

tcbi⁺mass⁺2026

Catalytic upgrading of
hydrothermal liquefaction-
derived biocrudes and
aqueous phase products

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Hydrothermal liquefaction (HTL) is a superior method, producing stable biocrudes



- HTL is conceptually simple and can accept a diverse range of wet feedstocks (no drying!)
- HTL produces a stable and high-energy-density biocrude with low oxygen content (3–10%)
- HTL results in high carbon yields to liquid hydrocarbons (up to 60%)
- Byproducts need processing

PNNL continues advancing HTL technologies

Feedstocks blending variation:

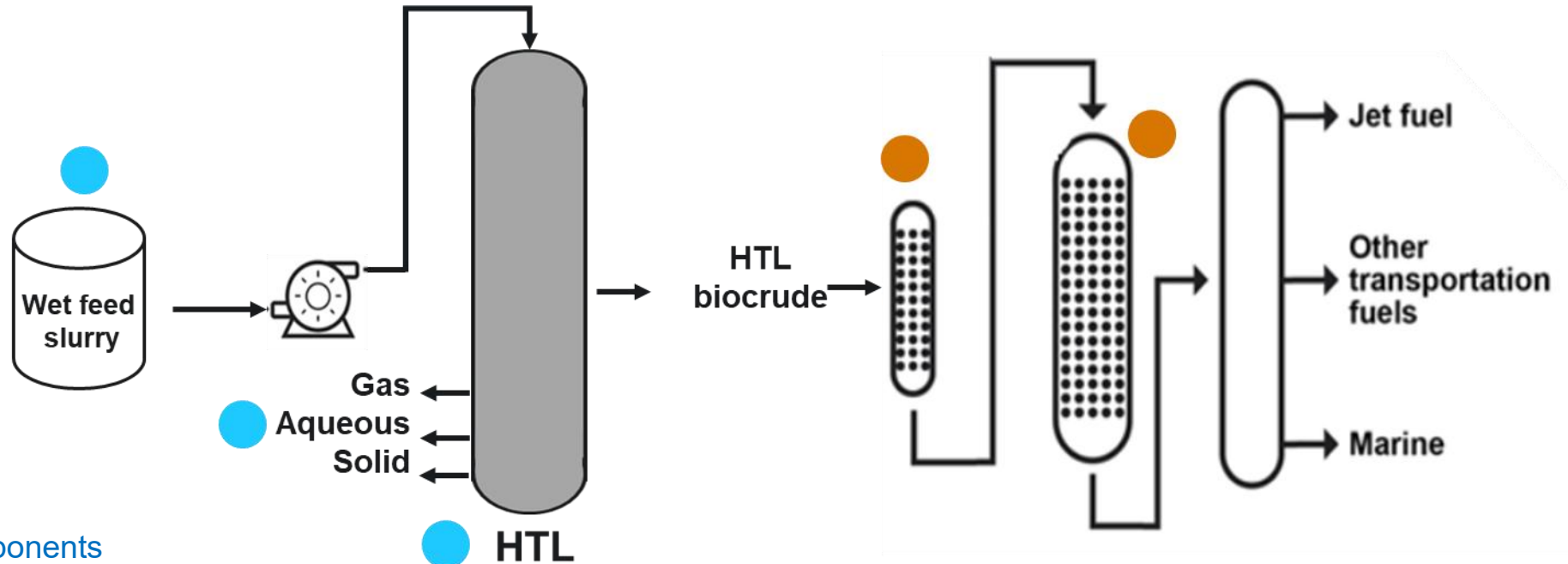
- Expand feedstock blends
- Assess synergy
- Establish correlations
- Seek opportunities for critical minerals harvesting

Aqueous product upgrading

- Understand the heavy components
- Sulfur-resistant CHG catalyst
- WAO: optimization and reaction kinetics
- Impacts of upgrading on recycling

HTL

- Scale up and enhance operation stability
- Explore possibilities to manipulate HTL chemistry



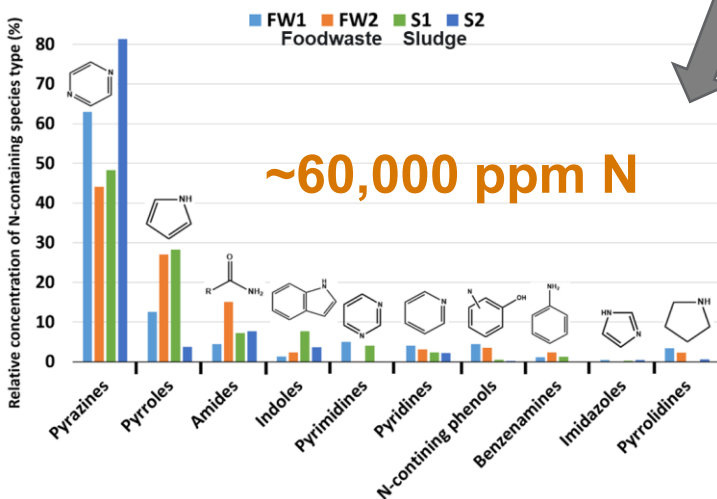
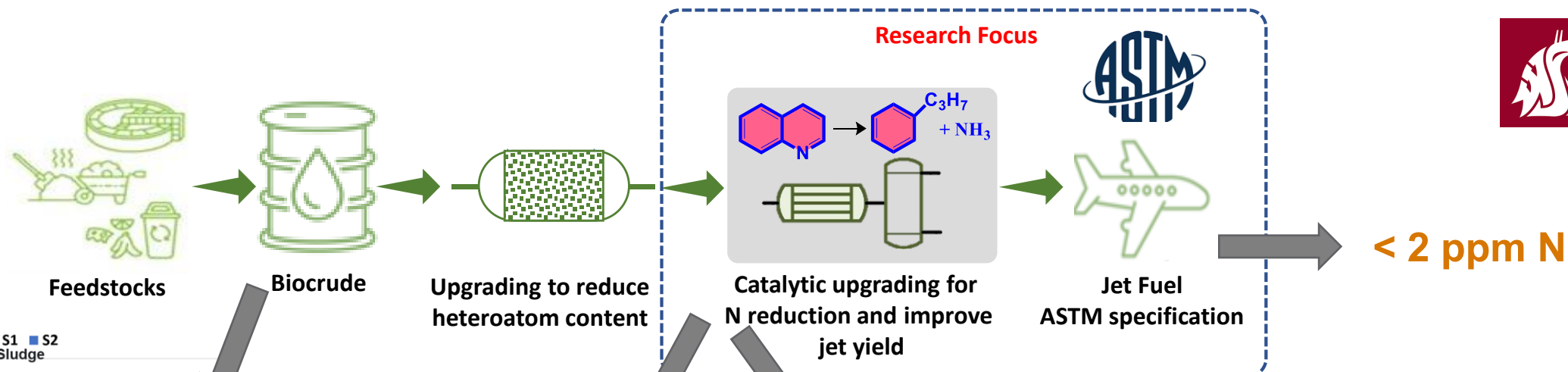
Biocrude pretreatment

- Focus on inorganics – correlation with feedstock
- Pretreatment and guard bed, enabling stable hydrotreating

