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2.3.3.301 Sustainable Aviation Fuel from Wet Wastes via Hydrothermal Liquification

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Organic Waste Conversion Technology Area

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Process Overview for Hydrothermal Liquefaction (HTL):
Transforming Wet Wastes to Transportation Fuels

HTL Plant

HTL Conditions
330-350°C / 2900 psig / 10-30 min
"Accelerating what the earth does"

HTL
Biocrude

Stable biocrude
60% C-yield
Thermally stable

Hydrotreater

Hydrotreater conditions
400°C / 1500 psig
"Standard refinery unit-op"

Hydrocarbon blendstock
(Diesel, Jet, Naptha)

Fuel Blendstocks
(95%+ C-yield)

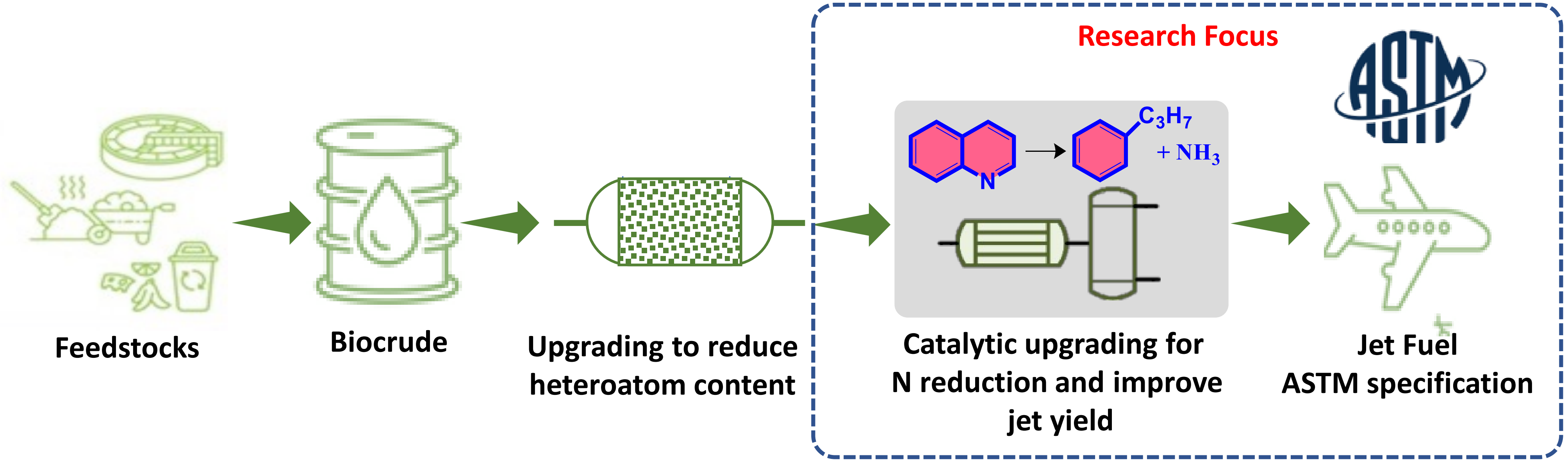
- Conceptually simple (i.e., heated pipe), continuous process for dirty, wet feedstocks
- High carbon yields to liquid hydrocarbons (**~78% GHG reduction**)

Benefit #1: **Potential for ~6 billion gallons/year of transportation fuel from wet wastes**

Benefit #2: **Alternative disposal processes expensive (~$4/gal fuel produced)**

Project Overview: **Producing Sustainable Aviation Fuel via Hydrothermal Liquification of Wet Waste**

- Potential for 1.5B gal/yr of SAF from HTL of wet wastes
  - ~25% in jet range → Hydrocracking could potentially increase this to >4B gal/yr
    - ✓ ~20% 2019 US jet fuel demand
- Jet Fuels (including SAF) have stringent fuel requirements
  - HTL SAF refining has lower TRL compared to HTL



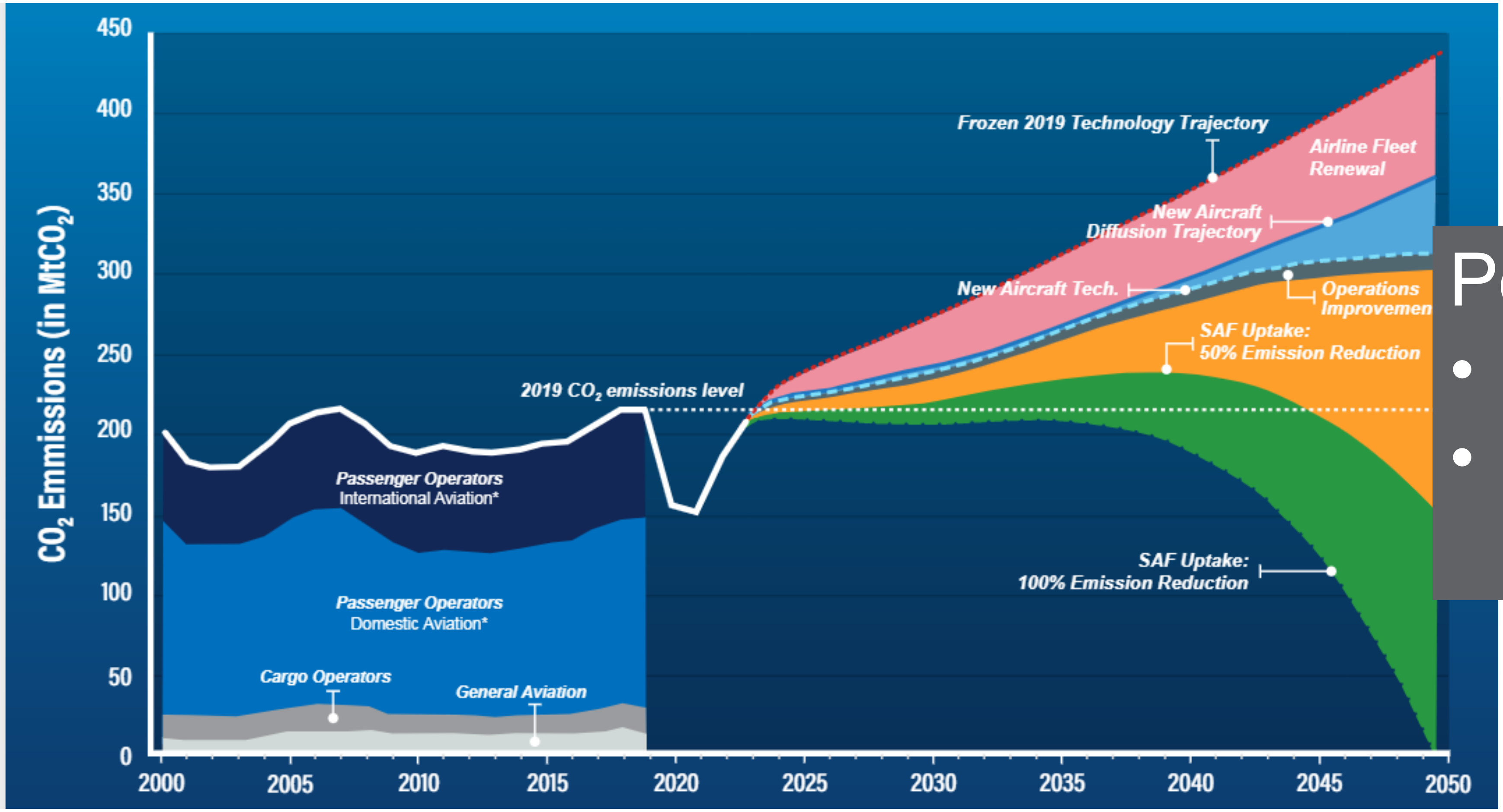
Objective: Address key jet fuel property uncertainties via hydroprocessing

