U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

BIOENERGY TECHNOLOGIES OFFICE

BIOPROCESSING SEPARATIONS CONSORTIUM

Adsorptive De-Nitrogenation (A-DN) to enable SAF pathway (Task 2.6)

BETO 2023 Project Peer Review

Performance-Advantaged Bioproducts and Bioprocessing Separations

April 6, 2023

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Argonne NATIONAL LABORATORY | BERKELEY LAB | Los Alamos NATIONAL LABORATORY | NREL NATIONAL RENEWABLE ENERGY LABORATORY | OAK RIDGE National Laboratory | Pacific Northwest NATIONAL LABORATORY

Overview of HTL pathway to decarbonize transportation sector

Hydrothermal Liquefaction (HTL) Overview: A promising pathway for wet-wastes

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

Stable biocrude
60% C-yield
Gravity-separable
Thermally stable

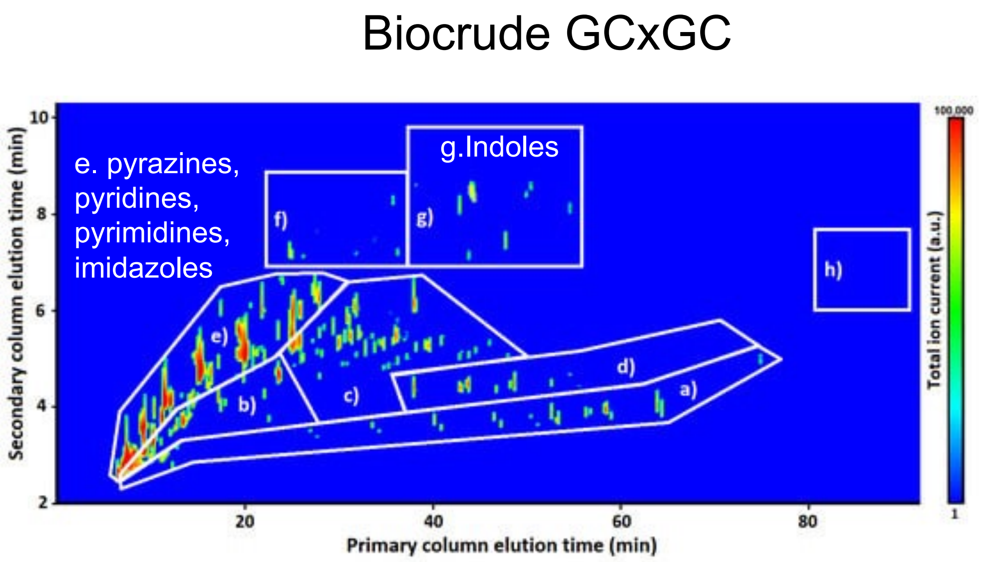
Hydrotreater
400°C / 1500 psig
"Standard refinery unit-op"

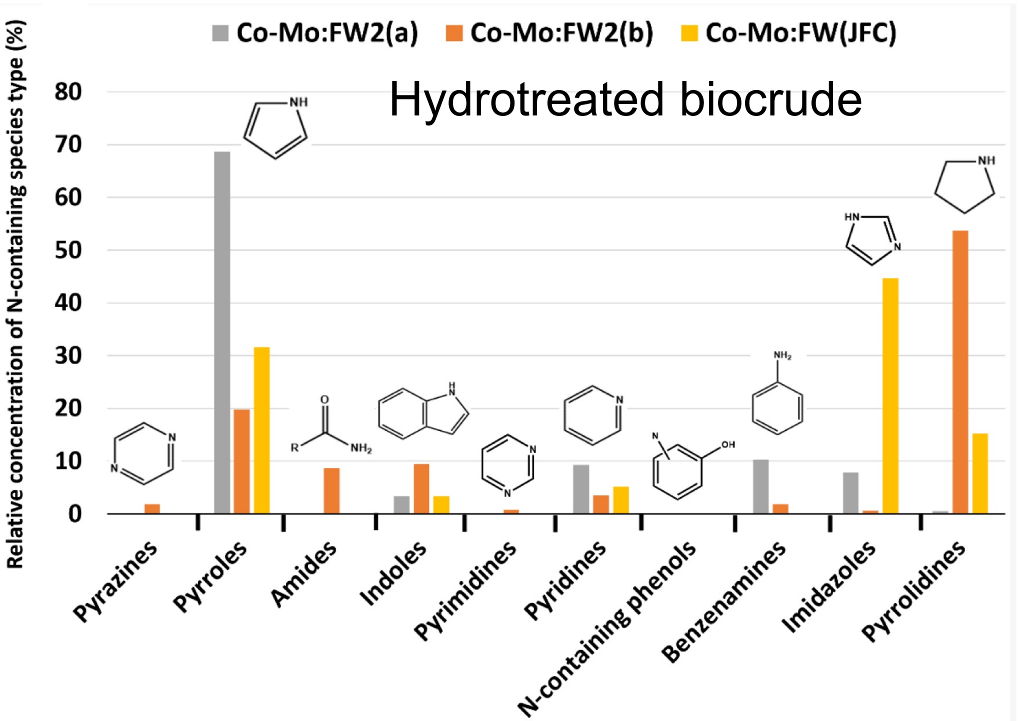
Fuel Blendstocks
(95%+ C-yield)

- ❑ Hydrothermal liquefaction provides a straightforward approach to producing *3.9 billion gal/y of SAF (>20% of 2019 US aviation demand) from wet wastes with >70% GHG reduction at $3.15/gge (projected cost per SOT 2022)
- ❑ Barrier for SAF deployment: SAF requires <2ppm N final content.

*3.9 billion g/y assumes additional SAF from cracking of the heavies from hydrotreater

Overview of N-species in SAF from upgraded biocrude





- N is a challenge for all protein bearing feedstocks (algae, manure, food, sludge)
- N in hydrotreated biocrude consist of large variety of nitrogenated compounds:
  - Amides and amines, but also non-basic and more refractory indoles, pyridines, pyrimidines, imidazole.
  - State of technology for removing N requires harsher operating condition with H_2 and high temperature and pressure – higher yield losses from undesired cracking*.