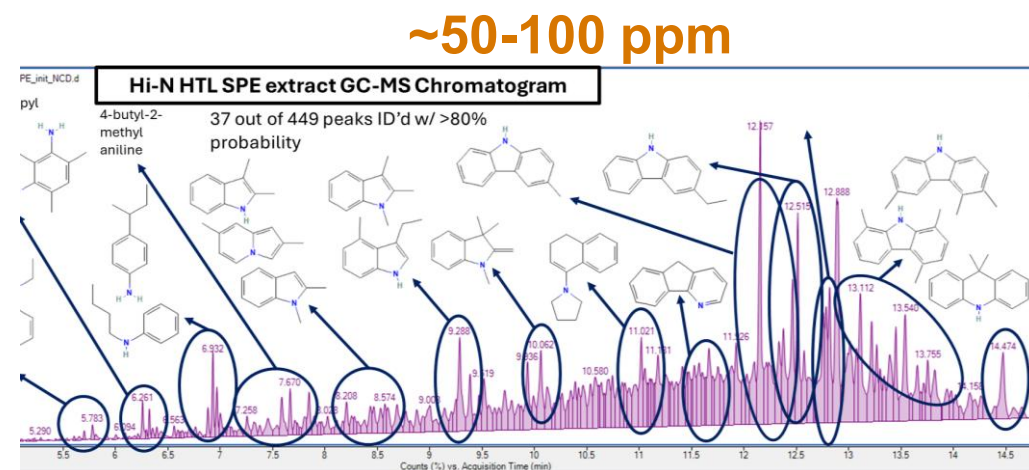
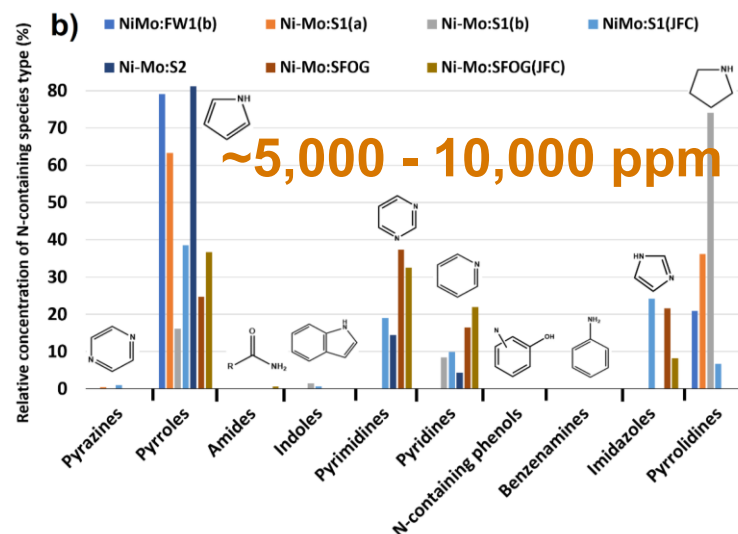
Biocrude hydrotreating

- Deep HDN to meet SAF requirements
- Hydrocracking to increase SAF yield
- Co-processing
- More effective catalyst for high N/O biocrude upgrading
- Product quality

Deep HDN is required to meet SAF specification



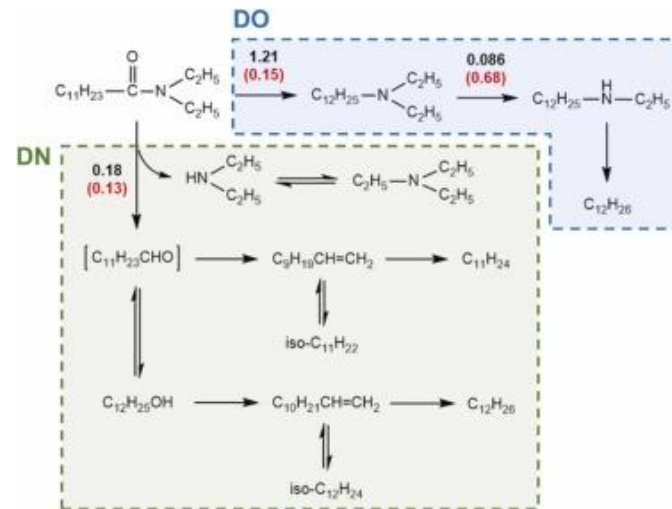
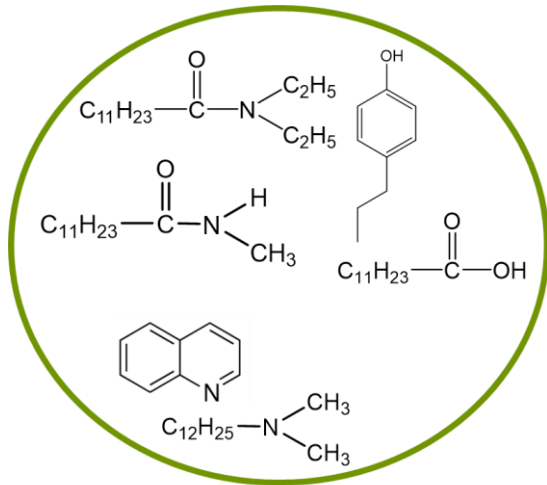
Nitrogen analysis by GC-MS, GCxGC-MS, trace N analysis, and GC-NCD



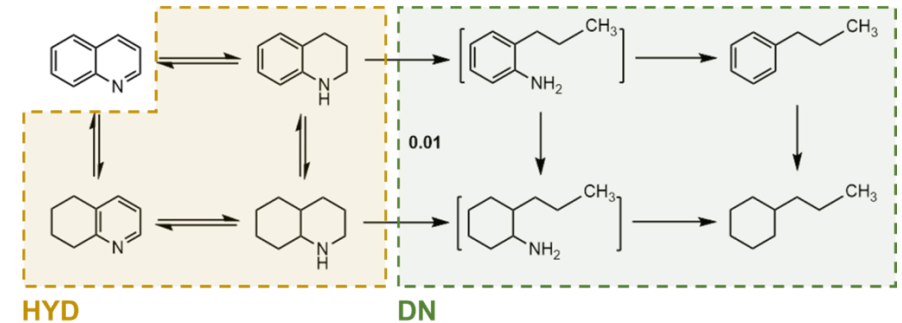
Diverse nitrogen-containing species in biocrudes and hydrotreated intermediates

Kinetic study to identify the most challenging species

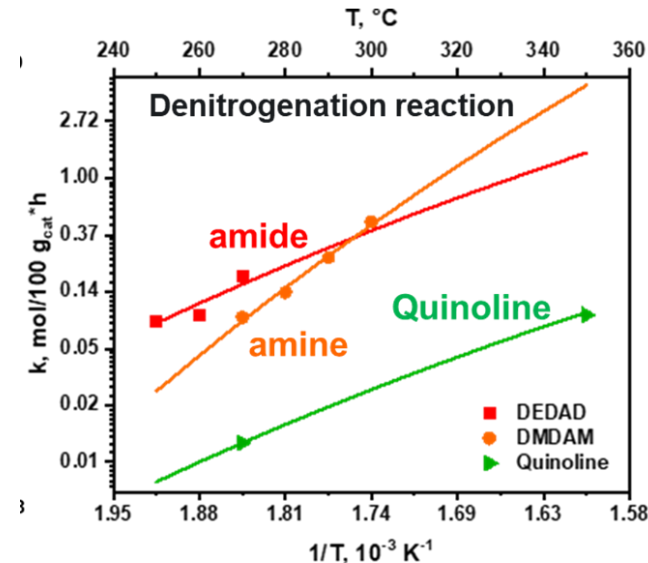
Biocrude introduces new N-containing species



