U.S. DEPARTMENT OF ENERGY

Office of ENERGY EFFICIENCY & RENEWABLE ENERGY

DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

Higher energy-content jet blending components derived from ethanol

April 3, 2023

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 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 – Approach: Team

Purdue

- Molecular level characterization of complex mixtures of hydrocarbons, including aviation fuels
- Techno-economic and life cycle analysis

Pacific Northwest National Laboratory

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

LanzaTech

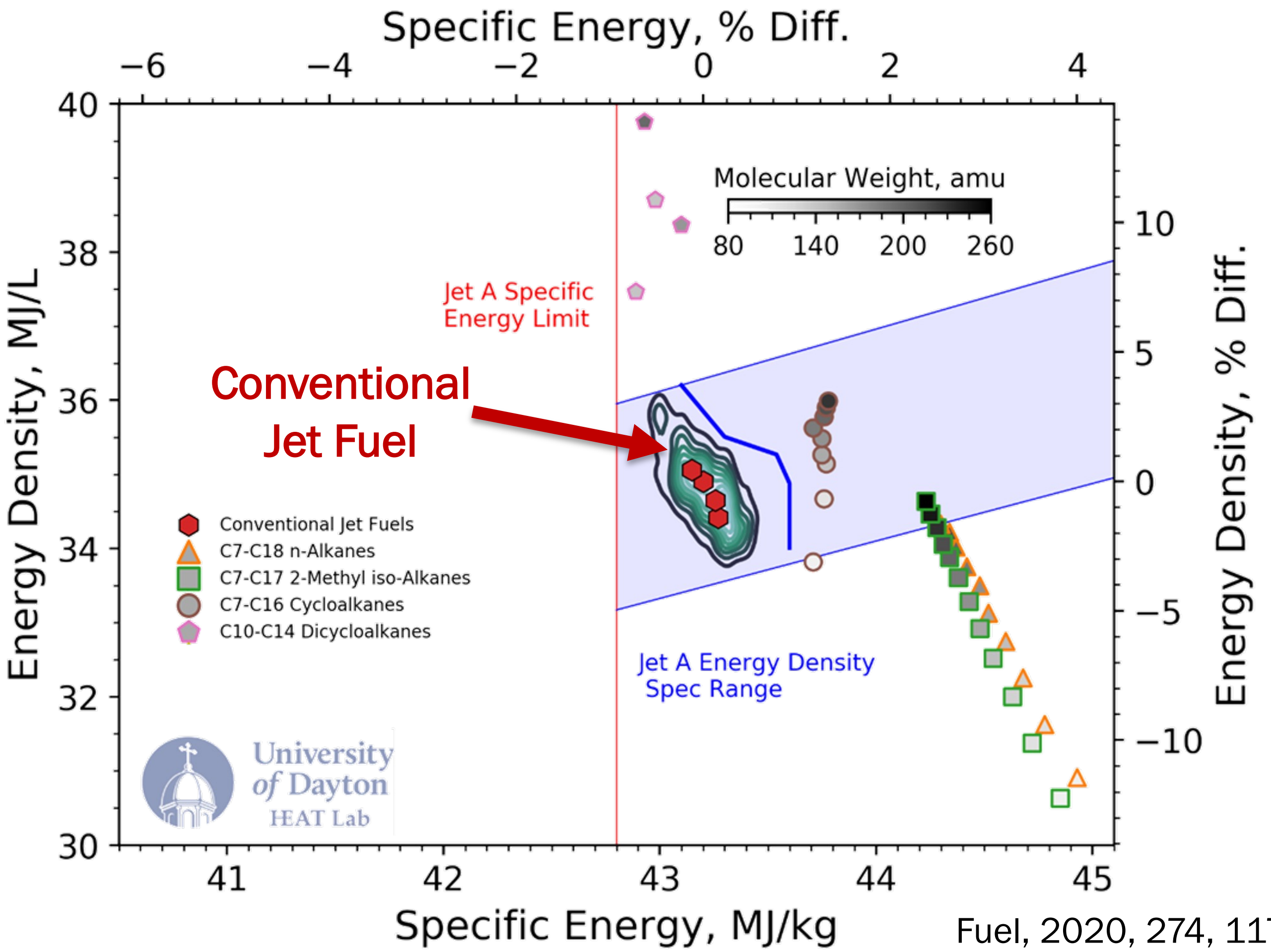
- Complementary commercial experience in catalyst scale-up, reaction engineering, and process engineering
- Commercializing a process for producing sustainable aviation fuels through spin-off company LanzaJet, aims to diversify its product offering to jet blendstocks that offer superior fuel properties to conventional jet fuel

1 – Approach: Motivation for Cycloalkanes

Project leverages PNNL-LanzaTech alcohol-to-jet process for making isoalkane-rich hydrocarbons, with new processing for cycloalkanes developed here.

By making fuels without aromatic compounds, performance is enhanced over conventional jet:

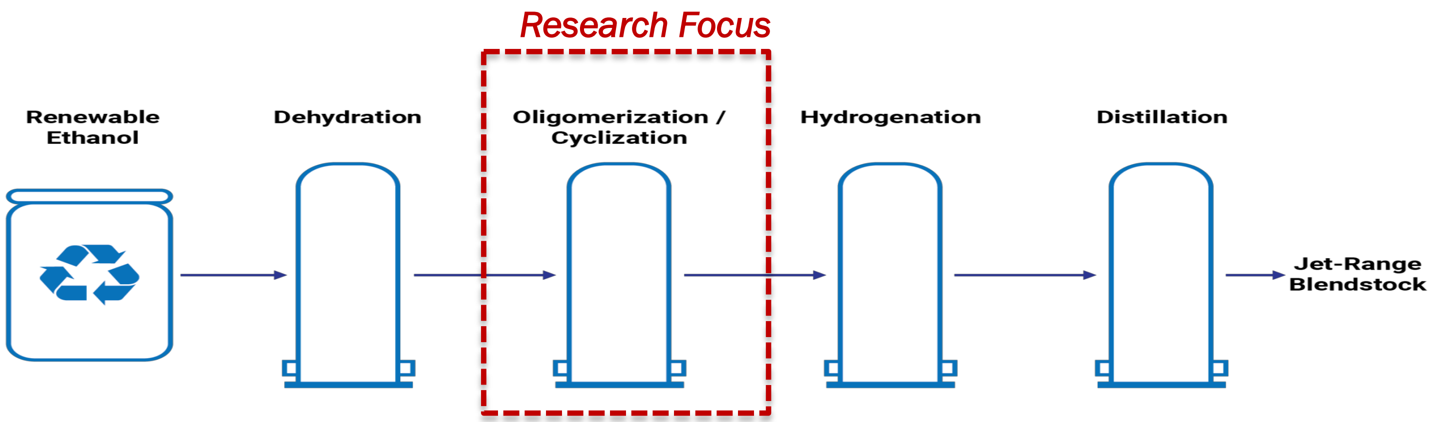
- Higher specific energy
- Energy density retained
- Cleaner burning



Fuel, 2020, 274, 117832

1 – Approach: Motivation for Sustainable Aviation Fuel (SAF) with Desirable Fuel Properties

- PNNL and LanzaTech have already developed a sustainable, non-petroleum route to synthetic **isoparaffinic** jet blendstock that provides favorable fuel properties, including clean burning, excellent thermal stability, and favorable cold flow performance.
- When blended with **isoalkanes**, **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 compounds.
- Here we are modifying the catalysis currently used for making isoalkanes to also making cycloalkanes, and therefore a more energy dense jet blendstock.



Commercial olefin cyclization processes exist for producing aromatic compounds* but <u>not</u> cycloalkanes.

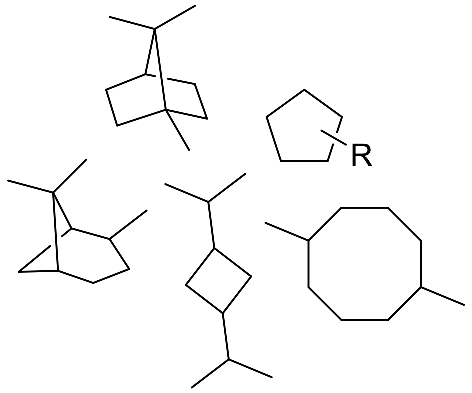
*Example aromatization processes: UOP Platforming and UOP BP-Cyclar.

1 – Approach: Technical Approach

Develop a commercially viable process to convert olefin intermediates into a cycloalkane-rich jet-range hydrocarbons and understand the properties of the resulting fuel and impacts on TEA/ LCA

- Develop robust analytical methodology for complex mixtures containing alkanes, alkenes, cycloalkanes, and aromatic compounds that provide information of degree of branching to guide catalyst development and correlate to fuel properties
- Explore the dependence of fuel properties on the blend ratios of produced alkane / cycloalkane streams
- Develop tunable production of a cycloalkane / iso-alkane jet fuel with optimized fuel properties
- Evaluate TEA and LCA impacts of new processing
- Screen the seal swell capability of the product and determine the optimum blend ratio with conventional jet fuel.

