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Syngas Derived Mixed Olefin Oligomerization for Sustainable Aviation Fuel

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Technology Area Session: Catalytic Upgrading

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Project Overview

Develop and demonstrate mixed olefin (C_2-C_5) co-oligomerization to enable multiple renewable feedstocks to produce SAF

Project Goal

Develop a C_2–C_5 co-oligomerization catalyst and demonstrate an efficient path to generating sustainable aviation fuel (SAF) from syngas via a mixed olefin intermediate

Outcome

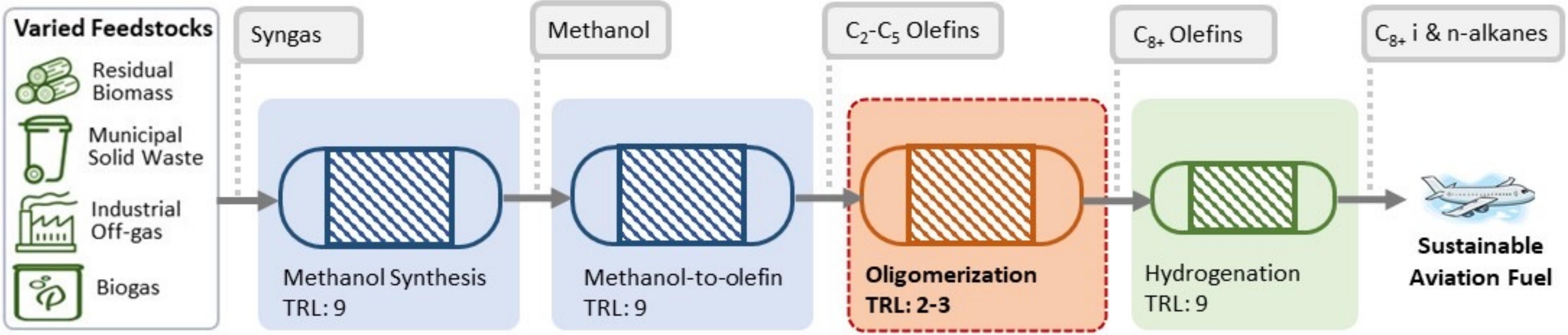
- Co-oligomerization catalyst development that is stable for mixed olefins derived form methanol to olefin process
- Produce >1 L finished jet fuel from this process that meet the ASTM standards for Tier α and β analysis

Relevance

Develop technologies that can achieve greenhouse gas (GHG) reduction of >70% for SAF production from renewable feedstocks

Source: https://www.energy.gov/sites/default/files/2022-09/beto-saf-gc-roadmap-report-sept-2022.pdf

Co-oligomerization of mixed olefins to demonstrate efficient path to produce SAF via syngas



- Leveraging existing commercial processes and feedstocks will be the most efficient path toward producing SAF in the near-term
- Developing mixed olefin co-oligomerization is key to achieve an end-to-end commercial pathway for producing SAF from syngas derived from various renewable feedstock

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1-Approach (Project Management)

Integrated work between PNNL, WSU and Haldor Topsoe

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- Project management
- Catalyst development
- Evaluation of catalytic activity – flow reactor testing
- Catalyst characterization
- Production of fuel sample for analysis
- Techno economic and life cycle analysis

WASHINGTON STATE UNIVERSITY

- Detailed analysis of fuel properties

TOPSOE

- Engineering catalyst development

- Integrated workflow and handoff points between the partners based on the core capability and the technical expertise
- Regular meetings between the partners for the technical updates

Diversity, Equity, and Inclusion (DEI) Plan: Hired a summer intern through PNNL's diversity internship program

Project DEI Task: Hire at least one student from groups under-represented in STEM

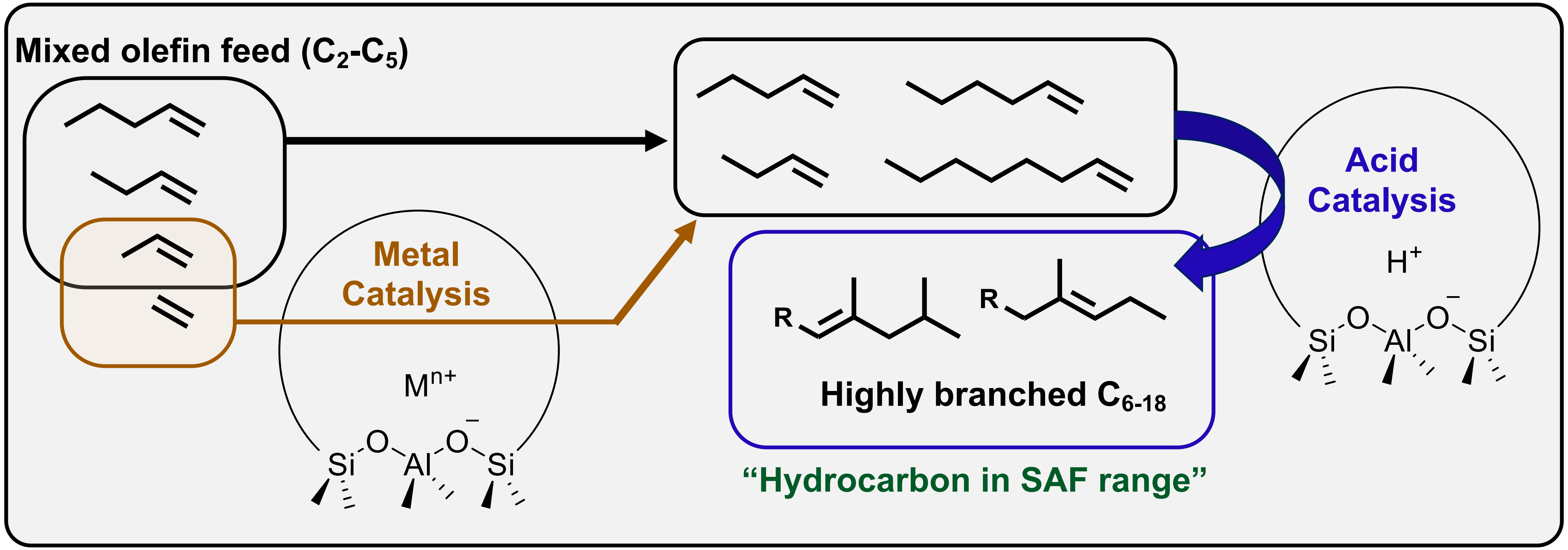
- PI of this project participated in The Energy and Environment Diversity Internship Program (EEDIP) program designed for students passionate about environmental and clean energy science
- This is a competitive opportunity supports traditionally under-represented students in target technical areas through a 10-to-12-week paid internship

Outcome:

- Hired a Bachelor of Science Chemical Engineering student through PNNL's EEDIP program
- Student is planned to work at PNNL between June – August 2023 to participate in the co-oligomerization catalyst/process development activities

1. Approach

Requires hybrid catalyst containing both metal and acid sites



- Activation of C_2 and C_{3+} goes through different reaction mechanism and active sites
- **Integrating** both **metal and acid catalysis pathways** are **key** to facilitate co-oligomerization of C_2 and C_{3+} olefins to **produce SAF**

1. Approach
Addressing risk and measuring progress

Milestone (Sep 2022): Produce 100 mL of finished jet fuel sample from the representative Methanol to Olefin (MTO) feedstock	Completed
Milestone (Sep 2023): Demonstrate the integration between Methanol-to-Olefin (MTO) reactor and oligomerization reactor to evaluate the feedstock impurity effect of the catalyst performance	**Ontrack**
Milestone (Sep 2024): Demonstrate extended operation (>500 hours) of an integrated process using engineered catalysts with on-stream regeneration	**Ontrack**