- Denitrogenation (<2ppm N), Thermal Stability, Tier α and Tier β analysis

Project importance:
Significant SAF volumes from wet wastes possible

Liquid transportation fuels are needed to decarbonize aviation transport

- Long distances/ weight limits electrification
- Existing fleet designed for liquid fuels and will take decades to replace



Potential SAF production:

- 1.5B gal/yr
- 4B gal/yr with cracking
  - >20% of 2019 US demand

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1 – Approach:
External input used to guide research needs

PNNL-31930 | Date: 09-16-2021

Hydrothermal Liquefaction: Path to Sustainable Aviation Fuel

November 17–19, 2020, Virtual Workshop in ZOOM Platform

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Key feedback from HTL SAF workshop:

Hydrodenitrogenation (HDN) is a significant concern for SAF from HTL of wet wastes

1 – Approach:
Jet fuel must meet detailed specs for safety

Assess Commercial Viability and Barriers

Aircraft and engines are certified for fuel (e.g., Jet A/A-1)
- A new SAF blend from HTL must be compatible with all infrastructure
- If not equivalent, it would require all new infrastructure and certifications

Engine Limitations

Aircraft Limitations

Aircraft Operator Limitations

ASTM INTERNATIONAL

Fuel specifications D7566-18

Areas of concern for SAF from HTL of wet wastes:
- High nitrogen content from proteins (Nitrogen: ~2000ppm)
  - All approved SAF pathways have a nitrogen spec of 2ppm
- Thermal stability concerns due to potential Nitrogen-Sulfur interactions

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1 – Approach: **Addressing Risk / Challenges with Defined Objectives and Milestones**

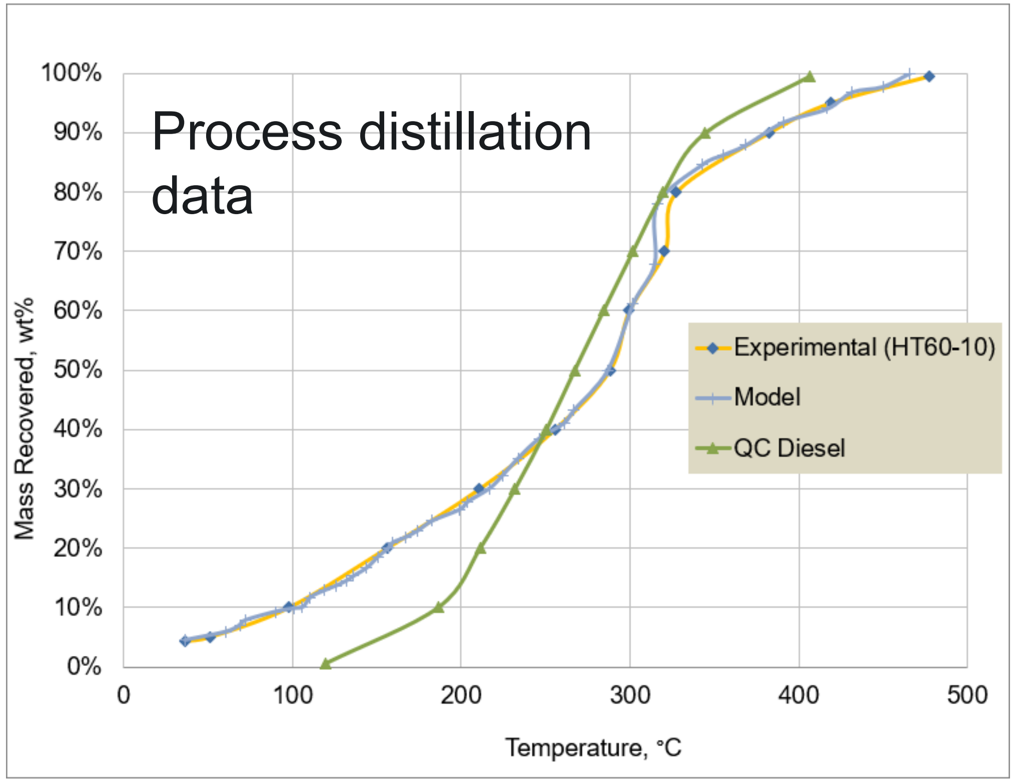
Develop Research Plans

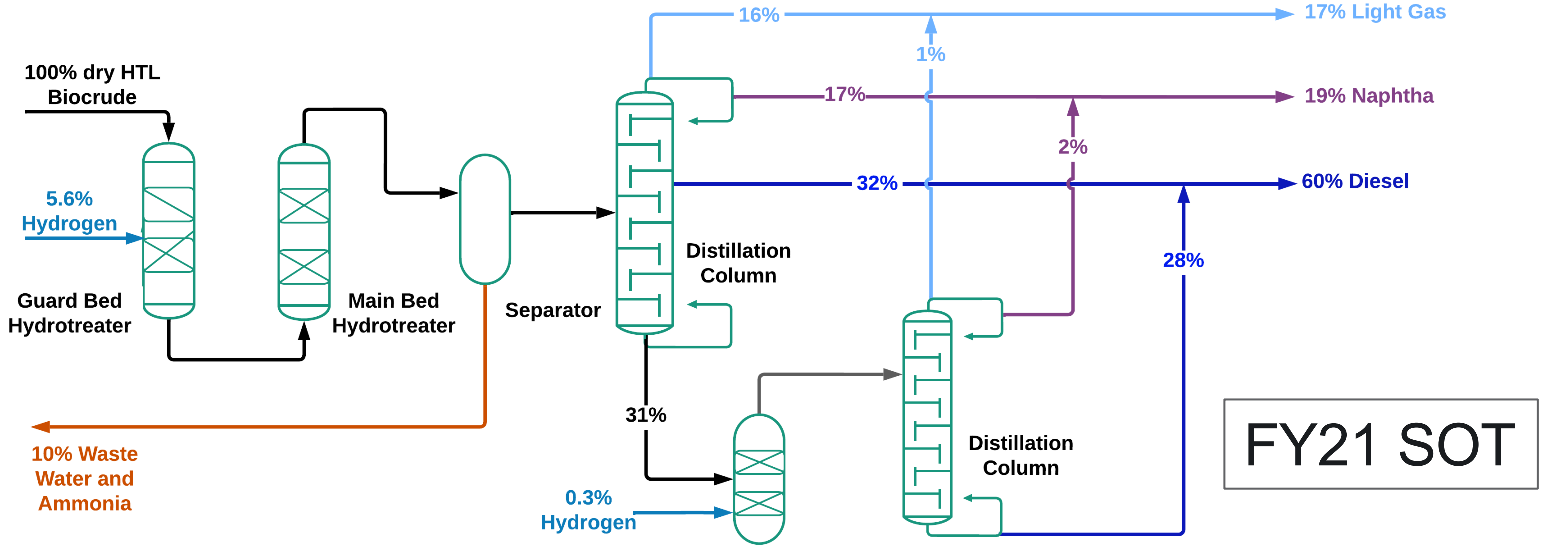
Tasks	Risks / Opportunity	Objectives	
Diversity, Inclusion	*Inclusive culture*	All PI(s) and task leads complete PNNL course Diversity, Inclusion, and Belonging with documentable action	✓
HDN	*Industrially relevant catalysts*	Acquire catalysts from Topsoe for HDN work	✓
HDN	*Deep N reduction*	Achieve nitrogen reduction to <50ppm	✓
Nitrogen and thermal stability analysis	*Meet required fuels properties*	Tier α and β testing on SAF cut with <50ppm nitrogen	On track
Nitrogen and thermal stability analysis	*Nitrogen speciation assessment*	Complete Nitrogen Chemiluminescence Detector (NCD) analysis of SAF for nitrogen speciation	On track
HDN	*Economic viability*	Complete preliminary TEA / LCA to guide the HDN process	On track
Diversity, Inclusion	*Tomorrow's workforce*	Hire a student from an underrepresented group in STEM	On track
Nitrogen and thermal stability analysis	*Fuel stability*	Conduct the thermal stability of the HTL -derived fuel compared to that of the conventional fuel (FY24)	On track
HDN	*Process viability*	Demonstrate the HDN process for >1000-hour stability while maintaining the N levels <2 ppm (FY25)	On track

