Co-processing wet waste hydrothermal liquefaction crudes with petroleum streams in refinery hydroprocessing

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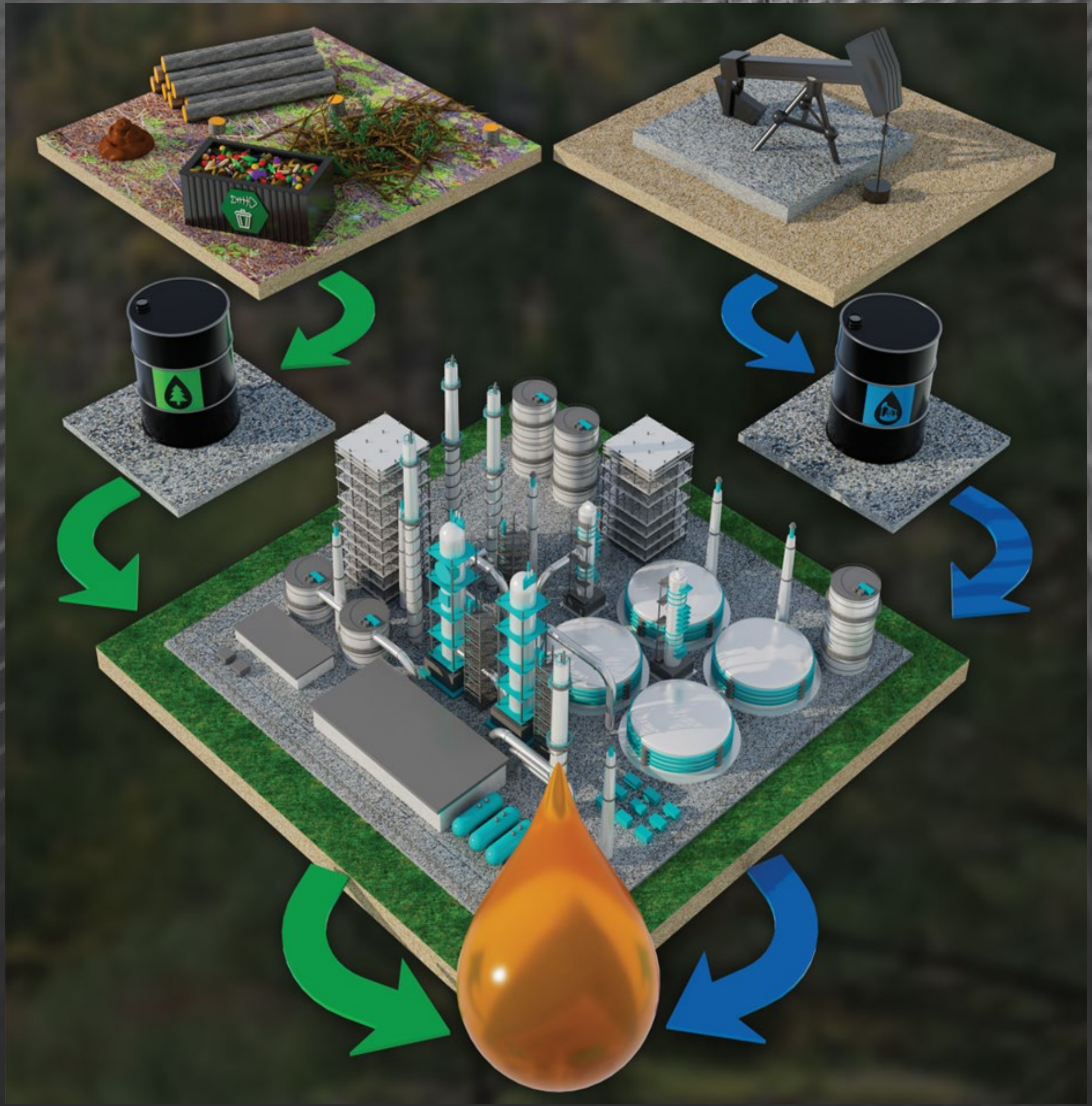
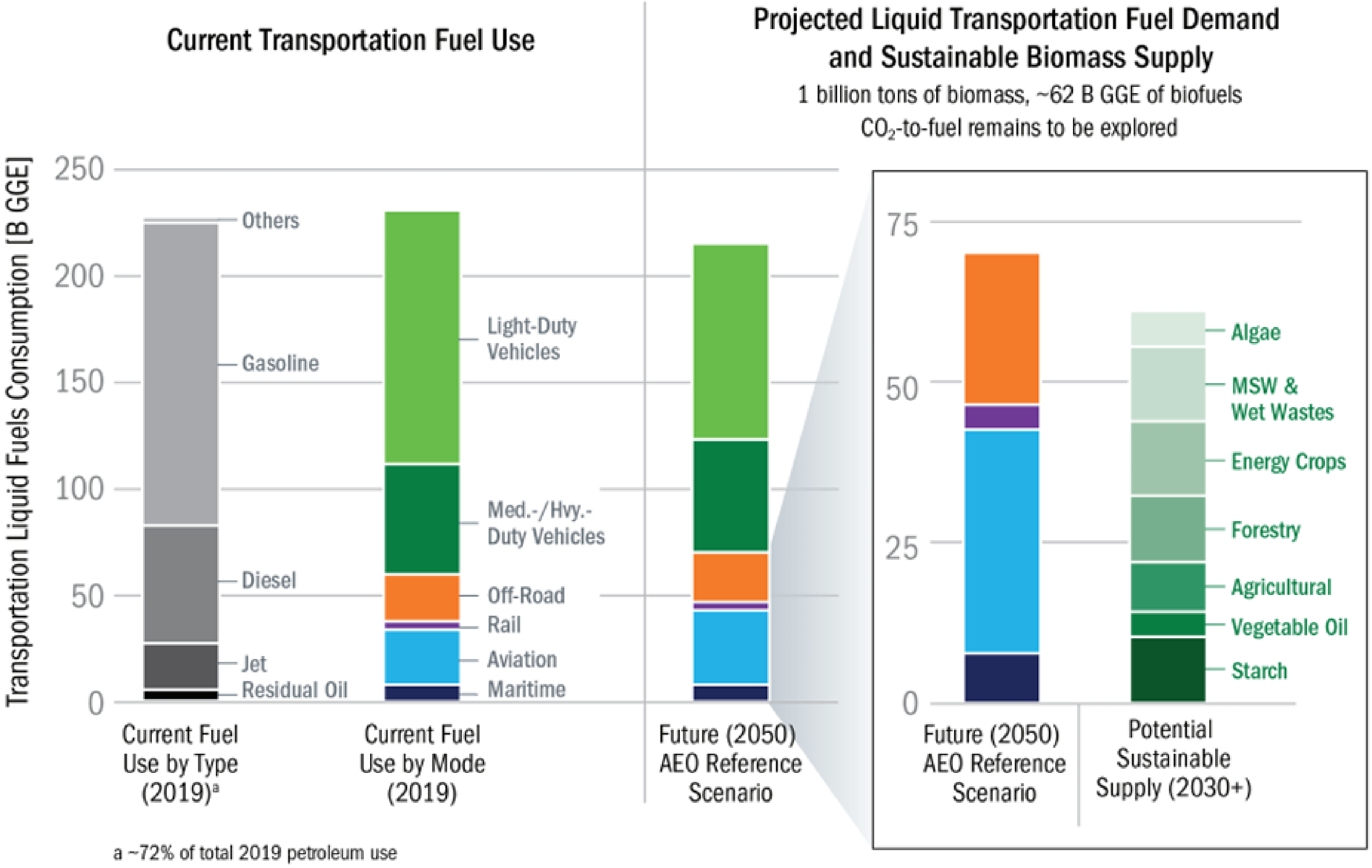
tcbiomass2024