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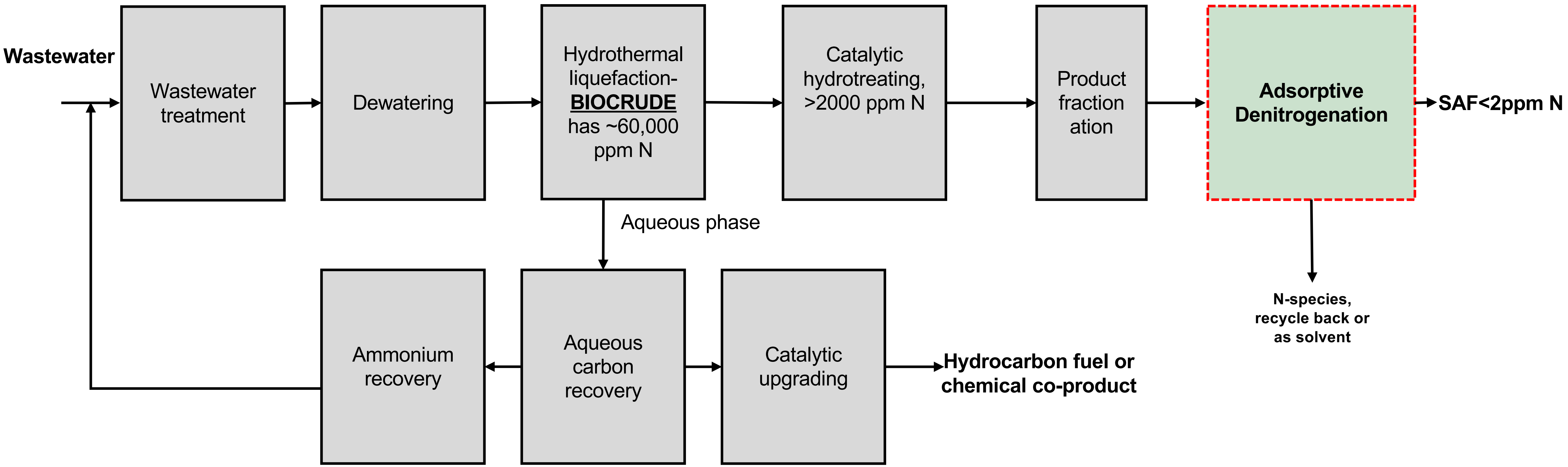
*Cronin, D. J et al. Energies 2022, 15 (4), 1306.

1- Approach:
Adsorptive Denitrogenation (A-DN)

Wet Feedstocks to Fuels/Products via High-Temperature Conversion



A-DN as an alternative to deep hydro-denitrogenation (HDN), is less severe and a more selective process.

1- Approach:
Adsorbent system development

Selective sorbent development- PNNL

Identify a selective sorbent system with high affinity and capacity for sorption of target N-molecules (Pyridine, indoles)

Adsorption cycle- PNNL & ORNL

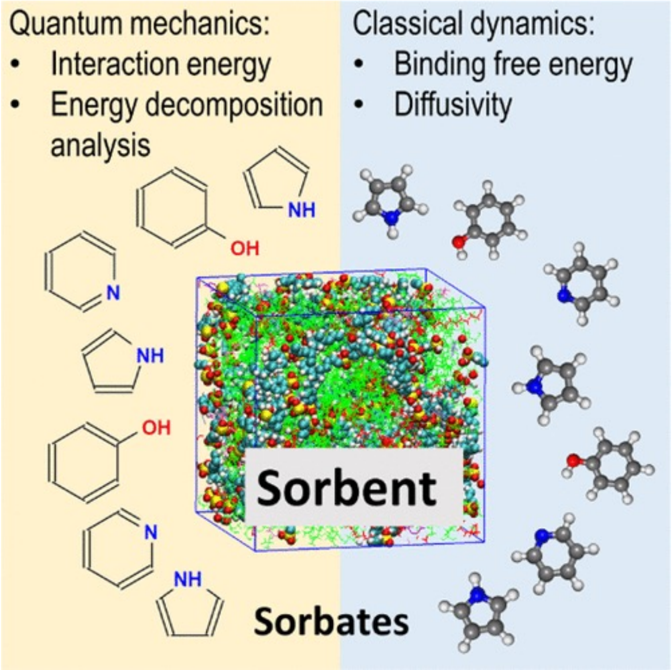
Demonstrate effective adsorbent regeneration mechanisms by utilizing knowledge of **surface functionality** (e.g., adsorb basic N such as pyridine with highly-acidic sorbents) and porosity to remove non-basic N such as indole. Current and earlier computational and experimental work will be leveraged*.

Continuous adsorption - ORNL

Demonstrate a cost-effective and continuous adsorption process via cyclic adsorption processes and apply knowledge of sorption isotherms and energy analysis to determine cost-effective thermal swing or solvent elution for desorption. (ORNL)

TEA- PNNL

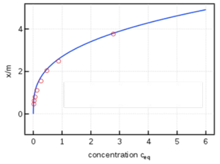
Optimize the economic impact or benefit of adapting adsorptive method and reduce the additional cost and environmental impact

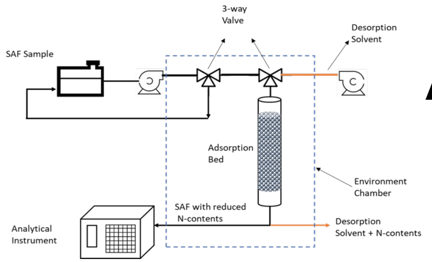


* Gurunathan et al. ACS Sustainable Chemistry & Engineering 2021, 9 (40), 13406-13413.