Risks: high mp, thermal stability



objective: understand properties and seek low-cost route

1 – Approach: Goals

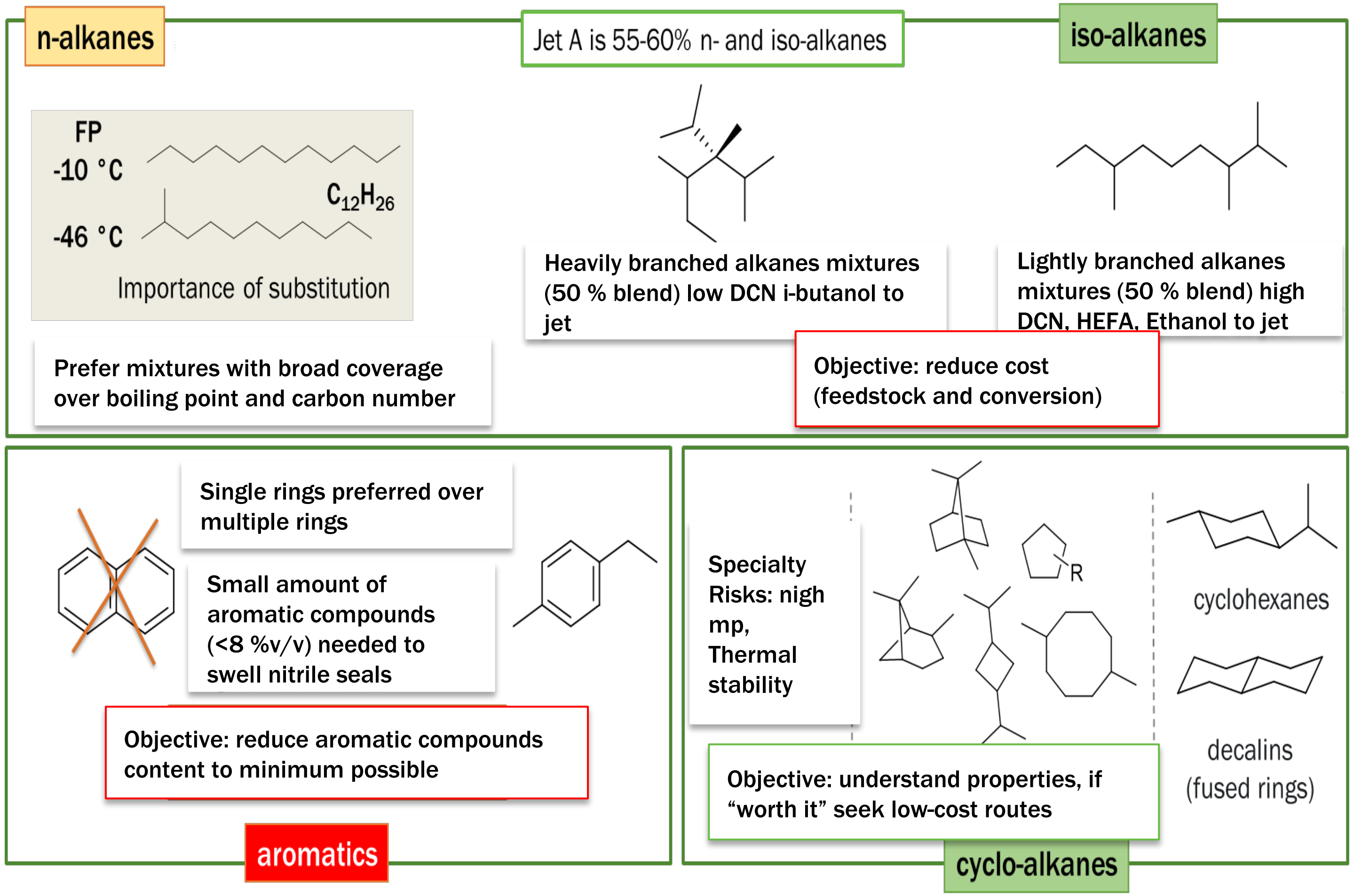
Biojet does not need to mimic the composition of petroleum-based fuel…but could have more favorable fuel properties and still needs to be of low cost

Goal 1

Develop new platform to produce jet blendstock consisting of cycloalkanes and isoalkanes

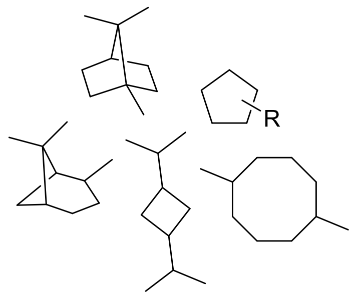
Goal 2

Understand properties of current and new mixtures of cycloalkanes



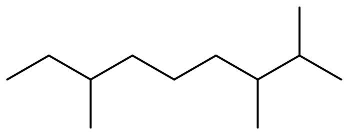
1 – Approach: Project Objectives

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/ alkanes) with conventional jet fuel that satisfy all ‘drop-in’ requirements
5. Quantify the economic and life cycle 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 and assess life cycle



Cycloalkanes

+



Isoalkanes

1 – Approach: Key Milestones and G/NG

Progressing toward process development for high cycloalkane content jet, fuel property analysis, TEA, and LCA

Milestone/ G/NG	Name	Description	Date	
G/ NG 1	**Initial Verification**	Duplicate experiment from proposal for ethanol conversion to cycloalkanes using the Amerberlyst-36 catalyst to demonstrate at least 25 wt.% selectivity to cycloalkanes.	**Summer 2021**	✓
Milestone	**Analytical Method Development**	Establish correlations between product properties and performance. Perform detailed hydrocarbon analysis of all reaction products provided by using at a minimum GC, IR, and NMR methods for analysis.	**April 30, 2022***	✓
G/ NG 2	**Cyclization Catalysis**	Evaluate if a bifunctional metal/acid catalyst can cyclize butene olefins to make a 60 wt.% cycloalkane stream to determine whether the focus should be redirected to two stage cyclization and oligomerization Criteria: Demonstrate >50 wt.% cycloalkanes.	**April 30, 2023 ***	
Milestone	**LCA analysis**	Using data obtained from this project perform the LCA for a 50 Mgal/yr plant scale.	**October 31, 2023***	
Milestone	**Cycloalkane Sample Production**	Deliver a minimum of **2 gallons of fuel blend-stock** with >60% selectivity to **cycloalkanes** in the jet range. Sample will be shipped to Purdue for ASTM analysis.	**January 31, 2024***	
Milestone	**Final TEA Analysis**	Using the TEA projections for a cyclization process at a 50 Mgal/yr plant scale, evaluate the process for applicability to its ethanol commercial platform,	**July 31, 2024***	

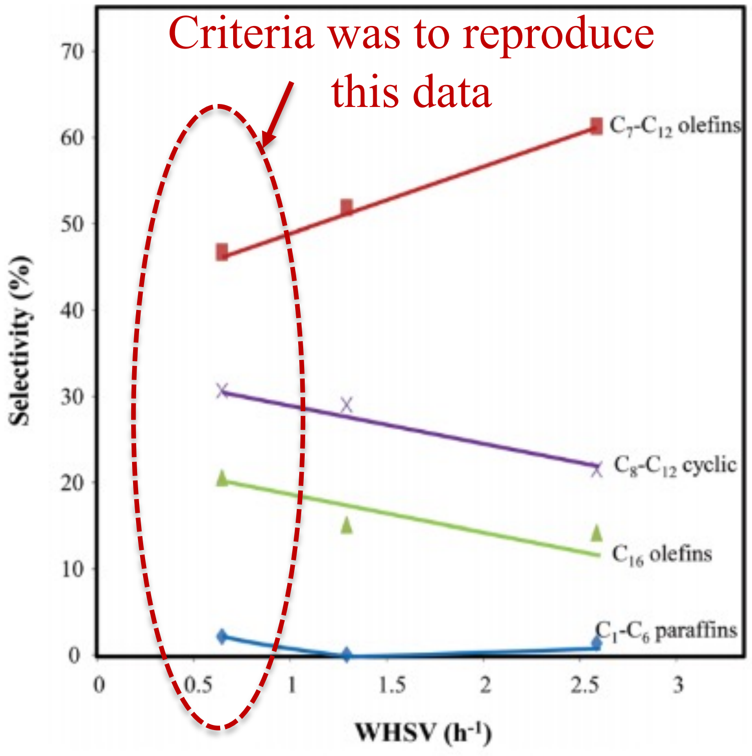
*** After no-cost time extension**

1 – Approach: Risk Management

Risk	Description	Mitigation Type	Mitigation Plans
Analytical Method Development	Development of robust analytical methodology for quantifying complex mixtures of cycloalkanes and olefins is difficult	Schedule	Catalyst development activities in Task 4 rely on the development of a a robust analytical method. If method development takes longer than anticipated, then Task 4 schedule will be pushed back accordingly. The analytical method development is a critical path item, and the catalyst development cannot proceed far without it in place.
Meeting cycloalkane selectivity target	Achieving **60% selectivity to cycloalkanes** in the jet range may be difficult to achieve	**Scope**	**Three 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 step to be evaluated by **TEA** • Finally, if both above routes are unsuccessful, we will evaluate producing **aromatic compounds** using known techniques and then hydrotreat for cycloalkane formation. This introduces additional process complexity, however, we note that the overall hydrogen requirement would not change, as cycloalkane are desired in all cases.
Aromatic compound production	Production of **aromatics** may be higher than anticipated	Scope	While aromatic compound formation will be avoided, if their production is higher than desired the use of hydroprocessing to reduce aromatic content will be investigated. TEA will also be utilized to analyze the effect of additional processing on cost and/ or if aromatic content in feed is acceptable without hydrotreatment. Note that some amount of aromatic compounds may be advantageous to address seal swelling issues and enabling regulatory approval for 100% SAF blendstock.

