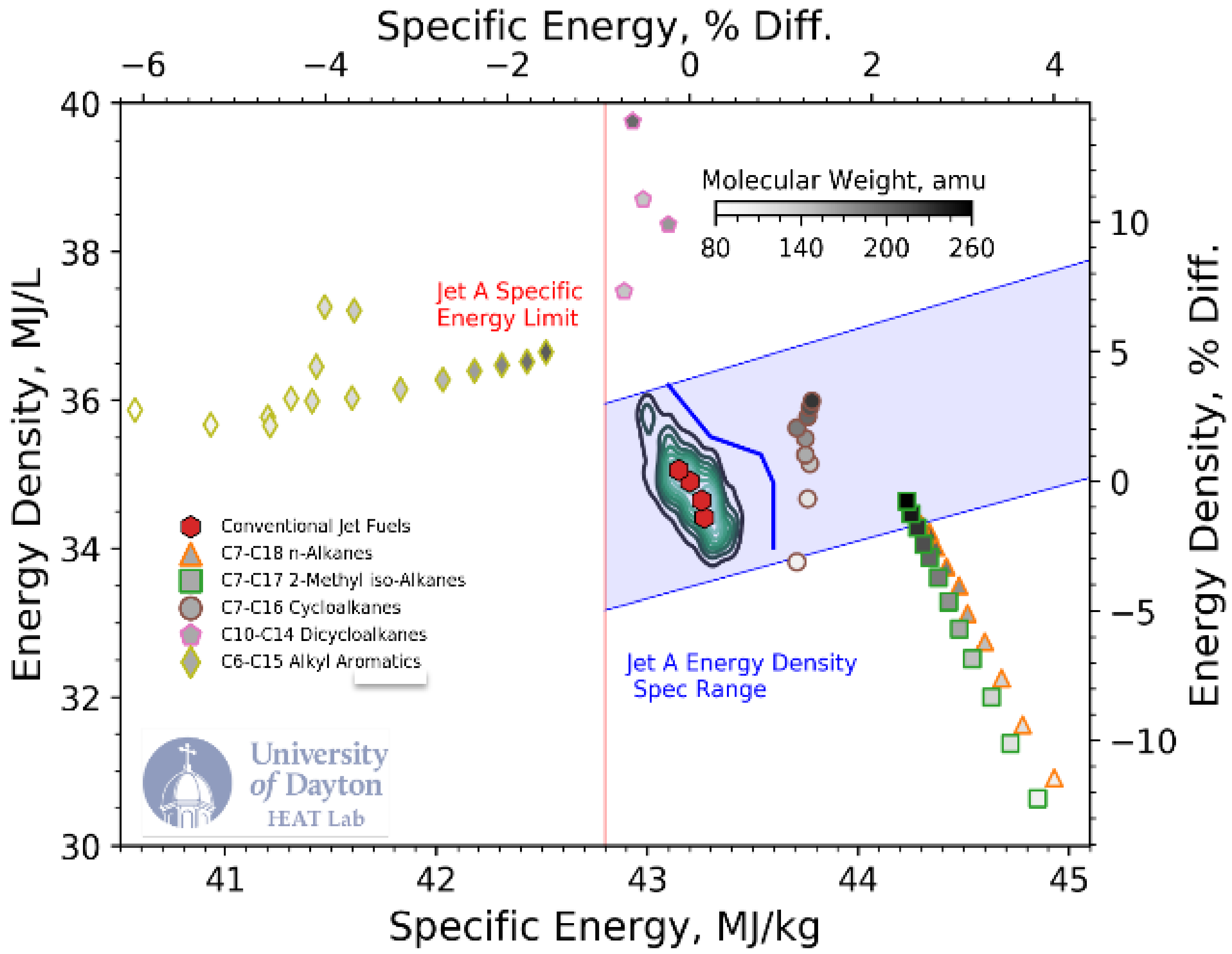
- control level of branching in alkanes

To achieve thermal stability

- No metals, no heteroatoms, no compounds that gum or break down (e.g., olefins)*

To maintain seal swelling in older planes

- Consider specific cycloalkanes**



*Research needs: will highly strained cycloalkanes have required thermal stability?