PNNL is operated by Battelle for the U.S. Department of Energy



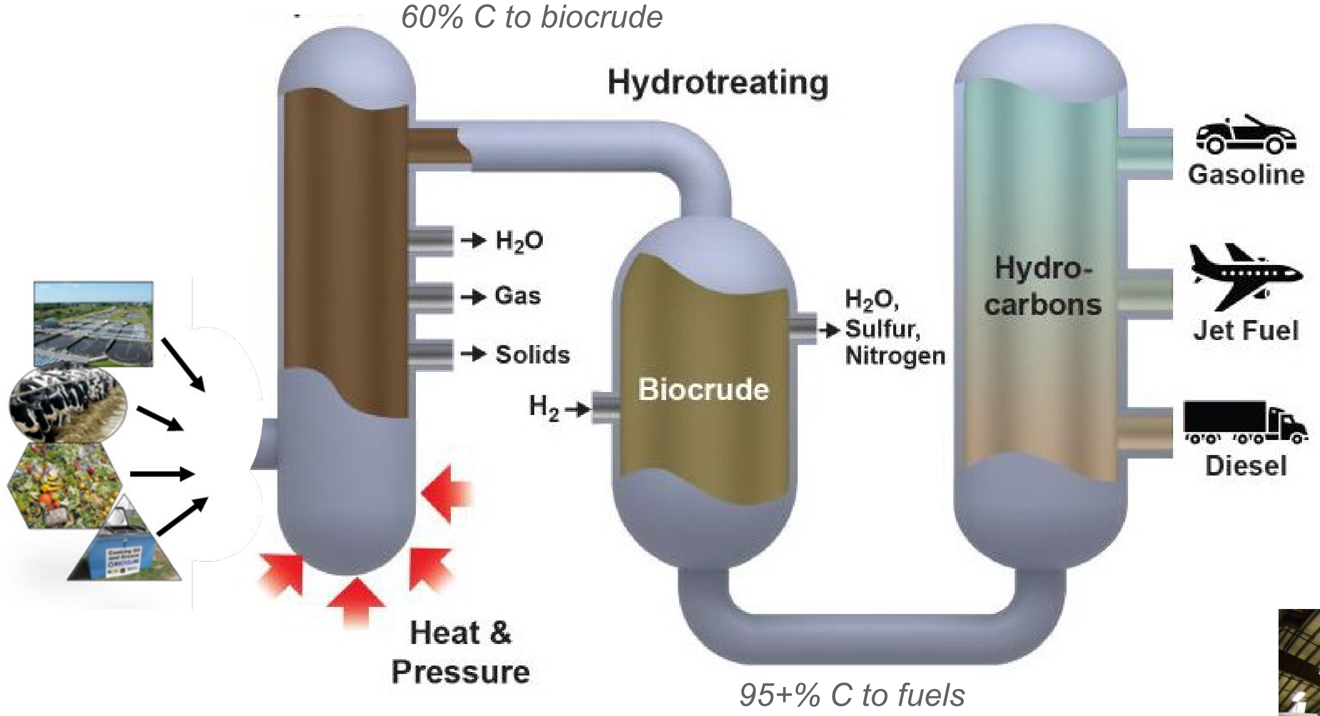
1 billion dry tons of potentially available biomass in 2030+ for the hard-to-electrify transportation sector



AEO = annual energy outlook | GGE = gasoline gallon equivalent | MSW = municipal solid waste

- Focusing on SAF and other strategic transportation fuels
- Unlocking the potential of the full range renewable carbon resources
- Leveraging existing industrial infrastructure supply chains

Transforming Wet Wastes to Liquid Fuels by Hydrothermal Liquefaction (HTL) and hydroprocessing



HTL

330-350 °C
20 MPa
10-30 min

Hydroprocessing

- Conceptually simple (i.e., heated pipe), continuous process
- High carbon yields to liquid hydrocarbons
- Tolerates dirty, wet feedstocks

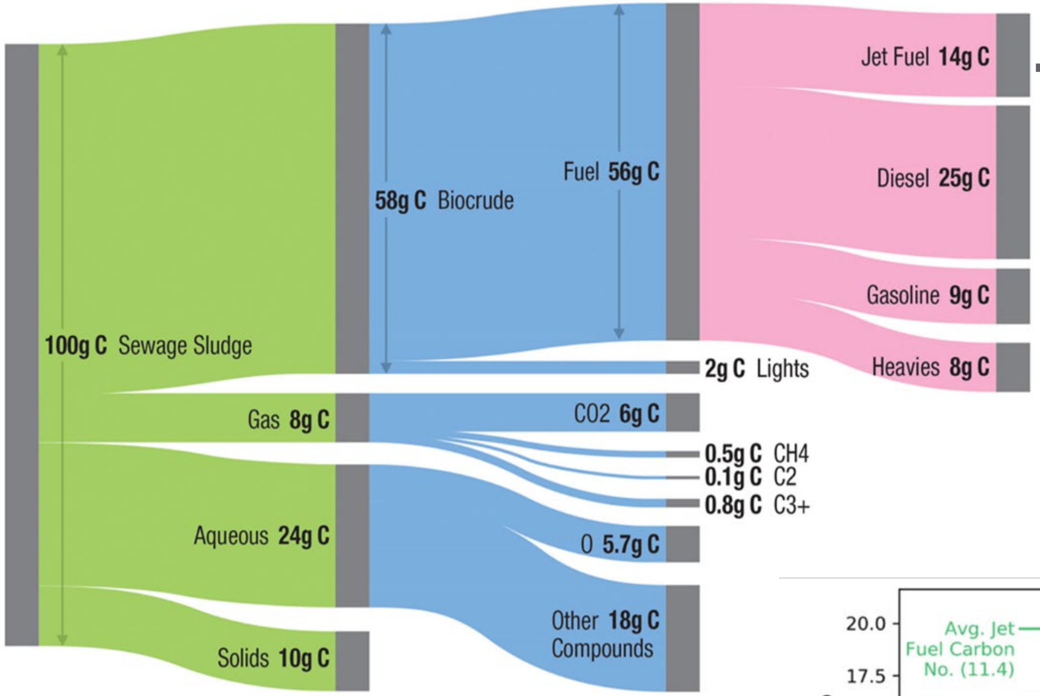
Benefit #1: **Potential for ~6 billion gallon/year of fuel in the U.S.**

Benefit #2: **Alternative disposal processes**

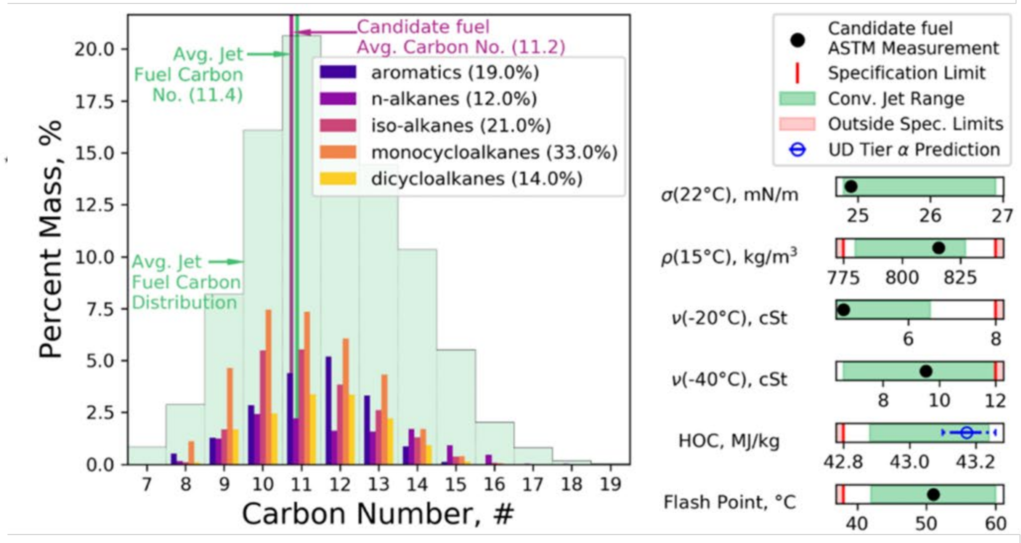
PNNL's HTL Process Development Unit (PDU)