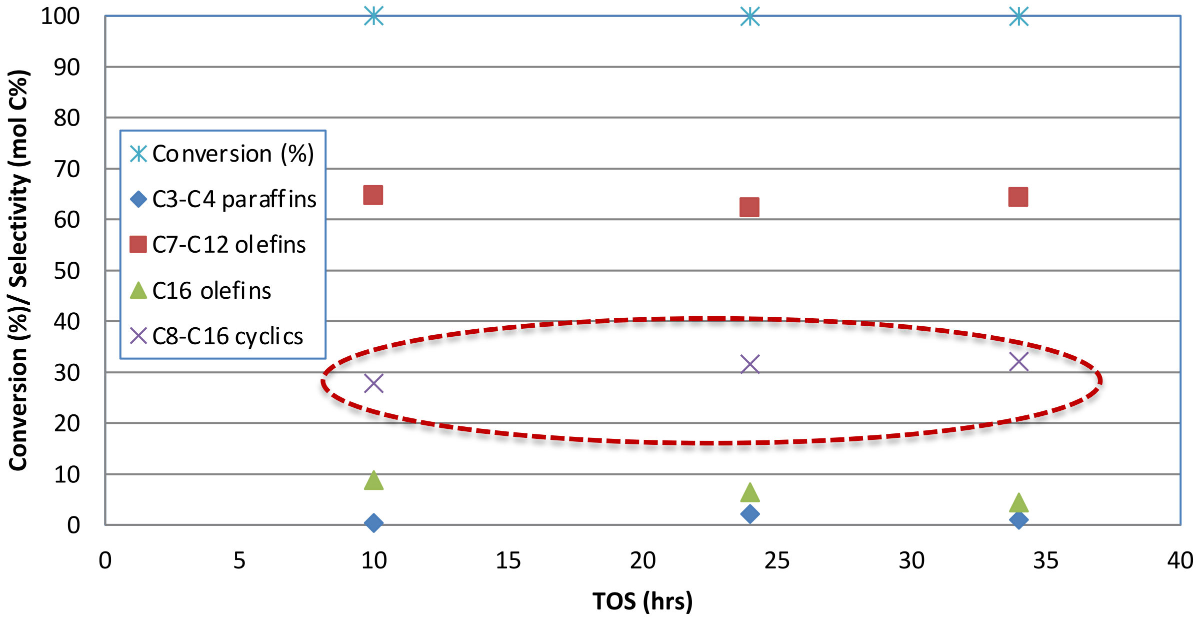
2 – Progress & Outcomes: Passed Verification G/NG 1

Verification Criteria



Green Chemistry, 2016, 18, 1880

Verification Results Met Criteria



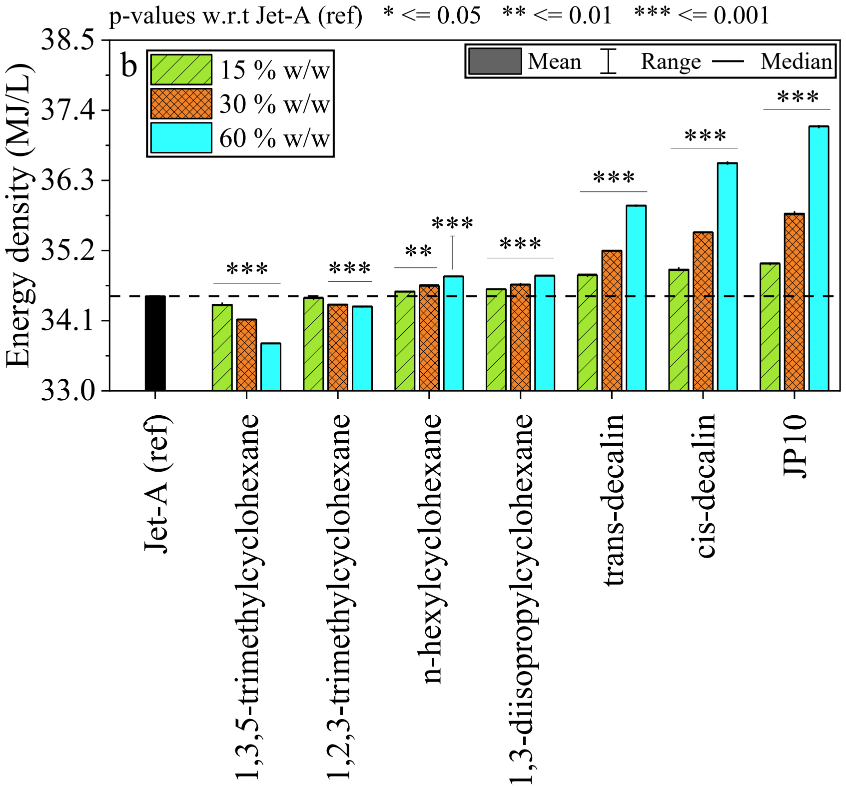
- 30 (mol C %) selectivity to cycloalkanes reproduced
  - Cycloalkanes; C8=2.3%, C12=26.2%, C16=3.2% (34 hrs TOS)

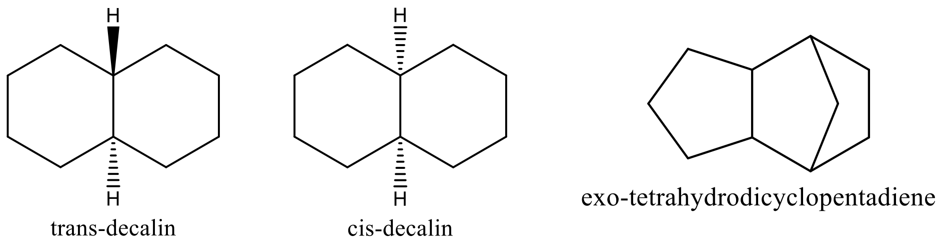
Reproduced cycloalkane data used in proposal and passed the verification G/NG 1 in Summer 2021

2 – Progress & Outcomes: Increased understanding for how blending of cycloalkanes with Jet-A affects fuel properties

Systematic study showing influence of cycloalkane additions into Jet-A as a function of amount and chemical structure

- Evaluated influence on gravimetric and volumetric energy content, density, and kinematic viscosity as a function of cycloalkane content with varying structural characteristics (alkyl chain length, number and type of substituents, and number of rings)
- Identified the most promising cycloalkane candidates
  - Maximizing energy content and density (metering and aircraft range)
  - Minimizing kinematic viscosity (atomization and pumpability at low temperatures)
- **A manuscript to be submitted to a high impact journal (95 % complete)**





Identified target cycloalkanes that maximize energy density up to 4 wt.% over current jet fuel

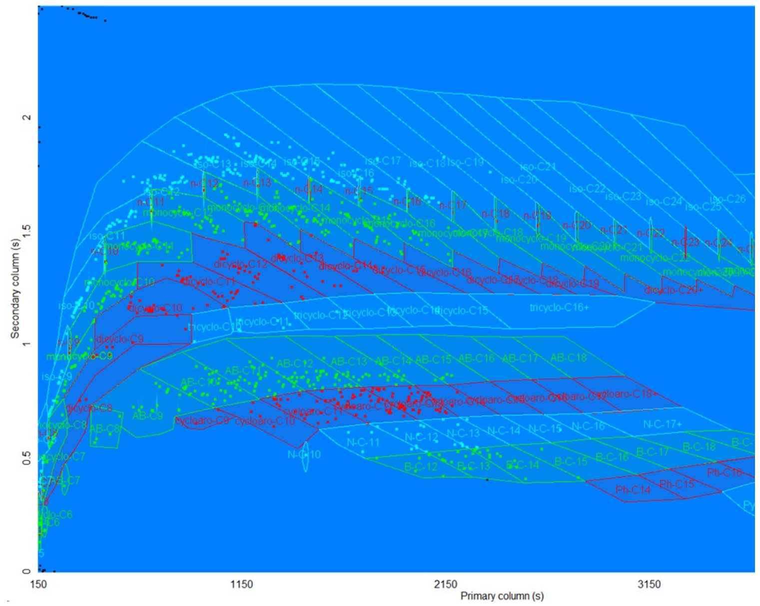
2 – Progress & Outcomes: Analytical Method Development

Results

- Identification and semi-quantitation of alkanes, cycloalkanes, alkenes, and aromatic compounds, including determination of the hydrocarbon group, carbon number distribution, and degree of branching for catalytic products via GCxGC/(+)EI TOF MS and GCxGC/FID
- Ionization efficiency of cycloalkanes as function of their molecular structure

Outcomes:

- Rapid characterization method using minimal amount of sample without requiring pre-separation methods
- Feedback for >90 liquid products provided by PNNL, understanding the chemistry relative to multiple catalytic conditions tested at PNNL
- **A manuscript to be submitted to high impact journal (40% complete)**
- ***Key challenge to overcome:*** *r*apid and complete analysis for complex mixtures of alkanes, alkenes, cycloalkanes, and aromatics



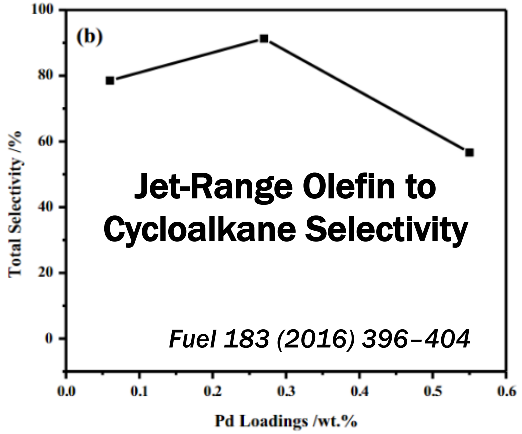
GCxGC classification map used for the characterization of jet and diesel fuels

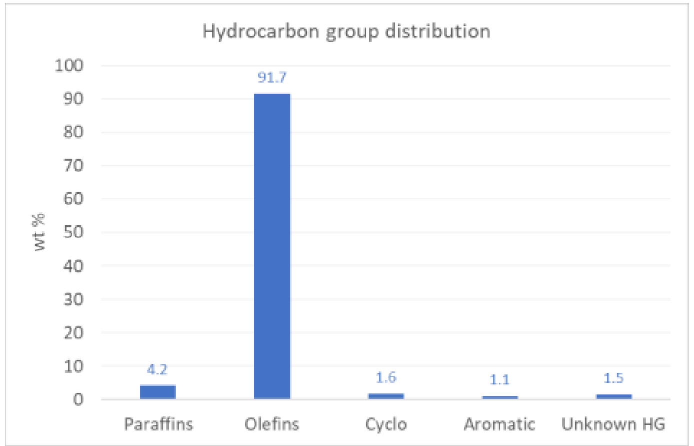
Comprehensive analytical method developed for complex mixtures being produced in this project, key for fuel property analysis and to guide catalyst development.