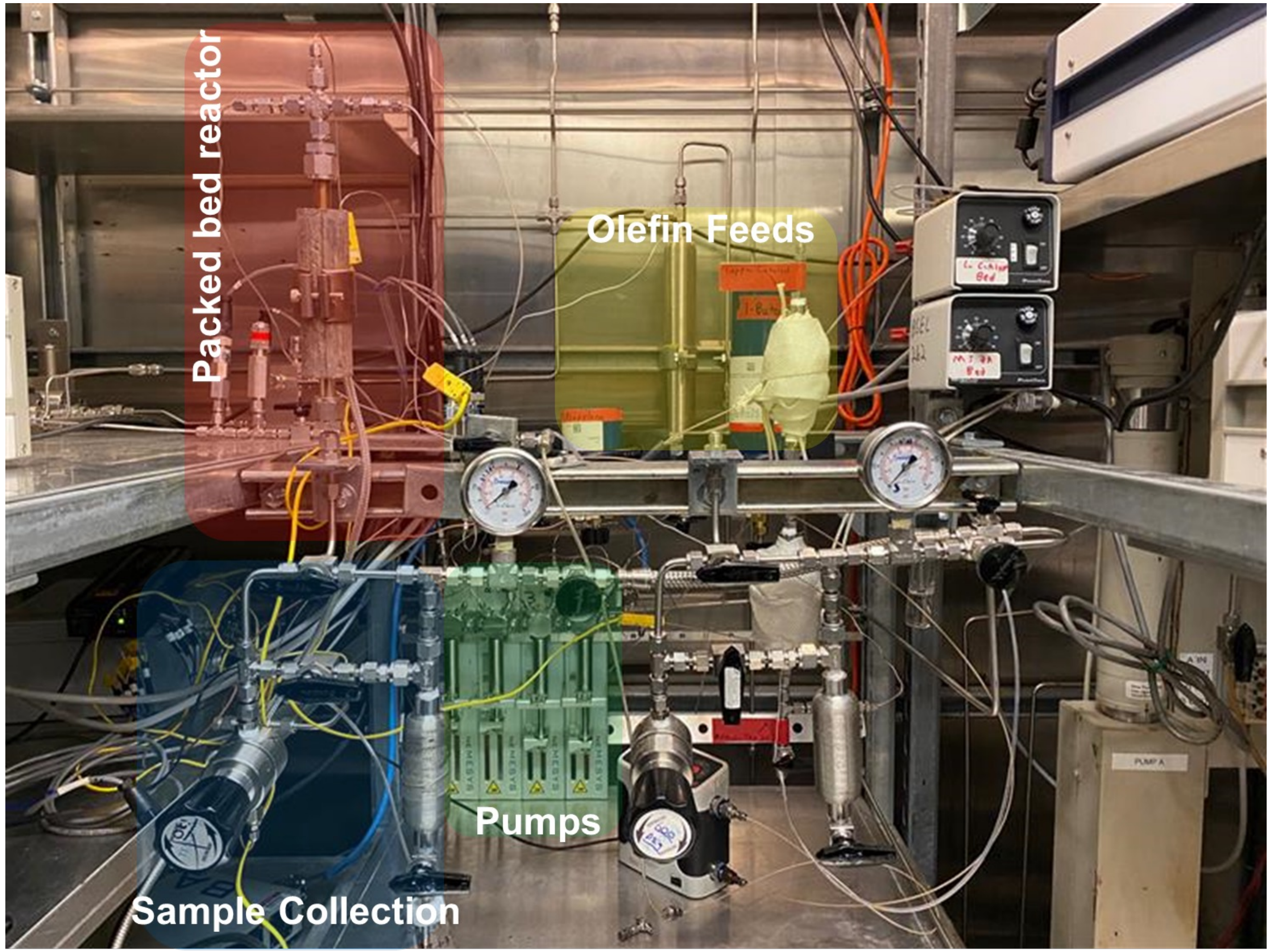
Risk Mitigation:

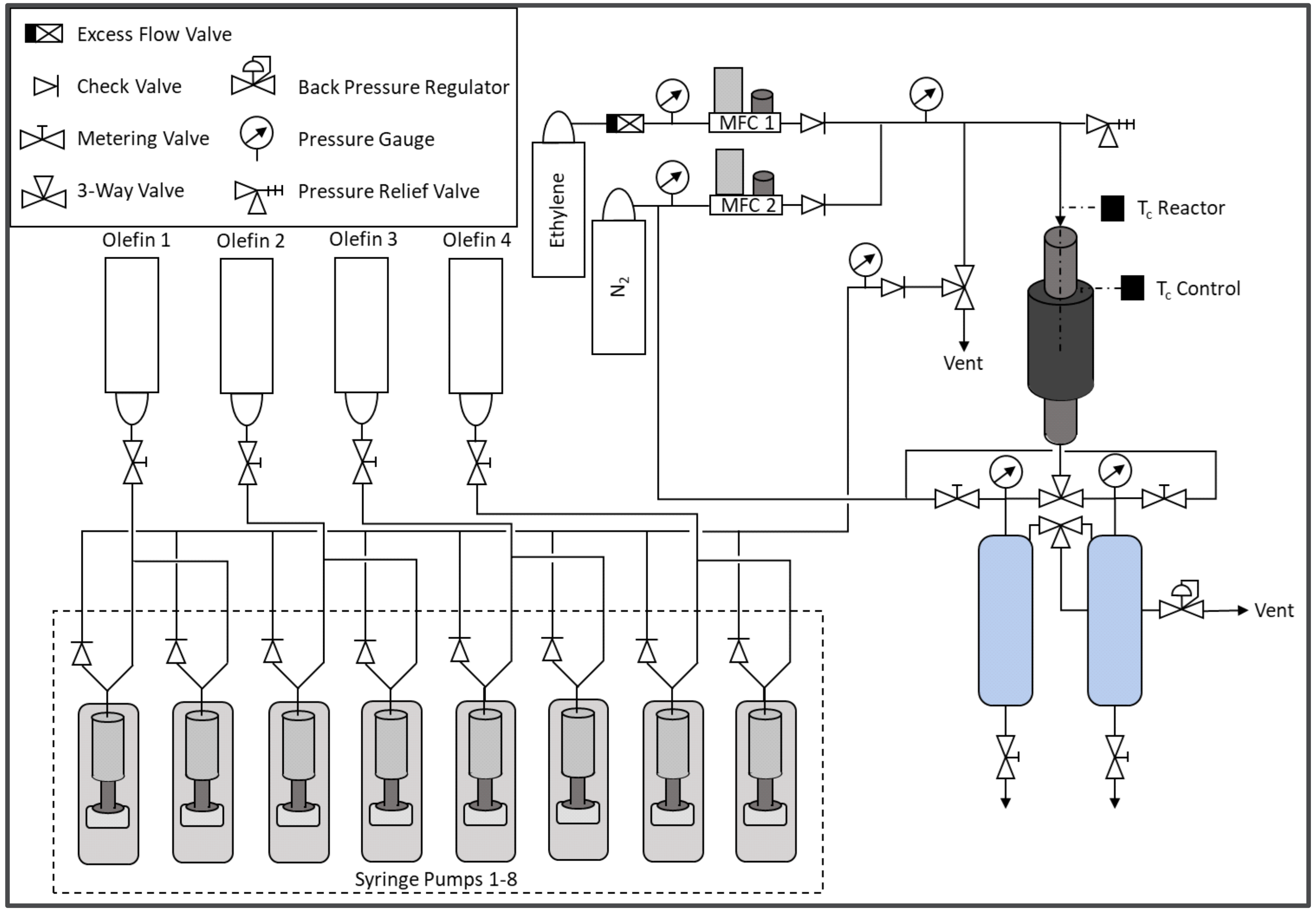
Low product yield and catalyst deactivation on single-step mixed olefin oligomerization:

Perform oligomerization in staged two-zone reactor with independently optimized catalyst, still achieving goal of significantly reducing process intensity.