HDN of polycyclic N-compounds is slow

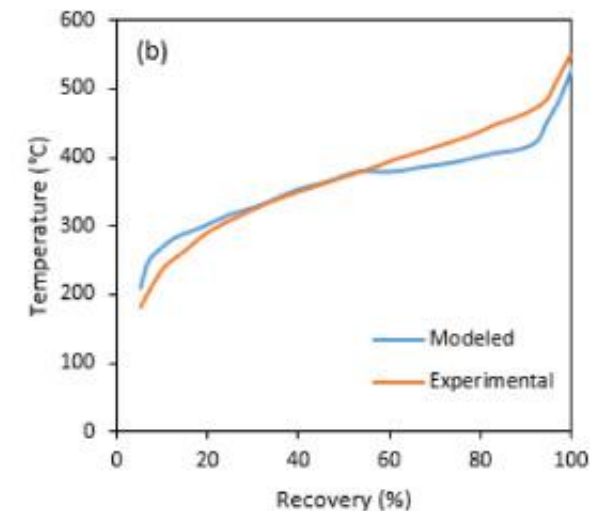


Kinetics



Appl. Catal. B,
2022, 307, 121197

Model for prediction



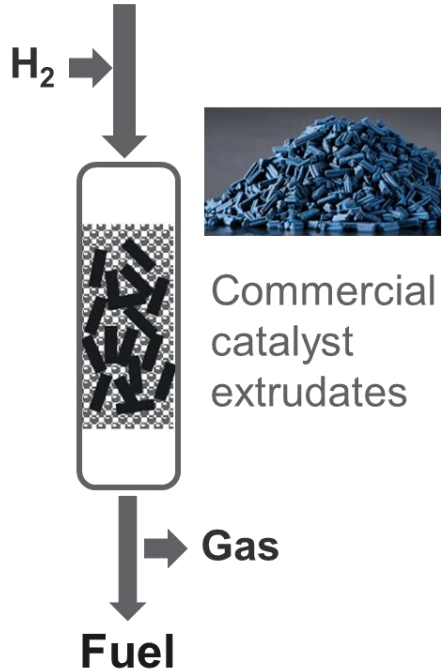
Biomass and Bioenergy,
2026, 208, 108839

- Biocrude introduces some unique N-containing species, but the indoles, quinolines, and carbazoles are still the most refractory compounds
- A kinetic-based reactor model for co-processing enables predictive capabilities and optimization for reactor configuration and operation conditions

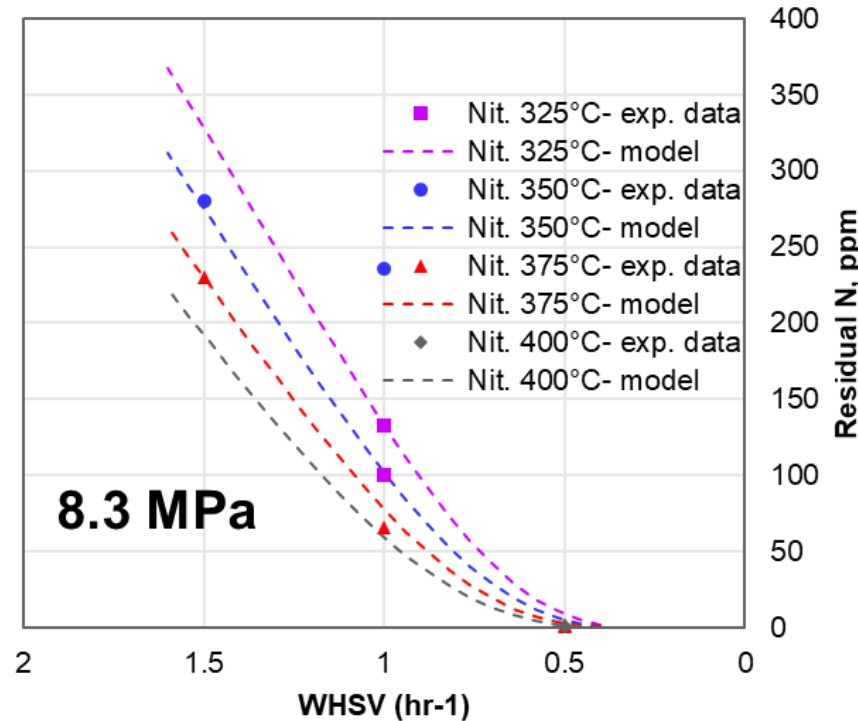
Deep HDN achieved with commercial catalysts