1- Approach:

Cost analysis to compare adsorbent system with hydrotreating (HDN)





Working capacity and selectivity
Removing efficiency

Bed size, flowrate
Adsorbent/Desorbent usage

Energy and Equipment cost

Productivity
Purity

Material cost

MFSP ($/gge)
Additional cost (A-DN)
Life-Cycle Inventory (CI)

- Baseline cost: An additional HDN may cost another $0.04/gge based on SOT prediction for a small HTL plant (110 dry tpd sludge).
- Adsorptive sulfur removal technology using a catalyst (<15ppm S) will cost an additional ~$0.04/gge and reduces CO_2 emission by 320 tons/day on a typical refinery scale (6000 bpd) due to less-hydrogen requirement**.
- AD-N has the potential to match the cost for additional unit ops (HDN), and to reduce CI of the overall process.

**https://www.aiche.org/resources/publications/cep/2017/november/catalyzing-commercialization-ultra-deep-desulfurization-diesel

1- Approach:

Project management

- Bi-weekly coordination meeting with ORNL, TEA and computational team.
- Industrial collaboration and Advisory Board interaction
- Collaborations/integration with other BETO projects on risk and mitigation
  - 3.4.2.301 (PDU for HTL Risk Reduction)
  - 2.3.3.301 (Denitrogenation of wet-waste-derived biocrude to meet SAF spec)
  - 2.2.2.302 (Bench Scale HTL of Wet Wastes Feedstocks)
- FY22 milestones: Participate in outreach activities and support student internship.
  - PNNL -3 outreach activities and 1 student intern in 2022.
  - For FY23, all labs will be participating in the Bioenergy to Bridge Program, which will be covered in more detail in the overview presentation.

1- Approach:

Project management (GNG) and risk management

Key Milestones	Task Details	Due Date
(GNG#1) Industrial relevance of Adsorptive de-N of fuels	Demonstrate support from refiners for potential adoption of adsorptive de-N of fuels	12/31/2022 Completed
Annual GNG#2	Down selection of starting adsorbent materials compatible with biocrude SAF and better than current HDN (97% removal) with less than 2wt% yield loss.	9/30/2023 On track- for completion

Risk	Response Plan
Ability to produce sufficient material for testing is limited.	Use whole upgraded biocrude for initial testing, and utilize surrogate feed
Recovery of SAF is <98%.	Consider process optimization to reduce hydrocarbon losses by maximizing N removal and adsorbent productivity.

1- Approach:

Go/No go completion and and industrial feedback

Decision	Description	Criteria
Industrial input regarding adsorptive technology to-reduce nitrogen in the SAF fraction	Receive feedback indicating the **relevance** of **adsorptive technology** to reduce Nitrogen levels and meet SAF nitrogen specifications	Industrial feedback indicates that ADN is an industrially relevant approach for nitrogen reduction - **GO**

Refinery Key concerns	Perspective on Adsorbents
• **Pyrazines, Pyrroles, Indoles,** etc. are a challenge for refiners due to their **inherent stability** and hierarchy in hydrotreating reactions. • **Sterically hindered versions** such as a **dibenzo pyrazine** are especially difficult to treat and can cause colored bodies that fails jet fuel oxidation (JFTOT) test.	Refineries are open to the possibility of adsorption processes if **catalytic routes prove too difficult to reach Nitrogen spec**. Adsorptive denitrogenation may require **additional treatment of the reject stream**. The cyclic nitrogen reject could be fed to the back end of the refinery where the heating content would add value and it would get converted to elemental gaseous nitrogen.

2- Progress and outcomes:

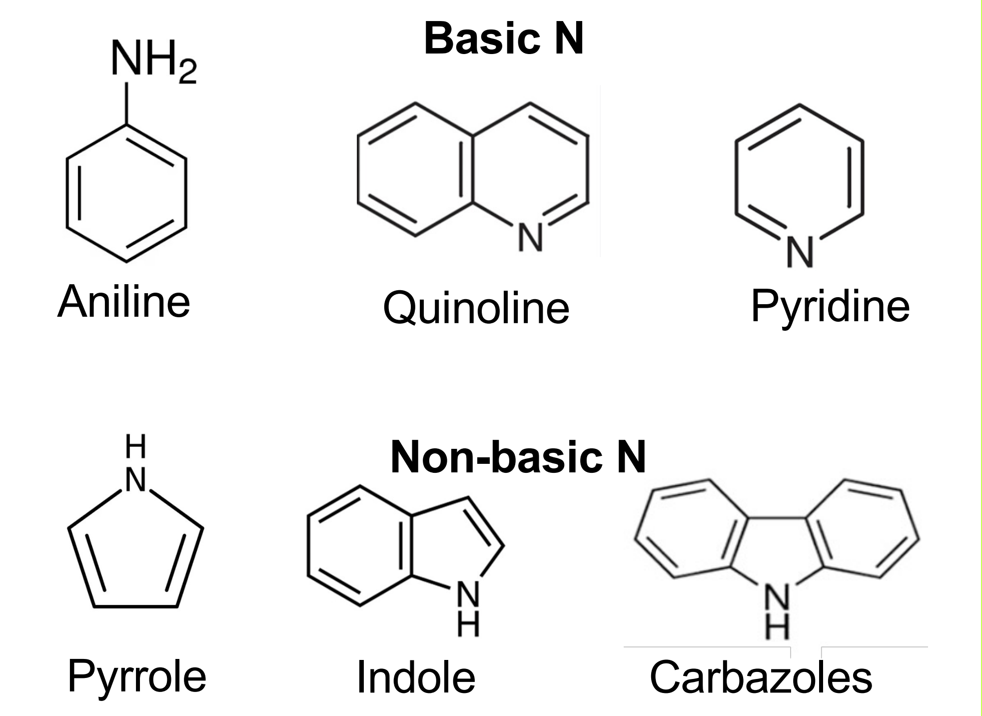
Bonding between adsorbent and adsorbate is via acid-base reaction and by static interaction