Go/ No-Go Completion: Production of 100 mL of finished jet fuel starting from MTO mixed olefin feed and complete analysis of Tier α and Tier β properties meeting ASTM standards at ≥50% blend level. **December 2022**

Construction of new reactor system that handles multiple olefin feed

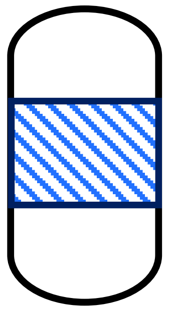


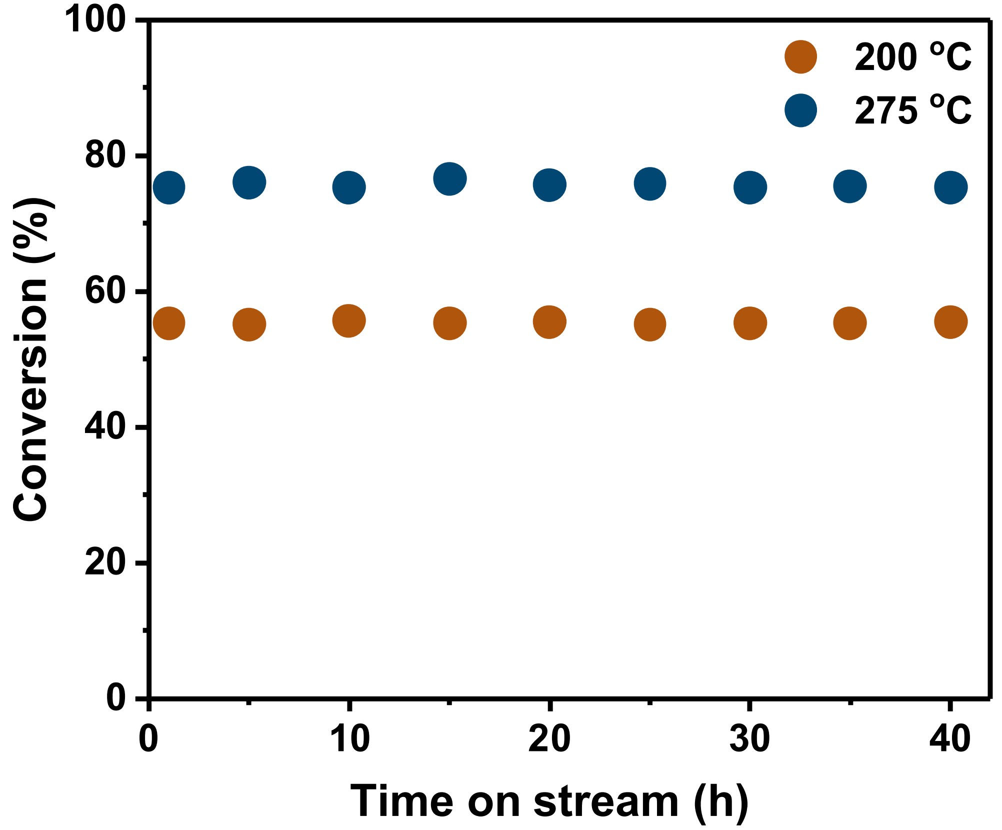


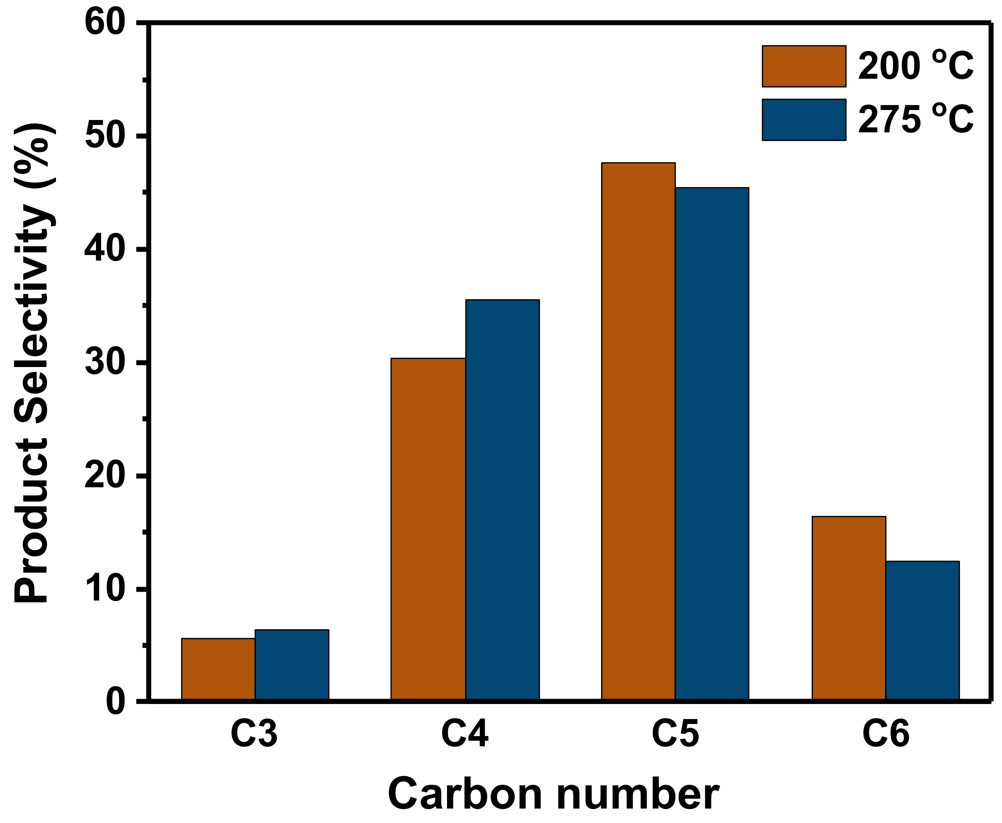
- Constructed new reactor systems to carry out co-oligomerization of C_2-C_5 mixed olefins

2. Progress and Outcome

Metal catalyst alone doesn't promote the chain growth beyond dimerization







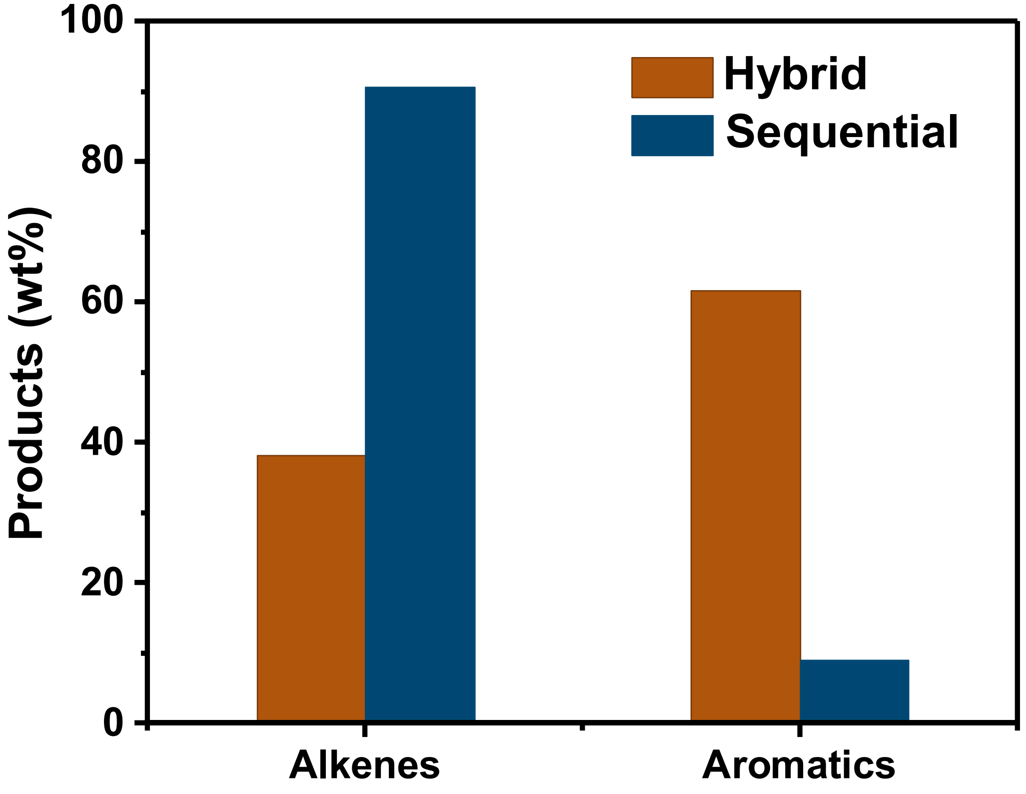
Operating Conditions: *WHSV: 0.8 h^{-1}, Feedstock: equimolar C_2-C_3, Pressure: 100 psi, Temperature: 200 - 275 °C*