2 – Progress and Outcomes: Catalyst Development Approach

Commercial processes do not exist for producing cycloalkanes from olefins but the oligomerization catalysis for producing isoalkanes can be tuned for cycloalkanes

- Current olefin PNNL-LanzaTech oligomerization process uses solid acid/ base surface reactivity to selectively produce jet-range isoalkanes
- Catalyst properties such as structure, reactivity, and adsorption/ desorption rates can be tuned to favor cycloalkanes





- >50 catalysts and process conditions evaluated
- Catalyst system developed with favorable properties for producing jet-range olefins with minimal branching and low aromatic content, ideal for subsequent ring closure to cycloalkanes (underway)
- ***Key challenge overcome***: avoiding production of aromatic compounds and alkanes

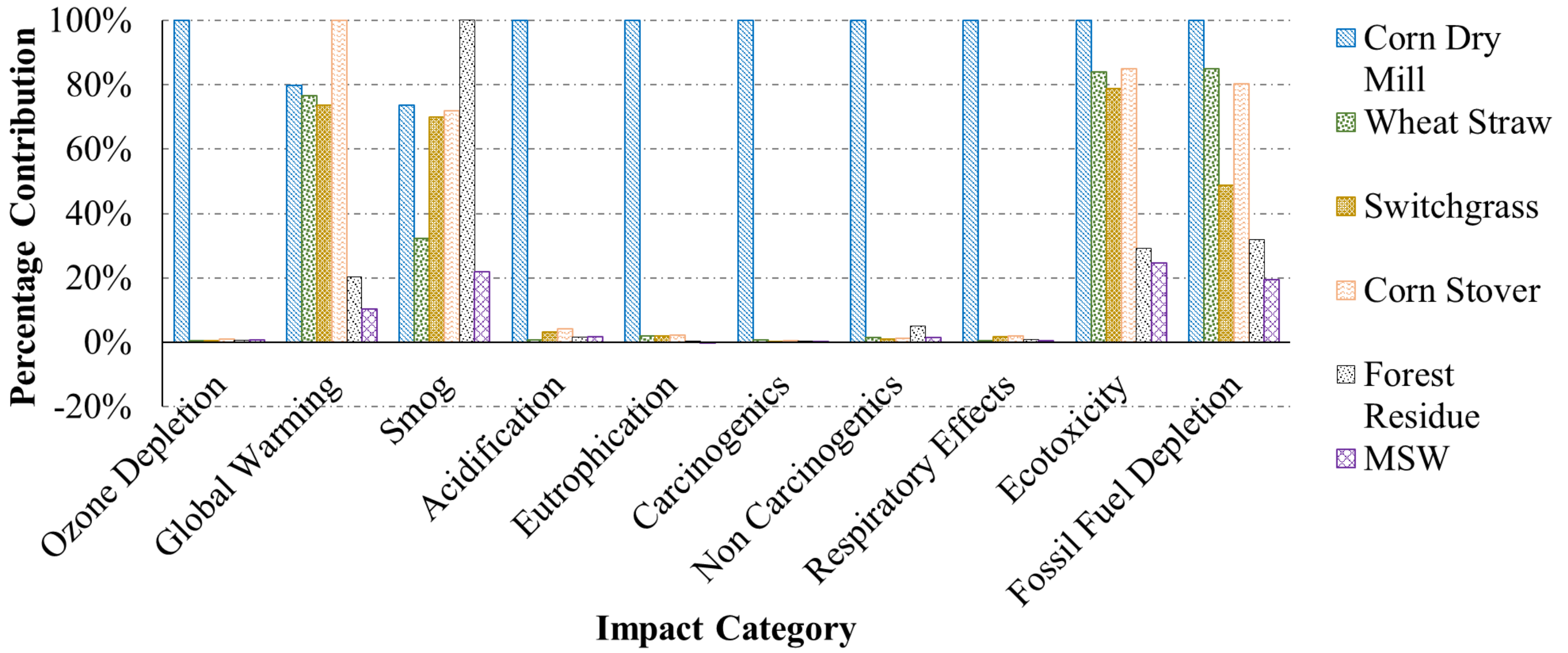
Catalyst developed for producing a jet-range olefin intermediate, ideal for selective cycloalkane formation. Currently working to develop the end-to-end processing for selective conversion of olefins to cycloalkanes.

2 – Progress & Outcomes: TEA/ LCA

- Process model developed for ethanol to jet conversion by using Aspen modeling to determine mass and energy balances and costing (TEA) and provide input for LCA
- LCA performed with system boundary including all inputs from choice of ethanol feedstock to combustion in aircrafts
- Comparison of life cycle impacts between first generation (corn) and second-generation feedstocks (lignocellulosic biomass and Municipal Solid Waste)

- **Municipal solid waste** has the lowest life cycle impact in all categories. **Corn** has the most impact in most categories except for global global warming and smog

- Moving forward, this approach will be extended to estimate the effect of **aromatic content** on the total emissions from bio-jet fuel combustion



* Normalized values with respect to highest contributing feedstock in each category

2 – Progress and Outcomes: Effects of Fuels on O-Ring Swelling

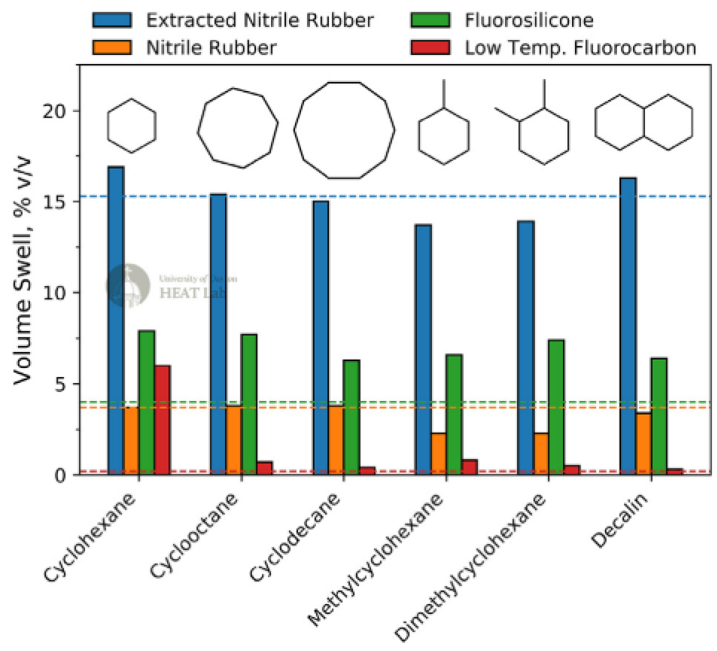
- Seals are a representative group of essential seals in the hydraulic and pneumatic components of aircraft fuel delivery systems
- O-ring seals are utilized to prevent fuel leakage within the pumps, metering devices, and connectors

- Identified ethylbenzene and indane as key aromatic compounds to swell acrylonitrile butadiene o-rings
- Steric hindrance as a key factor defining o-ring swelling characteristics

Source: Fuel 238 (2019) 483-492

- Cycloalkanes are less likely to induce swelling in fluorocarbon, poly(acrylonitrile), epoxide, acrylonitrile butadiene styrene, and fluorinated ethylene propylene o-rings
- Cycloalkanes are likely to induce swelling in silicon, extracted nitrile rubber, and poly(butadiene) o-rings
- Moving forward, target cycloalkanes will be evaluated on different o-ring materials to evaluate O-ring swelling potential

Source: Front. Energy Res. 9:771697. doi: 10.3389/fenrg.2021.771697



Volume swell of four o-ring materials in cycloalkanes blended at 30 % v/v with zero-aromatic SPK. Dashed lines represent conventional jet fuel lower limits, which many cycloalkanes exceed.

Source: Fuel 274 (2020) 117832

3 – Impact: LanzaTech ATJ Commercialization

LanzaTech successfully extended alcohol to jet conversion processes to include ethanol and increased the blend up to 50% to Jet-A

Industrial waste gas provides a low-cost route to ethanol

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

Source: LanzaTech

This technology enhances the value proposition of PNNL/LanzaTech's current Alcohol-to-Jet conversion process, by improving the fuel properties and subsequent value

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 amount of isoalkanes (specific energy)
- Increase amount of cycloalkanes (energy density)

To maintain low temperature fluidity

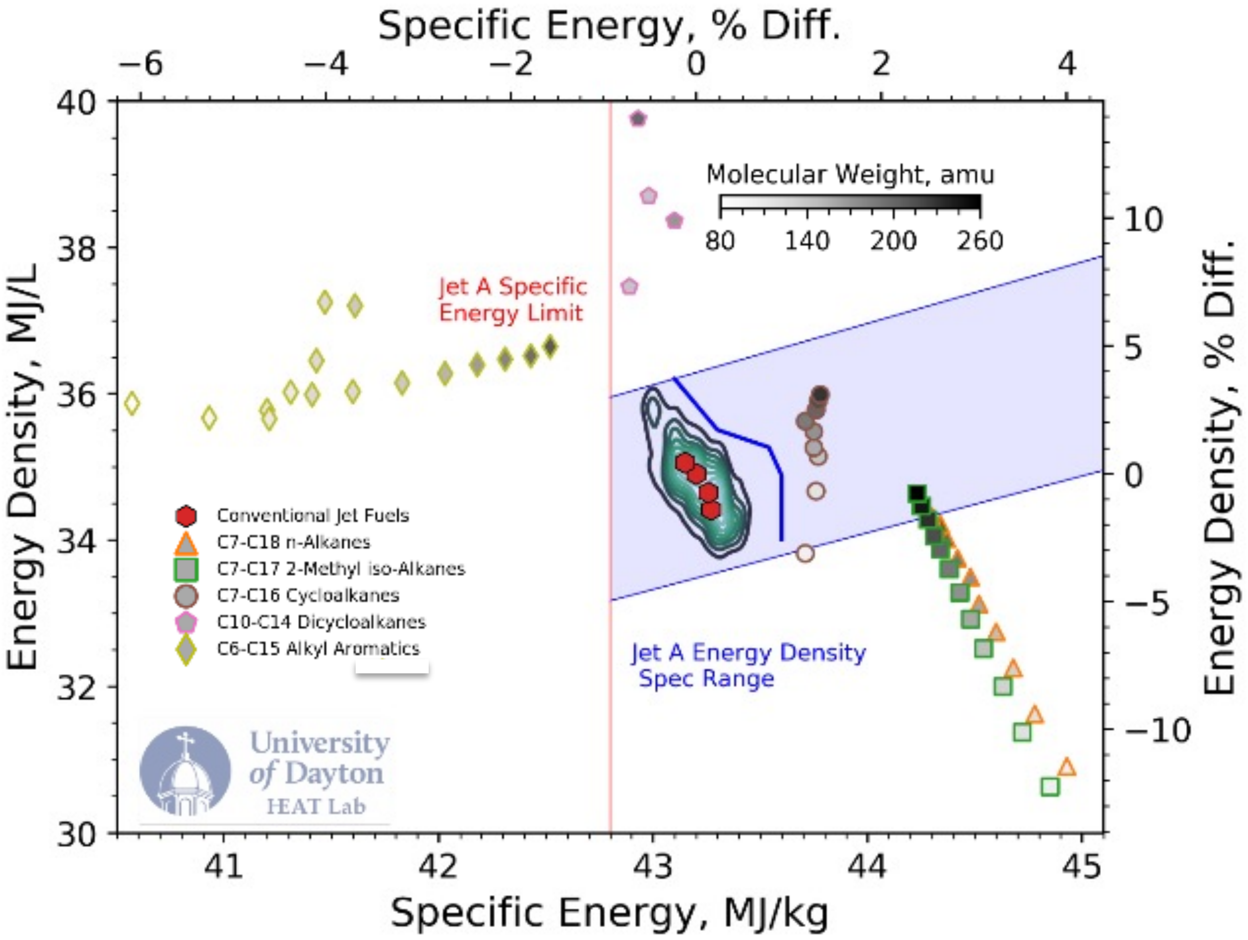
- control level of branching in alkanes

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

Quad Chart

Timeline

- Project start date: Not started
- Project end date: 3-year project duration

	FY21	Active Project
DOE Funding	$1,774,214	

Project Partners:

Purdue, 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 >60% 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

Acknowledgements

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Robert Dagle
Corinne Drennan
Dylan Cronin

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Mark Shmorhun
Liz Moore

Summary

- **Project Goal**
  - Develop a commercially viable process to convert an ethanol-derived olefin intermediate into **jet-range cycloalkanes/ alkanes**
- **Approach**
  - Discover the properties of cycloalkanes relevant as a fuel constituent
  - Provide a route to control the cycloalkane/n-alkane/isoalkane 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 up to 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**
  - Robust analytical method developed for characterizing **complex mixtures of** alkanes, alkenes, cycloalkanes and aromatics, to inform catalyst development and fuel properties.
  - Study on **influence of blending cycloalkanes with Jet-A** identified the most promising cycloalkane compounds that can **increase the energy density** of jet by up to 4 wt.%.
  - Catalyst developed for producing a jet-range olefin intermediate, ideal for ring closure and selective cycloalkane formation (underway)
  - LCA analysis found **municipal solid waste** has the lowest life cycle impacts among all ethanol feedstock sources evaluated. Analysis will be extended to estimate effect of **aromatic content** on the total emissions from bio-jet fuel combustion
  - O-ring swelling study identified the potential of cycloalkanes to swell silicon, extracted nitrile rubber, and poly(butadiene) o-rings (underway)

Thank you!

- Q&A

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Response to FY21 Peer Reviewer Comments

Note: work had not been initiated yet.

Comment:

- “This follows the research of others which has shown the advantages of cycloalkanes over aromatics in jet fuels. However, it looks like this project is advancing two well-known processes - E2E and cyclization of olefins.”
- “Ethylene-to-ethanol and cyclization are well known technologies; it is unclear what the innovation in this project it.”

Response:

- Indeed, others have reported how cycloalkanes would have advantages over aromatics and other constituents in a jet fuel. However, here our goals are to further develop the scientific basis and also quantify how cycloalkane-rich components could produce favorable jet blendstocks. Further, we will develop the tunable processing for producing different mixtures of cycloalkanes and paraffins–with selectively to the jet range–that can be optimized for the best combination of energy density and other characteristics. This is a distinctly different objective and approach from any known reports in the literature.
- Certainly there exist known catalysts and conditions that facilitate cyclization from olefins, and this these will be leveraged here. However, commercial systems have been optimized with different goals and using different feedstocks. For example, incumbent catalytic reforming processes convert low-octane linear alkanes into branched alkanes and cyclic naphthenes that are then partially dehydrogenated to produce high-octane aromatic-rich hydrocarbons. **This includes the UOP Platforming and UOP-BP Cyclar processes aimed at producing aromatics but not cycloalkanes.** Cyclization processes typically use homogenous catalysts and are employed at smaller scales.
- Here we leverage the alcohol-to-jet (ATJ) process that selectively produces iso-paraffins and was developed by PNNL and is being commercialized by LanzaTech. Our aim is to tailor the catalyst and conditions for the formation of cycloalkanes versus iso-olefins. To accomplish this goal, we are using newly developed multifunctional catalyst(s) and the same number of processing steps as the current ATJ process. Different from the aforementioned aromatization processes, here we aim to tune the olefinic distribution to cycloalkanes in the jet-range (C8–C16) and with minimal aromatics. This a stark contrast from the processes described above that typically produce aromatics in the C6–C8 range. Further, most of these traditionally used processes report up to 40% yield to aromatics. Our objective is to obtain at least 60% selectivity to cycloalkanes in the jet range.
- We are not aware of commercial-scale processes dedicated to the production of cycloparaffins from ethylene through cyclization or any other process (e.g., alkylation). Commercial uses for ethylene are currently aimed at the production of polyethylene, ethylene oxide, chloride, and styrene.

Response to FY21 Peer Reviewer Comments, cont.

Note: work had not been initiated yet.

Comment:

- “Significant need for hydrogenation of aromatics will be a further significant cost. It will also require hydrogen, which will require recovery and purification and possible incremental supply.”

Response:

- Our intent is to avoid the formation of aromatics either as a product or as an intermediate. By preferentially producing cycloalkanes over aromatics with hydrogen-neutral ring closure, we will limit the need for external hydrogen for hydrotreatment. If unsuccessful, one of our risk mitigation approaches is to hydrogenate produced aromatics as a path to selectively form cycloalkane. However, because of the additional processing costs incurred using this alternative approach, we will only consider it if other approaches cannot achieve the 60% cycloalkane selectivity target.

Comment:

- “The project management plan is lacking industry representative, at least in an advisory role.”

Response:

- LanzaTech is participating in this effort to ensure both the catalytic processing and jet fuel analysis efforts are successful. LanzaTech’s aim is to ultimately commercialize the technology developed here. Project management includes regular meetings with participation from all three project partners (as shown on slide 5). We also note that LanzaTech is already commercializing the benchmark ATJ process that was co-developed with PNNL; therefore, a track record for commercial offtake already exists in the project.

Response to FY21 Peer Reviewer Comments, cont.

Note: work had not been initiated yet.

Comment:

- “Is there any communication with the Bio-JET project, which is looking at direct biological routes to similar molecules. That project essentially proposes: sugar –> high-energy density jet fuel via fermentation. This project needs a fermentation to ethanol, dehydration to ethylene, oligomerization / cyclization, and then hydrogenation. There is also every likelihood that direct biological synthesis will produce a water-insoluble product, meaning that instead of distilling ethanol and then distilling the hydrocarbons at the end, the direct biological route will require only one simple decantation step after fermentation. The flowsheet here looks too complex.”

Response:

- Certainly there are many biomass-to-jet routes being investigated, using alcohols, oils, gasses, and sugars as feedstocks. Multiple processes exist, all at various technology readiness levels. The ATJ process being commercialized by LanzaTech has many benefits. First, it uses ethanol feedstock that is already produced and distributed at commercial scale. Second, it uses thermochemical processing that enables high throughput. Further, while multiple unit operations are required, it is selective toward producing an isoparaffinic hydrocarbon with >90% carbon efficiency to the jet range. Carbon efficiency is one of the most critical cost metrics when considering the use of biomass or recycled-carbon feedstock. Taken together, this process has many benefits and is currently being commercially deployed for sustainable aviation fuels.

Publications, Presentations, and Patents

- Caceres-Martinez, L.E., Saavedra, J., Dagle, R., Gillespie, R., Kenttämaa, H., Kilaz, G. Influence of Blending Cycloalkanes on the Energy Content, Density, and Viscosity of Jet-A. 2023. (submitted)

- Caceres-Martinez, L.E., Wan-Tang, J.Z., Saavedra, J., Dagle, R., Gillespie, R., Kenttämaa, H., Kilaz, G. Semiquantitation Method and Ionization Efficiencies of Alkanes, Alkenes, Cycloalkanes, and Aromatics via GCxGC/(+)EI TOF MS. 2023. (submitted)

Extra Slides

1 - Approach: Objectives for Budget Period 2 and 3

- BP2: Process development focus on catalyst and process development to increase the selectivity towards cycloalkanes to > 40 wt.%.
  - Produce at PNNL 100 ml of > 40 wt.% cycloalkanes with > 60 wt.% in the jet-range material from n-butene (primary intermediate in LanzaTech/PNNL ATJ process) and deliver to Purdue for fuel analysis
  - Purdue provide regular feedback to PNNL on fuels produced to ensure that final product comprises 4% net increase in combined (specific (MJ/kg) and volumetric (MJ/L)) energy content, without impacting ‘drop-in’ fuel requirements, and assess seal swelling without aromatics
- BP3: 2 gallons of a > 60 wt.% selectivity to cycloalkane to jet-range produced at PNNL and sent to Purdue
  - Fuel analysis to understand properties of cycloalkanes produced to inform process development/ TEA
  - Seal-swelling analysis will quantify the viability of the fuel blend with zero or minimal aromatics

1 – 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)