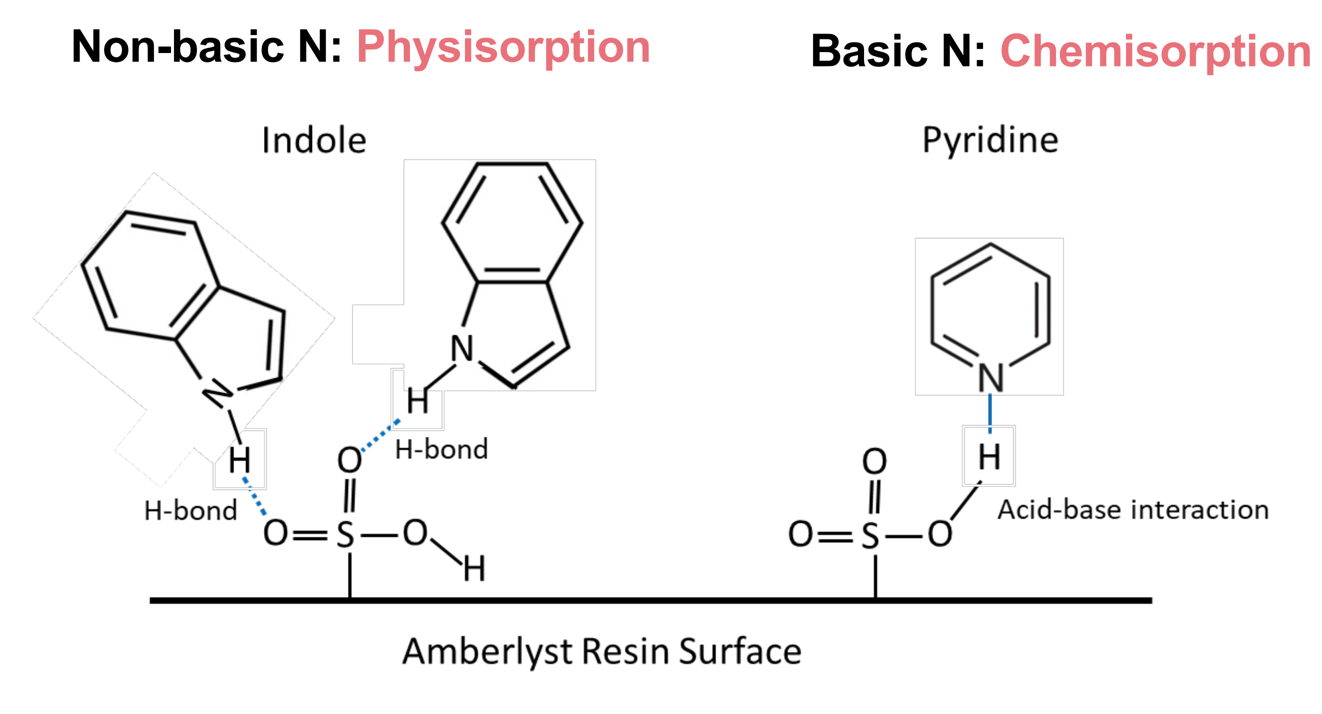
- For basic N-Containing compounds: Acidic functional group is the key to remove basic N*.

Acid-base reaction between the basic nitrogen compounds and the acidic groups on adsorbent.

- For neutral/non-basic nitrogen-containing compounds - Porosity is the key to remove neutral N.**

Hydrogen bond and Van der Waals force (Dispersion force, Dipole-Dipole force).