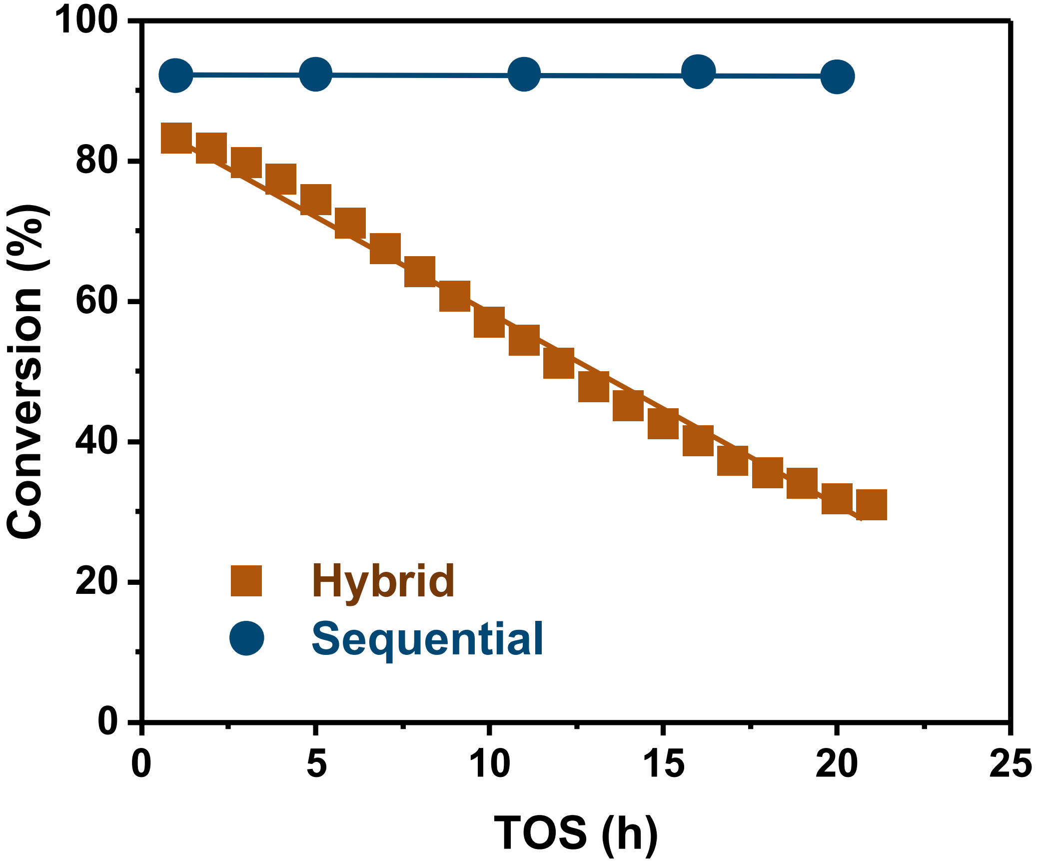
- Co-oligomerization of ethylene ($C_2^=$) and propylene ($C_3^=$) using the baseline metal catalyst at varying temperature in a plug flow reactor system

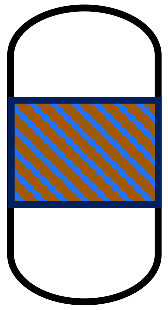
- Products obtained from $C_2^=$ and $C_3^=$ co-oligomerization are primarily between C_4-C_6 range with C_5 being the major project
- Significant **cross oligomerization** between **$C_2^=$ and $C_3^=$ with minimal chain growth**
- **Outcome: Optimized metal composition and loading for co-oligomerization of $C_2^=$ and $C_3^=$**

2. Progress and Outcome

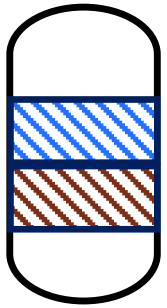
Sequential catalyst bed is active and selective to the oligomerized products







Hybrid: Metal supported on zeolite



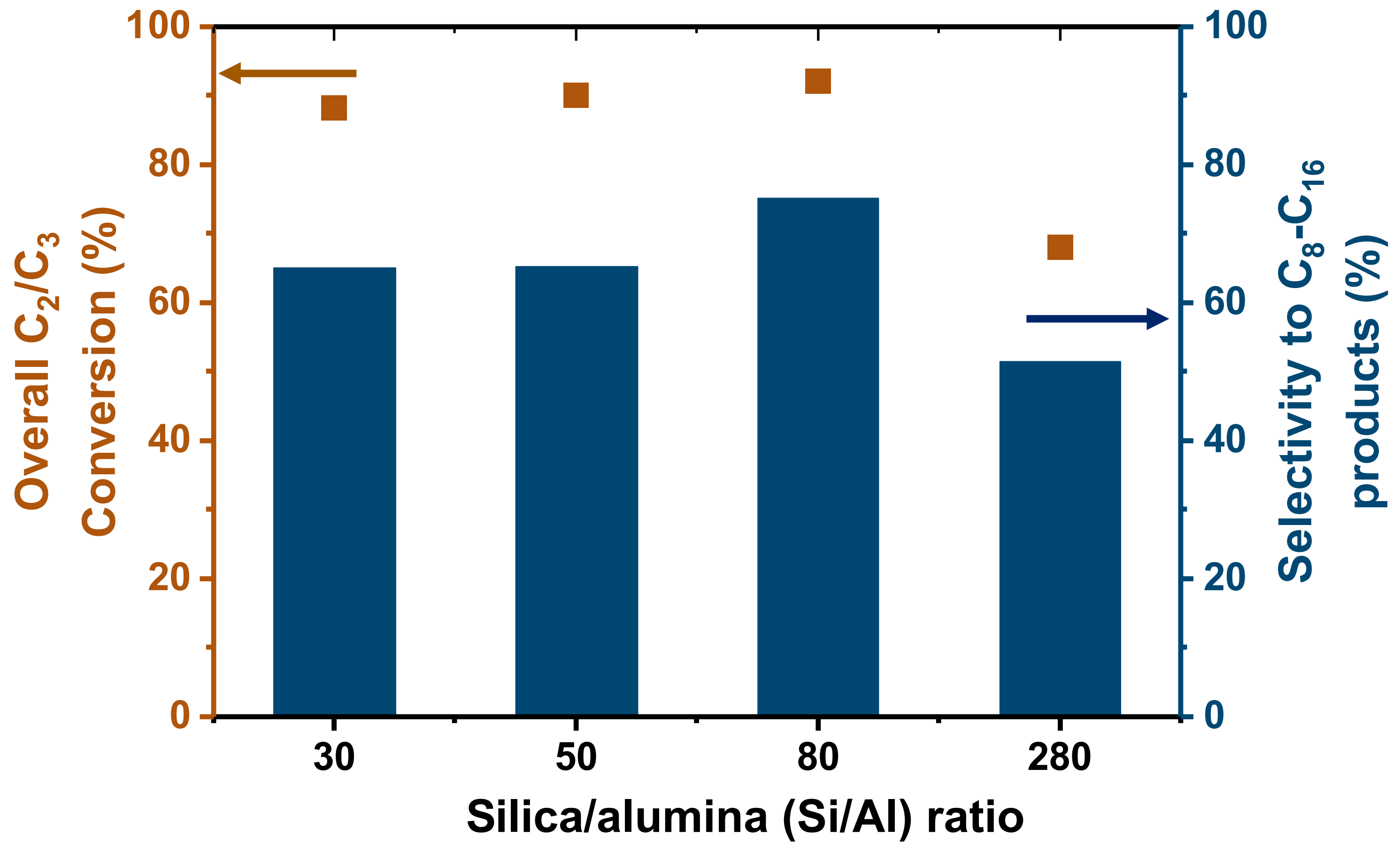
Sequential: Metal followed by acid catalyst

