Hydrothermal Liquefaction of wet wastes for SAF

June 20, 2023

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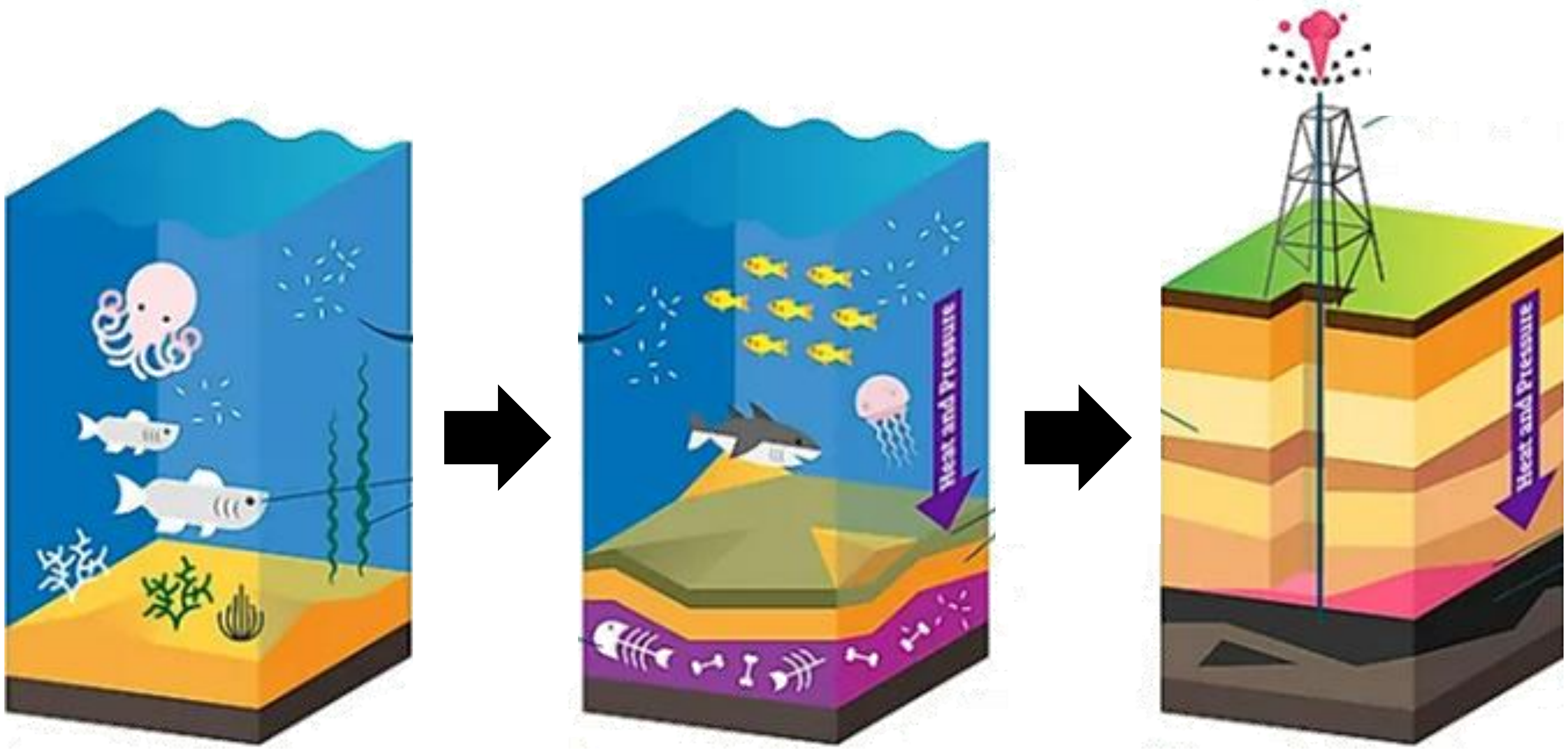
Pacific Northwest National Laboratory

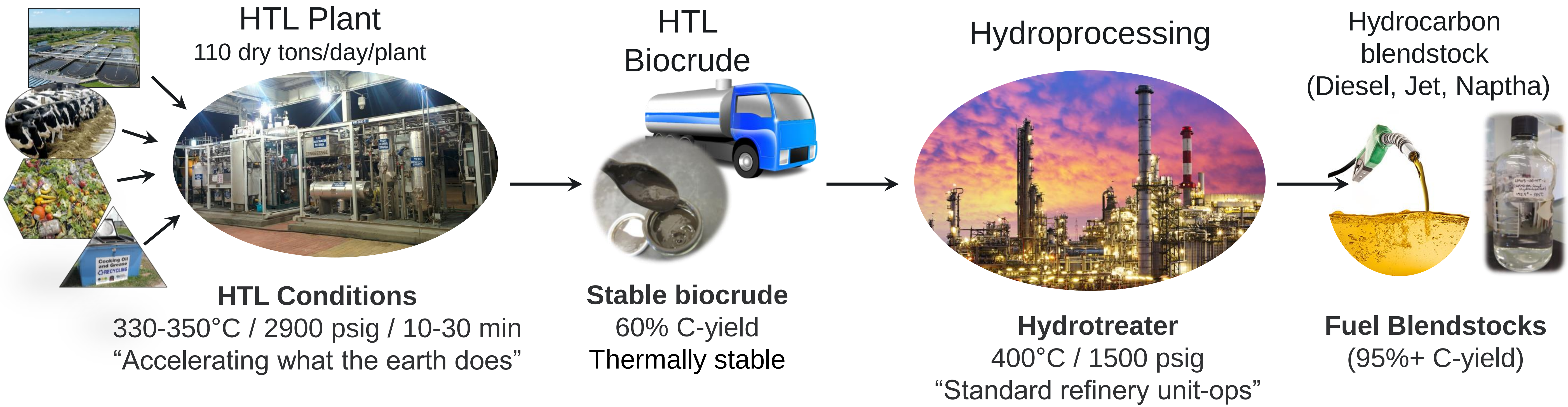
Hydrothermal Liquefaction (HTL)…



HTL speeds up the process:

350^{0}C @ 150 bar for 10 to 30 minutes

Hydrothermal Liquefaction
A pathway to fuel from sewage sludge



HTL Plant
110 dry tons/day/plant

HTL Biocrude

Hydroprocessing

Hydrocarbon blendstock
(Diesel, Jet, Naptha)

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

Stable biocrude
60% C-yield
Thermally stable

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

Fuel Blendstocks
(95%+ C-yield)

- HTL is **conceptually simple** ("a pressure cooker")
    - Can accept a diverse range of wet feedstocks (no drying!)
- Produces a **thermally stable** biocrude oil which can be upgraded to fuels, mostly diesel
- Tolerates moderate solids content
- HTL results in high carbon yields to liquid hydrocarbons (up to 60%)
- 81%* GHG reductions compared to fossil fuels for HTL of sewage sludge

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*Cai, Hao, et al., *Supply Chain Sustainability Analysis of Renewable Hydrocarbon Fuels via Hydrothermal Liquefaction, Combined Algal Processing, and Biochemical Conversion: Update of the 2022 State-of-Technology Cases*. 2023. doi:10.2172/1963599

Cost of sludge disposal is equivalent to the value of fuel that could be produced

Example:

Daily disposal costs[1]: $20,000 – $40,000

$2.30-4.70/gal of fuel produced

100 dry tons/day

→

~8,500 gallons fuel

Value of fuel[2]: ~$34,000/day

$4.00/gal

Costs of sludge disposal will grow as regulations increase due to environmental concerns

Maine bans use of sewage sludge on farms to reduce risk of PFAS poisoning

Sludge used as crop fertilizer has contaminated soil, water, crops and cattle, forcing farmers to quit

