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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

1-Approach

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.
1-Approach (Project Management)

Integrated work between PNNL, WSU and Haldor Topsoe

- 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
- Detailed analysis of fuel properties
- 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
1 – Approach (Project Management)

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**
2. Progress and Outcome

Construction of new reactor system that handles multiple olefin feed

- Constructed new reactor systems to carry out co-oligomerization of C₂-C₅ mixed olefins
2. Progress and Outcome

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

- Co-oligomerization of ethylene ($\text{C}_2^-$) and propylene ($\text{C}_3^-$) using the baseline metal catalyst at varying temperature in a plug flow reactor system

- Products obtained from $\text{C}_2^-$ and $\text{C}_3^-$ co-oligomerization are primarily between $\text{C}_4$-$\text{C}_6$ range with $\text{C}_5$ being the major project

- Significant **cross oligomerization** between $\text{C}_2^-$ and $\text{C}_3^-$ with minimal chain growth

- **Outcome:** Optimized metal composition and loading for co-oligomerization of $\text{C}_2^-$ and $\text{C}_3^-$
2. Progress and Outcome

Sequential catalyst bed is active and selective to the oligomerized products

- 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

**Operating Conditions:** WHSV: 0.8 h$^{-1}$, Feedstock: equimolar C$_2$-C$_3$, Pressure: 100 psi, Temperature: 275 °C
2. Progress and Outcome

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

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.

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**Sequential:**
Metal followed by acid catalyst
2. Progress and Outcome

Demonstrated the sequential catalyst bed system with high selectivity and activity

- >90% conversion of both ethylene and propylene; >75% selectivity to jet range (C₈-C₁₆) olefins
- Stability of the sequential catalyst system—~ 50 h continuous time on stream

Operating Conditions: WHSV: 0.8 h⁻¹, Feedstock: equimolar C₂-C₃, Pressure: 100 psi, Temperature: 275 °C
2. Progress and Outcome

Co-oligomerization of mixed olefins (C₂-C₅) performs similar to the C₂-C₃

<table>
<thead>
<tr>
<th>Ethylene conversion (%)</th>
<th>Selectivity to jet (C₈-C₁₆) products (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed - C₂/C₃ (equimolar)</td>
<td>Feed - C₂/C₃/C₄/C₅ (equimolar)</td>
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<tr>
<td>80</td>
<td>80</td>
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<tr>
<td>60</td>
<td>60</td>
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<td>40</td>
<td>40</td>
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<tr>
<td>20</td>
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</tbody>
</table>

Operating Conditions: WHSV: 0.8 h⁻¹, Feedstock: equimolar C₂-C₅, Pressure: 100 psi, Temperature: 250 - 275 °C

- Composition of olefin feedstock merely affect ethylene conversion and the selectivity to jet range (C₈-C₁₆) remains the same
- Higher selectivity obtained at lower temperature could be attributed to lower cracking activity
- Demonstrated co-oligomerization of mixed olefin (C₂-C₅) 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 \(\alpha\) and Tier \(\beta\) 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 \(\alpha\) and Tier \(\beta\) ASTM standard at \(\geq 50\%\) blend level
2. Progress and Outcomes

Research progress and timeline

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

**FY24:**
- Engineered catalyst development, process integration, and demonstration
- Catalyst deactivation – spent catalyst characterization
- Fine tuning catalyst structure and process parameters – improve catalyst lifetime
- Detailed process analysis
3. Impact

Supports near term decarbonization of aviation industry by maximizing SAF yield

- **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)

Jet fraction (SAF) yield from the major syngas conversion technologies compared to the Methanol-to-Olefin-and-Oligomerization (this work).
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 $\text{CO}_2$ conversion to syngas and then to SAF – further increase the global SAF contribution by 2050
<table>
<thead>
<tr>
<th>Summary</th>
<th>Enable the technology towards commercialization</th>
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<tbody>
<tr>
<td><strong>Overview</strong></td>
<td>Develop a C\textsubscript{2}–C\textsubscript{5} co-oligomerization catalyst and demonstrate an efficient pathway to produce sustainable aviation fuel (SAF) from syngas via a mixed olefin intermediate</td>
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<td><strong>Approach</strong></td>
<td>Developing catalyst that enables integrating both metal and acid catalysis pathways which are key to facilitate co-oligomerization of C\textsubscript{2} and C\textsubscript{3+} to produce SAF</td>
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<td><strong>Impact</strong></td>
<td>Demonstrated co-oligomerization process with mixed olefins (C\textsubscript{2}–C\textsubscript{5}) as feedstock to produce jet range hydrocarbons – Meeting Tier α and Tier β standard at ≥ 50% blend level</td>
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<td><strong>Progress &amp; Outcome</strong></td>
<td>Developed the hybrid catalyst system and optimized reaction condition to achieve C\textsubscript{2}–C\textsubscript{5} co-oligomerization with ≥75% selectivity to jet range (C\textsubscript{8}–C\textsubscript{16}) products</td>
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<td><strong>Future Work</strong></td>
<td>Demonstrate co-oligomerization to produce jet range product with catalyst lifetime &gt;500 h using engineered catalyst</td>
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Quad Chart Overview

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

<table>
<thead>
<tr>
<th>FY 22</th>
<th>Total Award</th>
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<tr>
<td>$530,000</td>
<td>$1,630,000 (FY 2022-2024)</td>
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DOE Funding

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
Acknowledgement

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- Washington State University: Joshua Heyne, Harrison Yang,
- Topsoe: Pablo Beato, Esben Taarning
- Bioenergy Technology Office: Sonia Hammache

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Thank you
C₂ oligomerization

Mixed olefin feed

C₃+ oligomerization

Highly branched C₆-₁₈