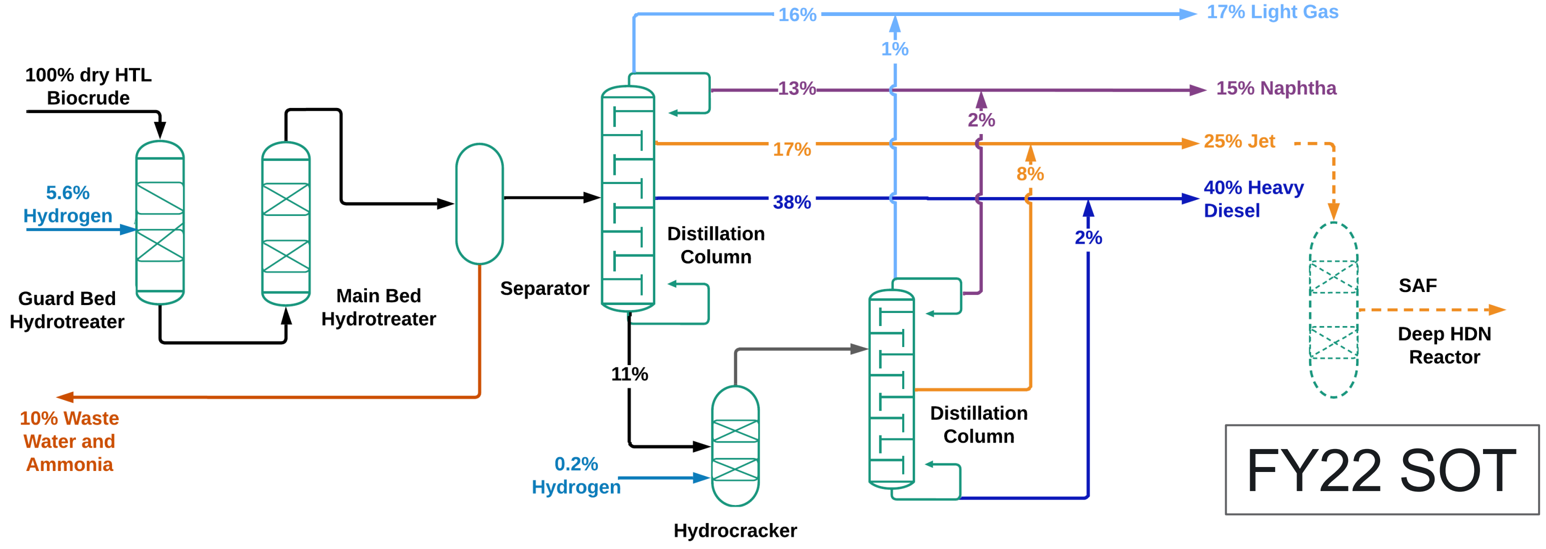
1 – Approach: **Execute Targeted Research Aligned to Commercial Embodiment**

Execute Targeted Research → Incorporate Learnings in State of Technology

Experimental data is incorporated into process design for TEA assessment





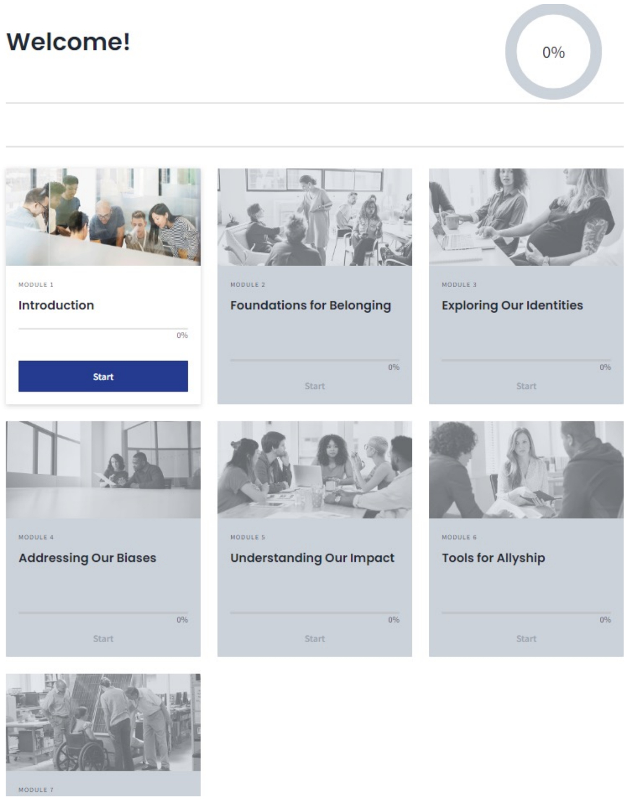


Incorporating **SAF production** in SOT updates (FY22 includes deep HDN step)