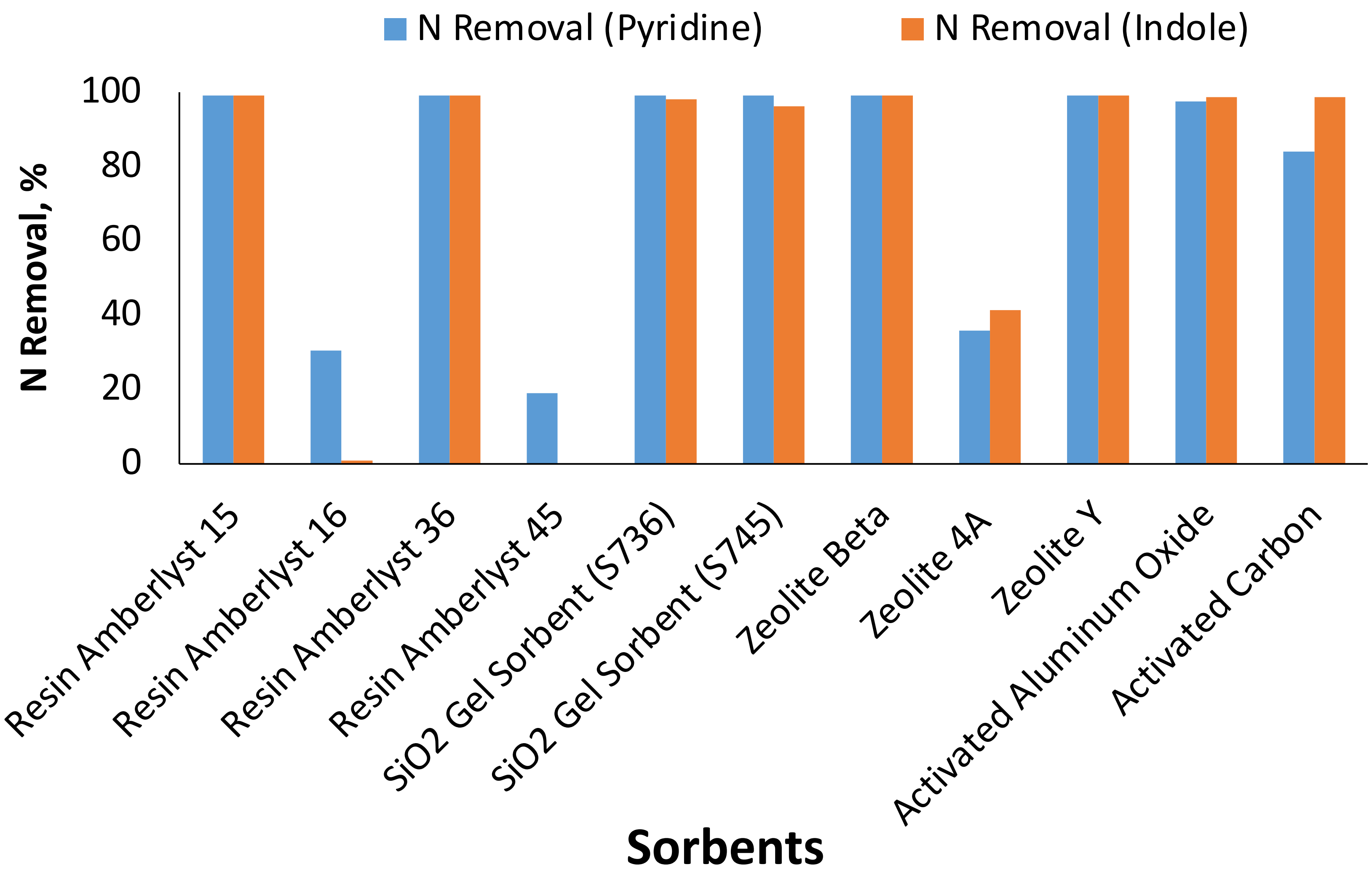




Non-basic N-Compounds: Physisorption, weaker, and usually occurs at low temperature.
Basic N-Compounds: Chemisorption, stronger, and usually occurs at high temperature.

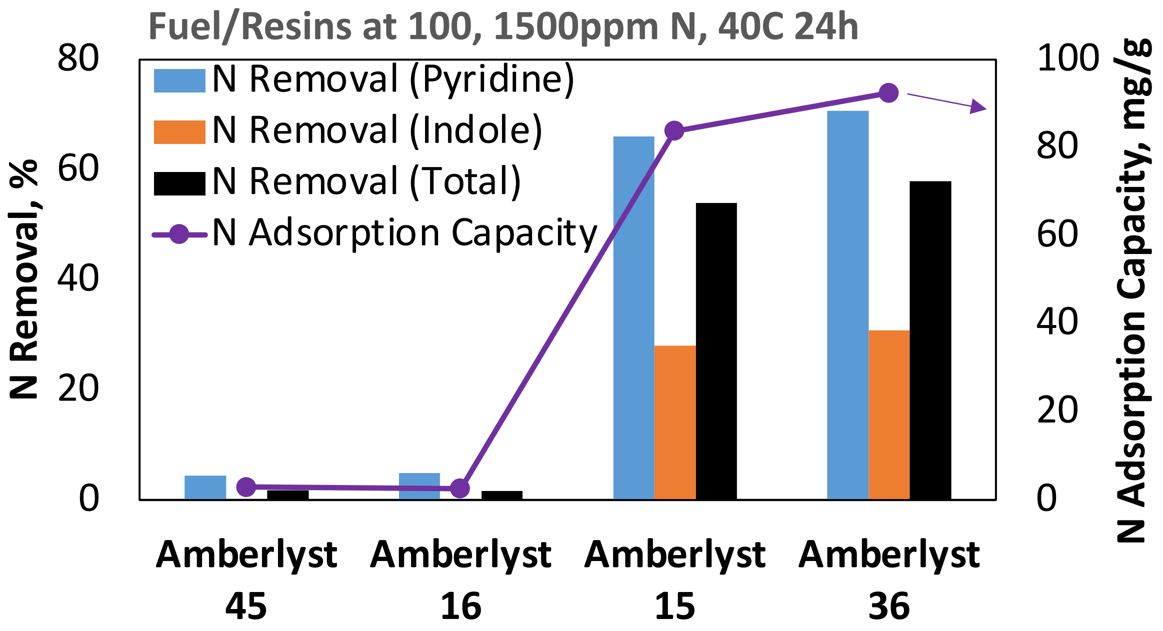
*I. Ahmed, S.H. Jhung / Journal of Hazardous Materials 301 (2016) 259–276 263 **Energy Fuels 2017, 31, 14−36

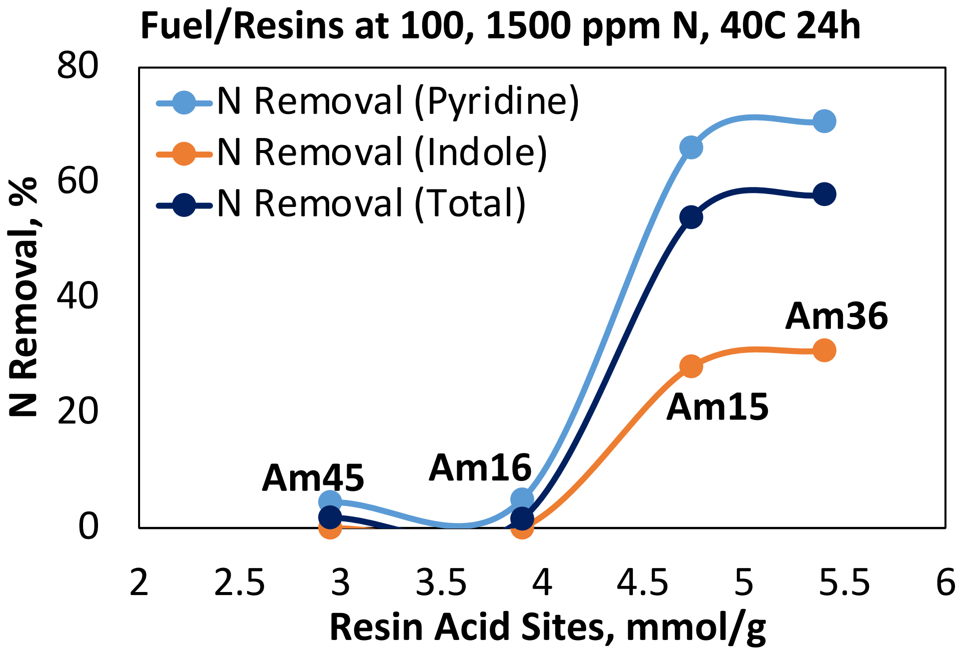
2- Progress and outcomes:
Polymeric resin demonstrate high selectivity to both N types



- Evaluated 11 adsorbent materials with various physicochemical properties for N removal.
- Most adsorbents achieve >**98% N removal,** but based on **the least fuel trapped**, resin is the better candidate.