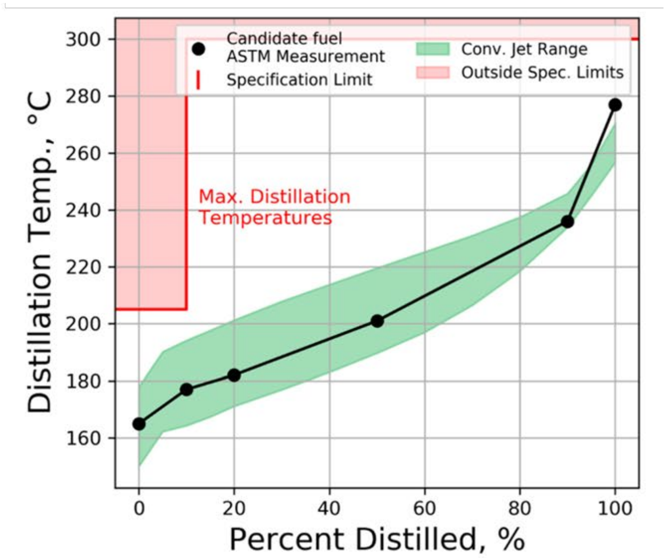
12-18 L/h slurry

SAF via HTL of wet wastes meets Tier α and β specs



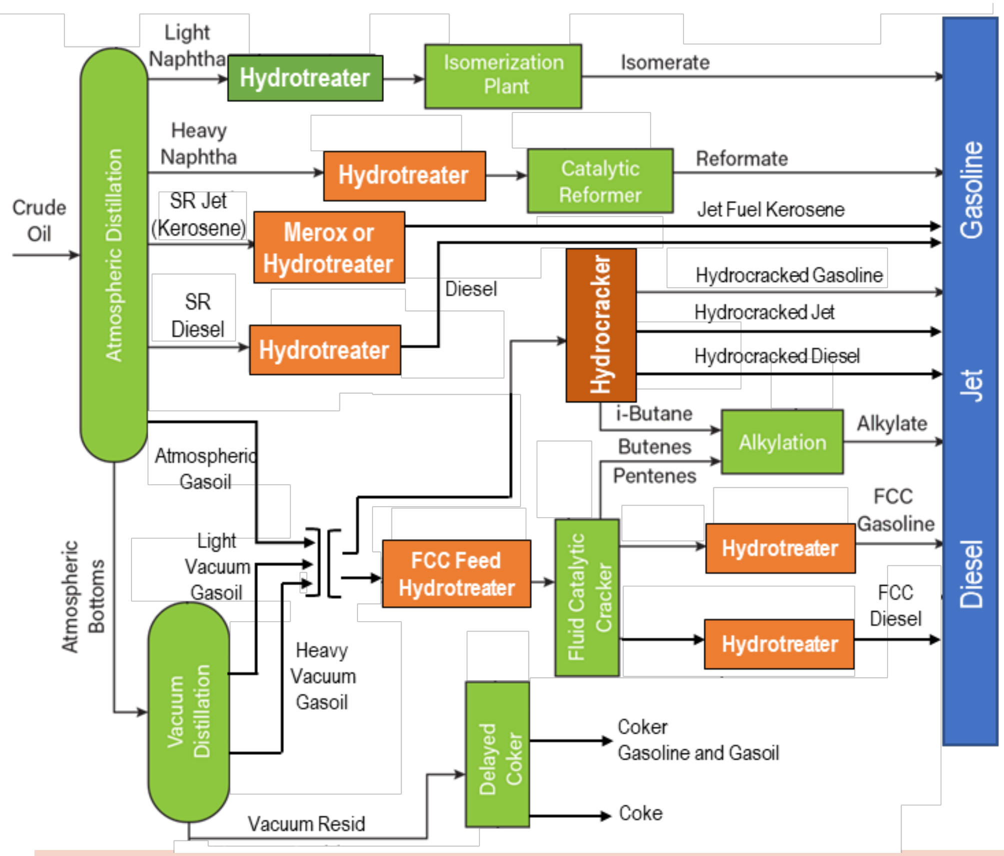
- ~25% of upgraded fuel in the jet range
- Similar mix of cycloalkanes, n-alkanes, iso-alkanes, and aromatics to traditional jet
  - Cycloalkanes and aromatics necessary to allow higher fuel penetration
- Positive Tier α and β jet fuel properties

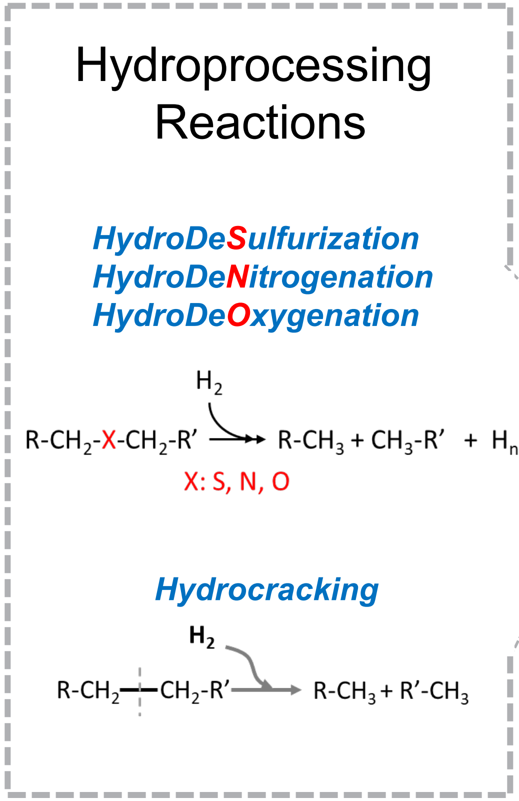




Hydroprocessing in refinery can co-process biocrudes

An example of a petroleum refinery





Hydroprocessing Reactions

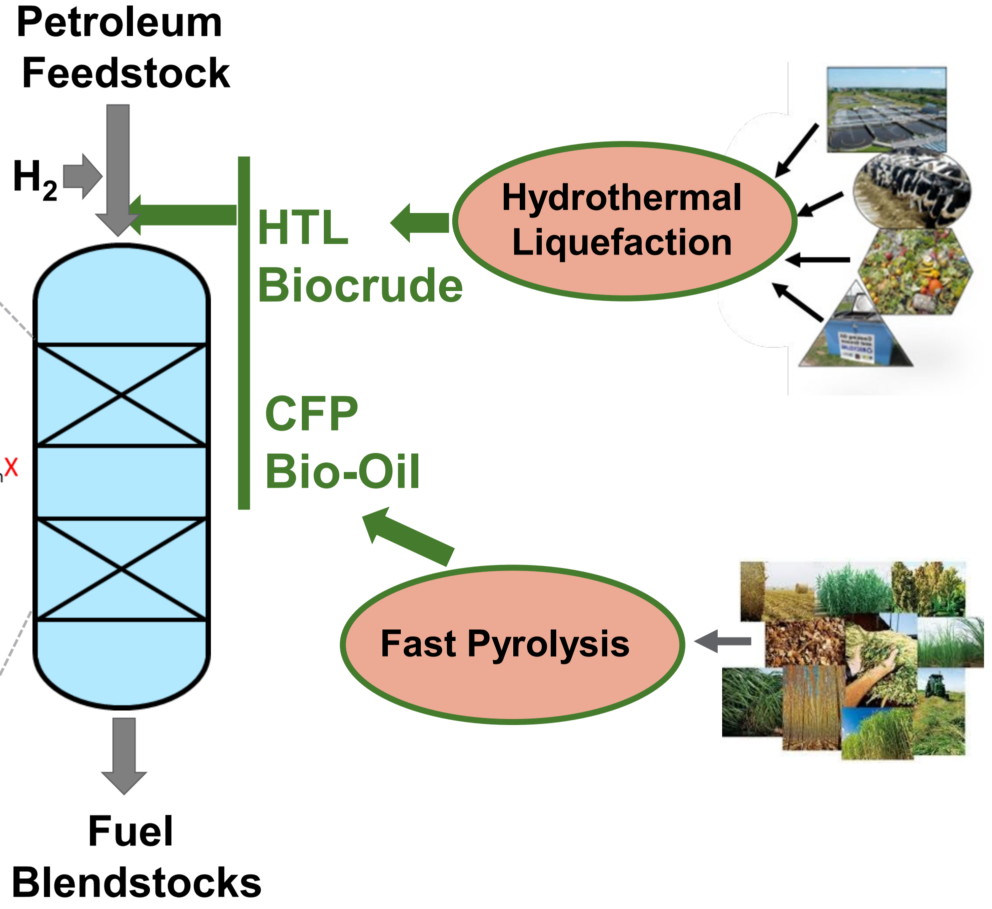
HydroDeSulfurization
HydroDeNitrogenation
HydroDeOxygenation

$$\text{R-CH}_2\text{-X-CH}_2\text{-R'} \xrightarrow{H_2} \text{R-CH}_3 + \text{CH}_3\text{-R'} + \text{H}_n\text{X}$$