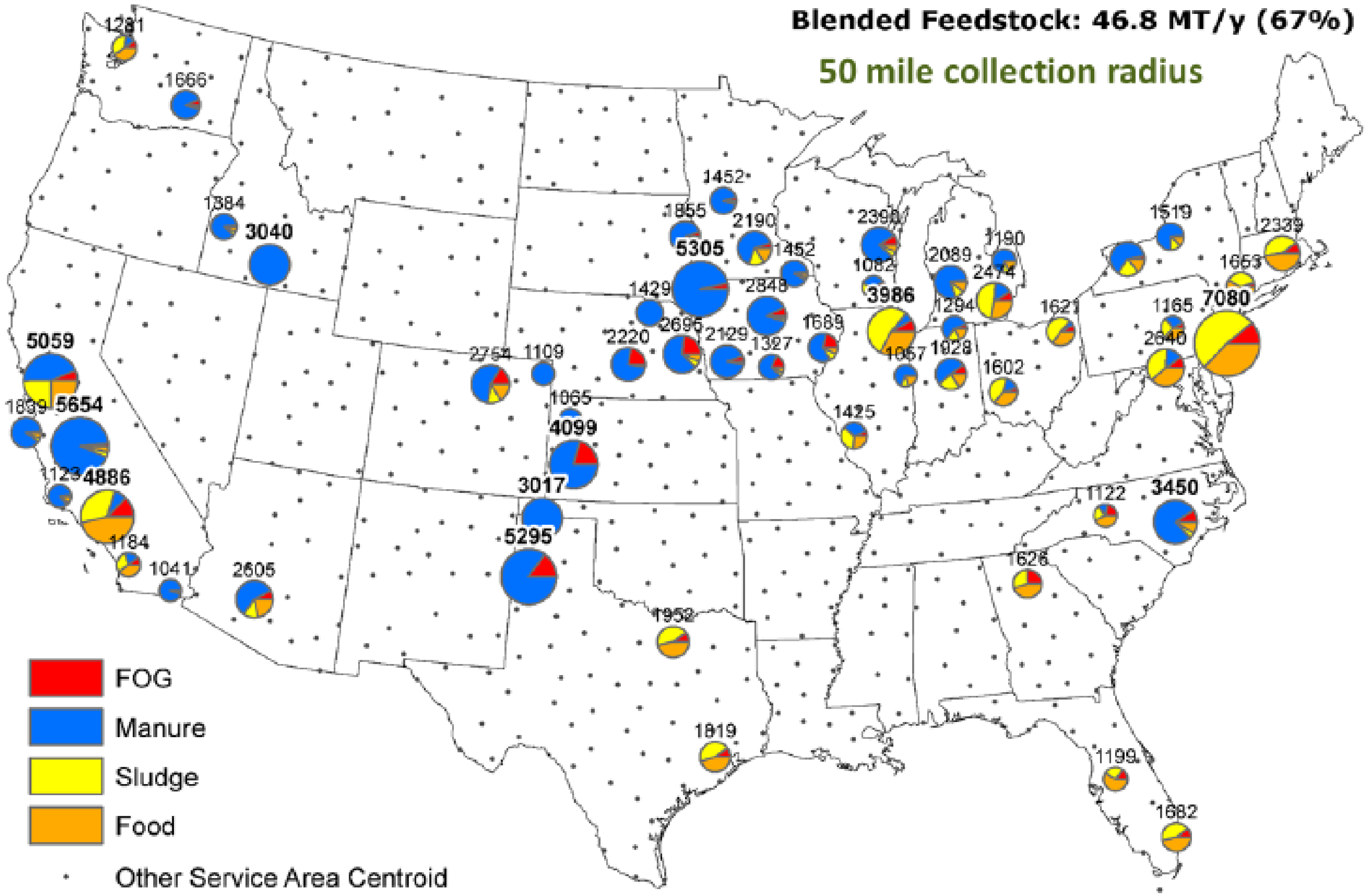
ENVIRONMENT

Colorado has been spreading biosolids with "forever chemicals" on farms, records show. How dangerous is it?

Environmental groups say there is no safe level for toxic PFAS chemicals in drinking water or on farm land. State regulators say they are studying it.

[1] Basis of disposal costs: $200-400/dry ton or $40/wet ton @ 10-20 wt% solids, [2] Value of fuel is $2-3/gal

Upwards of 77M dry tons of wet waste available – nearly 70% is within 50 miles of a WRRF



Urban wet waste composition:
40% food / 50% sludge / 10% FOG

Rural wet waste composition:
50% Manure / 20% food / 25% sludge / 5% FOG

Points

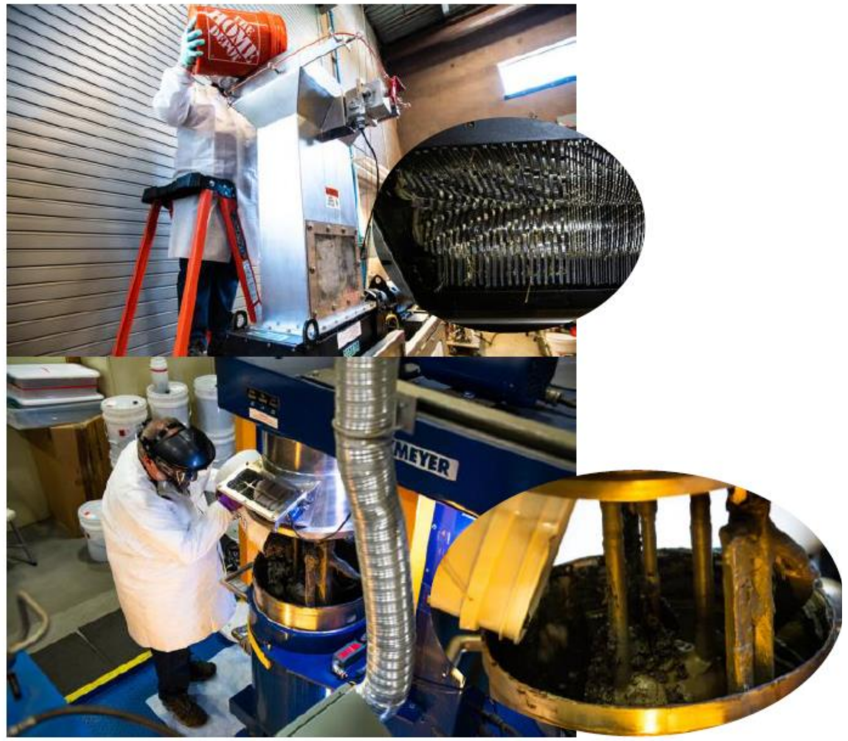
- Sludge makes a higher quality fuel than wood
- Sludge improves the processibility of wood
- Wood and stover increase the total fuel production potential

Potential for ~6 billion gallon/year of fuel in the U.S.
(~1.5 billion gallons per year in SAF range)