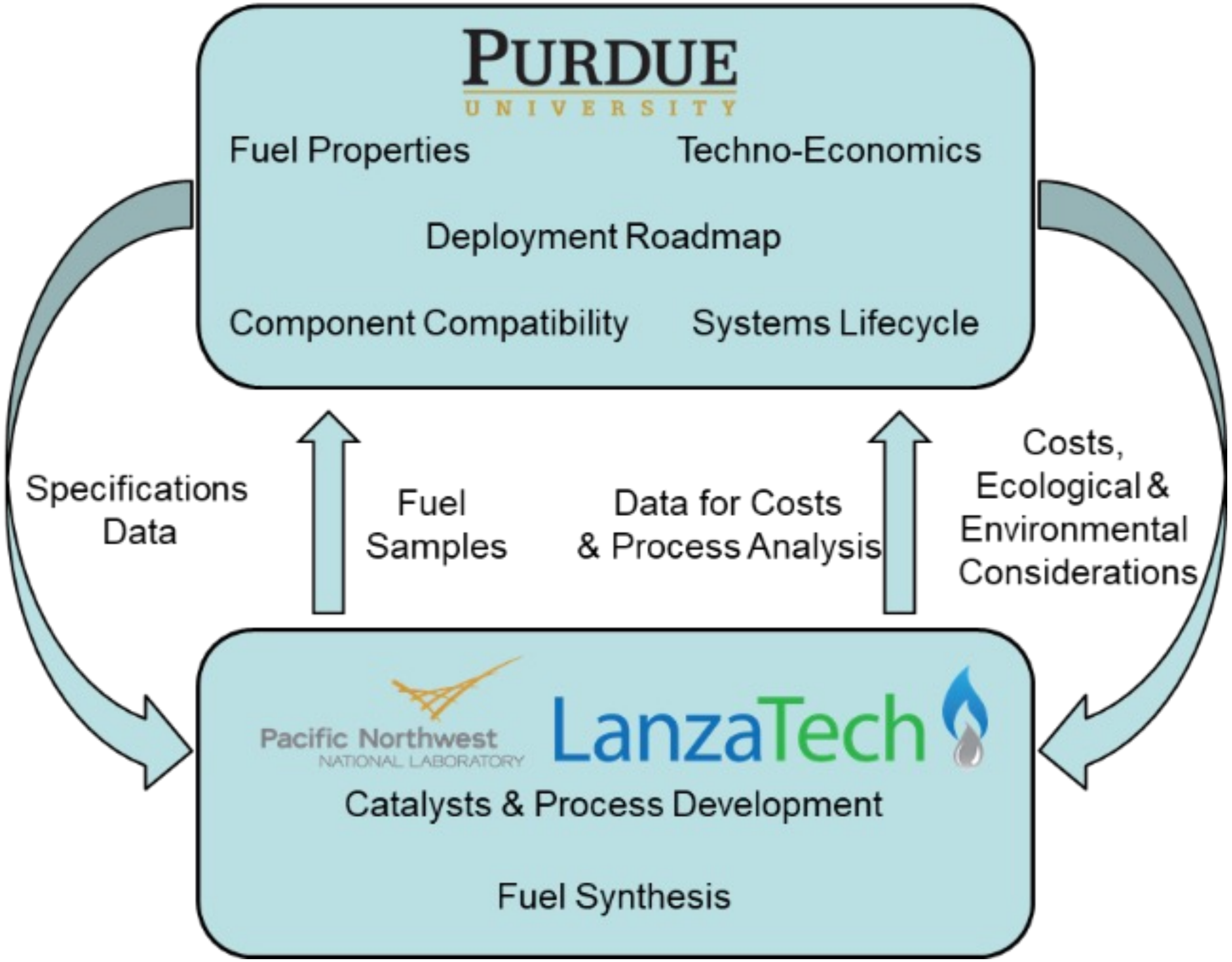
Property	Units	Description
Specific energy	[MJ/kg]	Enables fuel efficiency by lowering take-off weight, critical for mass-limited missions
Energy density*	[MJ/L]	Most important metric for volume-limited missions or military operations involving refueling
Thermal stability		Ability of fuel to sustain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

1 – Approach: Management of 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 – Approach: Collaboration Approach

- **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.
- Closely 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

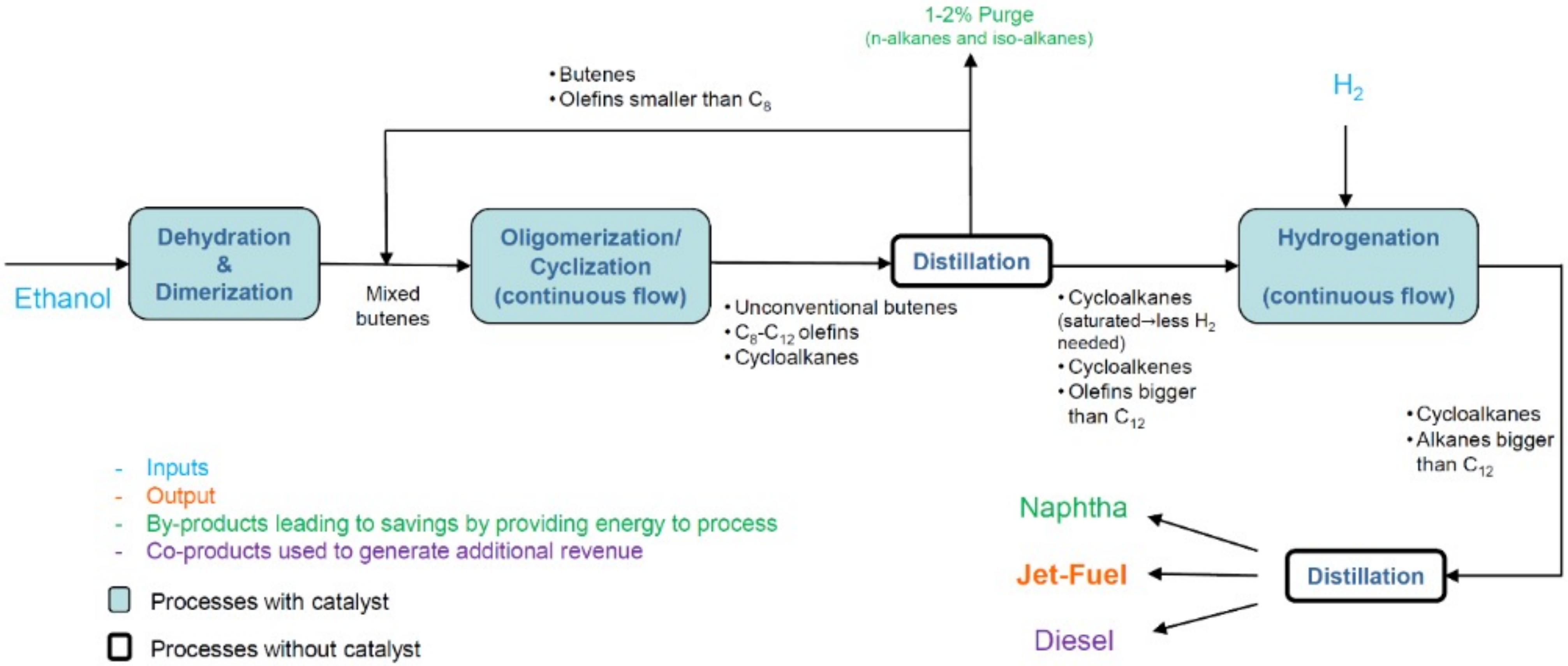


1 – Approach: ASTM Specification

- 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

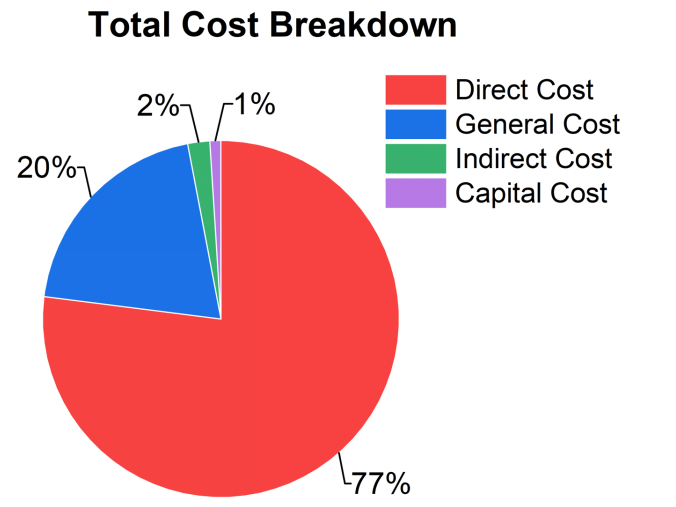
Property	Units	SPK + Jet A Blend ASTM D7566 Table 1	Description
Viscosity	mm^2/s	8 max (D445)	Flow performance especially at cold temperatures
Density	kg/m^3	775-840 (D4052)	Fuel tank volumes
Freeze Point	°C	-40 max (D5972)	Critical at high altitude
Flash Point	°C	38 min (D56)	Flammability
Distillation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

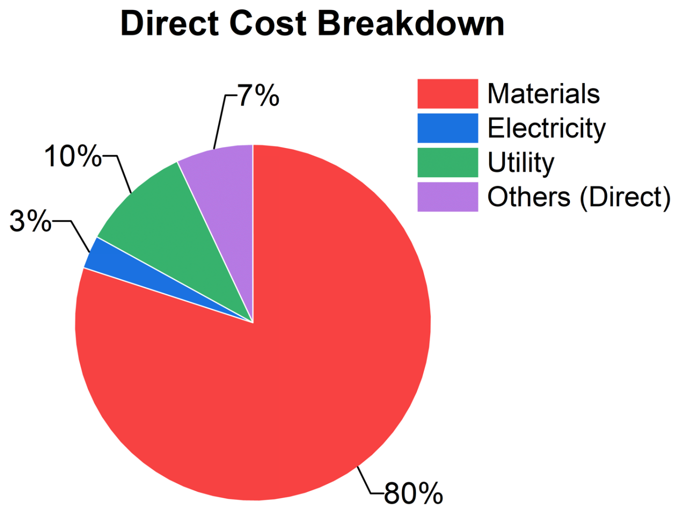
2 – Progress & Outcomes: Process Flow Diagram of Production of Jet Fuel from Bioethanol