X: S, N, O

Hydrocracking

$$\text{R-CH}_2\text{—CH}_2\text{-R'} \xrightarrow{H_2} \text{R-CH}_3 + \text{R'-CH}_3$$



Petroleum Feedstock

H_2

HTL Biocrude

Hydrothermal Liquefaction

CFP Bio-Oil

Fast Pyrolysis

Fuel Blendstocks

- Hydrotreating removes heteroatoms (S, N, O) and hydrocracking converts heavy gasoils into lighter fuel blends
- Hydrogen addition to prevent carbon rejection
- Fixed-bed operation, long catalyst lifetime, high pressure

The key challenges include N-containing species

High nitrogen content from protein

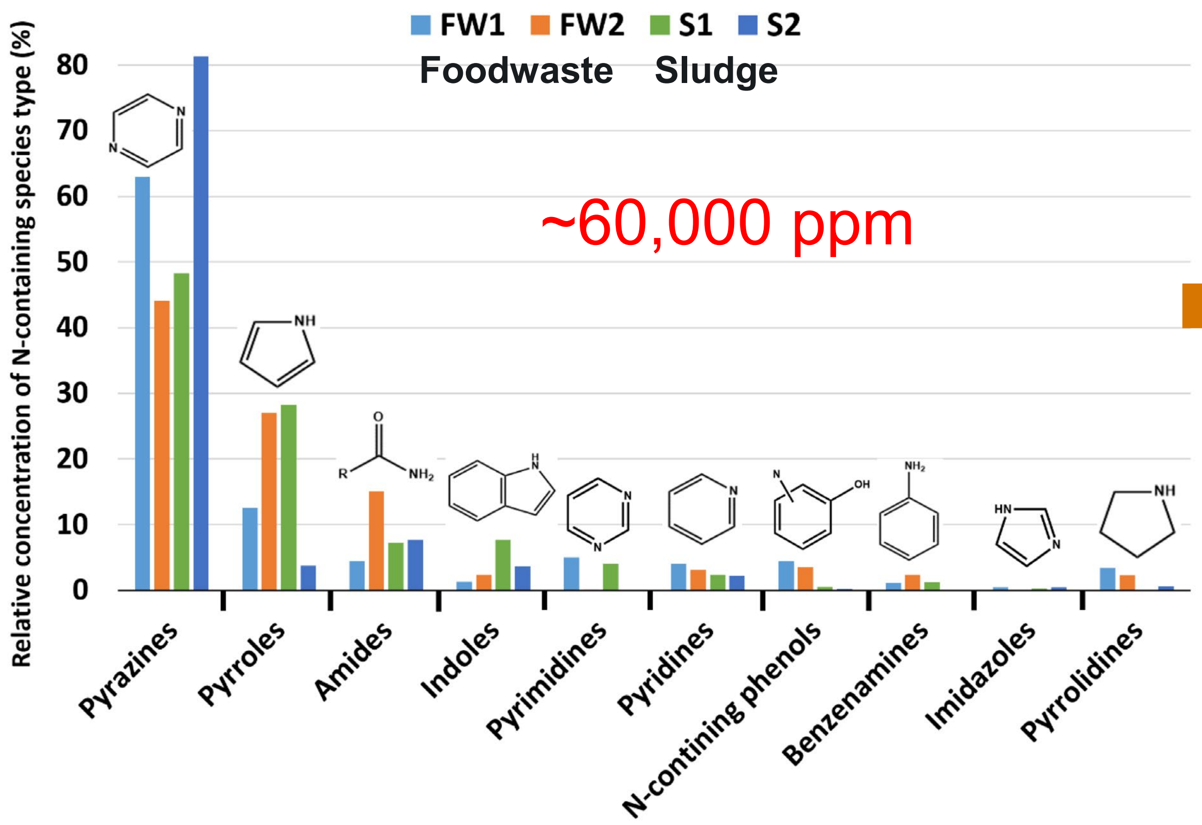
	VGO	Bio-crude
H/C	1.6-1.7	~1.5
O wt%	0.1-1.0	~2-8
S wt.%	0.1-2.5	~0.5
N wt.%	0.1-2	**~5**
H_2O Wt.%	<0.05	~1-5

Major Challenges

- **Deep N removal to meet SAF specification**
  - High nitrogen content in jet fraction after direct biocrude hydrotreating (Nitrogen: ~2000ppm)
  - All approved SAF pathways have a nitrogen spec of 2ppm
  - Thermal stability concerns due to potential Nitrogen-Sulfur interactions
- **Deep N removal to enable hydrocracking and co-processing**
  - Hydrocracking of heavier-than-jet fraction to increase jet yield
  - Co-processing biocrude with refinery hydroprocessing with minimal impact to hydroprocessing chemistry