1 – Approach:
Diversity, Equity, and Inclusion Plan

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

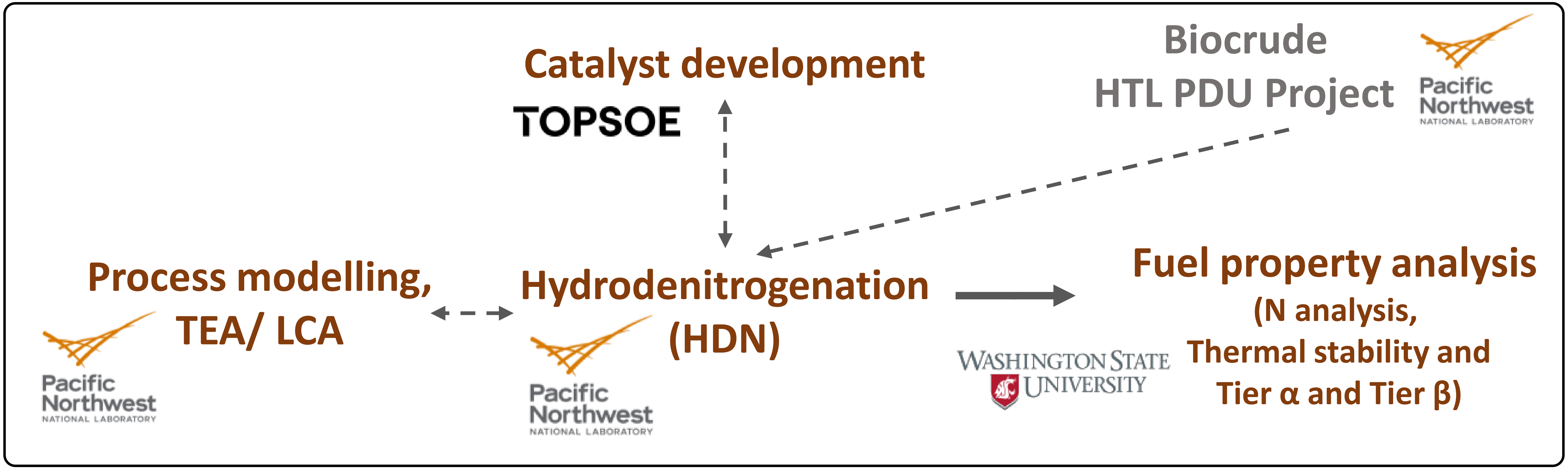
PI and task leads on this project completed PNNL course Diversity, Inclusion, and Belonging with documentable action



<u>Outcomes:</u>

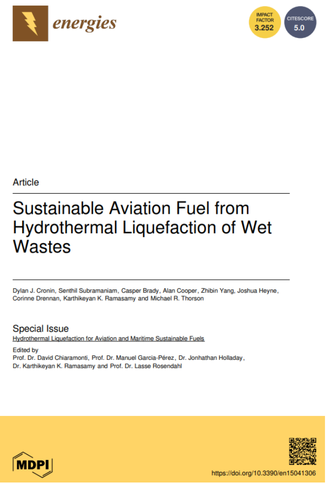
- Hired a Chemical Engineering Bachelor student through PNNL's EEDIP program
  - Student is planned to participate in fuel characterization activities
- All PI's and task leads completed training on Diversity, Inclusion and Belonging

1 – Approach:
Integrated workflow between PNNL, WSU and Topsoe

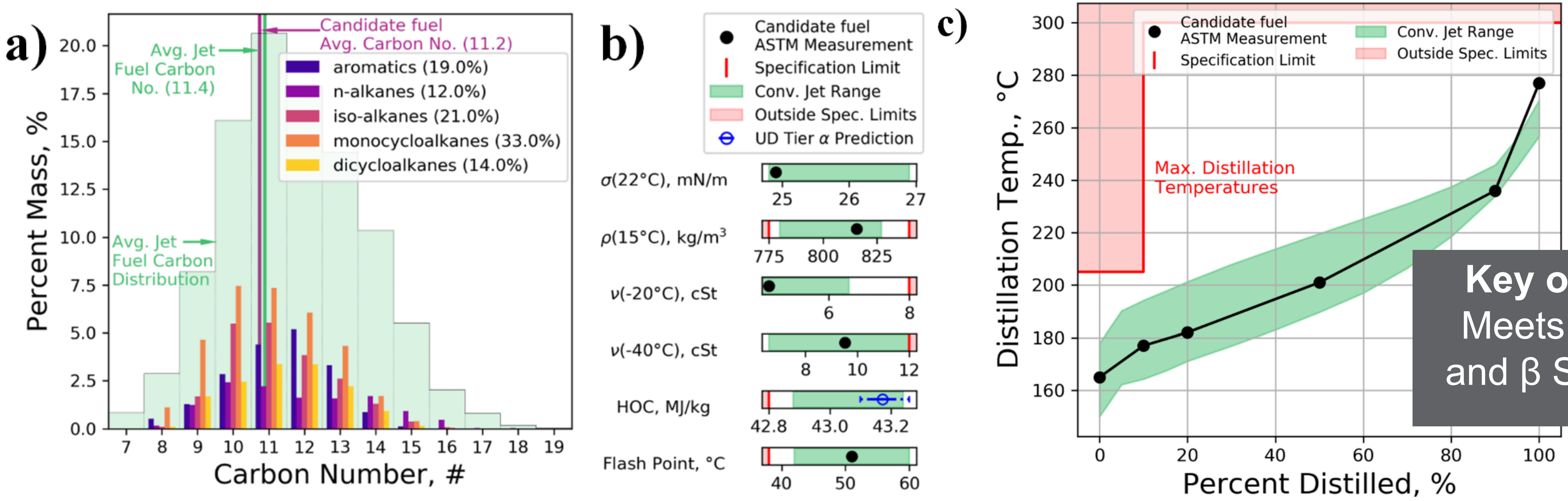


Integrated workflow and handoff points between the partners based on the core capability and technical expertise

2 - Progress and Outcomes:
HTL of Wet Wastes Meets Tier α and β Specs



- ~25% of upgraded fuel in jet range
- Similar mix of cycloalkanes, n-alkanes, iso-alkanes, aromatics to traditional jet
  - Cycloalkanes and aromatics necessary to allow higher fuel penetration
- Positive Tier α and β jet fuel properties[1]