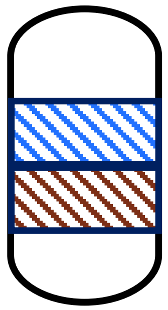
Operating Conditions: *WHSV: 0.8 h^{-1}, Feedstock: equimolar C_2-C_3, Pressure: 100 psi, Temperature: 275 °C*

- Both hybrid and sequential catalyst exhibited ~70% selectivity to C_8-C_{16} compounds
- Hybrid catalyst produced higher fraction of light olefins and **6x higher aromatics** compared to sequential catalyst
- **Hybrid catalyst suffers severe deactivation** compared to sequential catalyst

2. Progress and Outcome

Moderate acidity is required to maintain the balance between product selectivity and conversion





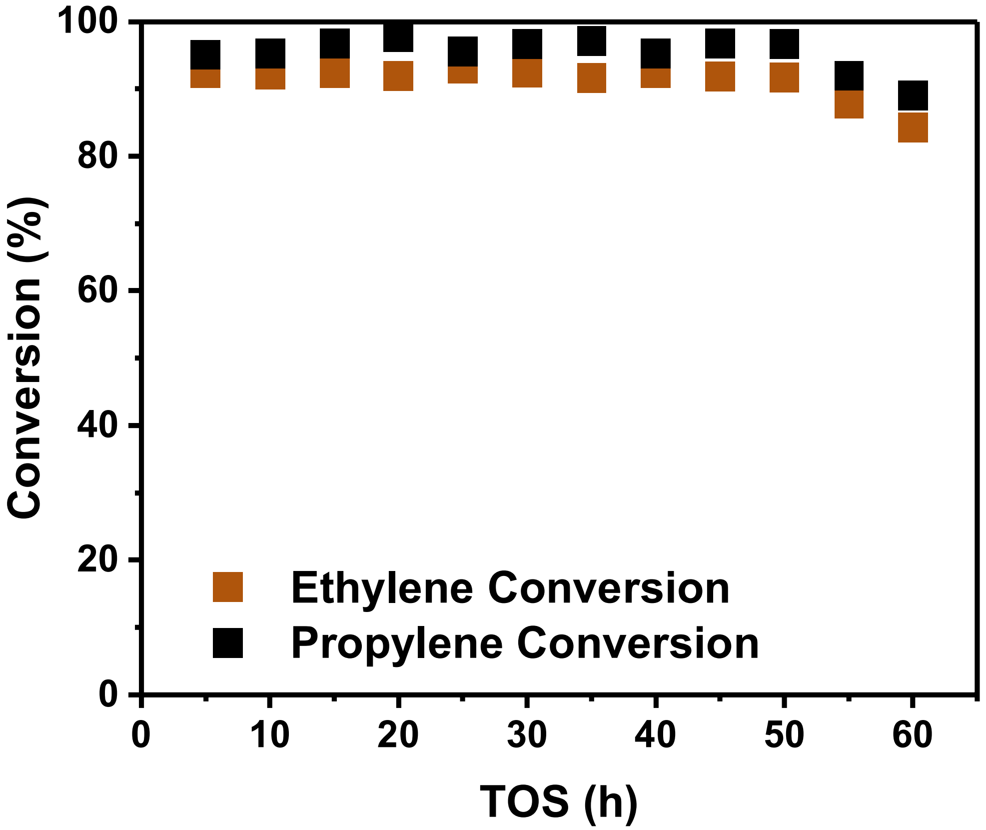
Sequential: Metal followed by acid catalyst

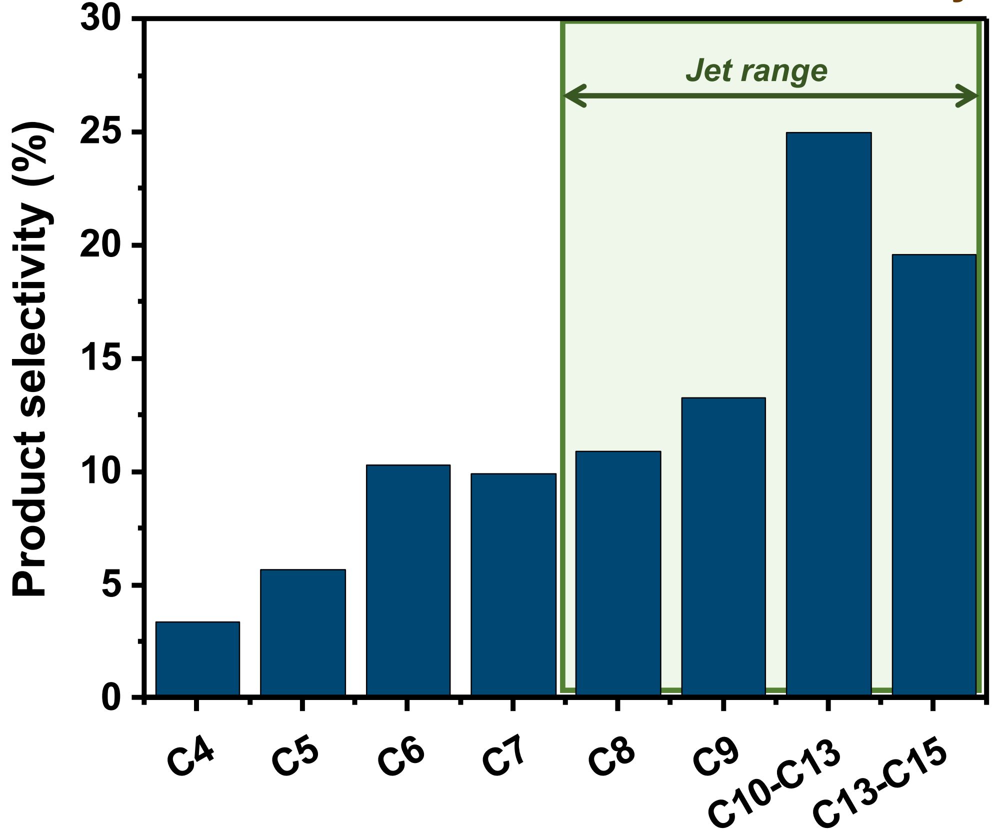
Operating Conditions: *WHSV: 0.8 h^{-1}, Feedstock: equimolar C_2-C_3, Pressure: 100 psi, Temperature: 275 °C*

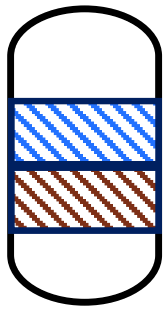
- Catalyst with moderate acidity exhibited both higher conversion and selectivity to desired jet range products
- Higher acidity (Si/Al:30) tend to have cracking as side reaction

2. Progress and Outcome

Demonstrated the sequential catalyst bed system with high selectivity and activity







Sequential:
Metal followed by acid catalyst

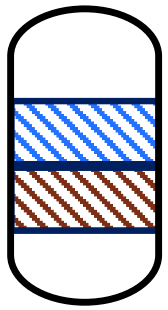
- Single step co-oligomerization of $C_2^=$ and $C_3^=$ using sequential bed containing metal and acid catalyst

Operating Conditions: *WHSV: 0.8 h^{-1}, Feedstock: equimolar C_2-C_3, Pressure: 100 psi, Temperature: 275 °C*