Achieving <1 ppm N at various conditions using extrudate catalysts

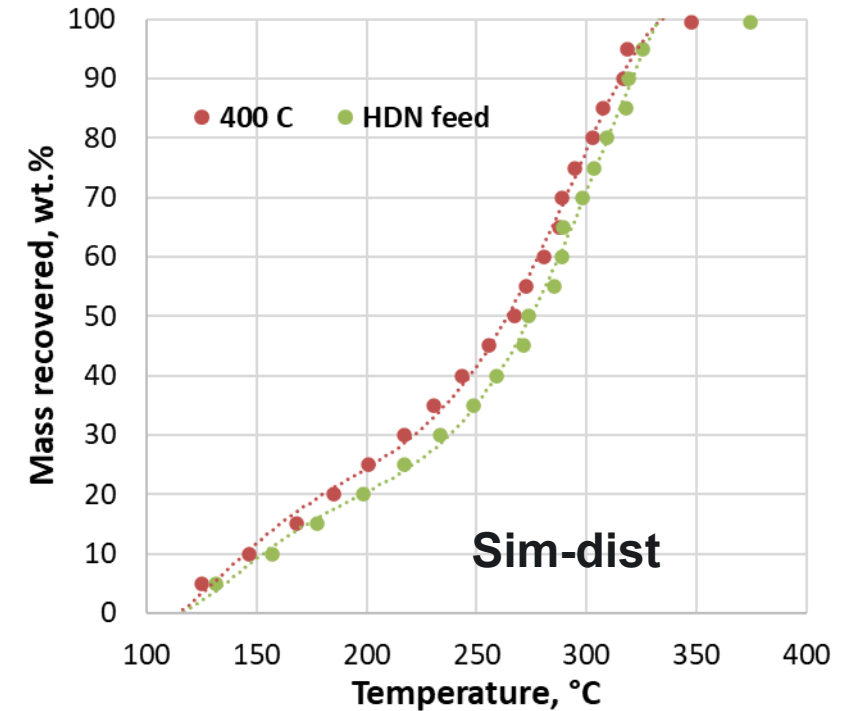
HTed biocrude
Jet or >Jet fraction



TOPSOE



Both temperature and WHSV play a big role in deep nitrogen reduction



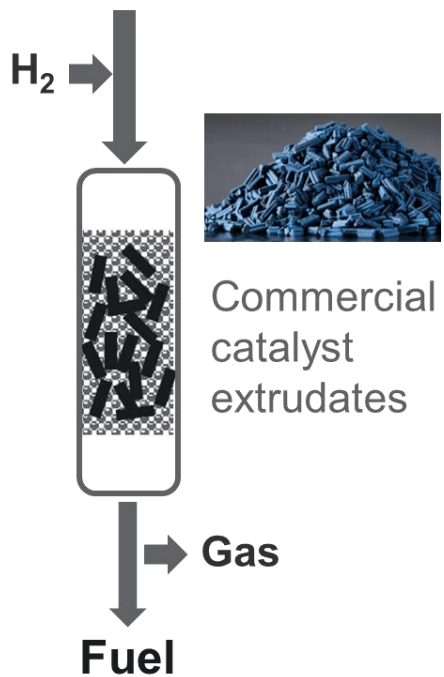
Gas yield is below 3% at the most severe conditions (400 °C and 0.5 h⁻¹ WHSV)

- TEA indicated an anticipated additional processing cost of <\$0.05/gal for deep HDN

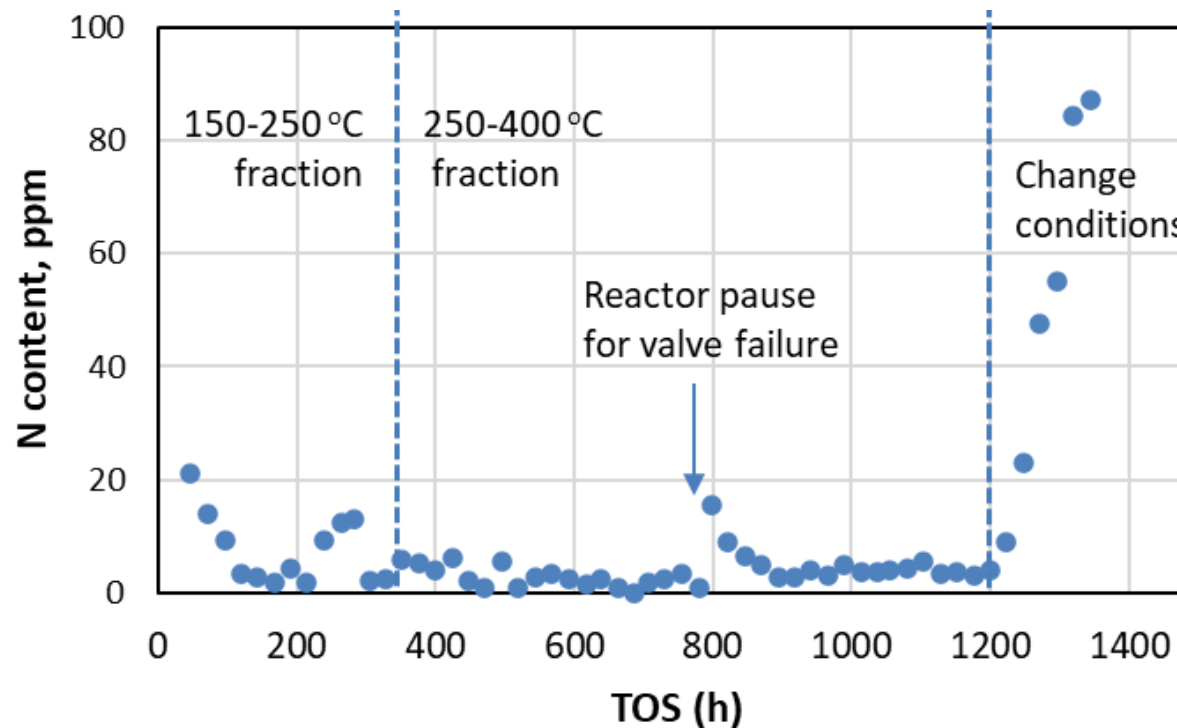
Deep HDN achieved and stability demonstrated

More than 1400 h of stable performance demonstrated

HTed biocrude
Jet or >Jet fraction



TOPSOE

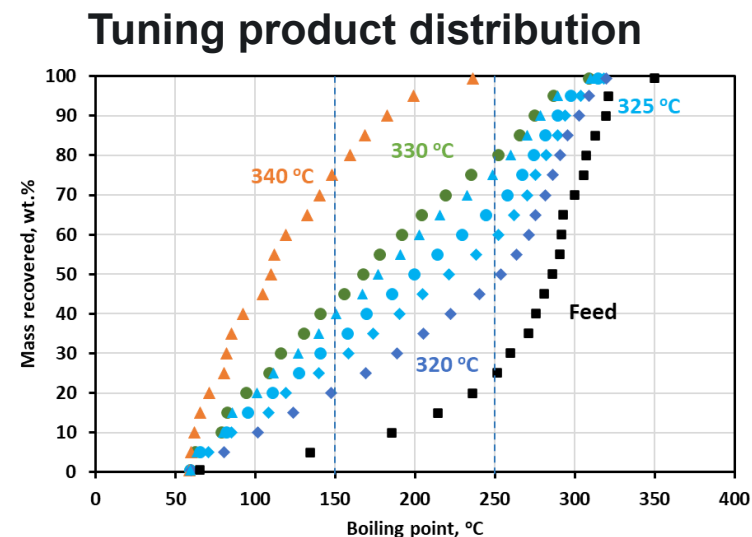
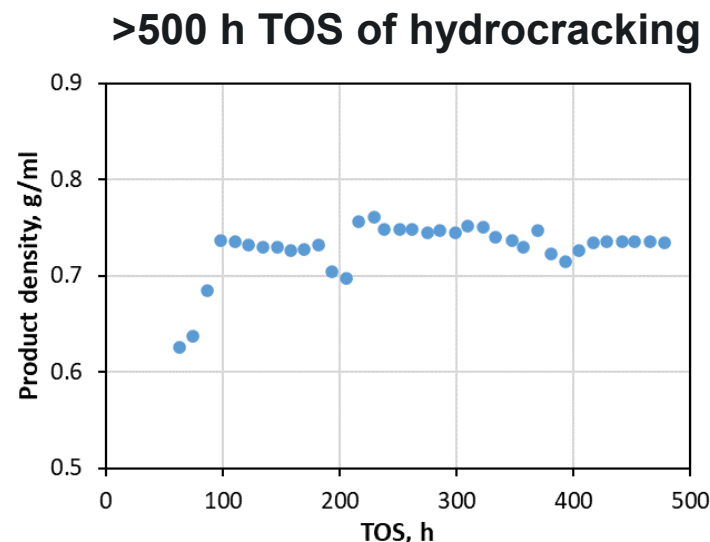


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Deep HDN of heavier-than-jet fraction enables hydrocracking