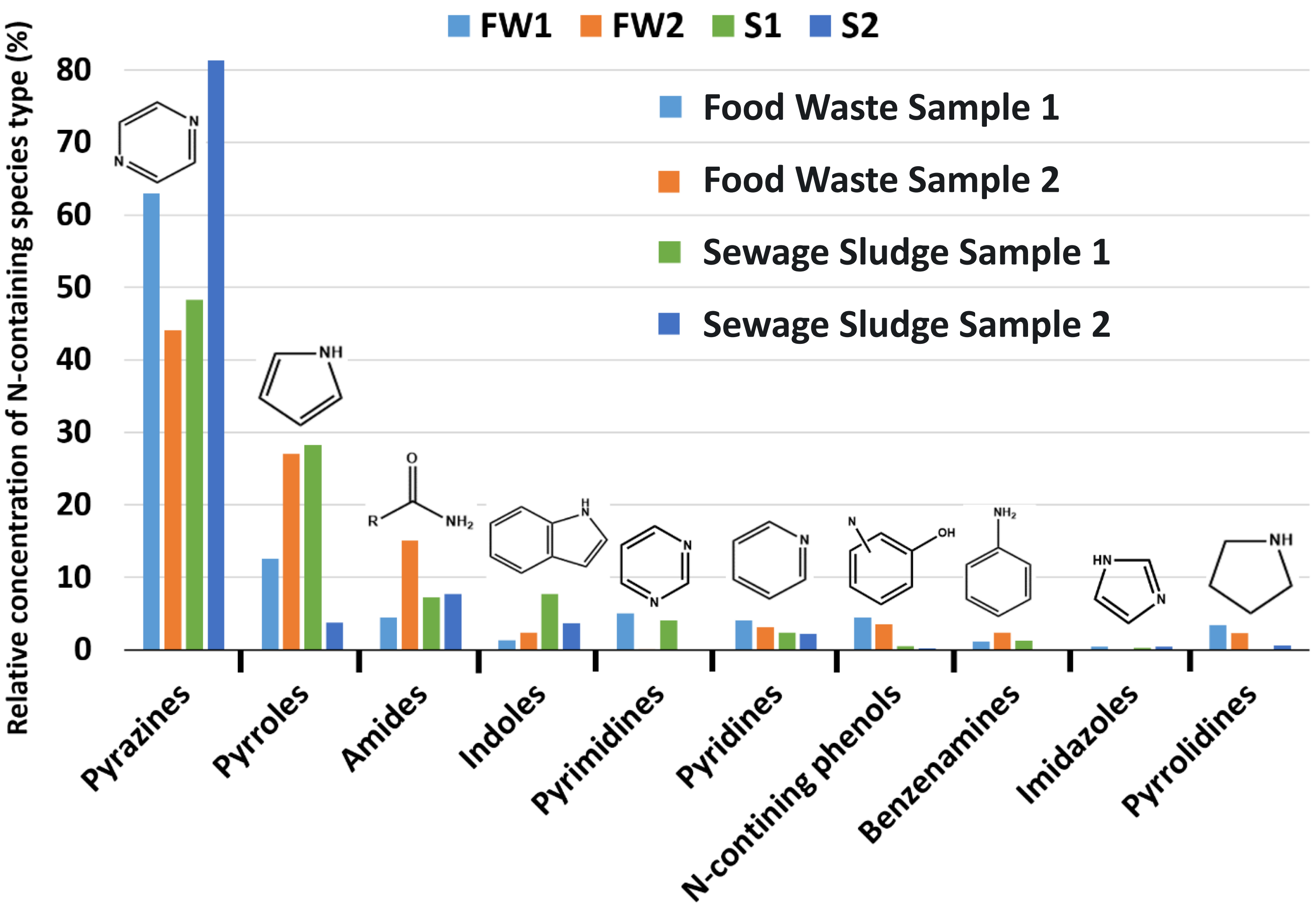


Key outcome:
Meets all Tier α and β SAF specs

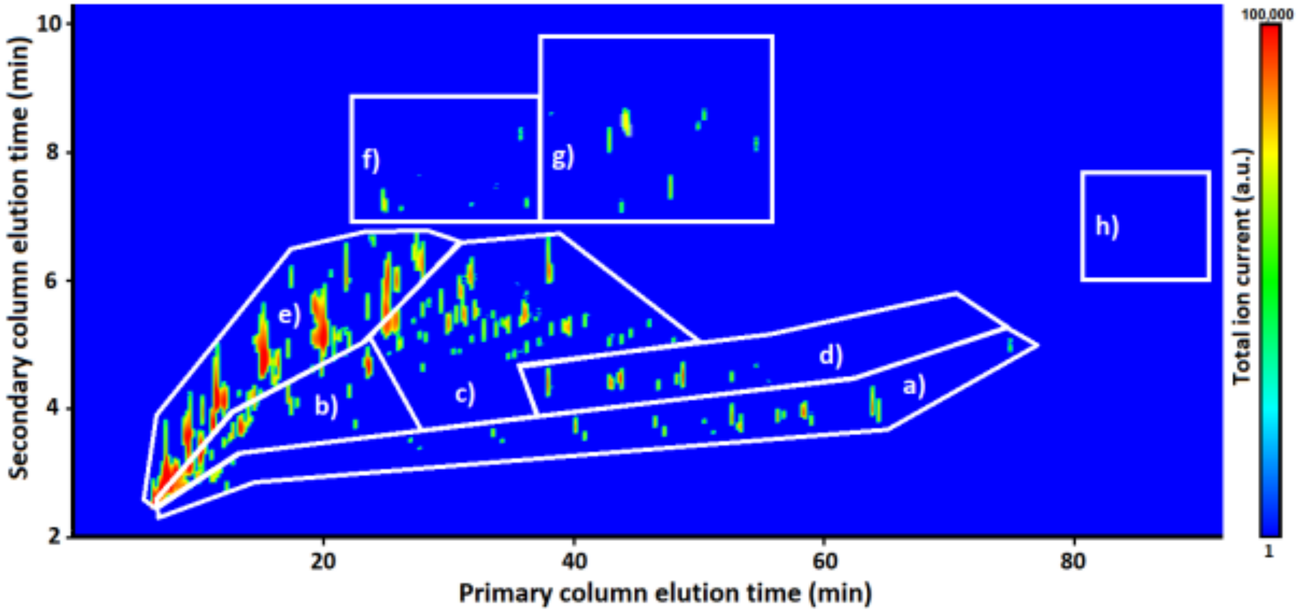
[1]Cronin, D. J., Subramaniam, S., Brady, C., Cooper, A., Yang, Z., Heyne, J., ... & Thorson, M. R. (2022). Sustainable Aviation Fuel from Hydrothermal Liquefaction of Wet Wastes. *Energies*, 15(4), 1306.

2 – Progress and Outcomes:
Identified the major Nitrogen-species in Biocrude

Biocrude is rich in Pyrazines, pyrroles, amides, indoles, etc.* as identified via GC/GCMS



GCxGC MS for speciation of N-compounds



Challenges for SAF:

- Nitrogen spec: <2ppm (expected)
- Concern with Nitrogen-Sulfur interactions that can lead to fuel instability issues in engine