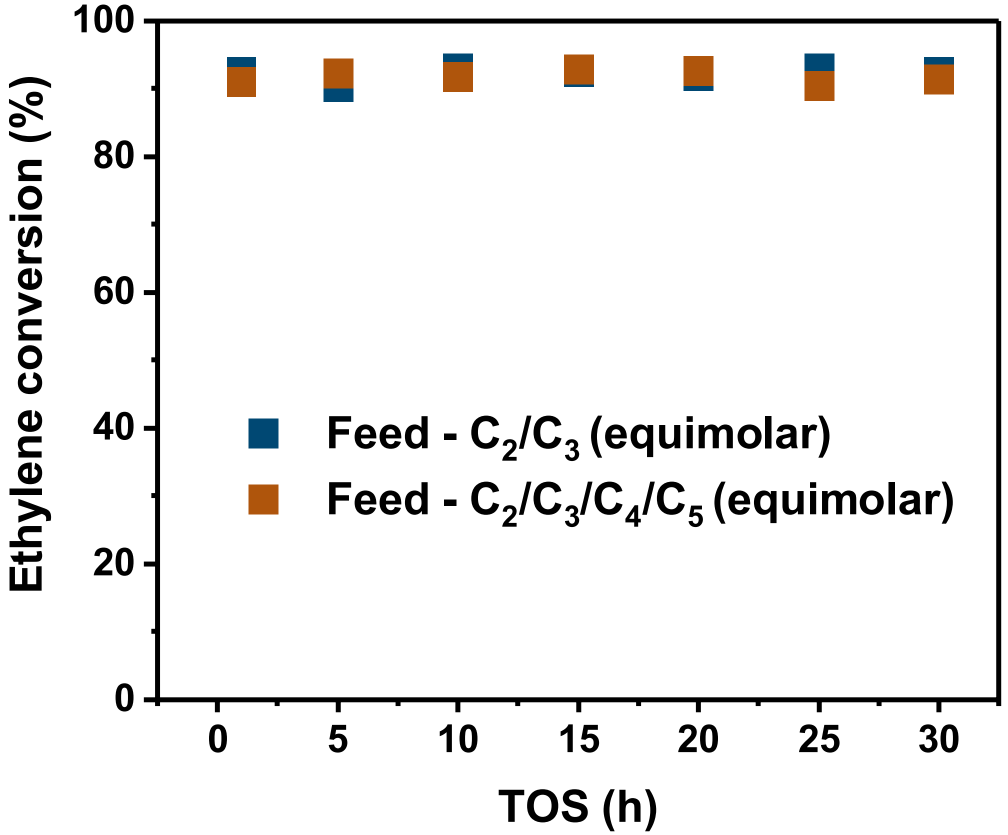
- >90% conversion of both ethylene and propylene; >75% selectivity to jet range (C_8-C_{16}) olefins
- Stability of the sequential catalyst system– ~ 50 h continuous time on stream

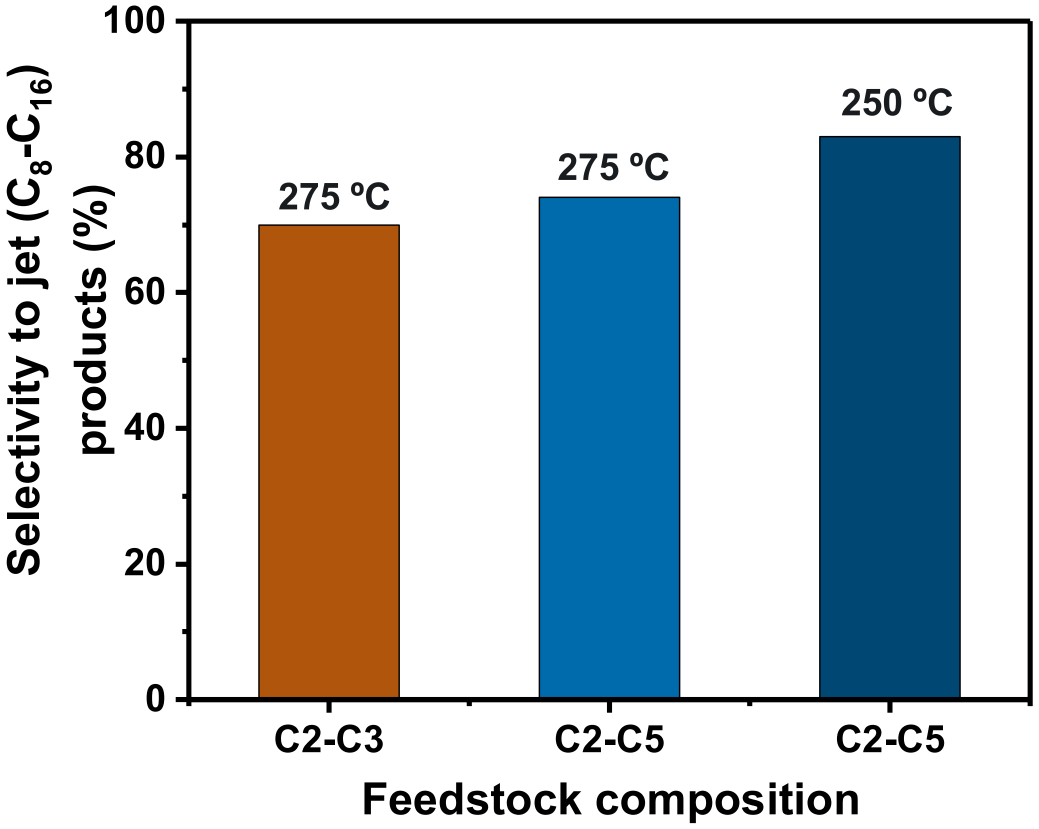
2. Progress and Outcome

Co-oligomerization of mixed olefins (C_2-C_5) performs similar to the C_2-C_3



Sequential: Metal followed by acid catalyst



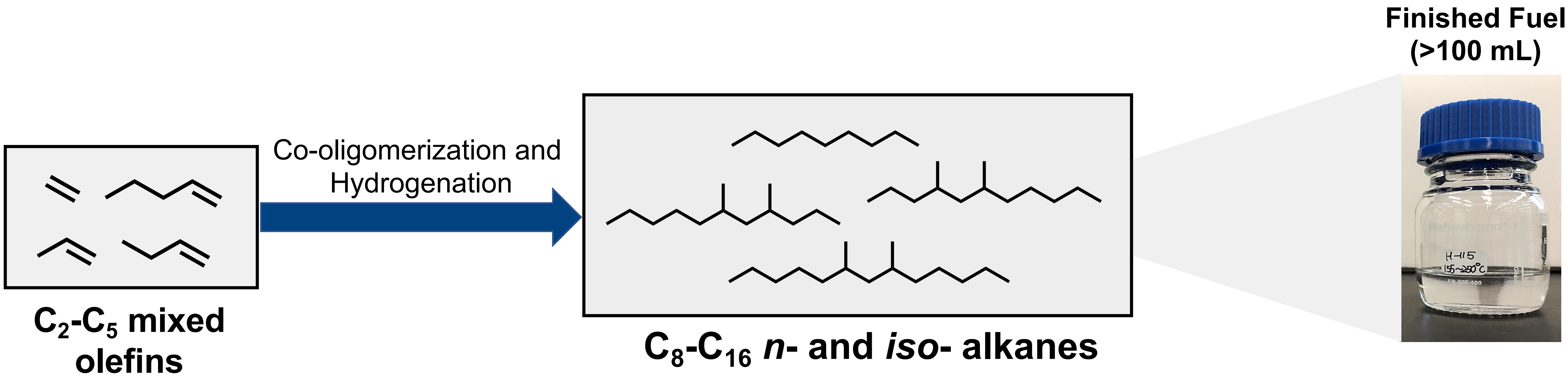


Operating Conditions: *WHSV: 0.8 h^{-1}, Feedstock: equimolar C_2-C_5, Pressure: 100 psi, Temperature: 250 - 275 °C*

- Composition of olefin feedstock merely affect ethylene conversion and the selectivity to jet range (C_8-C_{16}) remains the same
- Higher selectivity obtained at lower temperature could be attributed to lower cracking activity
- **Demonstrated co-oligomerization of mixed olefin (C_2-C_5) as feedstock**