** Boeing has shown seal swelling from decalin, a 10 carbon fused cyclohexane

Source: Fuel, 2020, 274, 117832

3 – Impact: Addresses gaps in understanding

Addressing current gaps in understanding of cycloalkane properties:

- Bulk properties of blends and blending behavior
- Fundamental properties of mono cycloalkanes and variation of properties with carbon atom number during combustion
- Impacts of alkyl chains, alkyl chain lengths, and isomerization on molecular properties
- Variations in properties and behavior of molecules having multiple rings, or the same carbon number, but different configurations
- While some results indicate favorable swelling characteristics associated with fused bicyclic alkanes, additional work is needed, including compatibility with other materials
- Viability of strained compounds for meeting aviation needs, including safety

Ethanol-jet reduces cost by recycling industrial gas

3 – Impact: Fuel Properties Effect on O-Ring Swelling

- Seals are a representative group of essential seals in the hydraulic and pneumatic components of aircraft fuel delivery systems

- O-rings are utilized to prevent fuel leakage within the pumps, metering devices, and connectors

- % swell percent of o-ring seals is the measure of essential seal properties – Purdue team has assembled a test rig where the seals can be suspended in various test samples; followed by gas chromatography head space analysis.

- Project will screen product streams' seal swell capability as well as assisting in determining the optimum blend ratio with conventional jet fuel.

4 – Progress & Outcomes

- The project has not started yet, as we are finalizing CRADA and SOPO agreements

- We anticipate the project to start in Q2 FY21

- 3-year project duration

Quad Chart

Timeline

- Project start date: FY21 Q2
- Project end date: 3-year project duration

	FY20	Active Project
DOE Funding	**$1,774,214**	

Project Partners:

Purdue University, Pacific Northwest National Laboratory, LanzaTech

Barriers addressed

Ct-F: Increasing the Yield from Catalytic Processes

Ct-E. Improving Catalyst Lifetime

Project Goal

Deliver a minimum of 2 gallons of fuel blend-stock with >70% yield to cycloalkanes in the jet range with a 4% net increase in combined energy content without impacting 'drop in' fuel requirements. Insights from in-situ analytical techniques will enable mechanistic understanding of chemistry and intermediates. Generate a Technology-to-Market analysis to evaluate the process for applicability to its ethanol commercial platform, assess potential for market viability. Report correlations between chemical composition and fuel performance.

End of Project Milestone:

Final report. Communicate the learnings in process development directed by fuel performance properties and process analytical. Provide insights on the chemistry via analytical of intermediate streams (e.g., in-situ or other intermediate stream analysis)

Funding Mechanism

FOA Project: FY20 Multi-topic FOA AWARD

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Summary

- **Project Goal**
  - Develop a commercially viable process to convert an ethanol-derived olefin intermediate into a **jet-range hydrocarbon**
- **Management**
  - Purdue: fuel characterization, TEA, LCA
  - PNNL: catalysis and process development
  - LanzaTech: ensure commercial viability
- **Approach**
  - Discover the properties of cycloalkanes relevant as a fuel constituent
  - Provide a route to control the cycloalkane/n-alkane/iso alkane content of a next-generation fuel with minimal or no aromatic content
  - Target **60 wt.% yield of** ethanol-derived olefin intermediate **to cycloalkanes**
- **Impact**
  - Cleaner burning biojet with a 4% net increase in combined – specific and volumetric - energy content
  - Understand impact on fuel swell properties
  - Compliant with all conventional jet fuel "drop-in" requirements
  - Commercial, environmental, and economic feasibility
- **Progress/ Outcomes**
  - CRADA and SOPO finalized, project is due to begin in Q2 in FY21