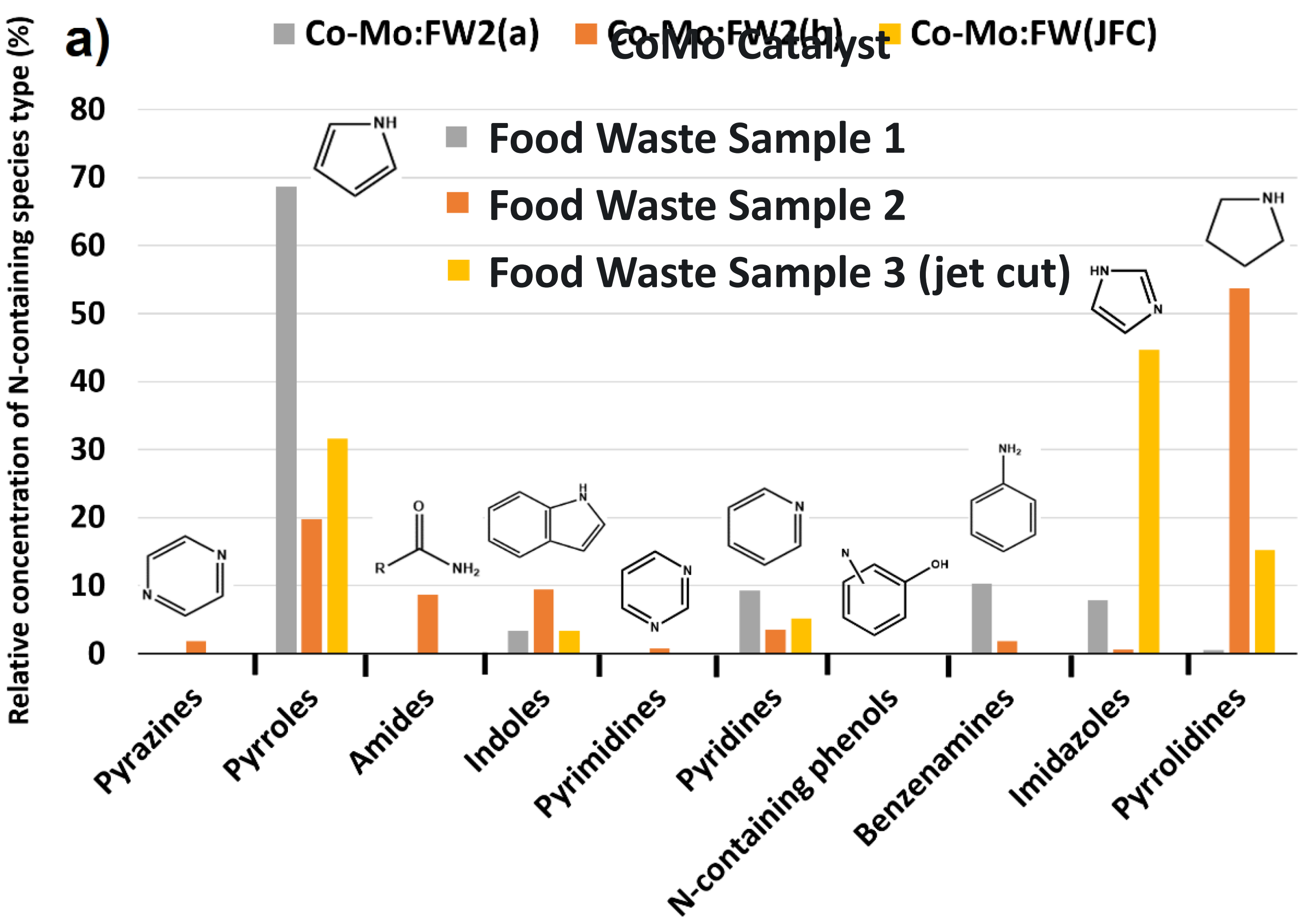
[1]Cronin, D. J., Subramaniam, S., Brady, C., Cooper, A., Yang, Z., Heyne, J., ... & Thorson, M. R. (2022). Sustainable Aviation Fuel from Hydrothermal Liquefaction of Wet Wastes. *Energies*, 15(4), 1306.

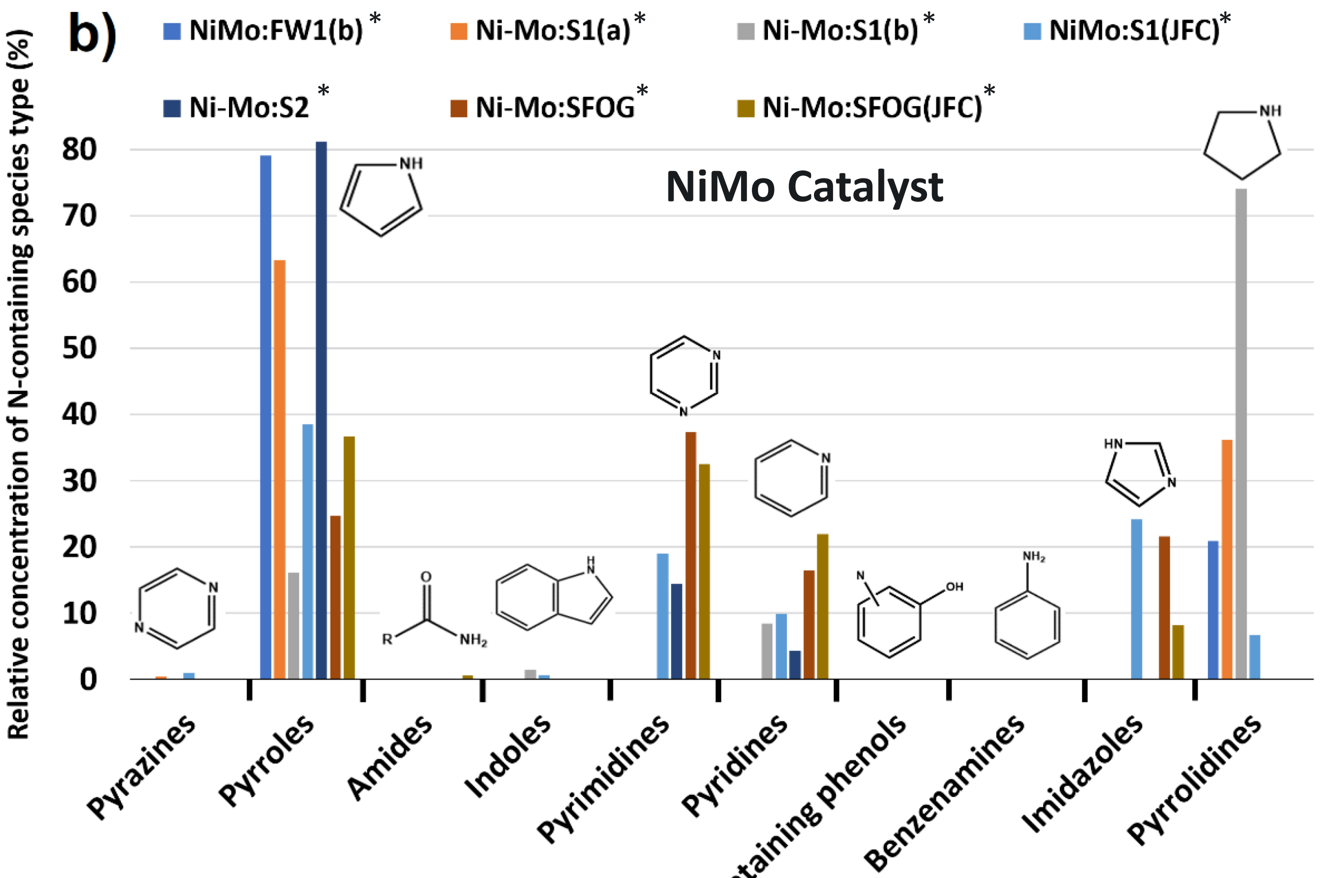
*Significant amount of the biocrude does not volatize in the GCxGCMS

2 – Progress and Outcomes:
Identified the challenging N-species in Biocrude

- Most challenging species to hydrotreat are the Pyrroles, Imidazoles, Pyrrolidines
- Will pursue further HDN to get to 2ppm N⁺