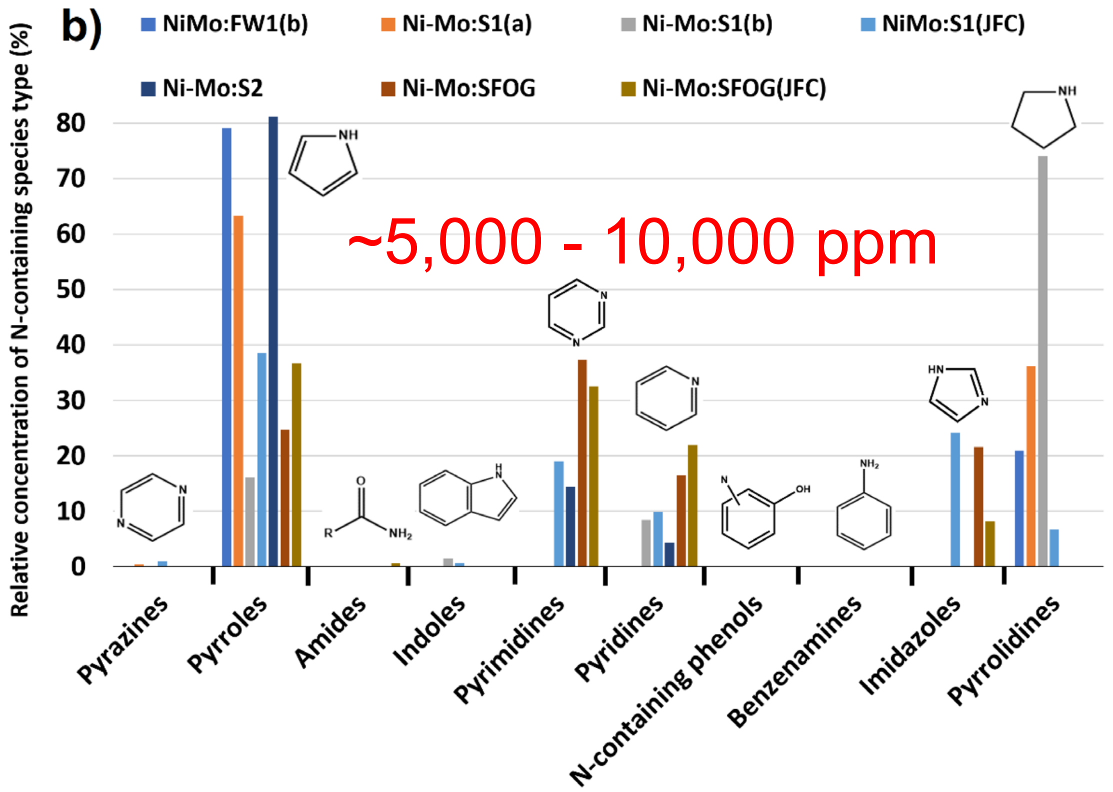
Deep HDN is required

Biocrude



~60,000 ppm

Hydrotreated biocrude



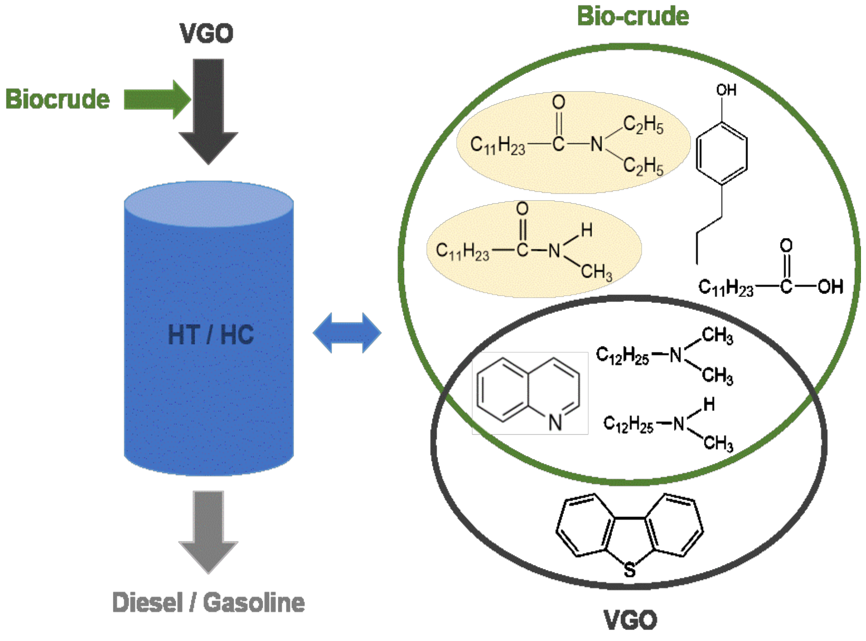
~5,000 - 10,000 ppm

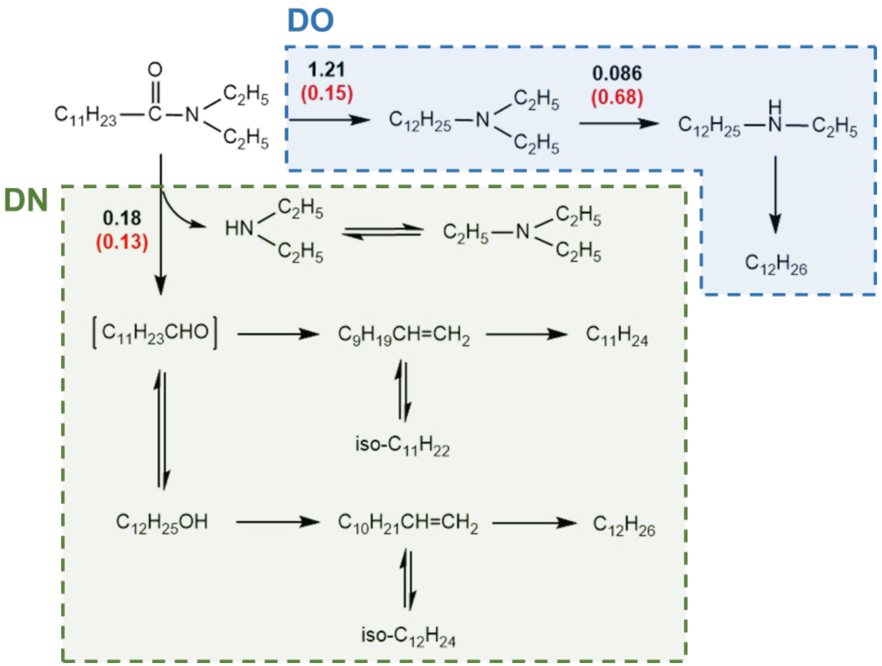
- Biocrude is rich in pyrazines, pyrroles, amides, indoles, etc. as identified via GC/GCMS

- Deep HDN is required to further reduce N

Kinetic study to identify the most challenging species

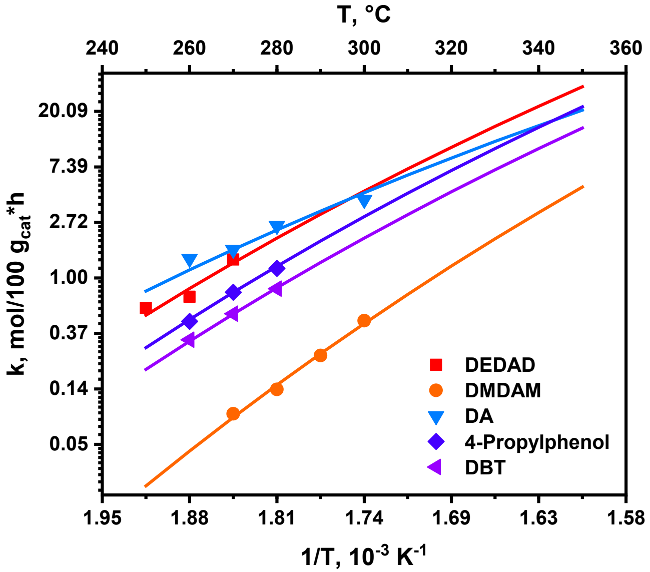
Biocrude introduce new N containing species

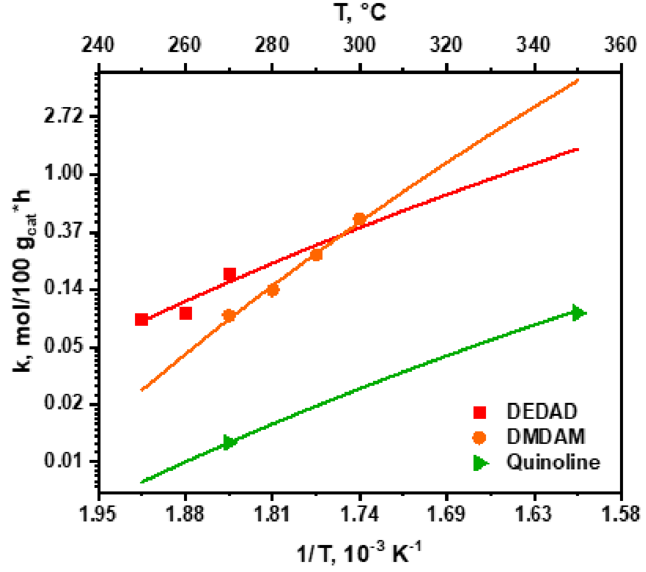




- Biocrude introduce some unique N containing species, but the indoles and quinolines are still the most refractory compounds
- A kinetic-based reactor model for co-processing enables predictive capabilities and optimization for reactor configuration and operation conditions