After deep HDN

Hydrocracking of heavier-than-jet fraction

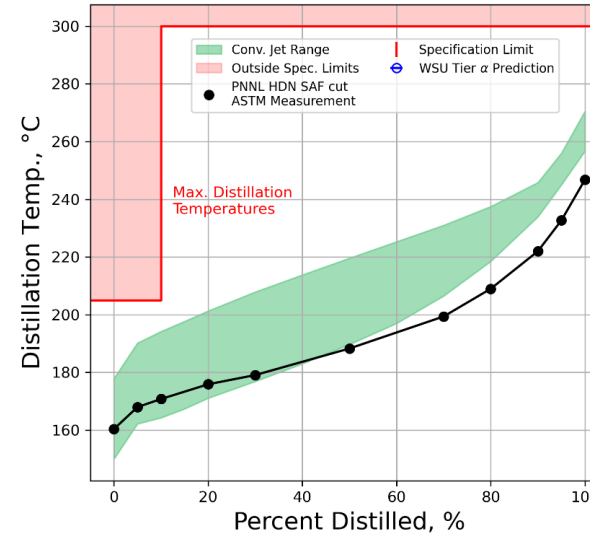
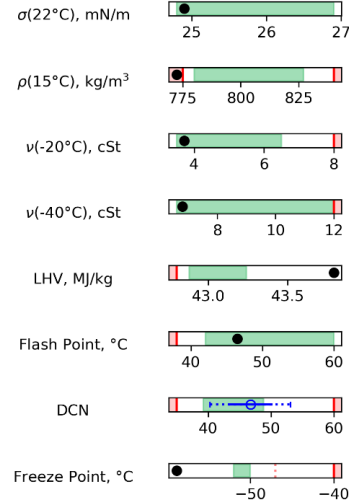
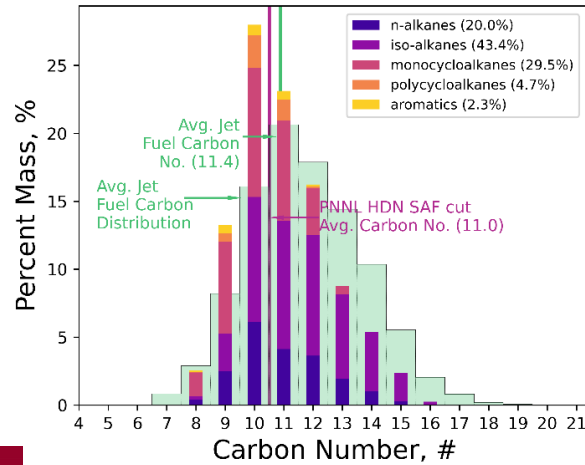


- Deep HDN of heavier-than-jet fraction, leading to <5 ppm N in the product, enables hydrocracking using commercial zeolite-containing catalysts
- Potential for a 100% increase in jet fuel yield from biocrude

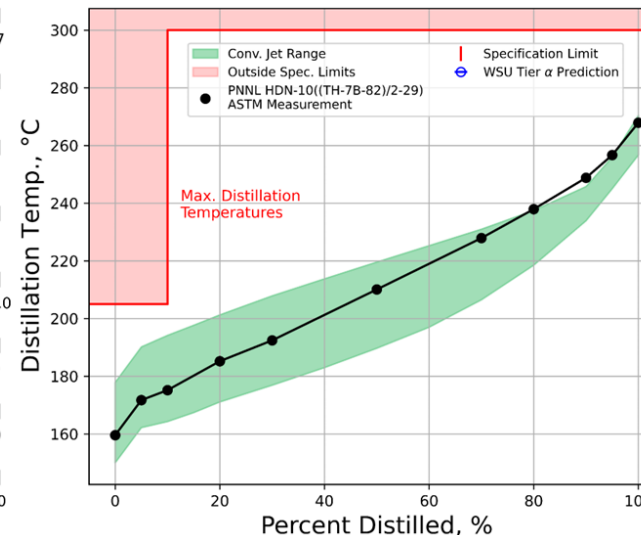
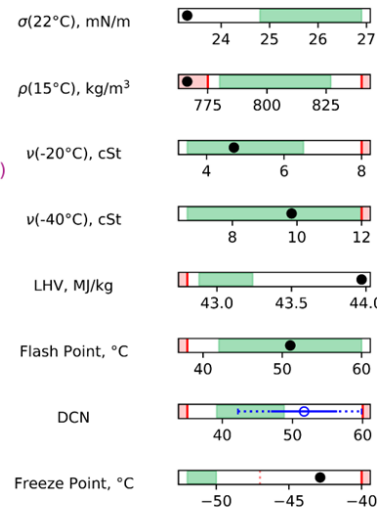
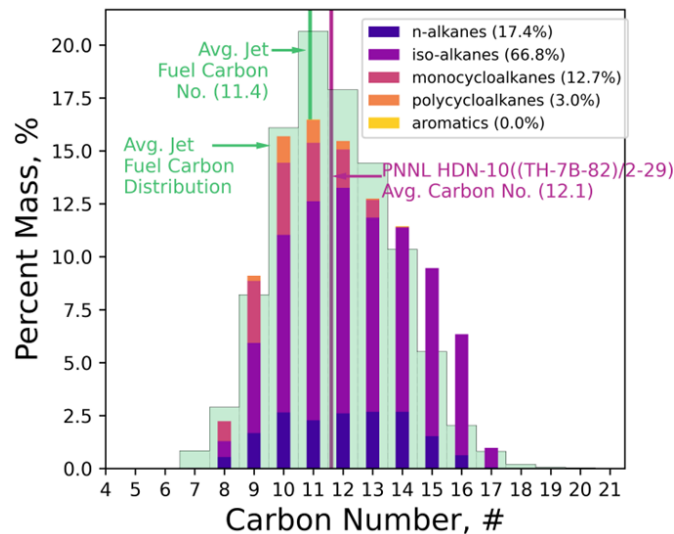