HTL's Main Process Areas

Wet feedstock formulation and formatting

Pumpable slurry



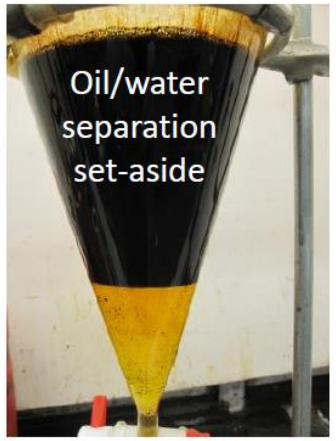
Liquefaction

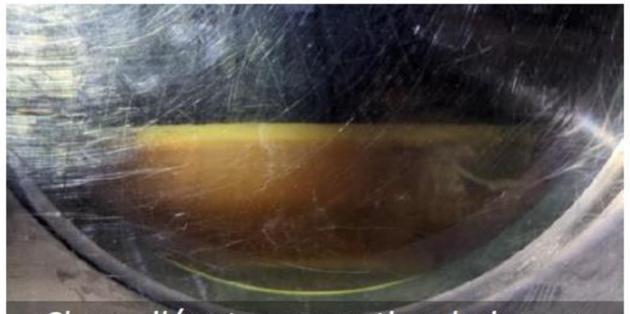
Heat exchange and reaction

350°C / 3000 psi

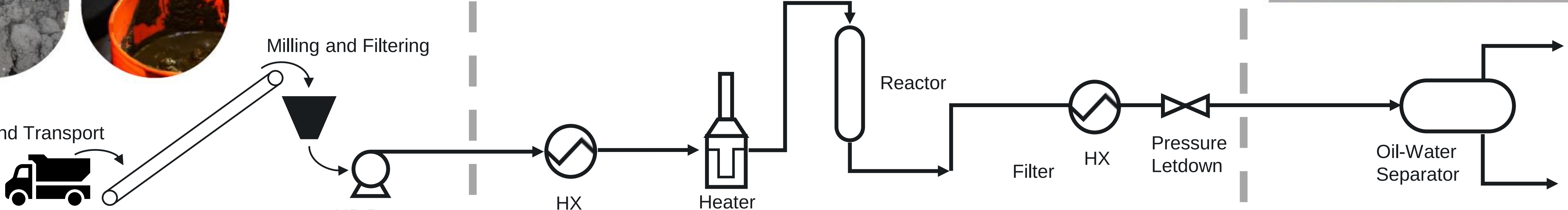
Product Separations

Oil / Solids / Gas

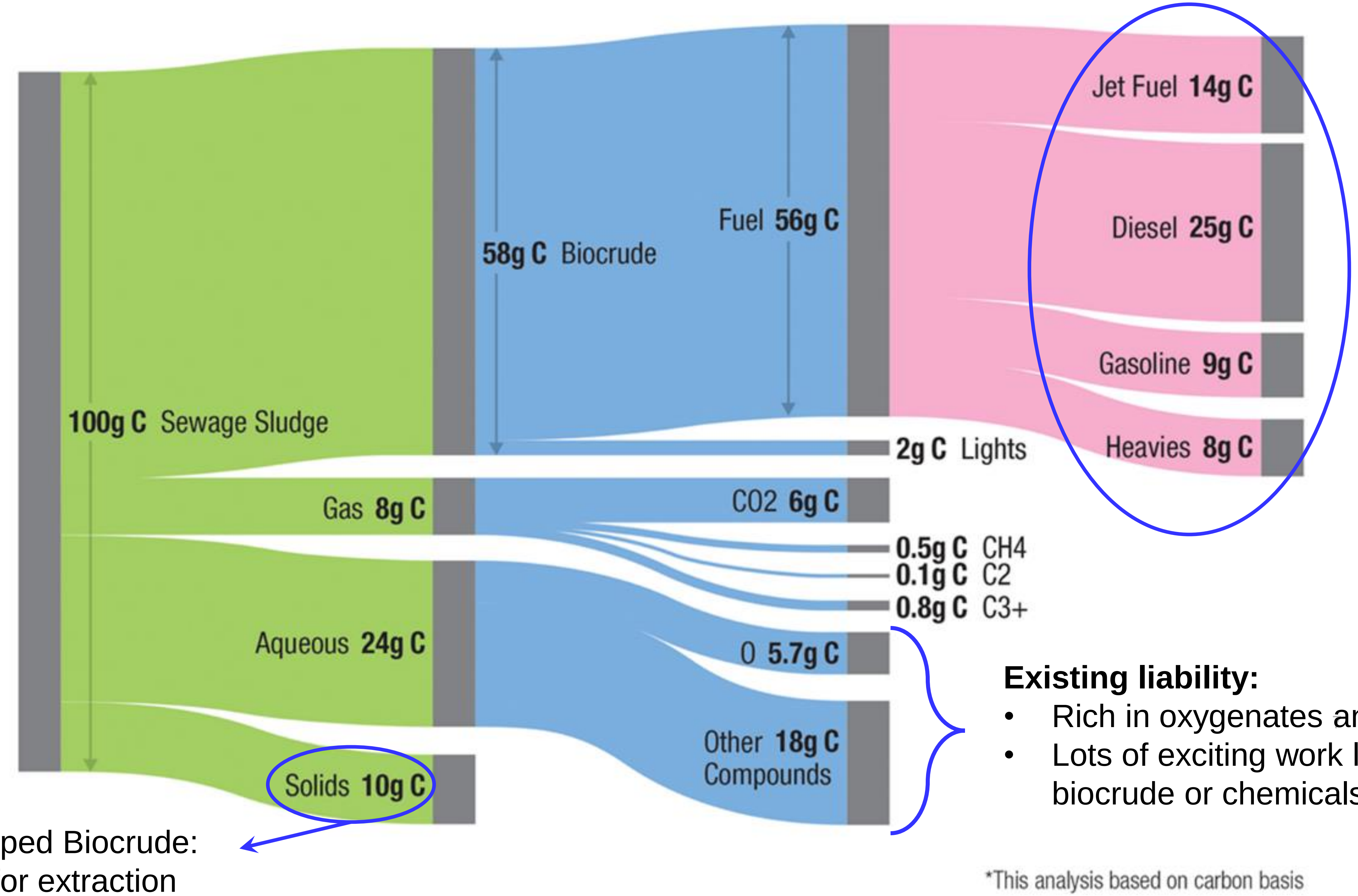




Clean oil/water separation during run



Breakdown of carbon balance for a typical HTL experiment (regional wet waste blend)



*This analysis based on carbon basis

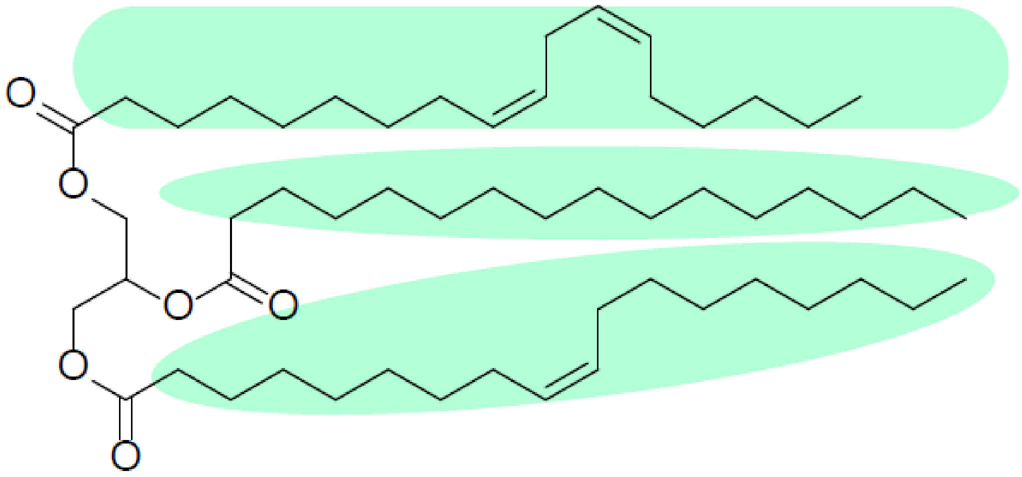
Fuel testing critical

Existing liability:

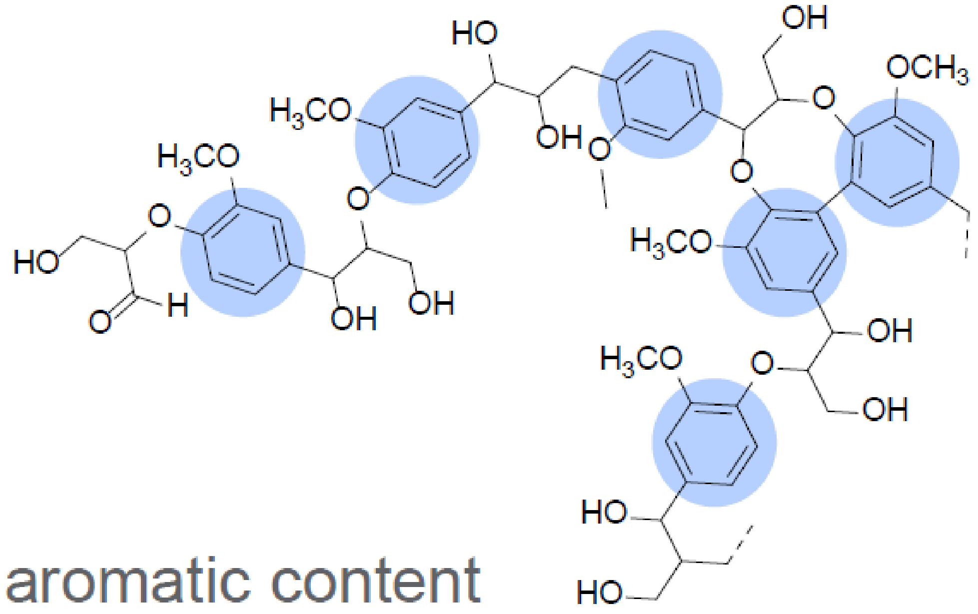
- Rich in oxygenates and nitrogen
- Lots of exciting work looking at extracting biocrude or chemicals

Includes trapped Biocrude: Opportunity for extraction

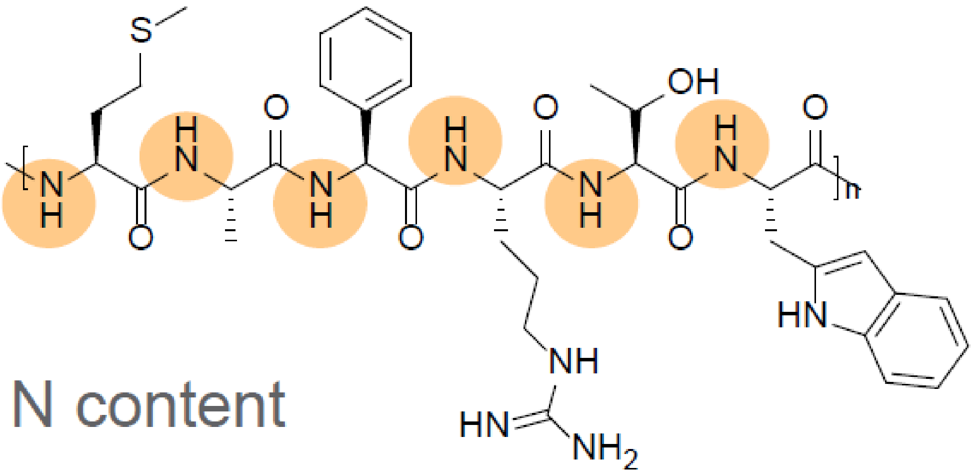
Feedstock impacts the biocrude: Hydrocarbon type, N content, % aromatic content



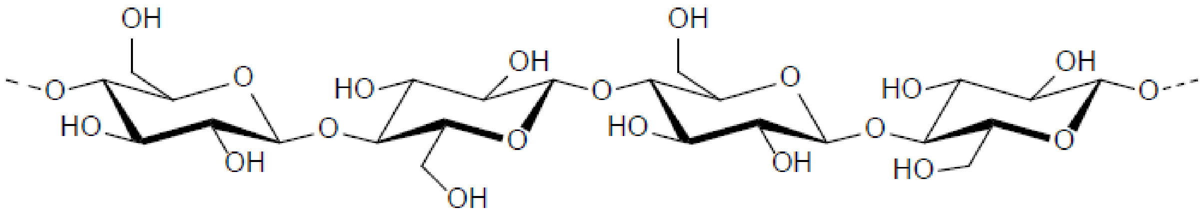
Fats –
increased long n-alkane (cetane)