Hydrodenitrogenation is slow

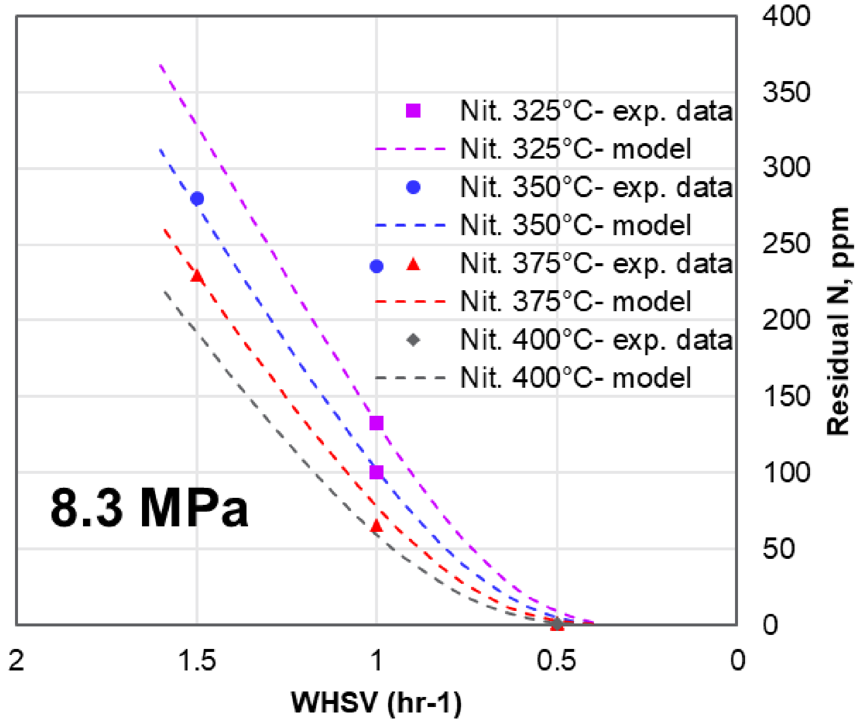




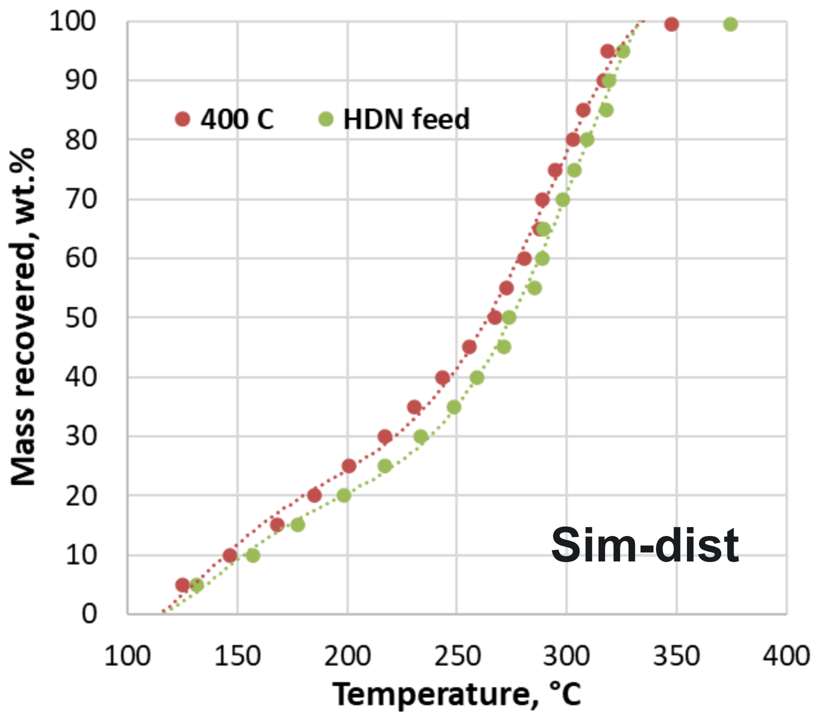
C. Zhu,… H. Wang, Applied Catalysis B: Environmental, 2022, 307, 121197

Deep HDN achieved with commercial catalysts

Achieving <1 ppm N at various conditions using extrudate catalysts



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



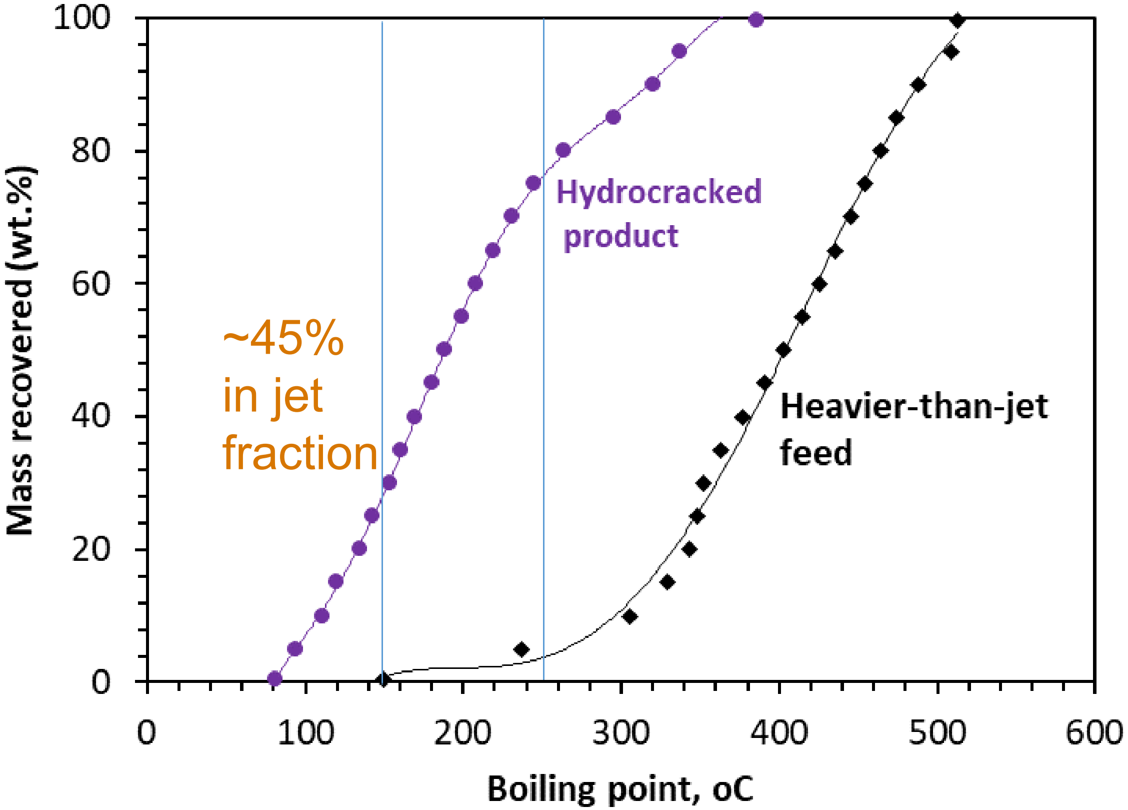
Gas yield is below 3% at the most severe conditions (400 ^{o}C and 0.5 h^{-1} WHSV)

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

Deep HDN of heavier-than-jet fraction enables hydrocracking

After deep HDN

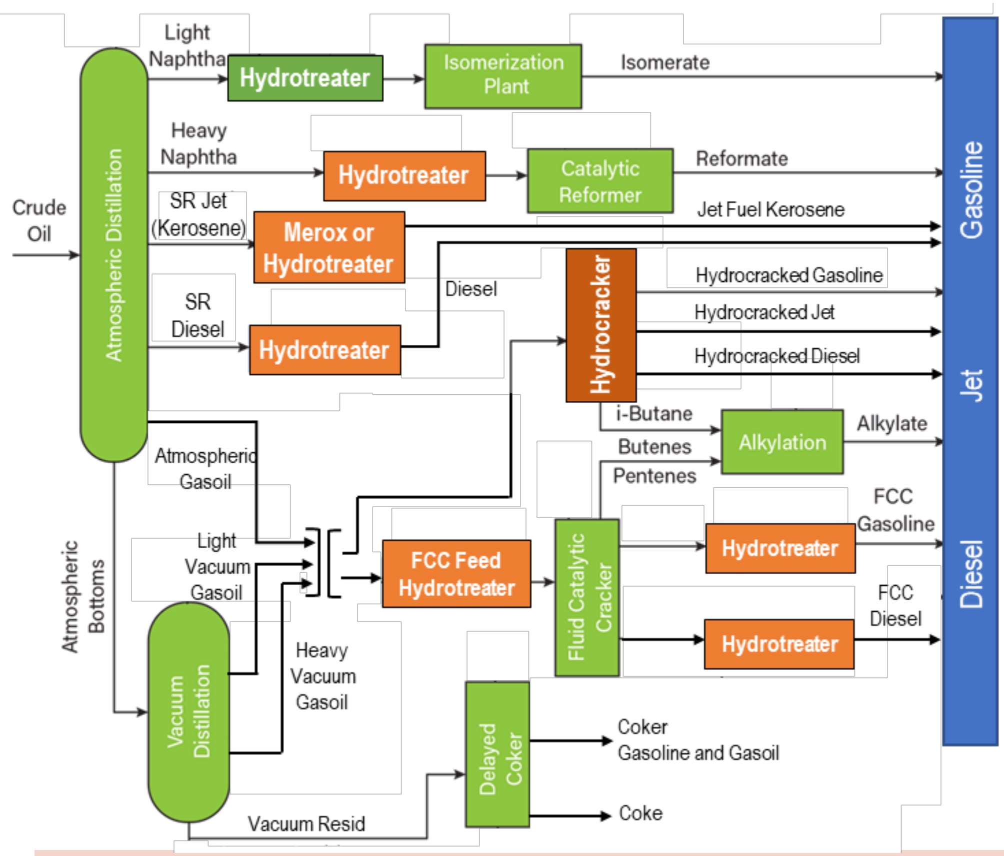
Hydrocracking of heavier-than-jet fraction