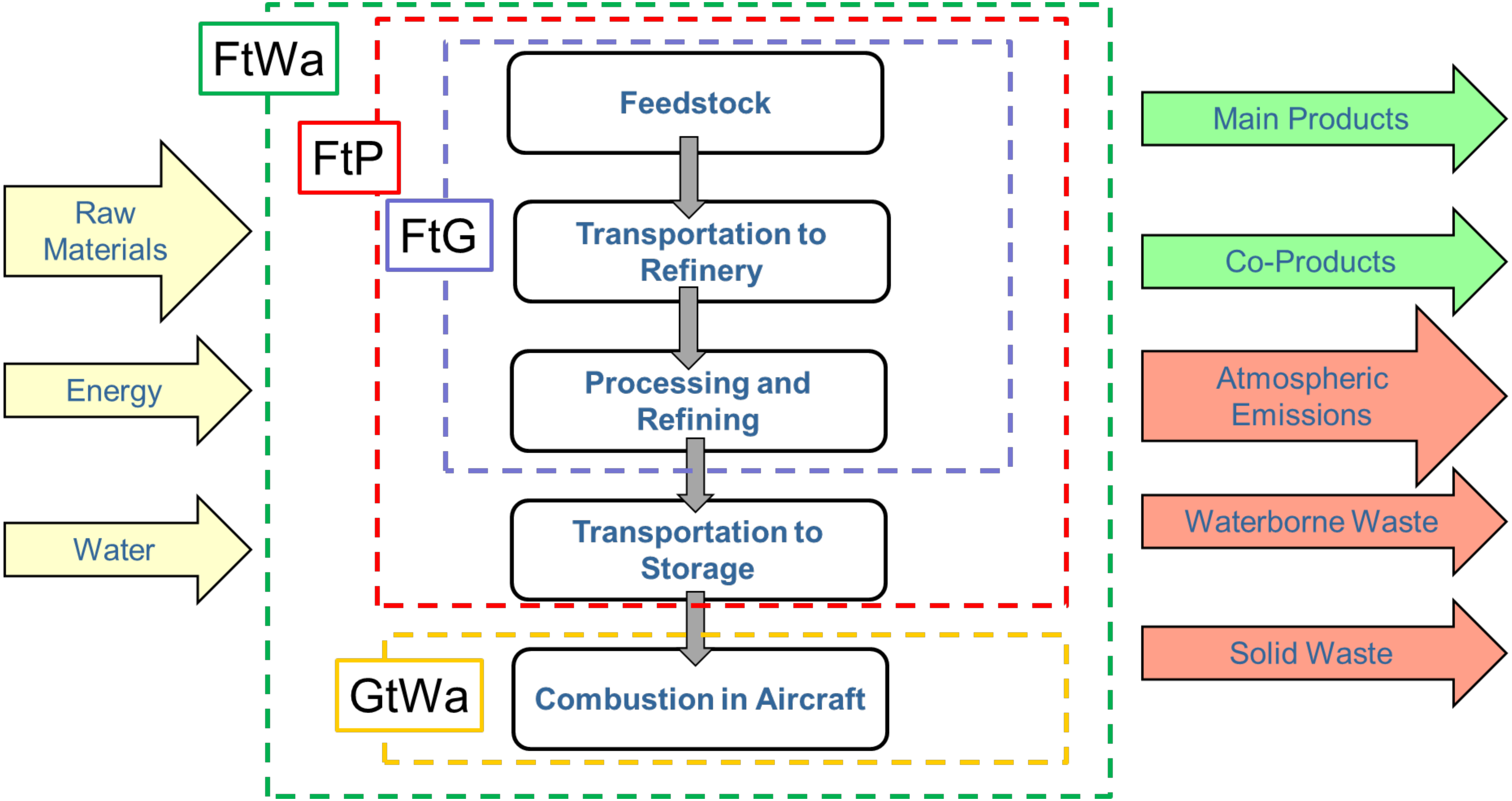
2 – Progress & Outcomes: Key Inputs for TEA

Category	Value	Category	Value
Operational days	330 days/year	Plant life	23 years
Working hours	24 hours/day	Salary; No. of operators	53,383 $/yr/opr; 21 Opr/shift
Debt/Equity ratio	1.5	Revenue during startup	50% of normal
Debt financing term	10 years	Operational cost during startup	75% of normal
Debt financing interest	8% per year	Administrative cost during startup	100% of normal
Compounds per year	1	Working capital	20% of fixed capital
Depreciation period	7 years	Financial debt	60% of total capital
Depreciation rate	Double declining balance (200%) (year 1-4) & straight line (year 5-7)	Financial equity	40% of total capital
Annual inflation	1.56%	Plant salvage value	$ 50,000

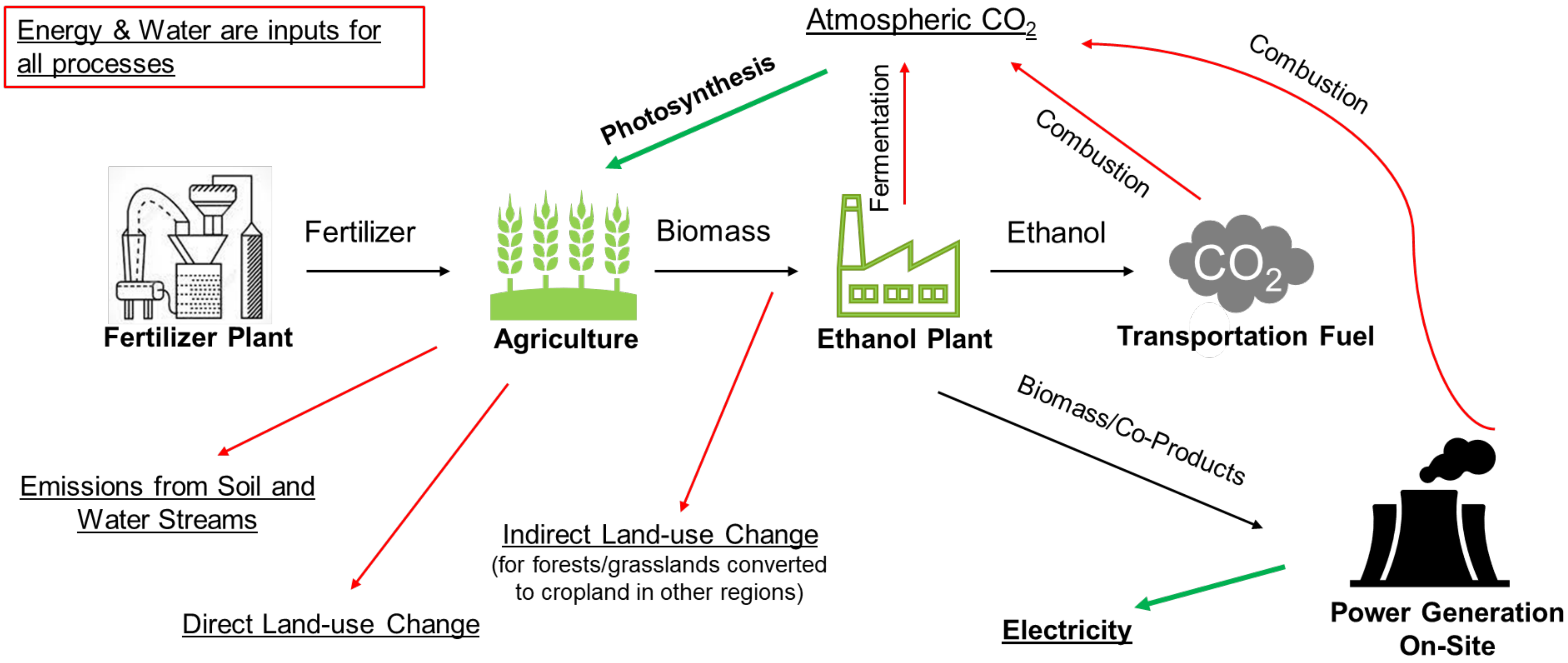




2 – Progress & Outcomes: LCA System Boundary



2 – Progress & Outcomes: Feedstock to Ethanol



M. Wang and J. Han, "ANALYSIS AND SUSTAINABILITY SESSION 2017 BETO PEER REVIEW GREET ® DEVELOPMENT AND BIOFUEL PATHWAY RESEARCH AND ANALYSIS," 2017.

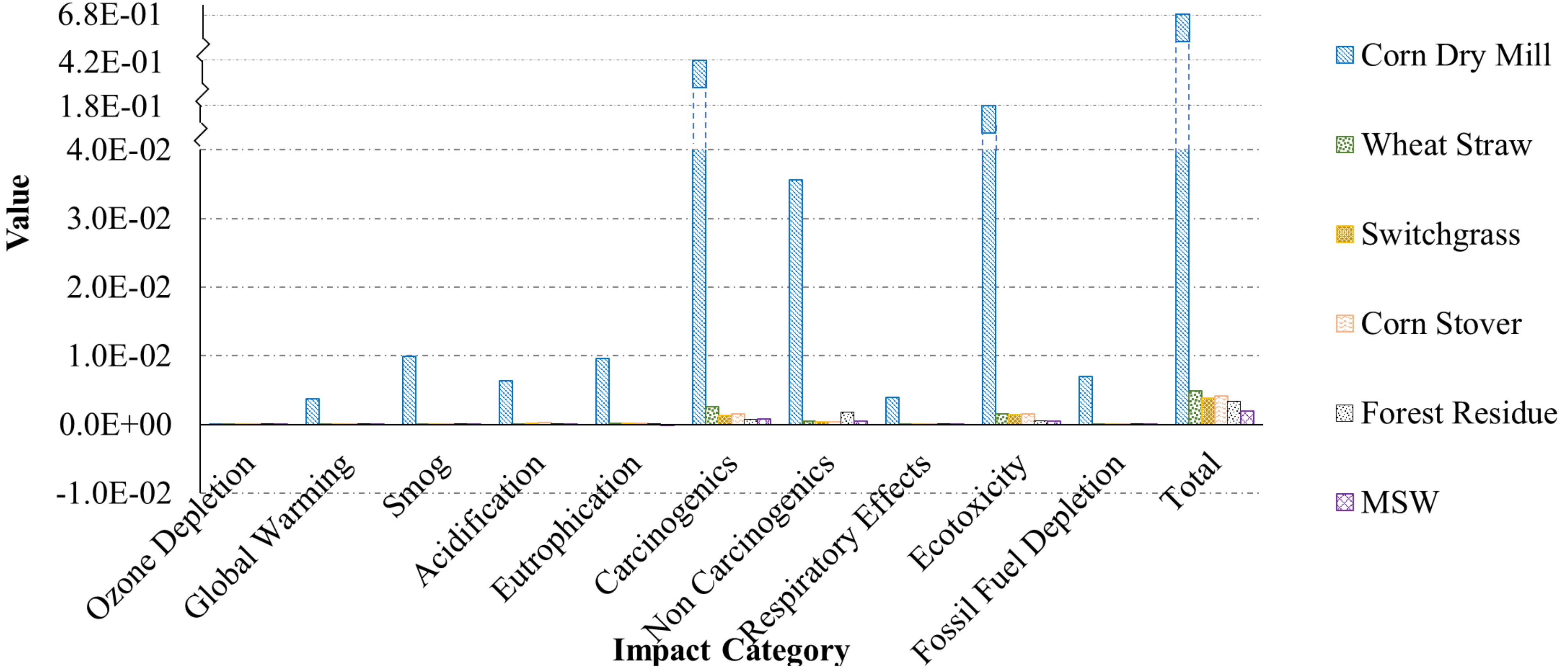
2 – Progress & Outcomes: Factors considered in LCA

- **Impact on environment:**
  - Global warming potential (CO_2 eq., black carbon)
  - Ozone depletion potential (CFC eq.)
  - Smog generation (O_3 eq.)
  - Acidification potential (SO_2 eq.)
  - Eutrophication potential (N eq.)
  - Ecotoxicity (CTUe)
  - Fossil fuel depletion (MJ surplus)
  - Black carbon, polycarbonate
- **Impact on <u>immediate</u> human health:**
  - Carcinogens released (CTUh)
  - Non-carcinogens harmful to human health (CTUh)
  - Factors affecting respiratory health ($PM_{2.5}$ eq.)