Fuel quality analysis showed promising results

Straight-run jet cut



Hydrocracked jet cut

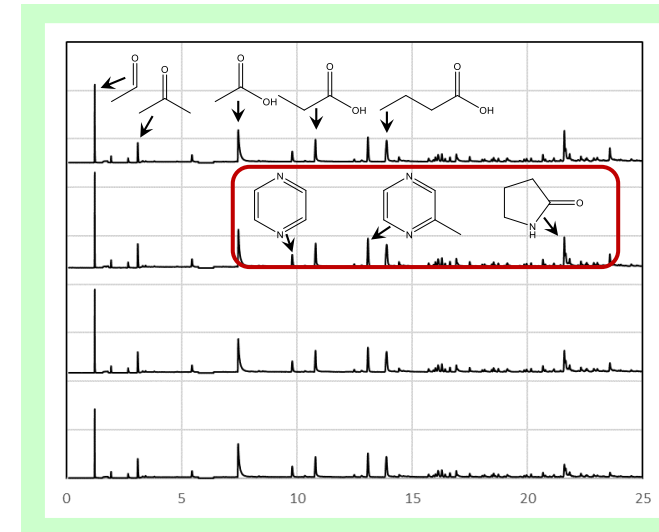
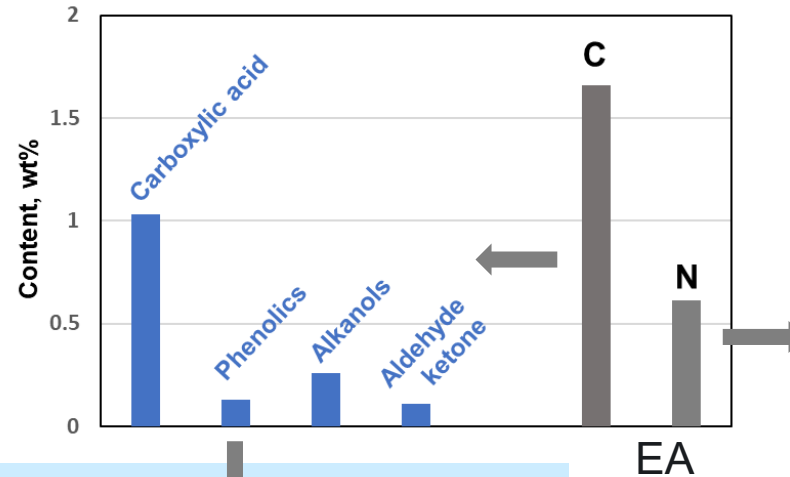


- Properties either within or better than the conventional fuel range based on Tier Alpha/Beta analysis
- A shortened JFTOT test result and the GC-NCD total nitrogen result suggest that thermal stability issues are likely not a major concern for this jet-cut sample

HTL aqueous stream is diluted, complex, and contaminated and its treatment is challenging

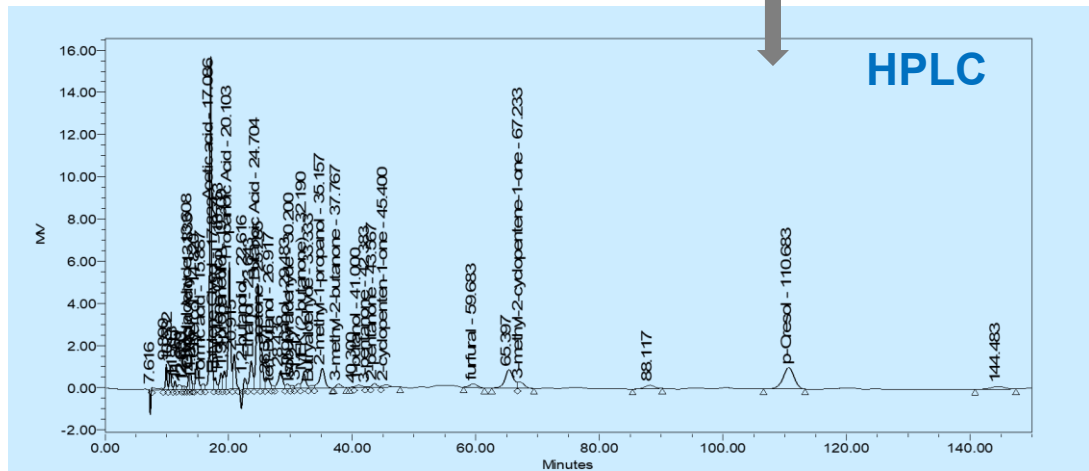


>95 wt.%
water



GC-MS

N-containing
species



Carboxylic acid: acetic acid, propanoic acid, butanoic acid

Phenolics: phenol, cresol

Alkanols: ethanol, propanol, butanol

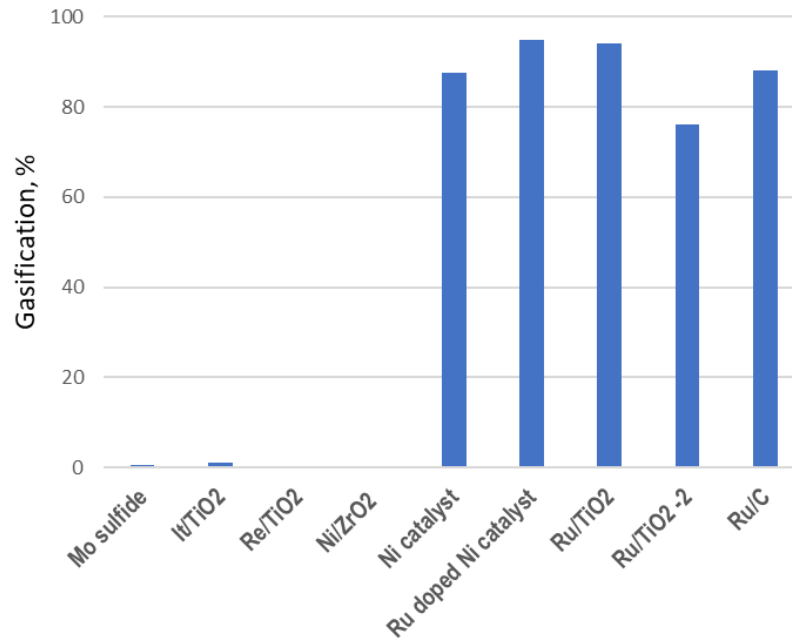
Aldehyde/ketone: butanone, cyclopentenone, furfural

ICP
S: ~100 ppm Si: ~150 ppm
K: ~150 ppm Na: ~120ppm

Problematic characteristics of HTL aqueous stream:

- Water-induced material degradation
- Diluted and complex oxygenates
- Stable nitrogen compounds
- Foulants and contaminants: inorganics and sulfur

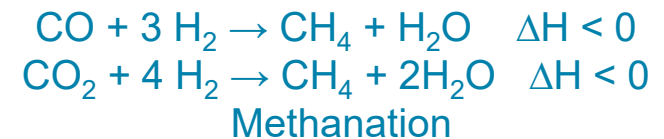
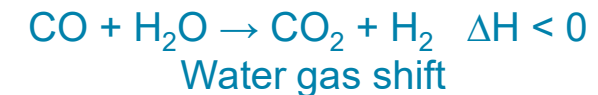
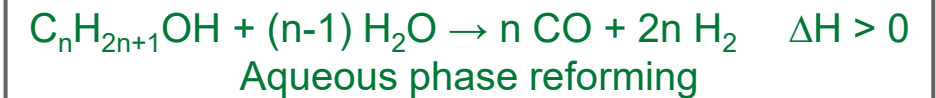
Catalytic Hydrothermal Gasification (CHG) converts HTL-AP to methane and clean water