2- Progress and outcomes:
N- Removal by resins highly correlates with adsorbent acid sites

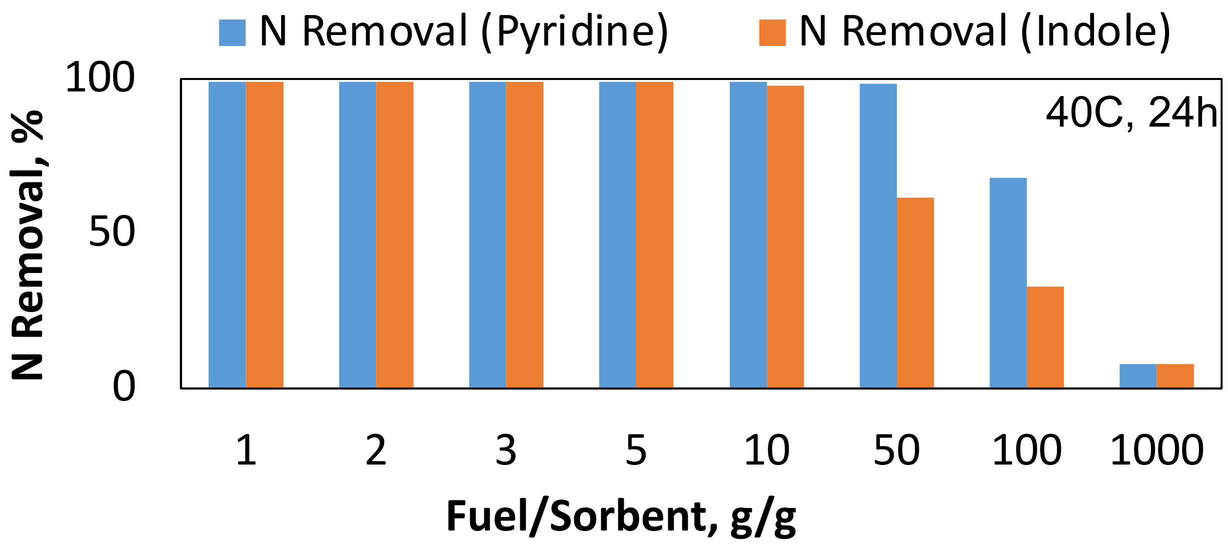


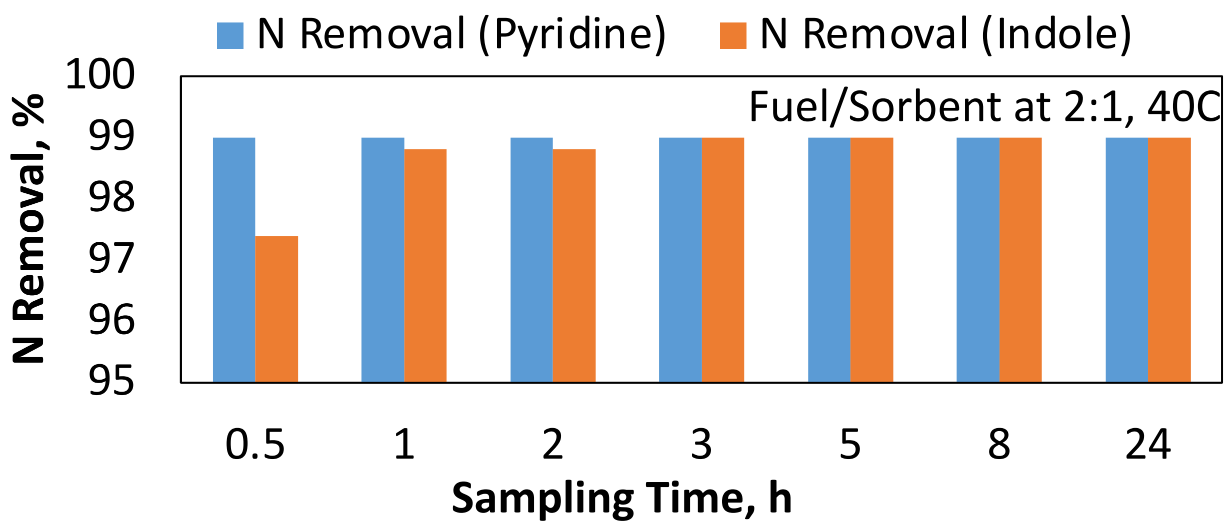


Resin	Acid Sites, mmol/g	BET Surface area, m2/g	Pore Diameter, nm	Maximum Operating T, C
Amberlyst 45	2.95	49	19	170
Amberlyst 16	3.90	30	25	130
Amberlyst 15	4.74	53	30	120
Amberlyst 36	5.40	33	24	150

Pyridine and Indole removal both increased with increased acid sites: Amberlyst 45 < Amberlyst 16 < Amberlyst 15 < Amberlyst 36.

2- Progress and outcomes:
Basic nitrogen adsorb much faster than non-basic N





Amberlyst 36 Resin

- At Feed/Sorbent ratio of 10 or lower,
  - **>99%** of the pyridine was removed.
  - indole removal rate is high at **98%**
  - Adsorbent saturated at lower Fuel/Sorbent ratio.
- Adsorption is time dependent.
  - Pyridine removal is within **30min**,
  - Indole took longer, about **2hrs** (4x).