Hydrotreating conditions:
~400°C / ~1500 psi / ~0.5hr^{-1} WHSV
Result: ~97% Nitrogen reduction





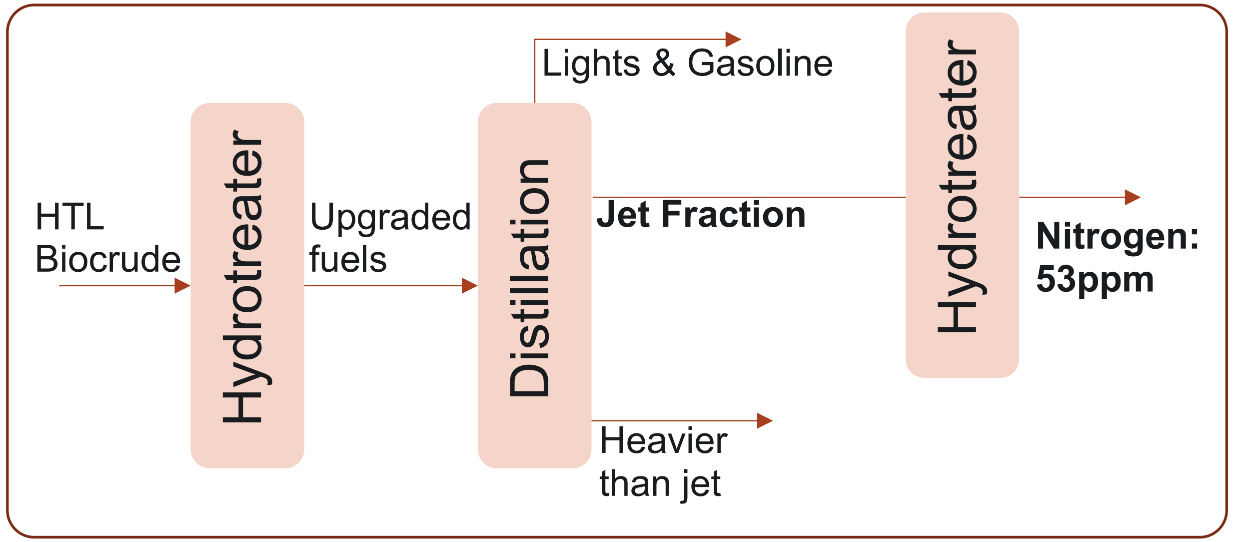
*FW: Food Waste, S: Sewage Sludge, SFOG: Sludge/FOG blend, JFC: Jet Fuel Cut

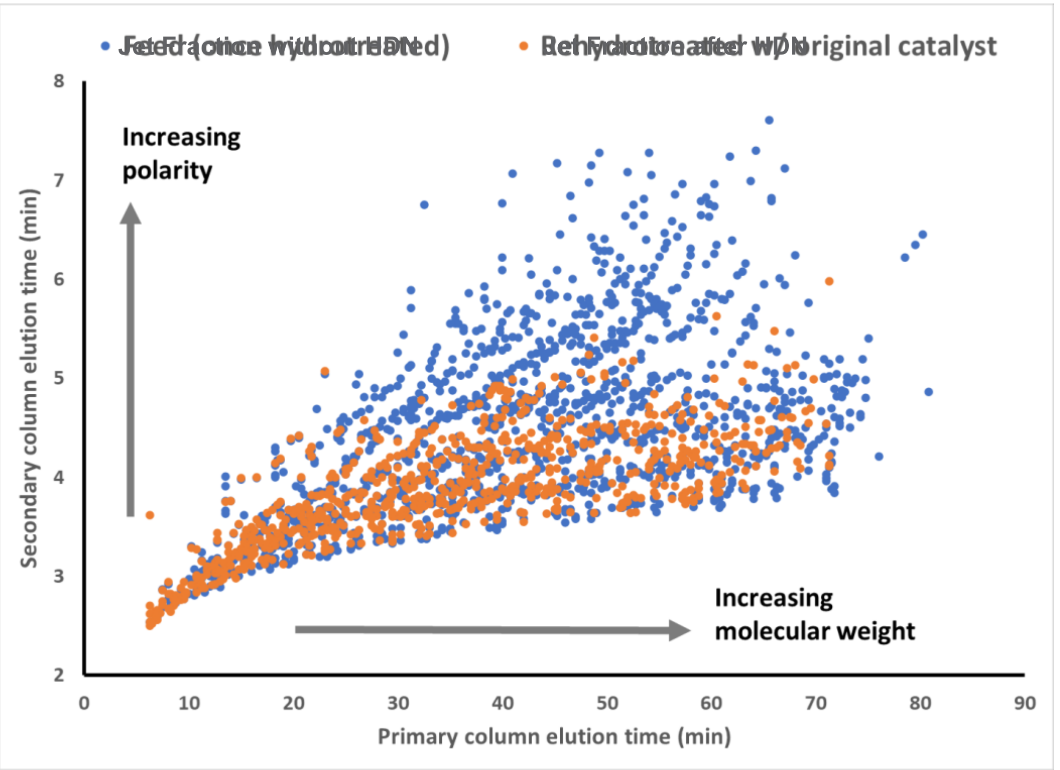
⁺ 2ppm N is the project goal based on the level achieved via other SAF pathways

2 – Progress and Outcomes

Reduced the Nitrogen Content in SAF to 53 ppm

- Reduce the N content to 53 ppm
  - 2-stage hydrotreating: 0.5 hr^{-1}, 400°C, 1500 psi
    - ✓Stage 1: ~60,000 ppm to 5100 ppm
    - ✓Stage 2: 5100 ppm to 53 ppm
- Estimated additional cost only $0.04/gge





Promising start: Initial data gives us confidence in the ability for further N reduction

Next step: Understand the impact of N on fuel thermal stability

3 – Impact: **Gathering crucial property data before HTL SAF specs are developed**

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Assess Commercial Viability and Barriers

Subset of Jet Fuel Specifications	Jet A	FT-SPK	SPK-HEFA	SPK/A	ATJ-SPK
Sulfur, mg/kg	**3000**	15	15	15	15
Nitrogen, mg/kg	**No spec**	**2**	**2**	**2**	**2**
Flash point, °C	38	38	38	38	38
Density, kg/m^3	775-840	730-770	730-772	755-800	730-770
Freezing pt, °C	-40	-40	-40	-40	-40
Thermal stability, mm Hg	**25**	**25**	**25**	**25**	**25**
Distillation residue, %	1.5	1.5	1.5	1.5	1.5
Acidity, mg KOH/g	0.1	0.015	0.015	0.015	0.015
Aromatics, vol%	25/26.5	0.5	0.5	20	0.5