Lignin –
increased aromatic content



Protein –
- increased N content
- does form oil



Short C length with many O

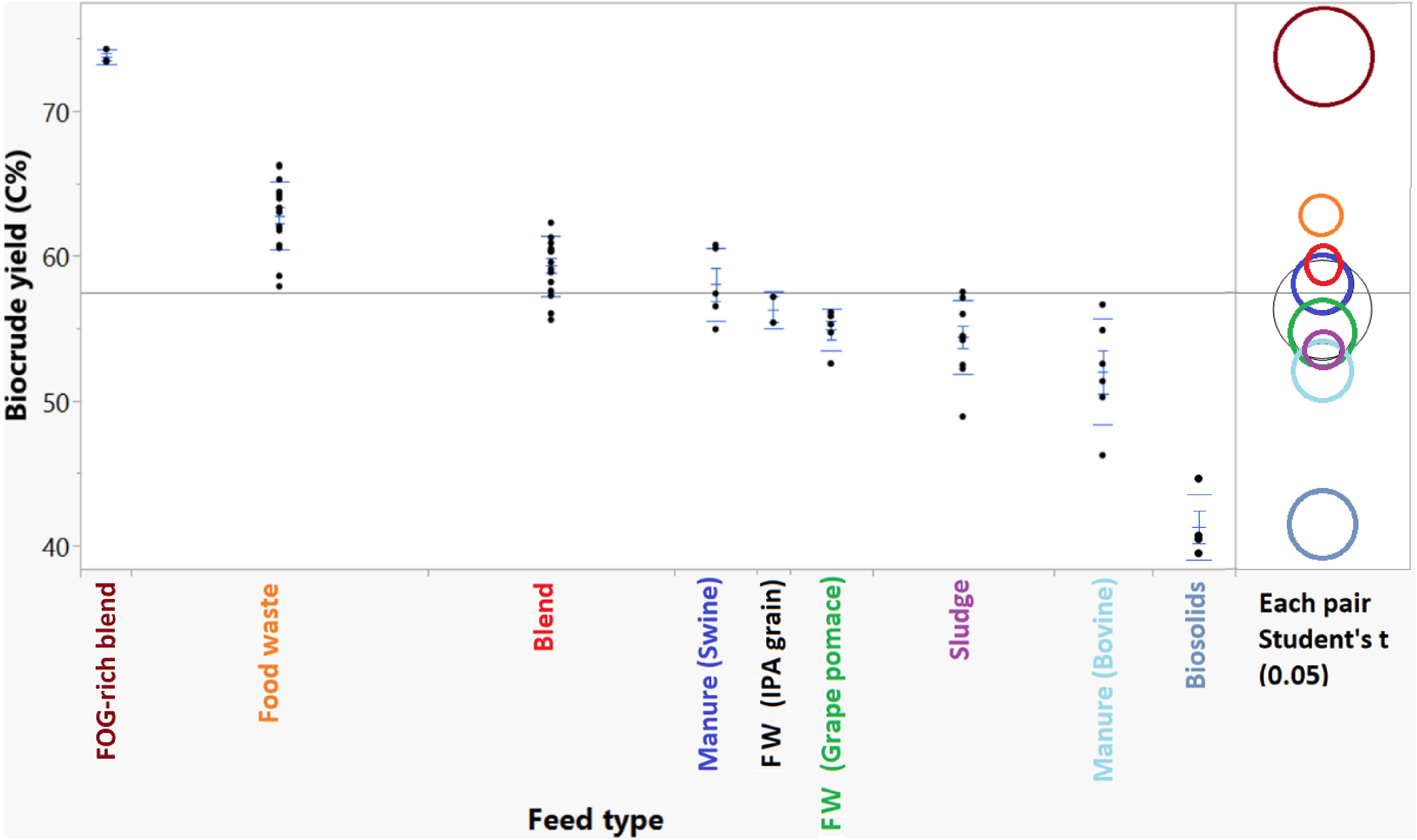
Cellulose –
- increased C to aqueous phase
- does form oil (Maillard reaction with protein)

Carbon yield comparison for multiple feedstocks

Wet wastes have high carbon yields to biocrude

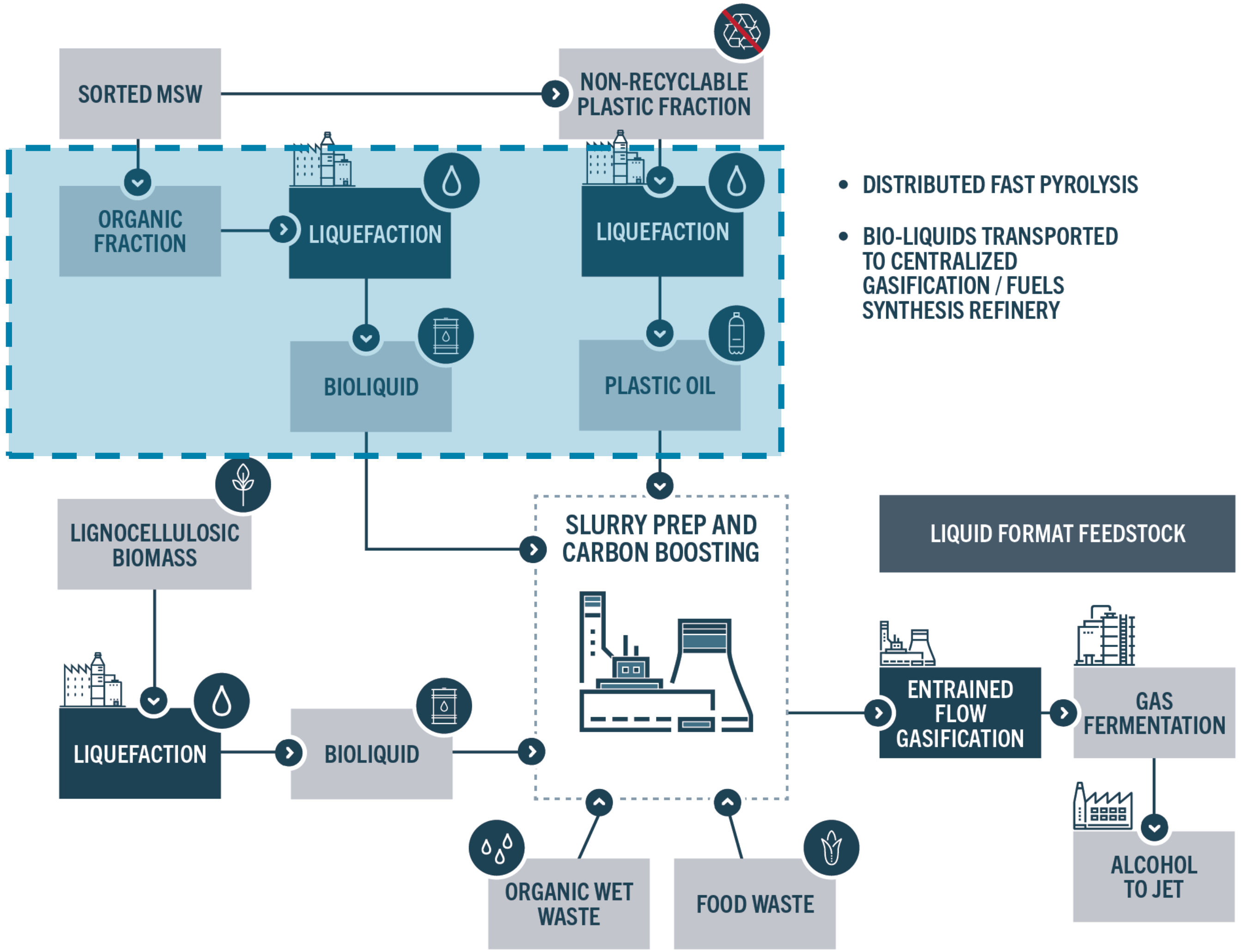
Increased *natural digestion* results in lower carbon yields to biocrude

Biosolids with high ash, have much lower carbon yields

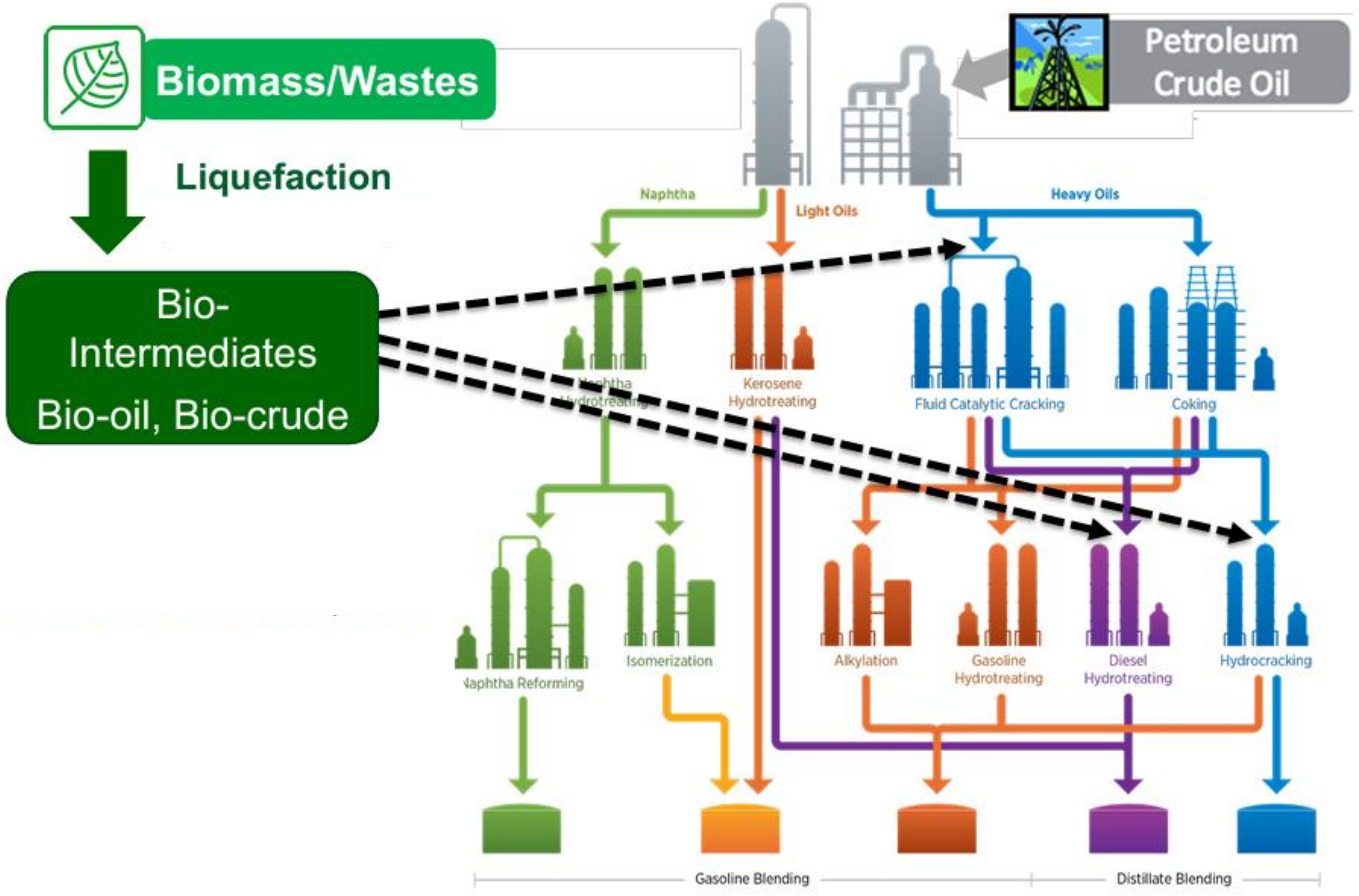


Two routes to SAF from HTL biocrude

Gasification of the Biocrude to fit into existing SAF pathways



Hydroprocessing – Traditional crude oil upgrading process*



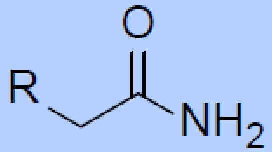
*This presentation will focus on hydroprocessing of HTL biocrude