- Deep HDN of heavier than jet fraction, leading to 20-200 ppm N in product, enables hydrocracking using commercial zeolite containing catalysts
- Potential for a100% increase in jet fuel yield from biocrude

Hydroprocessing in refinery can co-process biocrudes

An example of a petroleum refinery



Hydroprocessing Reactions

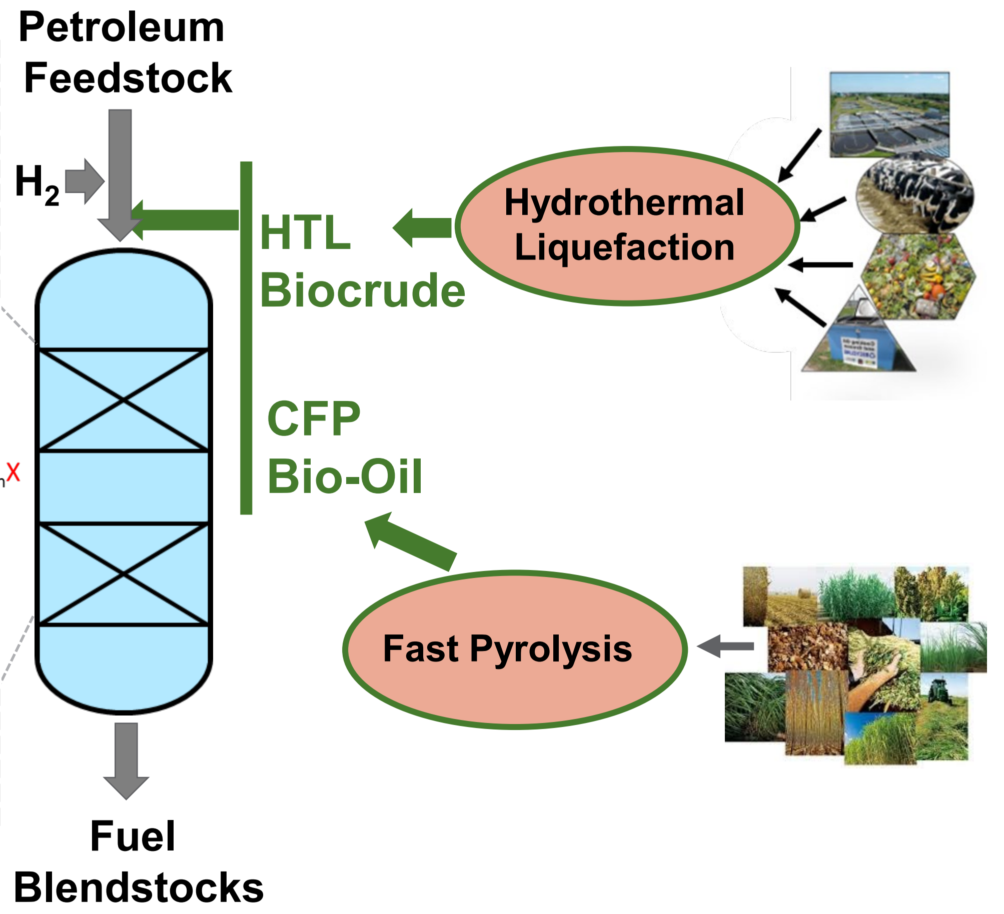
*HydroDe**S**ulfurization*
*HydroDe**N**itrogenation*
*HydroDe**O**xygenation*

$$R\text{-}CH_2\text{-}X\text{-}CH_2\text{-}R' \xrightarrow{H_2} R\text{-}CH_3 + CH_3\text{-}R' + H_nX$$

X: S, N, O

Hydrocracking

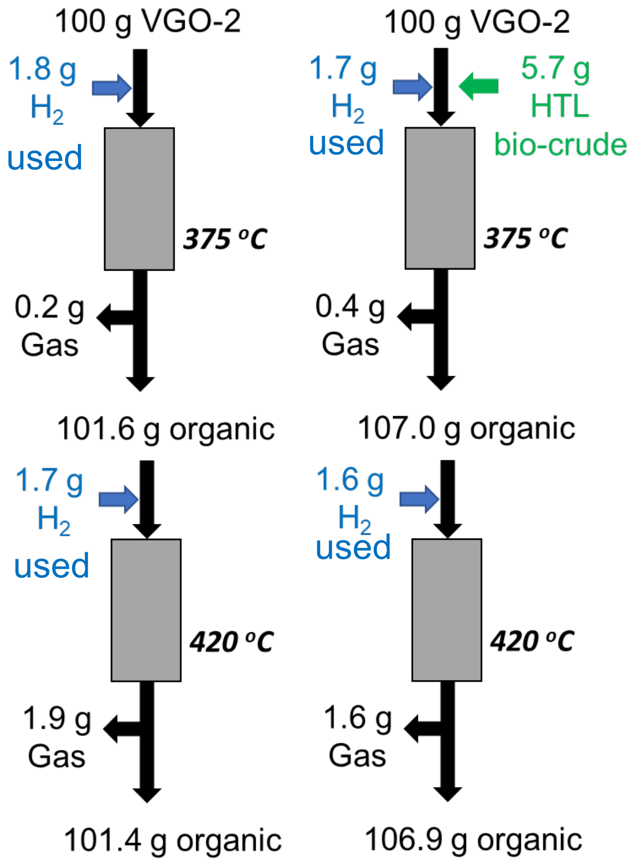
$$R\text{-}CH_2 \text{—} CH_2\text{-}R' \xrightarrow{H_2} R\text{-}CH_3 + R'\text{-}CH_3$$



- Hydrotreating removes heteroatoms (S, N, O) and hydrocracking converts heavy gasoils into lighter fuel blends
- Hydrogen addition to prevent carbon rejection
- Fixed-bed operation, long catalyst lifetime, high pressure

95+% Biogenic carbon incorporation demonstrated for the HTL biocrude

	Bio-crude	VGO
H/C	~1.5	1.6-1.7
O	~2-8	0.1-1.0
S	~0.5	0.1-2.5
N	**~5**	0.1-2
H_2O	~1-5	<0.05