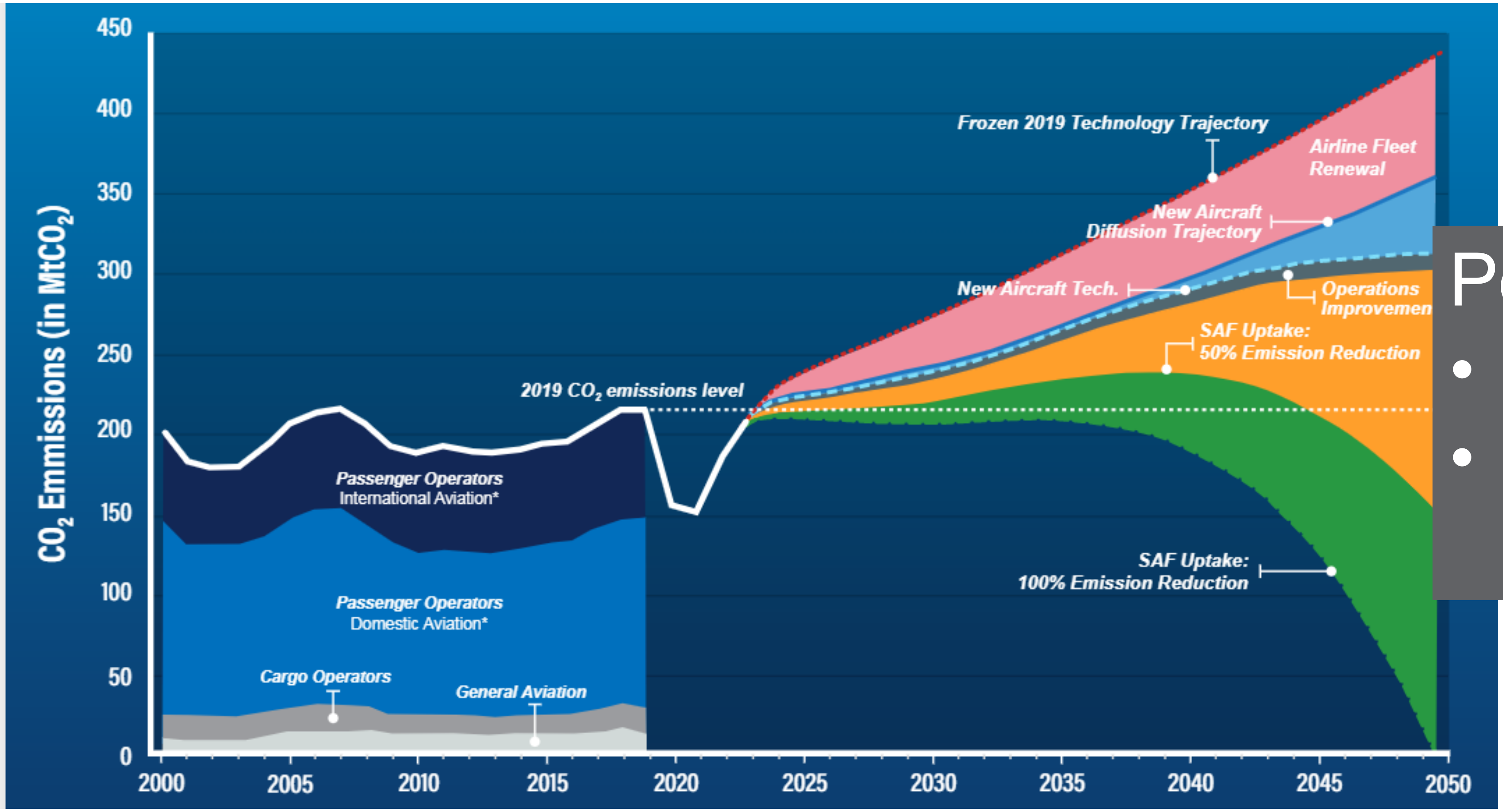
Addressing uncertainty regarding SAF from HTL of wet wastes:

- The impact of N on fuel stability in SAF derived from HTL
- The technical challenges with deep denitrogenation
- Addressing the technical uncertainty regarding the need for reduced N

Project importance:
Significant SAF volumes from wet wastes possible

Liquid transportation fuels are needed to decarbonize aviation transport

- Long distances/ weight limits electrification
- Existing fleet designed for liquid fuels and will take decades to replace



Potential SAF production:

- 1.5B gal/yr
- 4B gal/yr with cracking
  - >20% of 2019 US demand

3 – Impact: **HTL solves two crucial challenges to society:** *Sustainable Aviation Fuel & Sewage Sludge Disposal*

Value #1: Low GHG fuels

- Potential for 1.5 to 4B gal/year of SAF
- 81% reduction in GHG

Value #2: Sludge disposal

- Sludge disposal represents ~50% of wastewater costs
- Provides destruction of forever chemicals
- Costs expected to continue to increase as land application becomes illegal

3.1 M gal fuel/yr[2]
$12.4M/yr

Two potential revenue streams
Example:100 dry tons/day plant

HTL provides a disposal solution in addition to sustainable fuel production

Offset sludge disposal costs[1]:
$7.3-14.6M /yr

[1]Basis of disposal costs: $200-400/dry ton or $40/wet ton @ 10-20 wt% solids, [2]Assumed fuel value of $4/gal

Quad Chart Overview

Timeline

- Original Project start date: Oct 1, 2022
- Project end date: Sept 30, 2025

	FY 22	Total Award
DOE Funding	$0	$1,150,000 (FY23-FY25)
Project Cost Share*	$0	$0

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

Project Goal

This project will determine the impact of N on fuel stability in SAF derived from HTL and develop a pathway to reduce the N content to <2ppm.

End of Project Milestone

Demonstrate hydrodenitrogenation (HDN) with over 1000 hours of stable operation while maintaining the Nitrogen levels in the fuels <2 ppm.

Funding Mechanism

Lab Call

Project Partners

- Topsoe
- Washington State University

*Only fill out if applicable.

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Summary
Enable SAF production via HTL of wet wastes

Overview	• Determine the impact of N on fuel stability in SAF derived from HTL • Develop a pathway to reduce the N content to <2ppm
Approach	• Close partnership with industry, TEA and resource assessment teams to prioritize and target research • SMART milestones to ensure successful impact
Progress and Outcome	• Well defined partnership with catalyst manufacturer and fuel testing experts • Detailed characterization of the nitrogen species in jet cut • Promising preliminary
Impact	• Wet-waste feedstocks have the potential to produce 1.5-4.0B gal/y of SAF from wet-wastes • >20% of 2019 US aviation demand
Future Outcomes	• Achieve deep denitrogenation (<2ppm N) with an economic impact <$0.04/gge • Assess key jet fuel property for SAF • Assess the impact of Nitrogen on fuel thermal stability

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Acknowledgements

- Beau Hoffman, BETO Technology Manager

Experimental Team:
- Mike Thorson
- Andy Schmidt
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- Sam Fox
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- Igor Kutnyakov
- Matt Flake
- Mariefel Olarte
- Lisa Middleton Smith

Analysis Team:
- Yuan Jiang
- Shuyun Li
- Yunhua Zhu
- Aye Meyer
- Lesley Snowden-Swan

Waste Resource Team:
- Tim Seiple
- Andre Coleman

Additional Slides

Publications, Patents, Presentations, Awards, and Commercialization

Publications / Presentations:
None → the project kicked-off in FY23

Commercialization Efforts:
1. Metro Vancouver is building a demonstration HTL plant based on PNNL's technology
2. Aloviam is scaling up the HTL process via an awarded FOA

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Thank you