2. Progress and Outcome

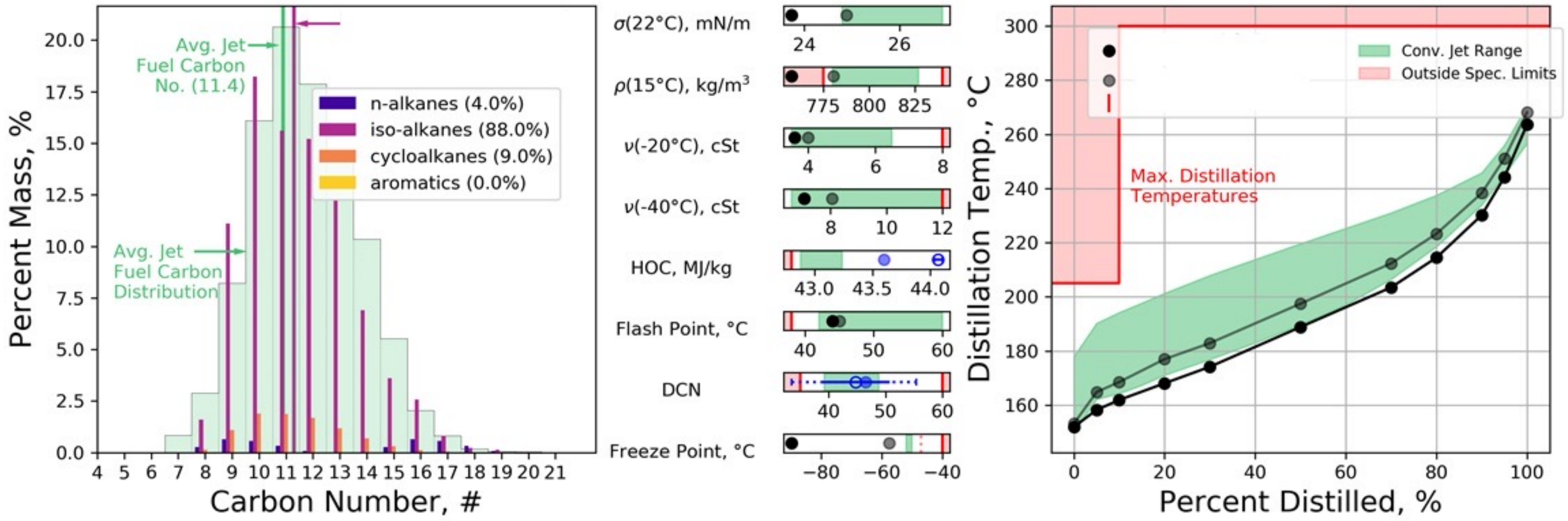
Produced SAF sample >100mL for the fuel property analysis



- Completed the co-oligomerization followed by hydrogenation to generate the finished fuel
- Generated > 100mL of finished fuels to conduct the initial Tier α and Tier β sustainable aviation fuel property analysis at Washington State University

2. Progress and Outcome

Co-oligomerized samples met the Tier α and Tier β fuel property requirements at 50% blend level



- Density of neat fuel low – further adjustment in composition (n-, iso- and cycloalkane) is required
- Properties of jet fuel produced by co-oligomerization process meeting Tier α and Tier β ASTM standard at ≥50% blend level

2. Progress and Outcomes

Research progress and timeline

Start — End

October 2021 — September 2024

FY22: Optimization hybrid and /or sequential catalyst to demonstrate co-oligomerization of mixed olefins (C_2-C_5) to produce ~75% jet range compounds.

- Developed sequential catalyst containing both metal and acid sites and demonstrated co-oligomerization
- **Successfully completed Go/No-Go**

FY23: Demonstrate 100 h time-on-stream using an integrated reactor system (metal and acid catalyst bed) and fuel properties meeting Tier α and Tier β ASTM standards, and complete process analysis

- Catalyst deactivation – spent catalyst characterization
- Fine tuning catalyst structure and process parameters – improve catalyst lifetime
- Detailed process analysis

FY24: Engineered catalyst development, process integration, and demonstration

- Synthesize powdered catalyst and provide to industrial partner
- Engineered catalyst testing and demonstration

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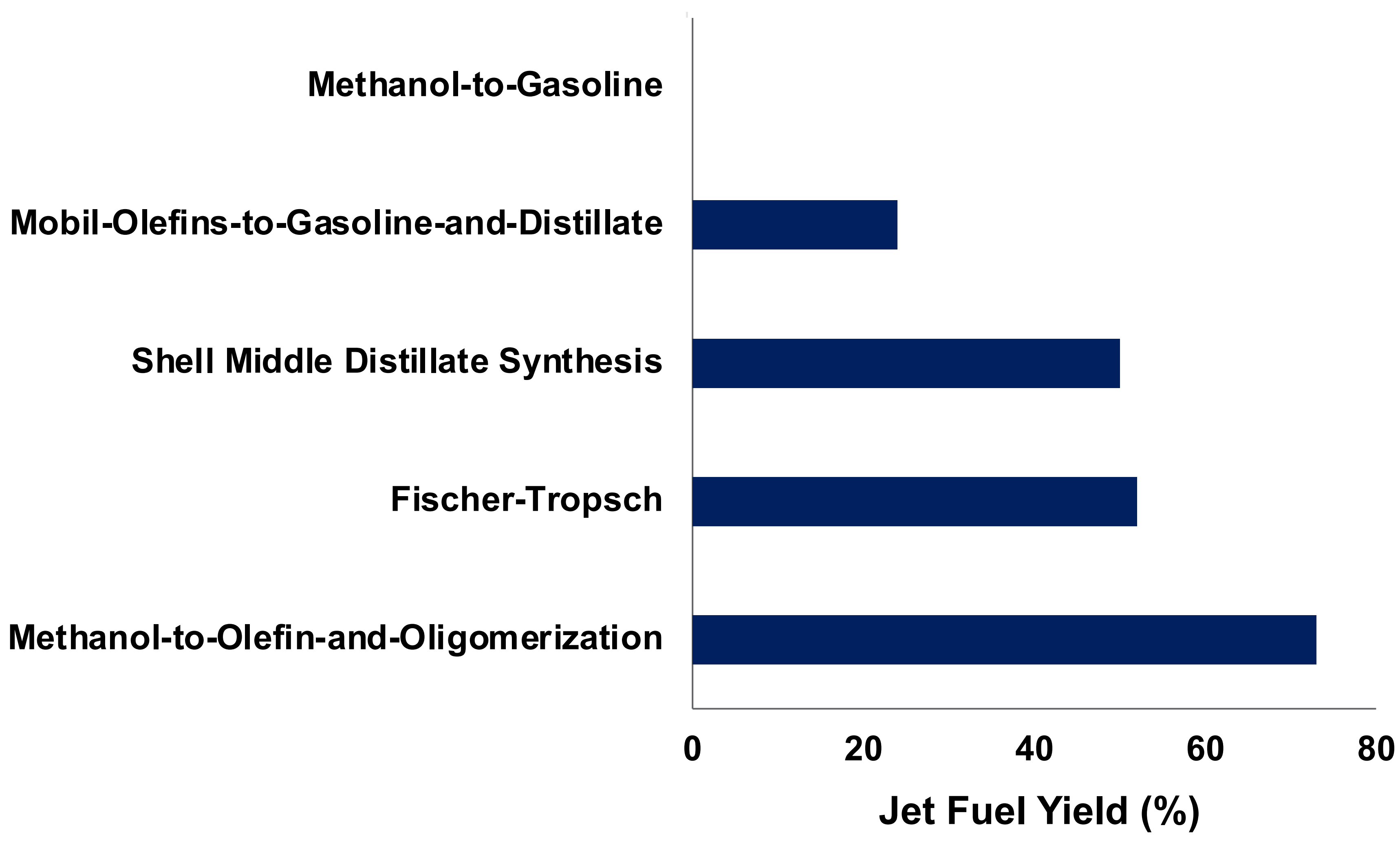
3. Impact