2 – Progress & Outcomes: LCA

Function Unit:

Production of 1 gallon ethanol from feedstock in the US



2 – Progress & Outcomes: Functional Unit and Ethanol Transportation Metrics

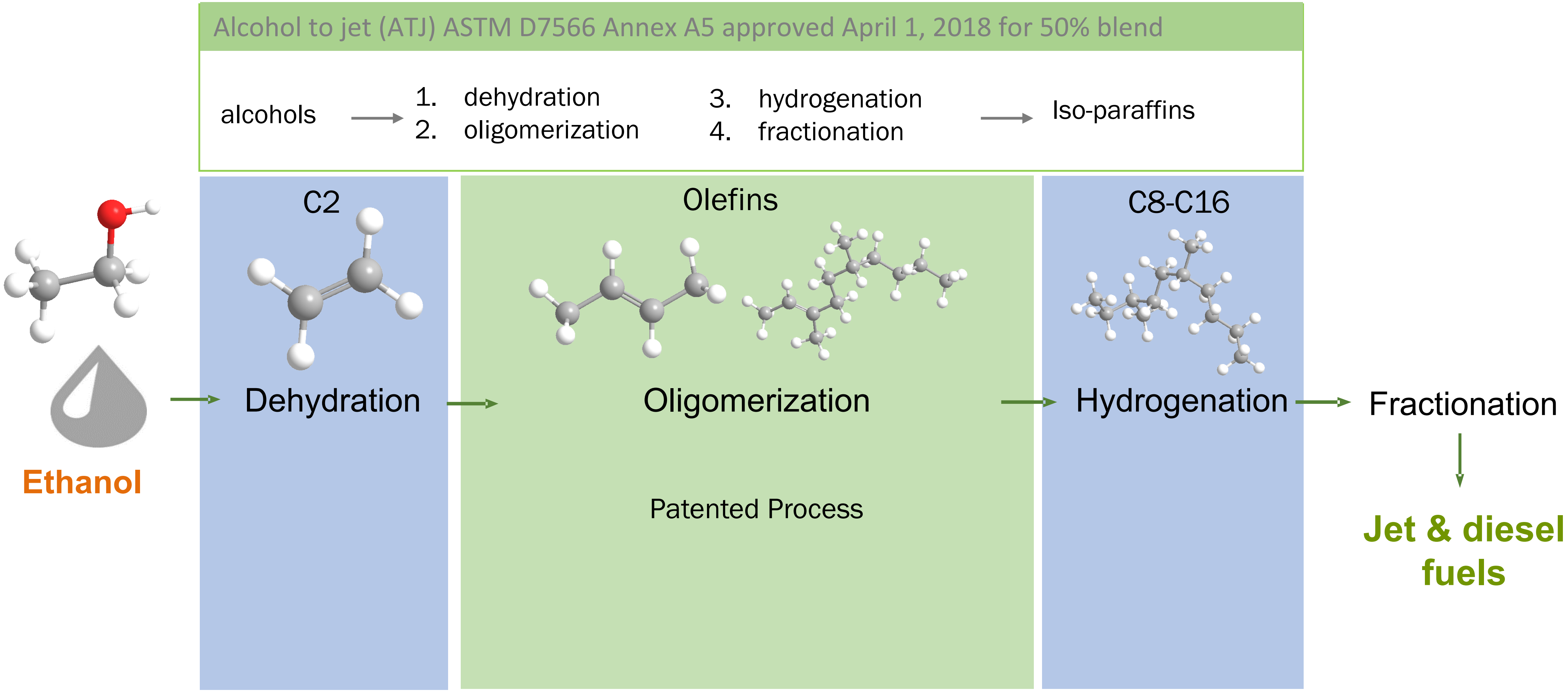
- **Ethanol transport contribution:**
  – Barge - 10%; Train - 40%; Truck - 50%
- **Average distance transported by each mode:**
  – Barge - 200 mi; Train - 800 mi; Truck - 1000 mi

- **Functional Unit:**
  – Manufacturing and transporting of 1 gallon ethanol from bio-feedstocks.

- "Alternative Fuels Data Center: Ethanol Production." https://afdc.energy.gov/fuels/ethanol_production.html.
- "Freight Rail Facts & Figures - Association of American Railroads." https://www.aar.org/facts-figures.

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

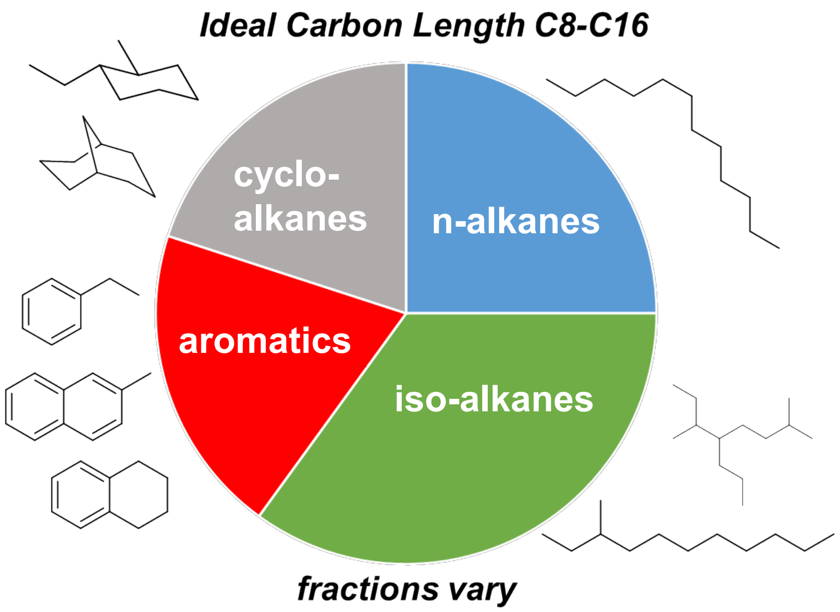
Ethanol to Diesel

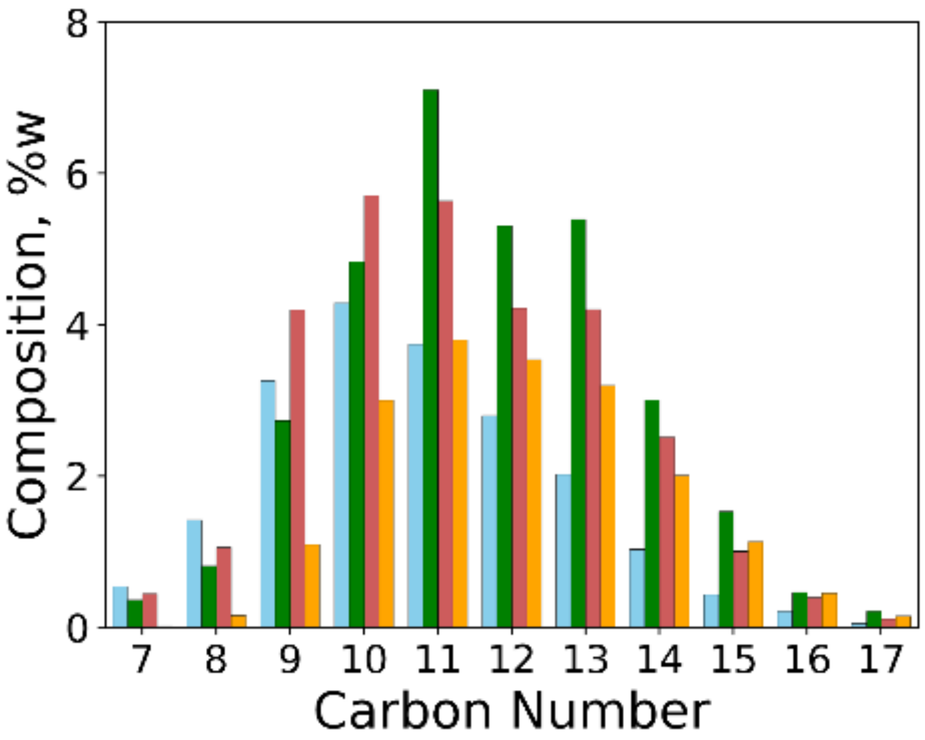
- High Cetane
- Excellent Cold Flow properties

✓ Isoalkane-rich

3 – Impact: 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

3 – Impact: Addresses gaps in understanding

Addressing current gaps in understanding of cycloalkane properties and their production

- Technology enhances the value proposition of PNNL/LanzaTech's Alcohol-to-Jet process, by improving the fuel properties and subsequent value
- Commercial processes exist for producing high octane aromatic product (e.g., UOP Platforming, and UOP BP-Cyclar) but not cycloalkanes selectively from olefins.
- Bulk properties of blends and blending behavior, including 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

Ethanol-jet reduces cost by recycling industrial gas