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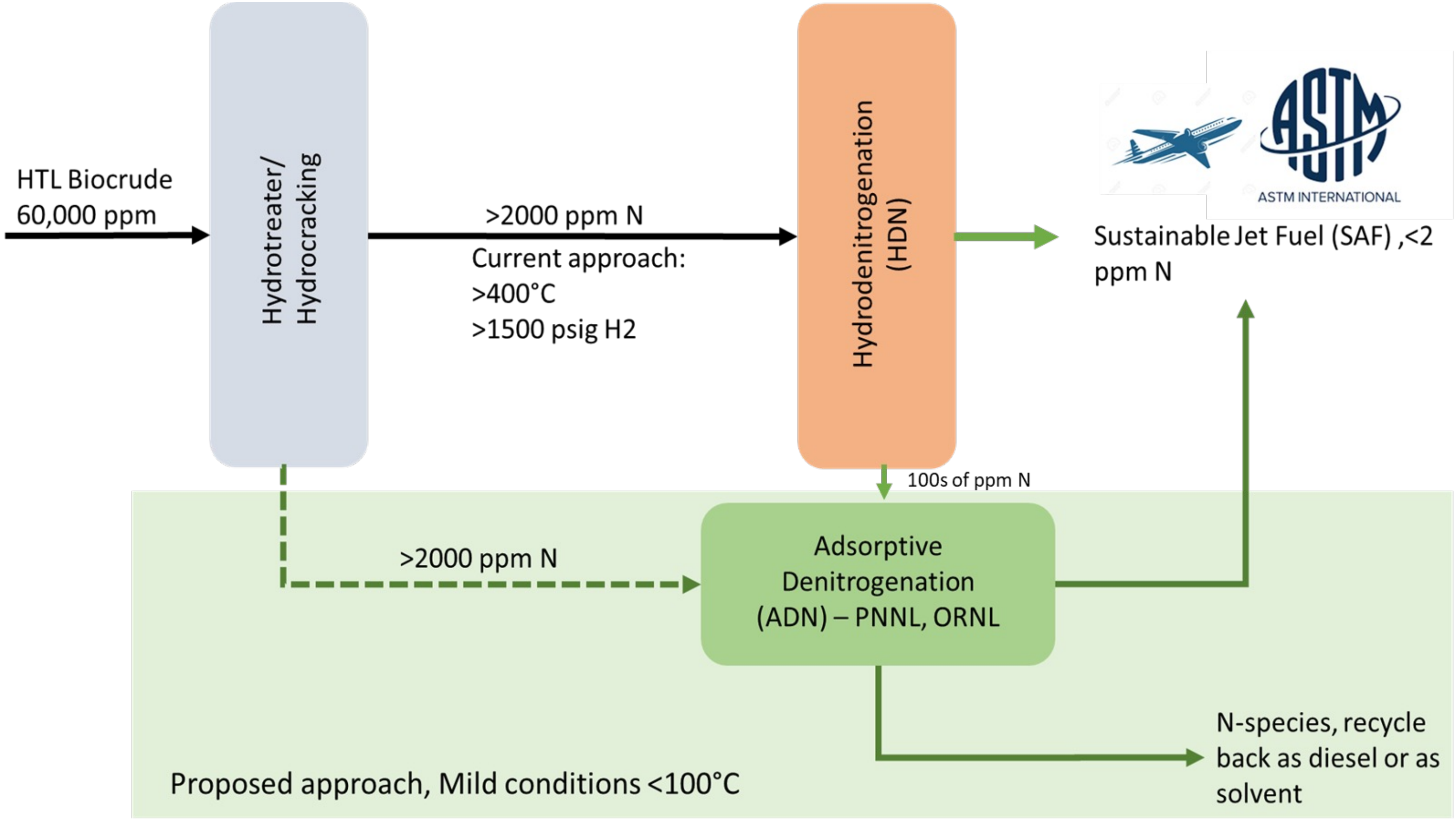
3- Impact:
Selective sorbent development is key in enabling SAF

- A selective separation of N-containing species from hydrotreated biocrude minimizes **yield loss from cracking** and have **lower CI due to lower hydrogen consumption.**
- Utilizing more environmentally friendly material such as resins will further reduce CI of the overall process.
- A **continuous process** will generate relevant data for use in scale-up of a commercial process.
- **Ongoing collaboration with industry** and dissemination of results via conference presentations and peer-reviewed journal articles facilitate technology transfer.

3- Impact:

Commercially relevant data is key in de-risking industrial adoption and industrial decarbonization



- HTL-SAF pathway will enable **76 MT/y* of wet waste in the US to be converted to ~400 kbd SAF (~25% US Jet fuel** demand).
- **Enable refineries with limited access to HDN** units to meet the stringent N specification.
- **Utilized industry engagement to guide the FY23 Q1 GNG.**

*https://doi.org/10.1016/j.rser.2017.09.107

Summary

Goal

- Demonstration of a selective adsorbent system with lower fuel lost and <2 ppm N in the final fuels to meet SAF requirement.

Approach

- Adsorption and desorption test with known materials with high selectivity towards basic and non-basic N
- Develop fundamental understanding in close collaboration with computational team.
- Develop optimized economic and carbon footprint in a continuous process.

Outcome

- A selective material towards N impurities resulting in <2ppm N.
- Address SAF grand-challenge by enabling Hydrothermal liquefaction to produce *3.9 billion gal/y of SAF (>20% of 2019 US aviation demand) from wet wastes with >70% GHG reduction at $3.15/gge (projected cost per SOT 2022).

Future Work

- Demonstrate N-adsorption on SAF fraction from upgraded biocrude (Q4 milestone).
- Optimize removal efficiency, bed size, and selectivity.
- Demonstrate continuous system including regeneration for scale-up.

Acknowledgements

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KERN ENERGY We Fuel the Future

- Jake Bishop

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Thank you!

Quad Chart Overview

Timeline
- Project start date: 10/1/2022
- Project end date: 9/31/2025

	FY 22	Total Award
DOE Funding	$0	$1,341.6K (FY 2022-2025)

TRL at Project Start: 2
TRL at Project End: 3

Project Goal
Demonstration of an adsorbent system with low yield lost and <2 ppm N in the final fuels to meet SAF requirement by selective adsorption process using knowledge of adsorption and surface functionalities and optimization by using a continuous process.