Supports near term decarbonization of aviation industry by maximizing SAF yield

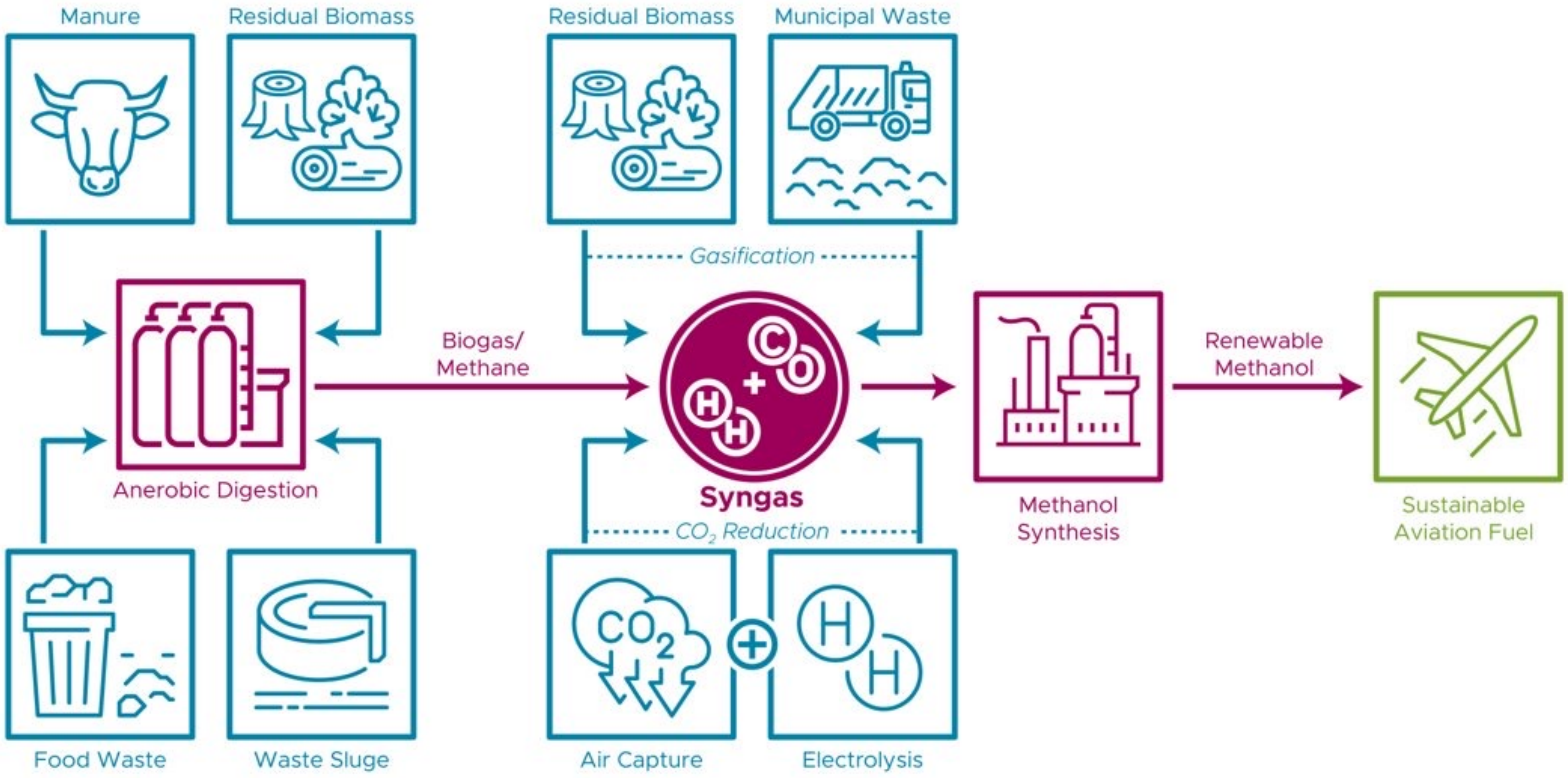


Jet fraction (SAF) yield from the major syngas conversion technologies compared to the Methanol-to-Olefin-and-Oligomerization (this work).

- **Maximize** the carbon efficiency from syngas to **SAF** and reduce/ eliminate the other fuel fractions
- Leverage **existing commercial process** for the transformation of **syngas intermediate to produce SAF**
- Potential to de-risk and **integrate the unit operations at a rapid rate** to support the aviation industries net zero emission goals
- **Industrial institution** interest (to convert methanol to SAF

3. Impact

Supports the long-term aviation industry decarbonization goals



- Syngas obtained from waste source (e.g., MSW) can potentially provide ~65% of the global aviation fuel requirement by 2050
- Renewable electricity can enable the CO_2 conversion to syngas and then to SAF – further increase the global SAF contribution by 2050

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Summary

Enable the technology towards commercialization

Overview	Develop a C_2–C_5 co-oligomerization catalyst and demonstrate an efficient pathway to produce sustainable aviation fuel (SAF) from syngas via a mixed olefin intermediate
Approach	Developing catalyst that enables integrating both metal and acid catalysis pathways which are key to facilitate co-oligomerization of C_2 and C_{3+} to produce SAF
Impact	Demonstrated co-oligomerization process with mixed olefins (C_2-C_5) as feedstock to produce jet range hydrocarbons – Meeting Tier α and Tier β standard at ≥ 50% blend level
Progress & Outcome	Developed the hybrid catalyst system and optimized reaction condition to achieve C_2–C_5 co-oligomerization with ≥75% selectivity to jet range (C_8–C_{16}) products
Future Work	Demonstrate co-oligomerization to produce jet range product with catalyst lifetime >500 h using engineered catalyst

Quad Chart Overview

Timeline

- Project start date: October 2022
- Project end date: September 2025

	FY 22	Total Award
DOE Funding	$530,000	$1,630,000 (FY 2022-2024)
Project Cost Share*	NA	NA

TRL at Project Start: 2
TRL at Project End: 4

Project Goal:

Develop sustainable aviation fuel (SAF) production process from syngas derived mixed olefins and demonstrate the commercial path to achieve 70% reduction in greenhouse gas emissions.

End of Project Milestone:

Production of 1 L of finished jet fuel from syngas derived mixed olefins with fuel properties meeting Tier α and Tier β standard and completion of 500 hours continuous operation (with intermittent regeneration) using engineered catalysts with >75% yield to fuel-range products.

Funding Mechanism: AOP *Lab Call*

Project Partners

- Washington State University
- Topsoe

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Acknowledgement

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Thank you

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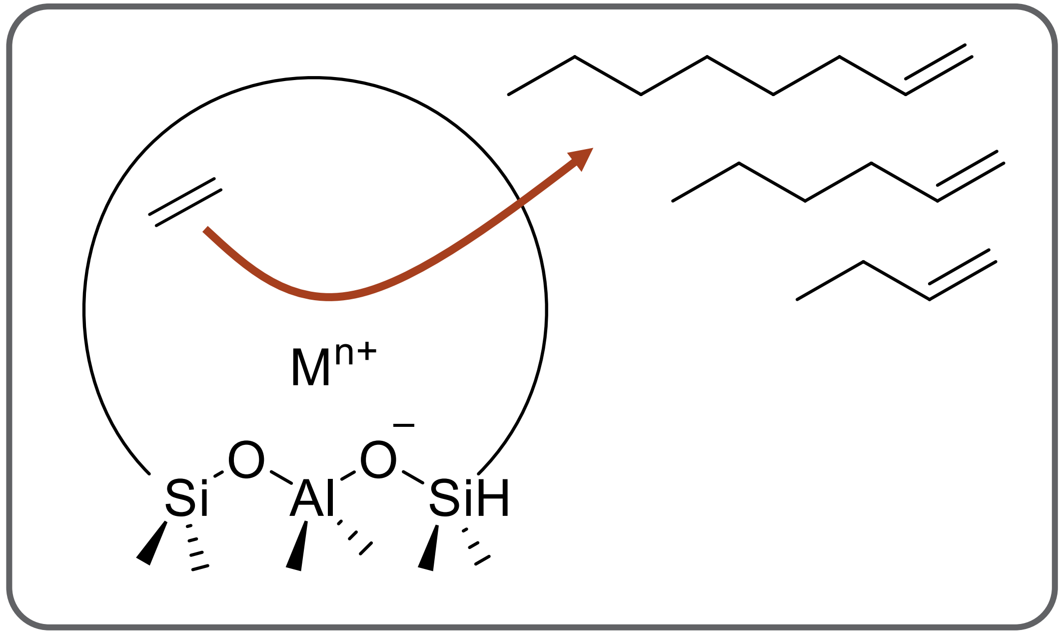
C_2 oligomerization



C_{3+} oligomerization