Biocrude has higher O and N content and higher acidity than petroleum crude oil

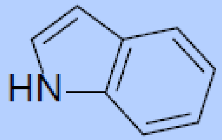
	O%	N%	S%	TAN*
Petroleum*	0.5	0.1-2	0.05 - 6	0.2 - 5
Biocrude				
Sludge	8	4	1	65
Chlorella	4	6	1	53
Pine	10	0	0.01	53

* The heteroatom content into unit operations (after atmospheric distillation) is much lower

Organic N is in two forms



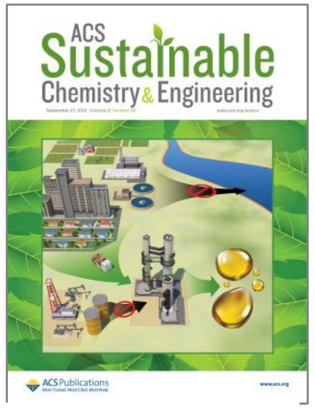
Amides (easily hydrogenated)



Cyclic amines (more difficult to hydrogenate)

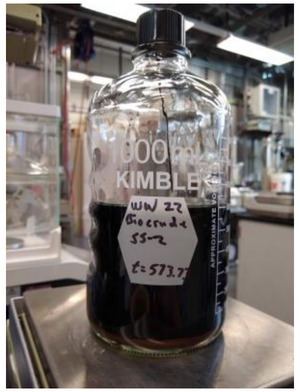
- N content is an issue if cracking is needed (cracking catalysts have acidic sites)
- The heteroatom content is outside of what refiners are comfortable, so they dilute

Stable, Scalable Hydrotreating



Assessed extended time-on-stream hydrotreating of biocrudes from mixed fuels.

Biocrude

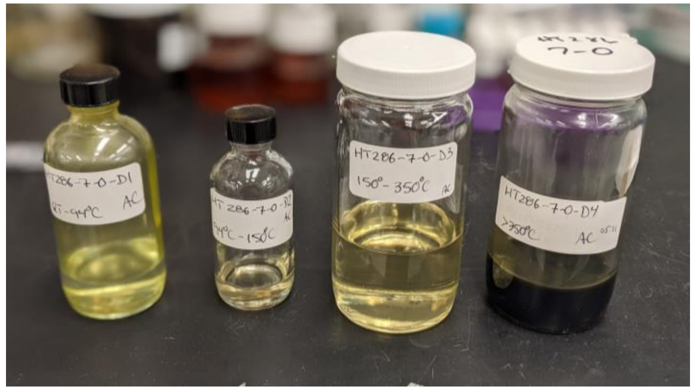


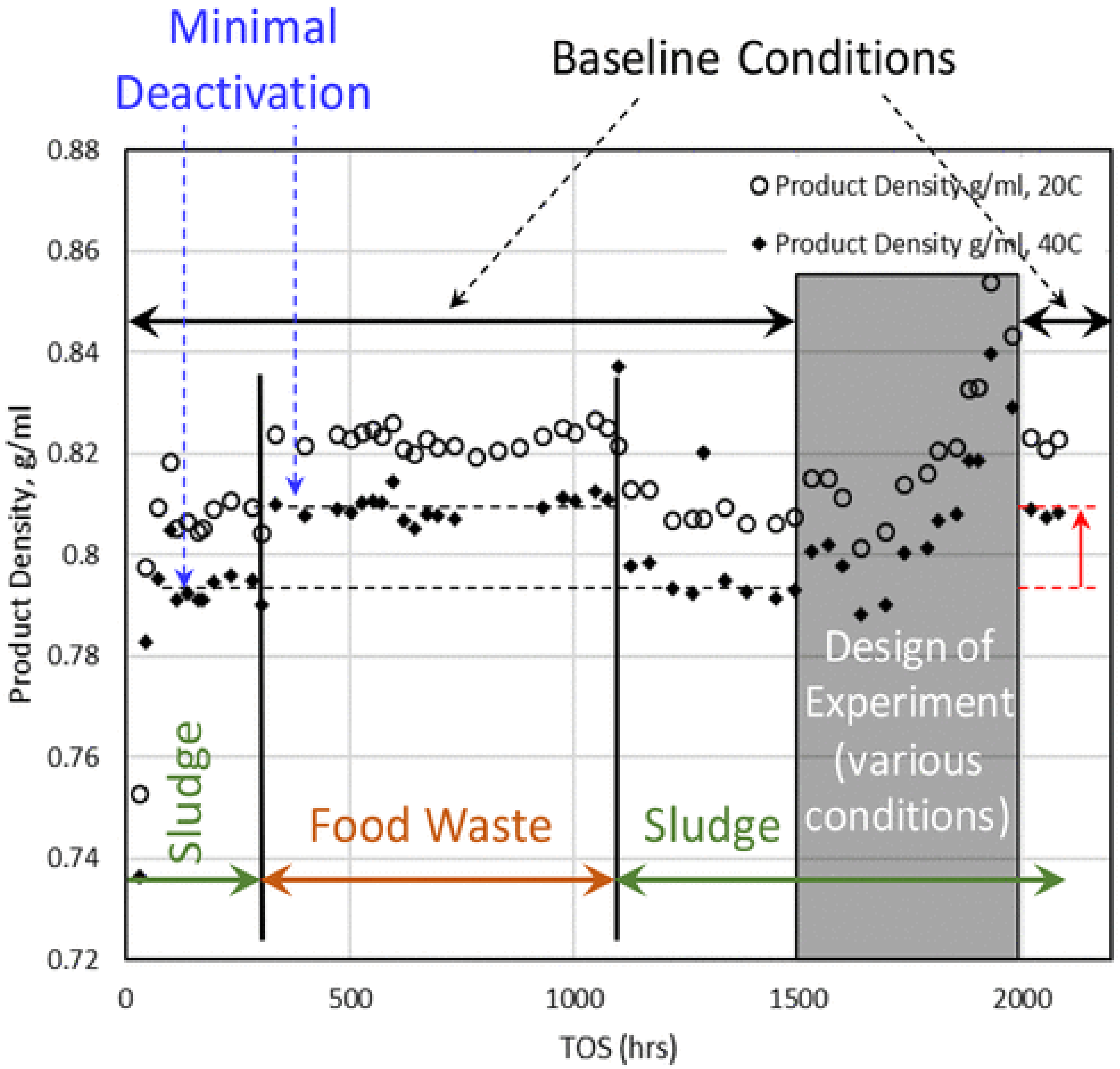
→

Upgraded

→

Distilled





Key outcome:

- Stable continuous hydrotreating: 1500+ hrs

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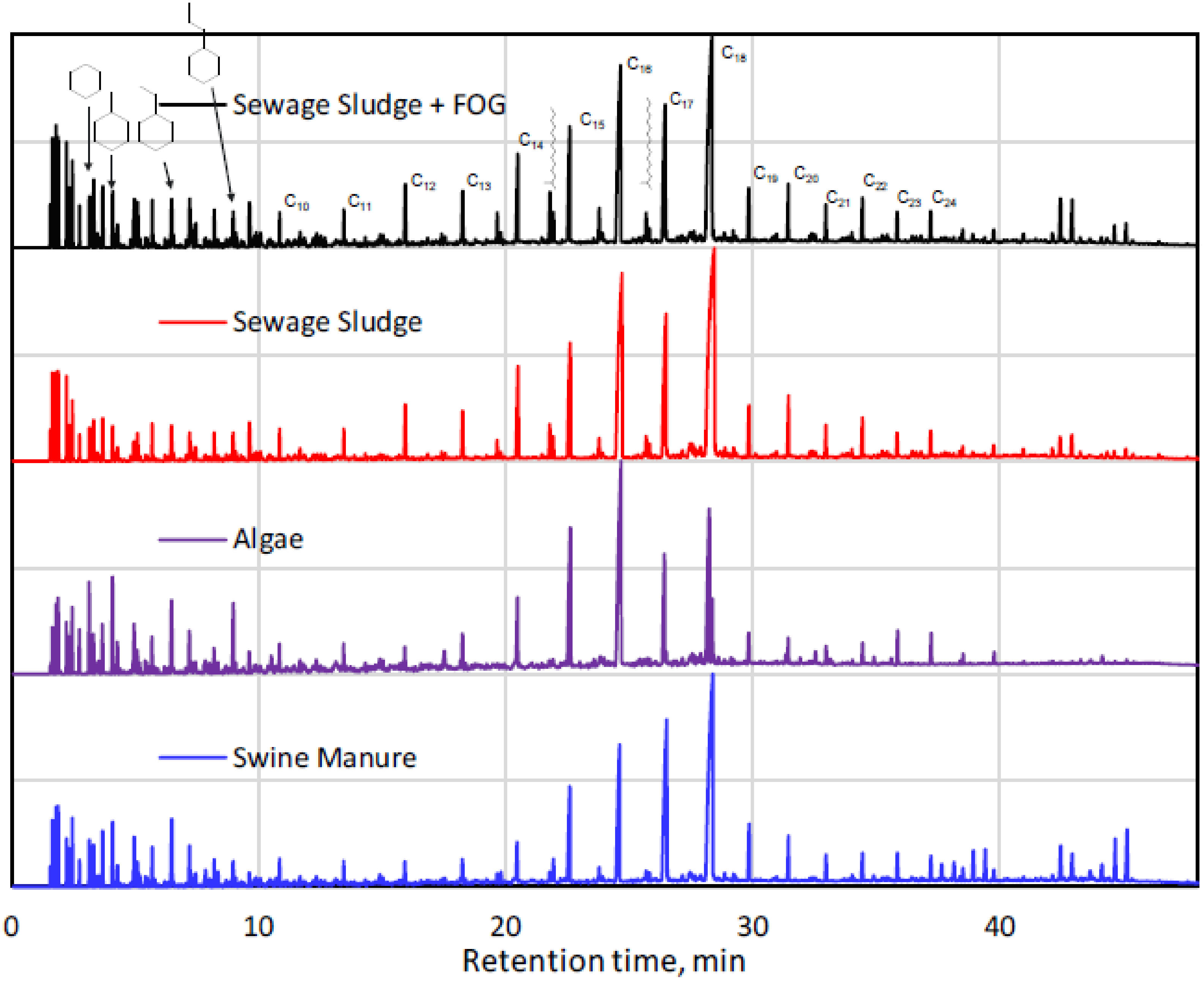
[1] Cronin, D. J., Subramaniam, S., Brady, C., Cooper, A., Yang, Z., Heyne, J., ... & Thorson, M. R. (2022). Sustainable Aviation Fuel from Hydrothermal Liquefaction of Wet Wastes. *Energies*, 15(4), 1306.