100 g VGO-2

1.8 g H_2 used

375 °C

0.2 g Gas

101.6 g organic

1.7 g H_2 used

420 °C

1.9 g Gas

101.4 g organic

100 g VGO-2

1.7 g H_2 used

5.7 g HTL bio-crude

375 °C

0.4 g Gas

107.0 g organic

1.6 g H_2 used

420 °C

1.6 g Gas

106.9 g organic

95+%

biogenic carbon incorporated into fuels

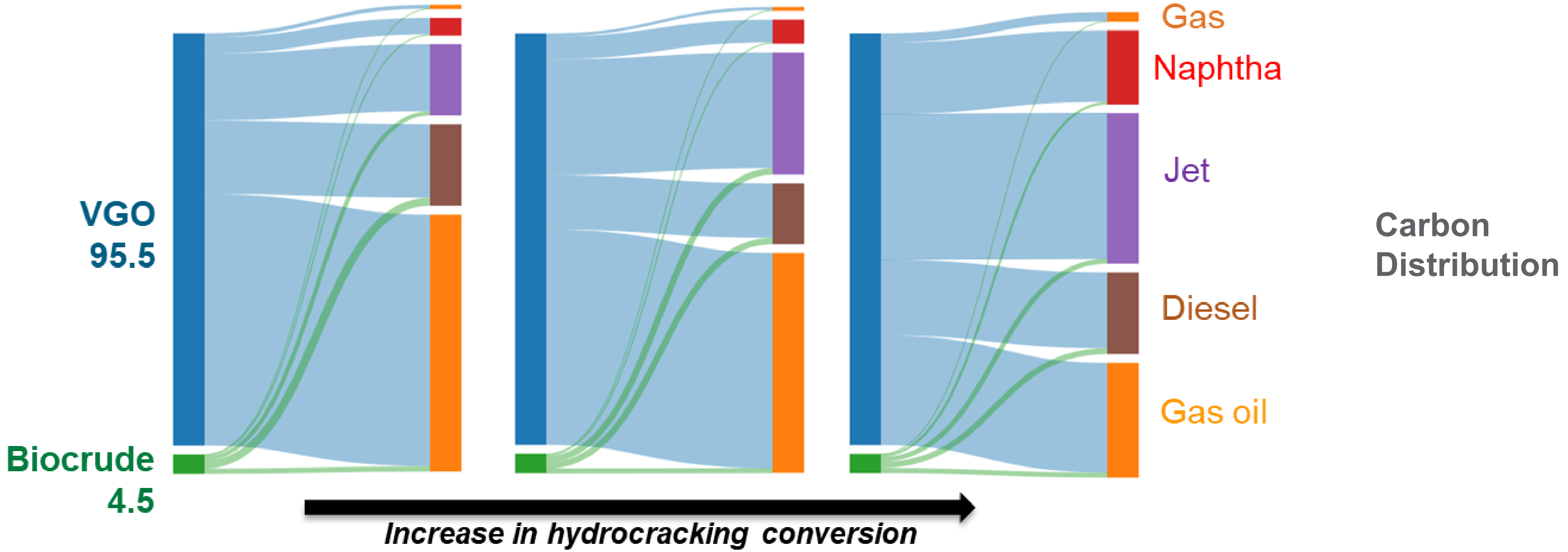
Improved diesel (184-350 °C) quality

	VGO only	5.7/100 HTL/VGO
Cetane Number	**42**	**47**
S, ppm	**<15**	**<15**
N, ppm	**30**	**93**
Biogenic C, % (AMS)		**7.3** **(~60% of total bio-C)**

M. Santosa, … H. Wang, Manuscript in preparation

- High N in biocrude leads to competition among heteroatom (S, N, O) removal when co-processing
- A hydrotreating step is required to mitigate N issues of biocrude and enable co-processing in hydrocracking
- High biogenic carbon incorporation and improved diesel fuel quality through co-processing biocrude

Tuning biogenic carbon distribution in co-hydrocracking



- Deep HDN in VGO + biocrude hydrotreating enables hydrocracking using the conventional zeolite-containing catalyst for a greater yield of jet and diesel range fuels
- Biogenic carbon is largely incorporated into the mid-distillate range fuel (jet and diesel)
- Biocrude is less sensitive than VGO on the hydrocracking severity

H. Wang, Manuscript in preparation

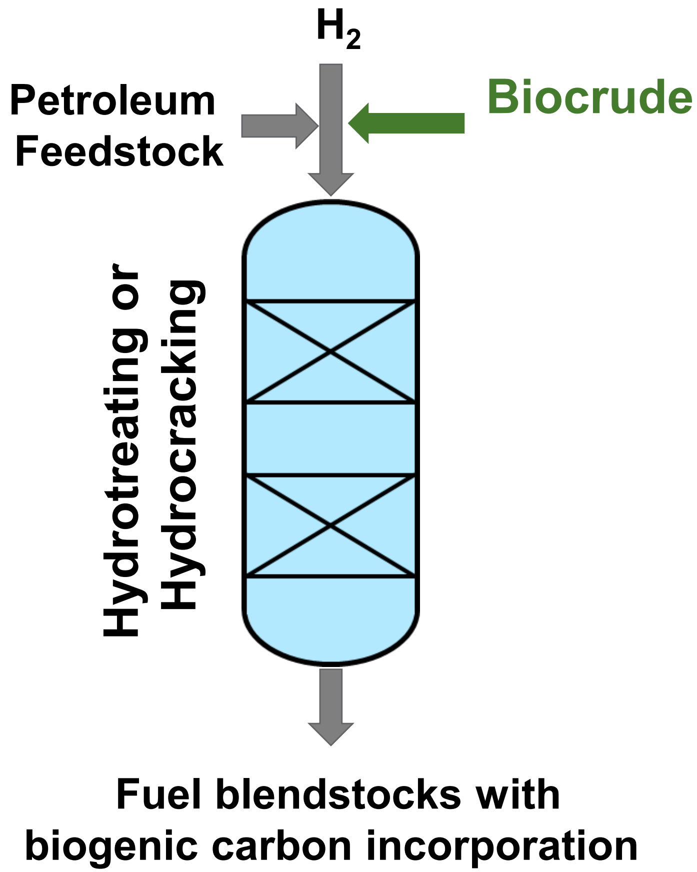
We evaluate co-processing of bio-liquids in various hydroprocessing units

	Woody FP bio-oil	**Woody CFP bio-oil**	**Sludge HTL biocrude**	**Hydrotreated HTL biocrude**
Diesel HT	🔴 • Instability requires pre-stabilization • High water and O • Low (~70%) bio-carbon incorporation into fuel	🔵 • Mild impact on HT chemistry • High (80-95%) bio-carbon incorporation into fuel • Water, O, long-term “coke” formation	🔴 • Strong N inhibition of HT chemistry	
VGO HT	🔴	🔵	🔵 • HT pretreatment to mitigate N issue • High (>95%) bio-carbon incorporation into fuel • Increased fuel quality • Faster catalyst deactivation at long-term	
VGO HC			🔵	
Fuel oil HT			⚫ • Enable N and S reduction • Issues in homogeneity	
Kerosene HT				🔵 Synergy enables deep HDN (<1 ppm N for SAF)

- The feasibility of co-processing bio-oil and biocrude feedstocks with different petroleum streams in hydroprocessing greatly depends on their heteroatom content and speciation

🔴 *More challenge* 🔵 *Less challenge* ⚫ *More data needed*

HDN to meet SAF requirement and enable co-processing



Deep HDN

- Biocrude introduce some unique N containing species, but the indoles and quinolines are still the most refractory compounds
- Deep HDN using commercial catalyst can reach <2 ppm N in SAF, meeting SAF specification
- Deep N removal to enable hydrocracking heavier-than-jet fraction to increase jet yield

Co-processing biocrudes in hydroprocessing have great potential

- High biogenic carbon incorporation
- HDN addresses high N challenges
- Co-processing can offer benefits to both the biorefinery and the refinery

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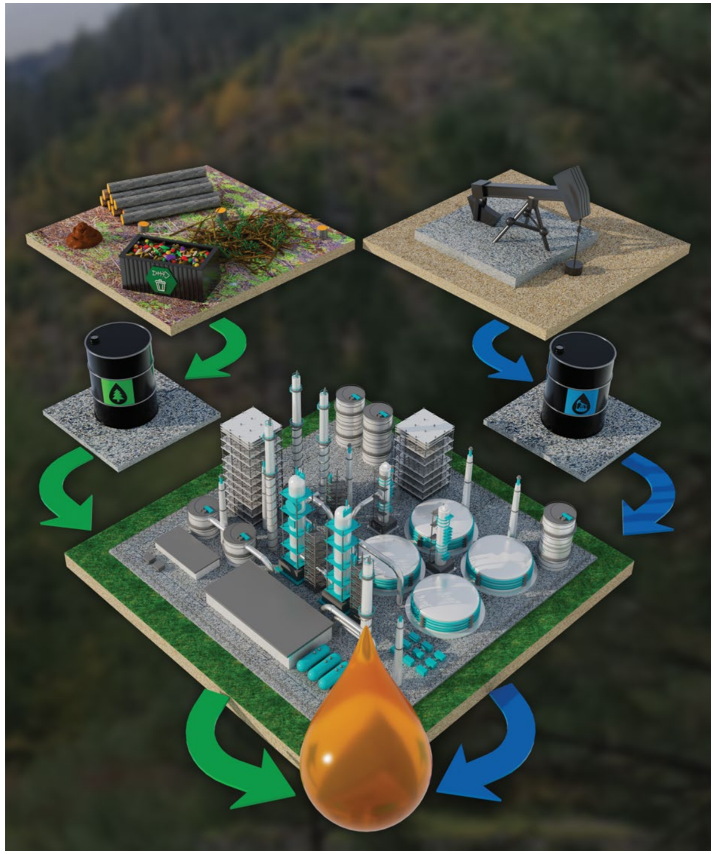

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