End of Project Milestone

Demonstration of an adsorbent system with low yield lost and <2 ppm N in the final fuels to meet SAF requirement.

Funding Mechanism
Sepcon AOP

Project Partners
- ORNL

*Only fill out if applicable.

Additional Slides

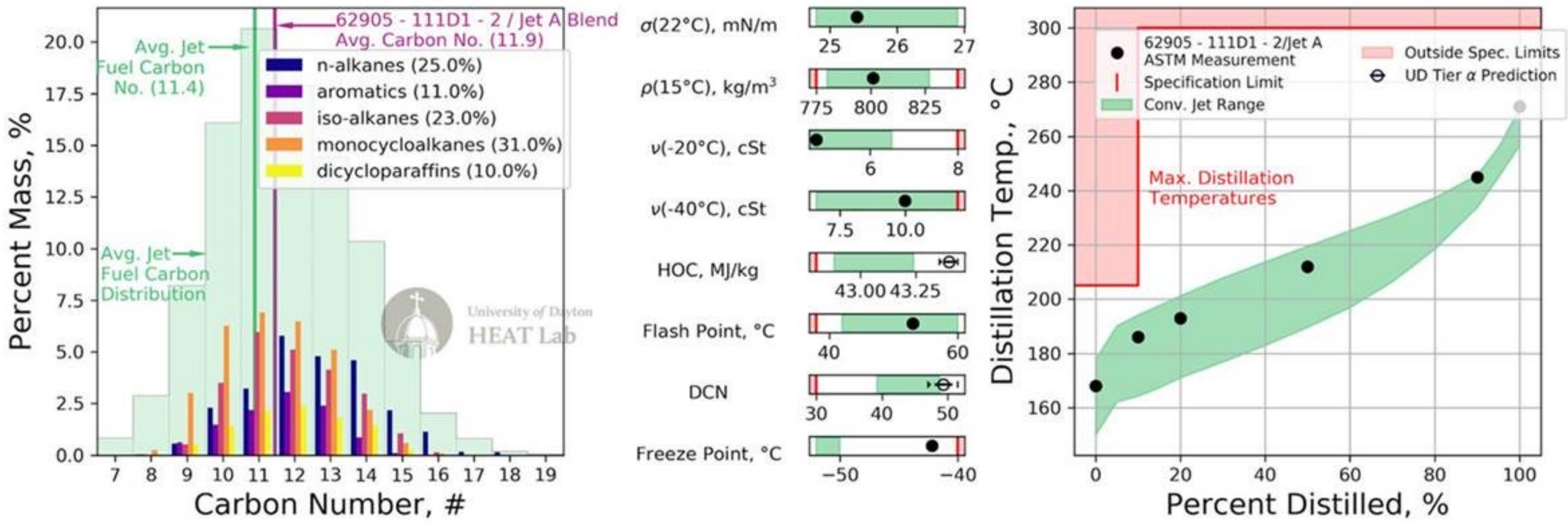
Abbreviations

- AOP: Annual Operating Plan
- SOT: State of Technology
- LCA: Life cycle analysis
- TEA: Techno economic analysis
- CI: Carbon Intensity
- GWP: Global Warming Potential
- GHG: Green House Gas
- PNNL: Pacific Northwest National Laboratory

Extra slides

- Additional overviews
- Refinery detailed feedback
- Adsorption methodology

Overview of SAF fraction properties from HTL



50% HTL SAF and Jet A blend alpha and beta-tier test result

- 2021 HTL SOT demonstrates ~97% removal of the N-content in two stage process for jet fuel fraction.
- HTL Jet fuel fraction has a positive alpha and beta jet fuel properties, but still has problem with high N.
- HTL SAF is anticipated to have a lower N specification than other fuels:
  - Need to get approval from engine manufacturers, airlines, oil refiners, etc.
  - Expect N specification to be around 2ppm (Josh Heyne, WSU).
  - <2ppm N is required per ASTM D7566 due to potential fuel instability caused by N-compounds.

*Cronin, D. J et al. Energies 2022, 15 (4), 1306.

2- Progress and outcomes:

Refinery and Industrial Advisory Feedback

Current State-of-the-art:

- Nitrogen byproducts of thermochemical conversion processes are increasingly relying on refinery processes that include hydrotreating, hydrocracking and destruction in Sulfur Recovery Units. N removal requires high severity hydrotreaters and most high severity hydrocrackers.
    - Only a few refining processes can handle these Nitrogen compounds in these concentrations
- Strategy: Higher hydrogen partial pressure, higher catalyst activity, alloyed for corrosion resistance, and already mitigating risks with industry standard design and operating practices.
- Corrosion issue mainly due to ammonium bisulfide.

Primary concern:

- Nitrogen compounds in a hydrotreater inhibit other desired reactions, are often difficult to convert to ammonia, and can limit process throughput.
    - Pyrazines, Pyrroles, Indoles, etc. are a challenge for refiners due to their inherent stability and hierarchy in hydrotreating reactions.
    - Sterically hindered versions such as a dibenzo-pyrazine are especially difficult to treat and can cause colored bodies that fails jet fuel oxidation (JFTOT).
- Adsorption alternatives for Nitrogen have industrial relevance, and their development is encouraged.

On adsorption:

- Adsorptive denitrogenating requires additional treatment of the reject stream.
    - The cyclic nitrogen reject could be fed to the back end of the refinery where the heating content would add value and it would get converted to elemental gaseous nitrogen.
- IAB recommend using polymeric resin which is more environmentally friendly.

Continuous Adsorption/Desorption Test System

Test Parameters:

- Adsorption breakthrough curves
  - Adsorbent working capacity (mol N/kg adsorbent)
  - Selectivity towards N species
  - Adsorption bed size estimation
- Regeneration test (solvent, temperature, volume)