[2] Kallupalayam Ramasamy, K., Thorson, M. R., Billing, J. M., Holladay, J. E., Drennan, C., Hoffman, B., & Haq, Z. (2021). *Hydrothermal Liquefaction: Path to Sustainable Aviation Fuel* (No. PNNL-31930). Pacific Northwest National Lab.(PNNL), Richland, WA (United States).

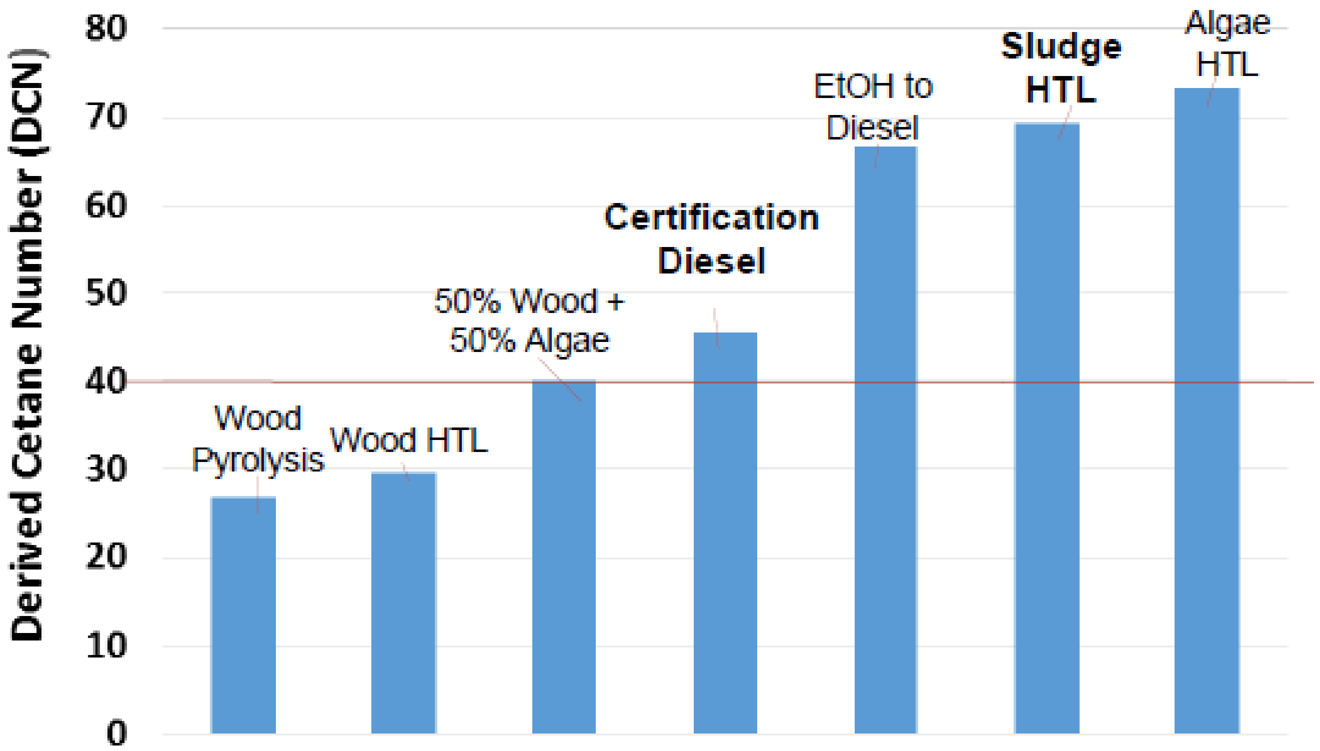
[3] Subramaniam, S., Santosa, D. M., Brady, C., Swita, M., Ramasamy, K. K., & Thorson, M. R. (2021). Extended Catalyst Lifetime Testing for HTL Biocrude Hydrotreating to Produce Fuel Blendstocks from Wet Wastes. *ACS Sustainable Chemistry & Engineering*, *9*(38), 12825-12832.

[4] Thorson, M. R., Santosa, D. M., Hallen, R. T., Kutnyakov, I., Olarte, M. V., Flake, M., ... & Swita, M. (2021). Scaleable Hydrotreating of HTL Biocrude to Produce Fuel Blendstocks. *Energy & Fuels*, *35*(14), 11346-11352.

Upgraded fuel is rich in n-alkanes

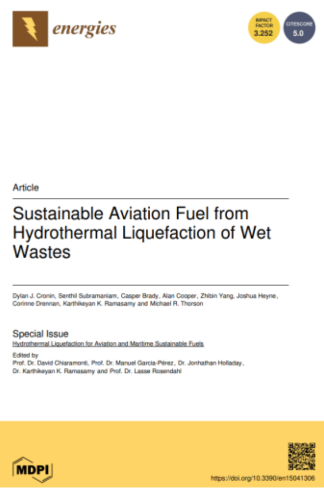


- Minimal impact from feedstock variability on product composition
  - Typically high derived cetane number (DCN)
    - ✓ Except wood



**Analysis by Colorado State University

SAF via HTL of Wet Wastes Meets Tier α and β Specs



energies

Article

Sustainable Aviation Fuel from Hydrothermal Liquefaction of Wet Wastes

Dylan J. Cronin, Senthil Subramaniam, Casper Brady, Alan Cooper, Zhibin Yang, Joshua Heyne, Corinne Drennan, Karthikeyan K. Ramasamy and Michael R. Thorson

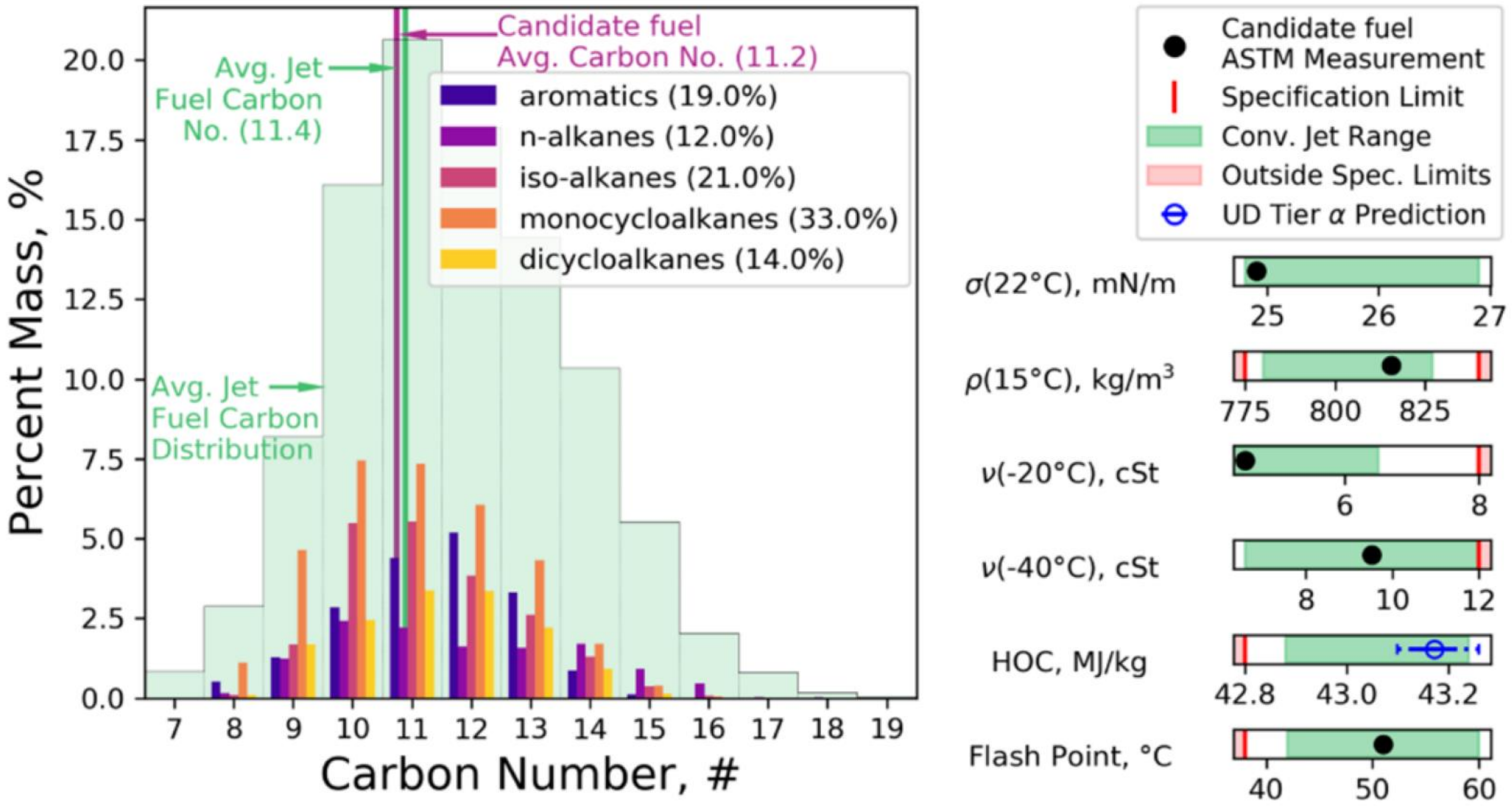
Special Issue
Hydrothermal Liquefaction for Aviation and Maritime Sustainable Fuels