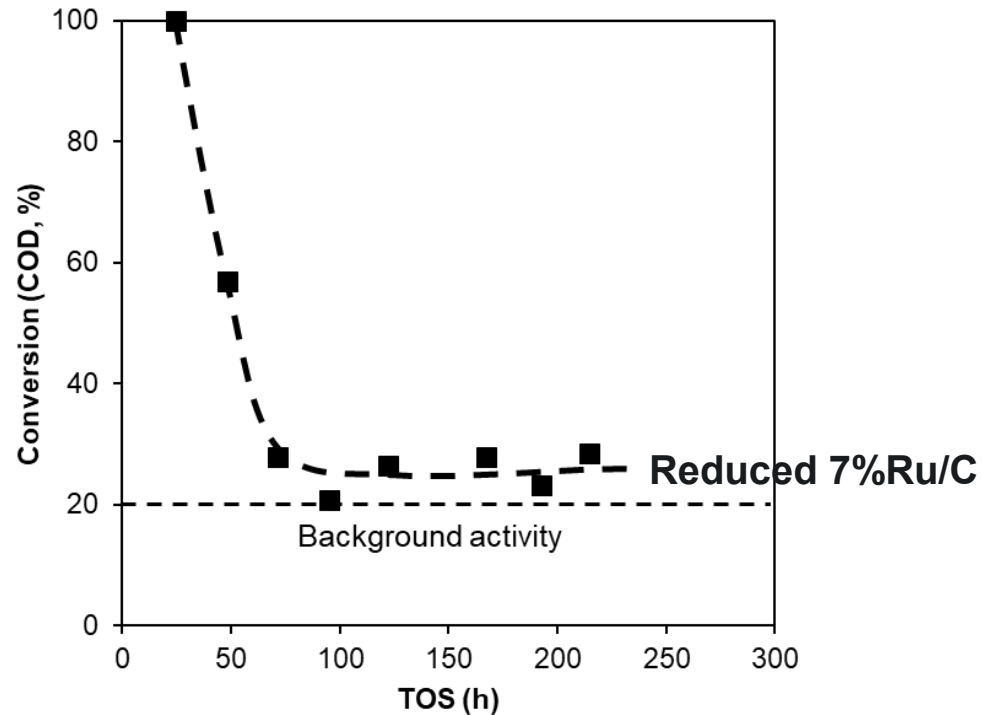
350 °C, 10% phenol, batch reactor, by Doug Elliott et al.

- Ru-based catalyst provides superior activity for CHG

Key reactions in CHG

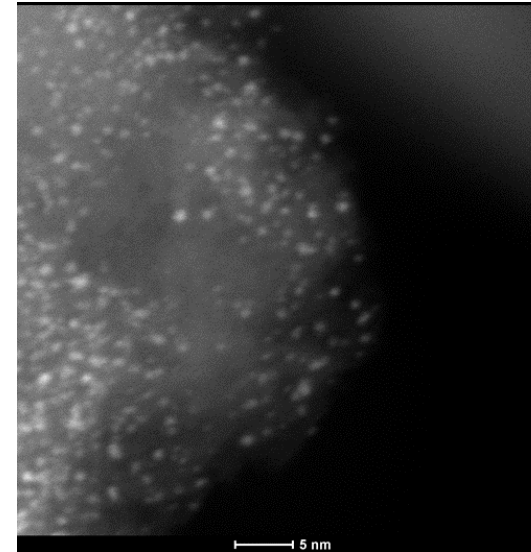


Significant catalyst deactivation by sulfur poisoning



350 °C, 20 MPa, real HTL-AP, fixed bed flow reactor

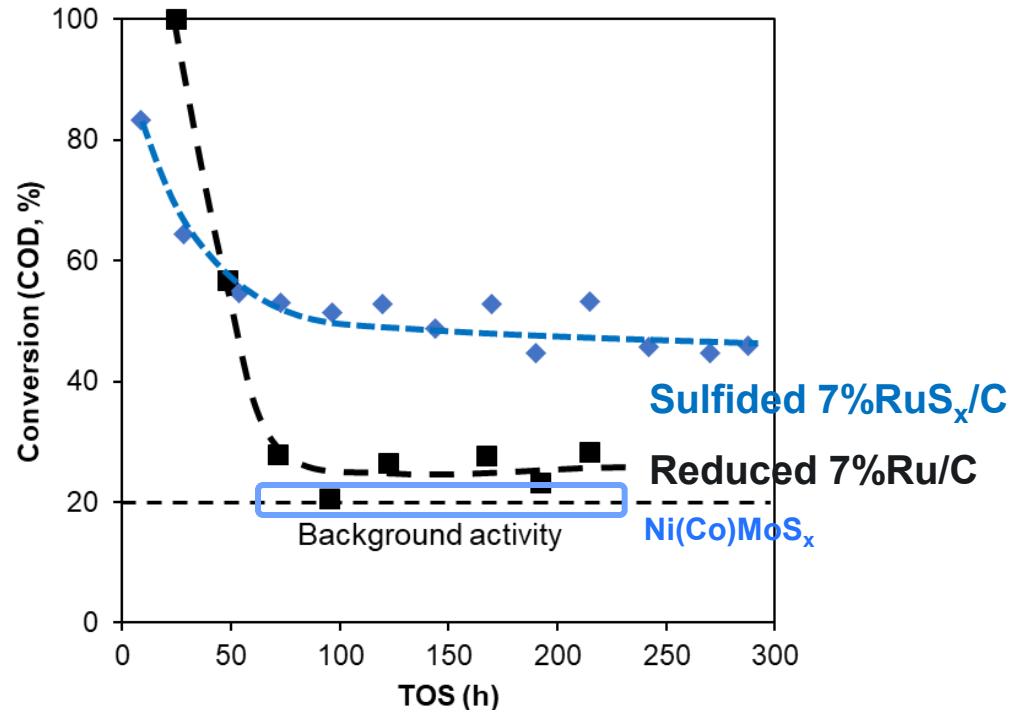
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- Stable Ru NPs at ~ 1.5 nm
- Inorganic deposition on the entrance
- Significant sulfur poisoning

Feed ICP
S: ~100 ppm Si: ~150 ppm
 K: ~150 ppm Na: ~120ppm

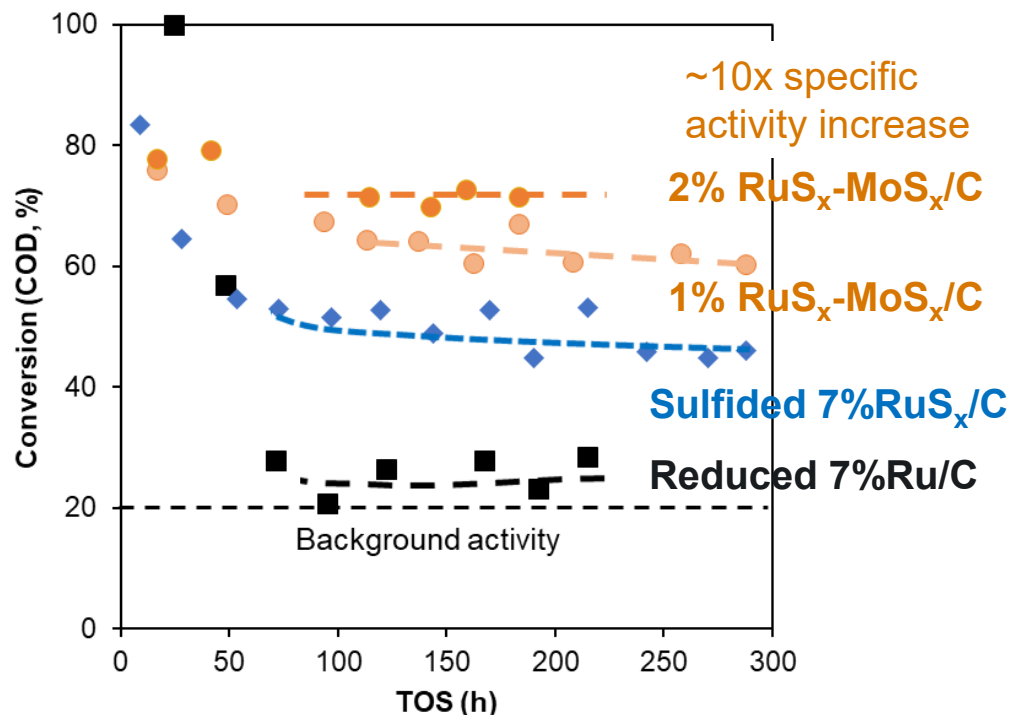
Ru-MoS_x based catalyst for stable and efficient CHG



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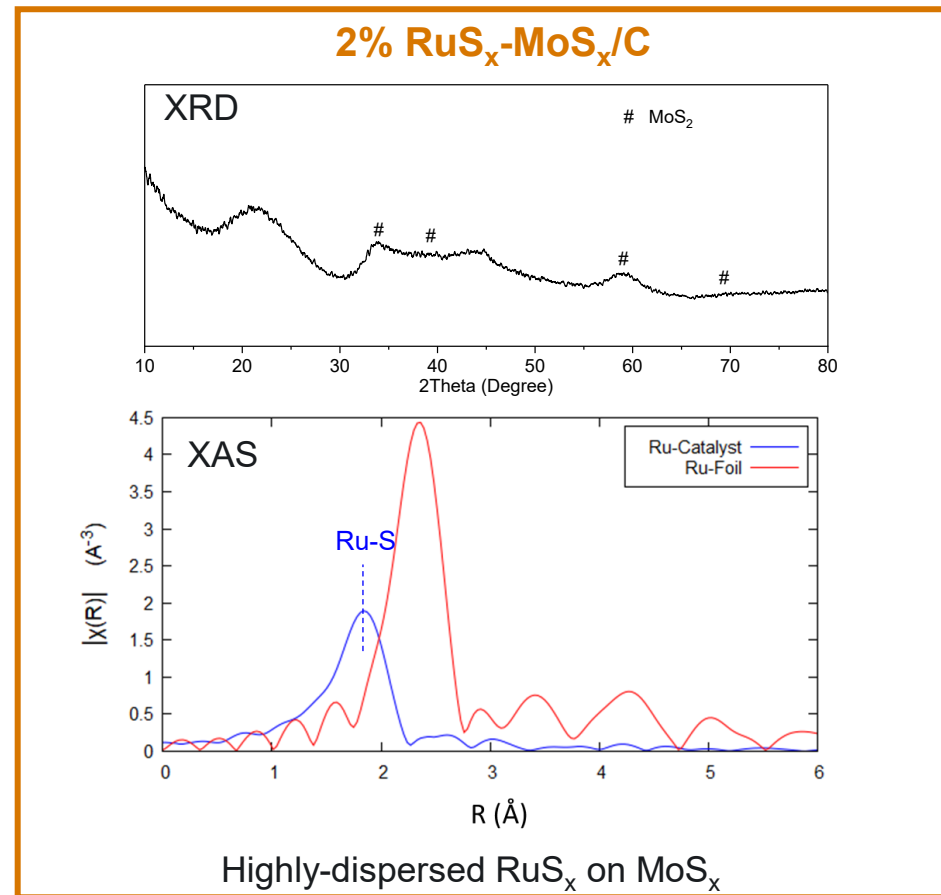
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350 °C, 20 MPa, real HTL-AP, fixed bed flow reactor

- Ru-based catalyst provides superior activity for CHG
- Significant catalyst deactivation by sulfur poisoning
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- New RuS_x-MoS_x/C catalyst showed enhanced activity at low Ru loading



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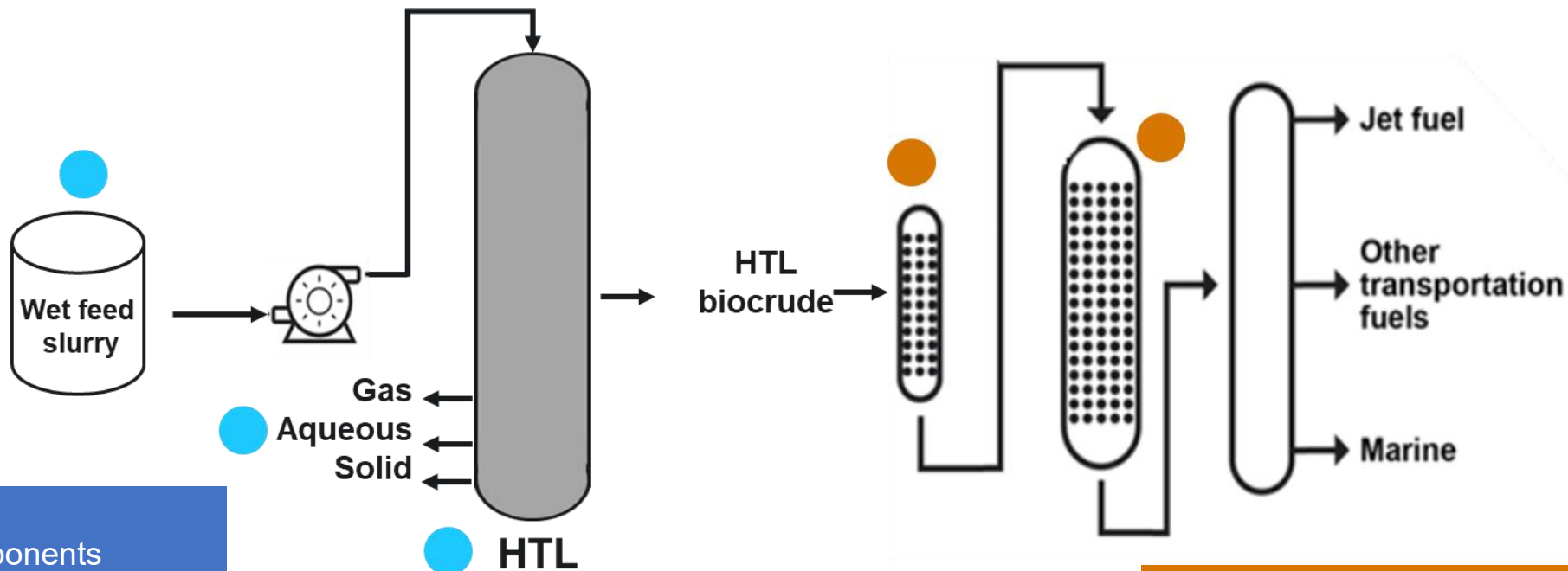
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CHG:

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Mariefel Olarte
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Conor Faulhaber
Zhibin Zhang

Topsoe for hydrotreating catalyst

Alternative Fuels and Feedstocks Office

Ben Simons, Robert Natelson



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and Energy Innovation

Alternative Fuels and Feedstocks Office

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