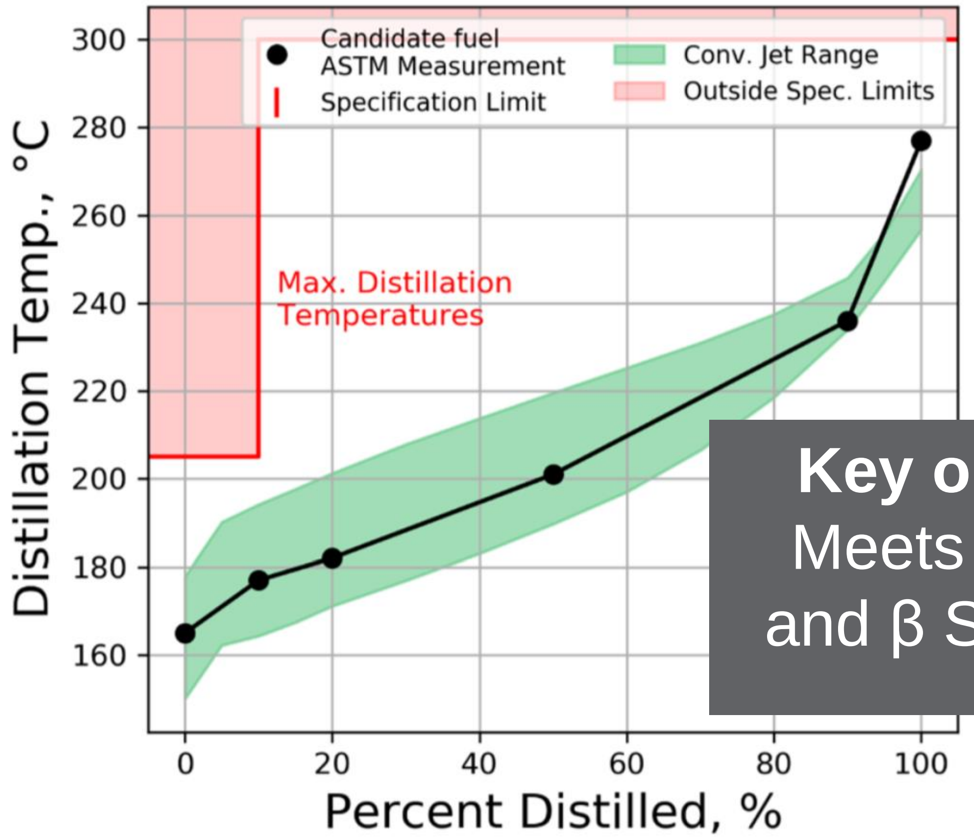
Edited by
Prof. Dr. David Chiaramonti, Prof. Dr. Manuel Garcia-Pérez, Dr. Jonhathan Holladay, Dr. Karthikeyan K. Ramasamy and Prof. Dr. Lasse Rosendahl

MDPI

https://doi.org/10.3390/en15041306

- ~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

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Need for crucial property data before HTL SAF specs are developed

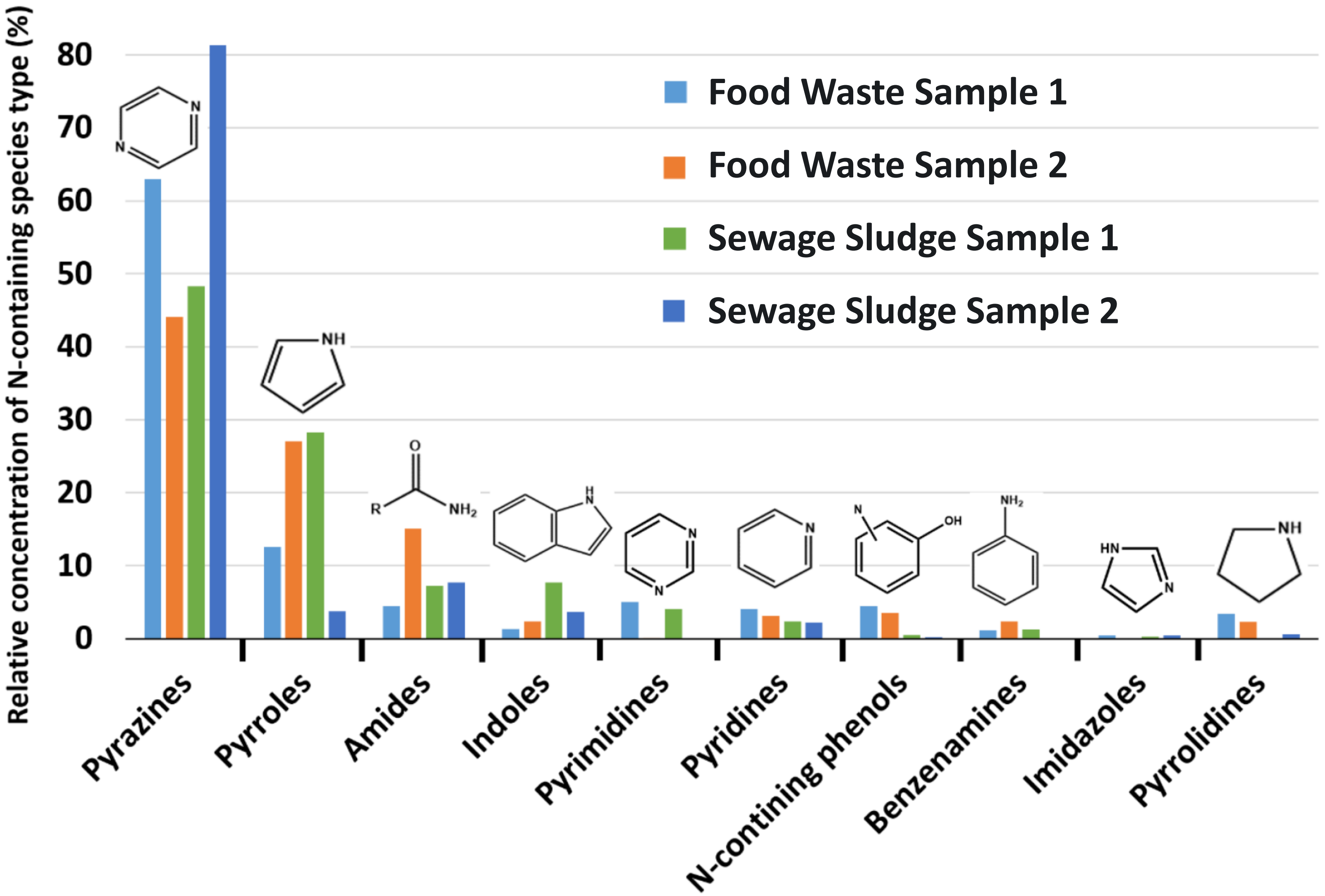
Subset of Jet Fuel Specifications	Jet A	FT-SPK	SPK-HEFA	SPK/A	ATJ-SPK
Sulfur, mg/kg	**3000**	15	15	15	15
Nitrogen, mg/kg	**No spec**	**2**	**2**	**2**	**2**
Flash point, °C	38	38	38	38	38
Density, kg/m^3	775-840	730-770	730-772	755-800	730-770
Freezing pt, °C	-40	-40	-40	-40	-40
Thermal stability, mm 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:

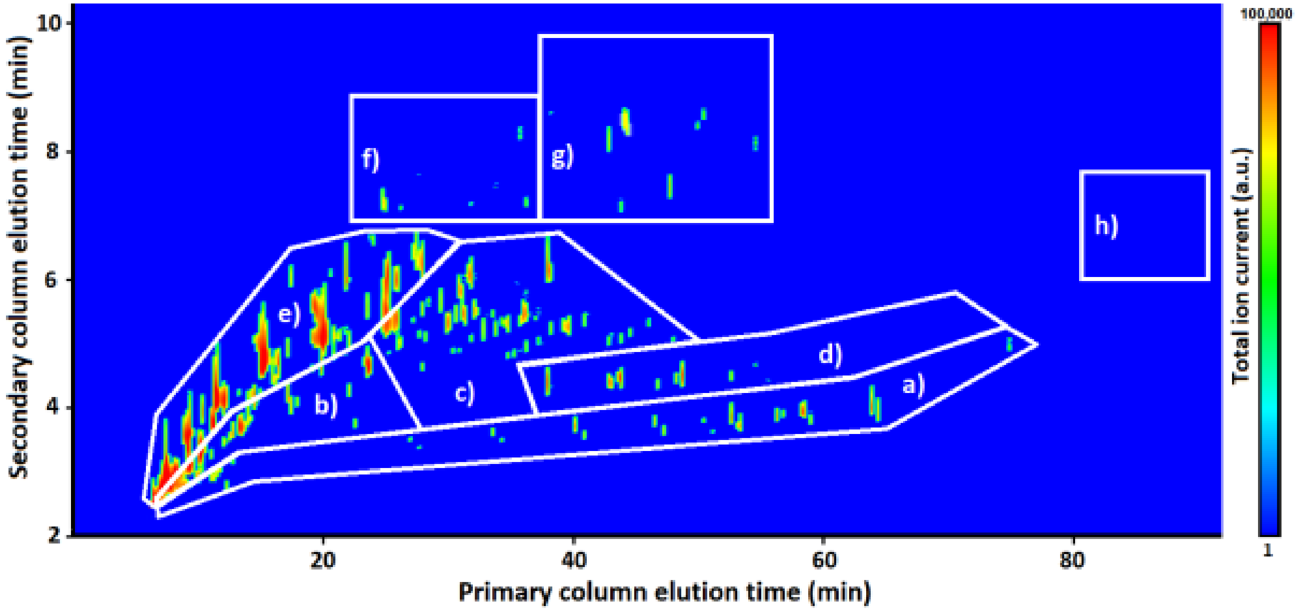
- The impact of N on fuel stability in SAF derived from HTL
- The technical challenges with deep denitrogenation
- Addressing the technical uncertainty regarding the need for reduced N

Nitrogen-species in Biocrude – A possible challenge for SAF from HTL of wet wastes

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



GCxGC MS for speciation of N-compounds



Challenges for SAF:

- Potential Nitrogen specification
- 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

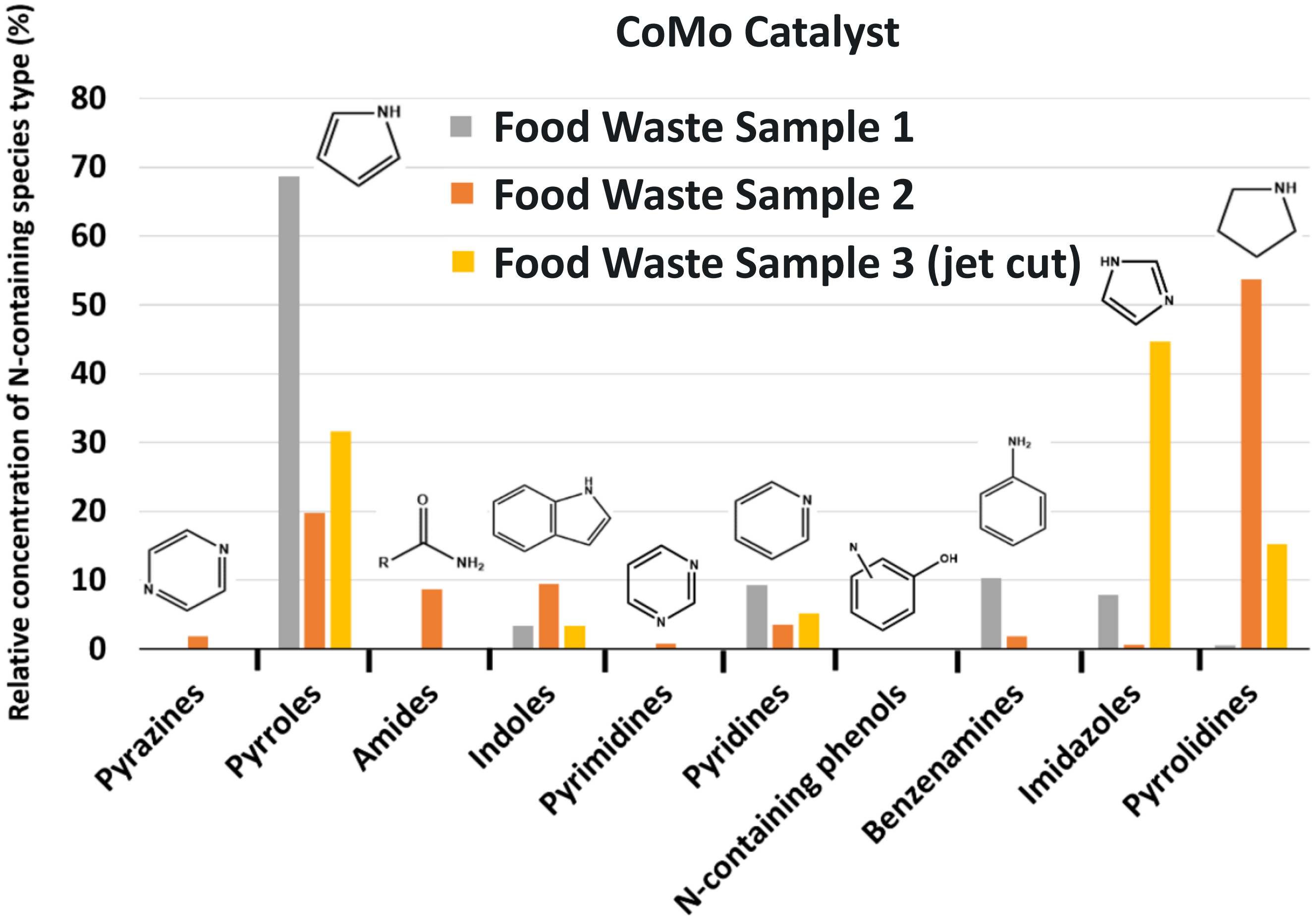
Challenging N-species to hydroprocess in Biocrude

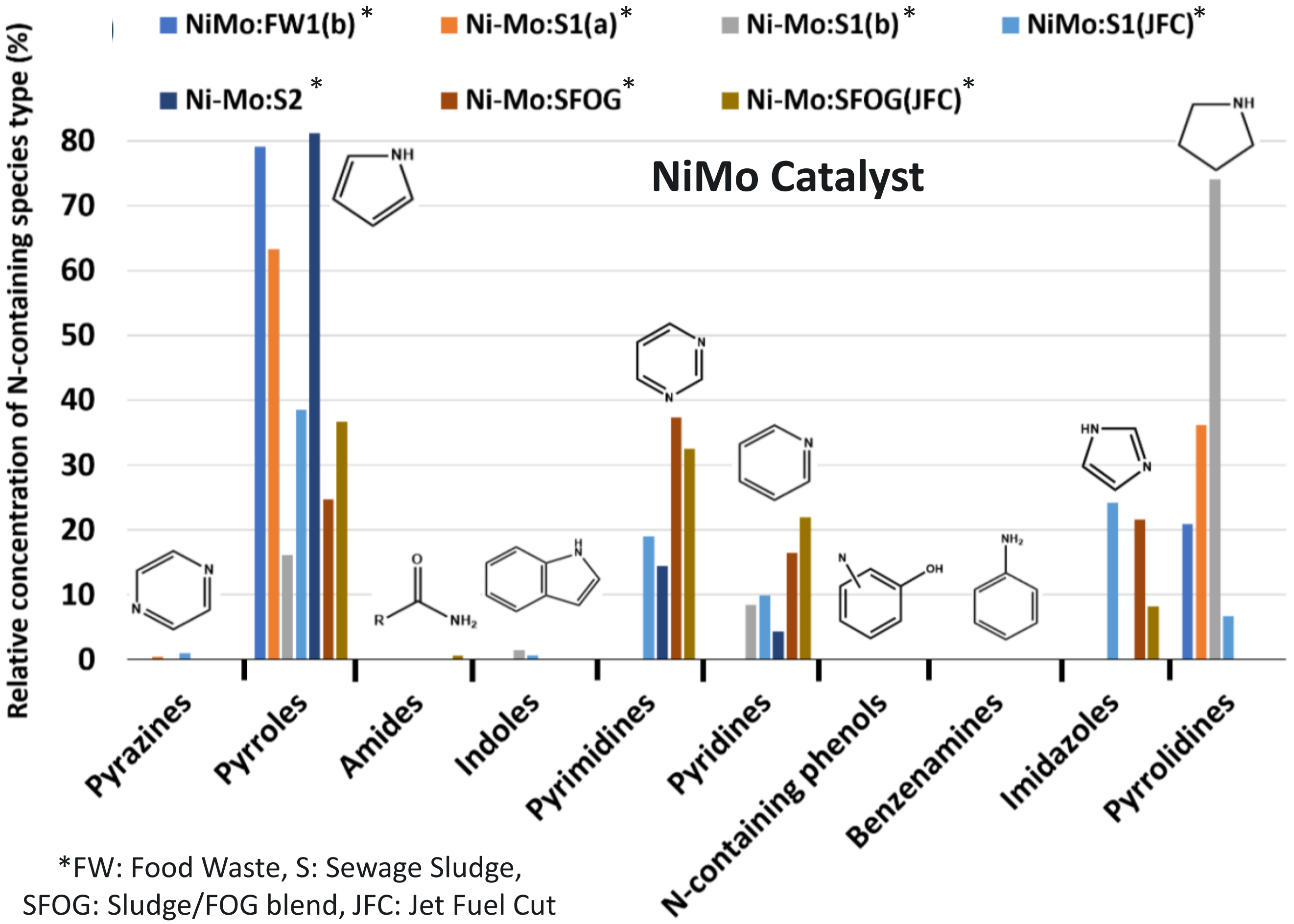
- Most challenging species to hydrotreat are the Pyrroles, Imidazoles, Pyrrolidines
- Will pursue further HDN to get to 2ppm N[+]

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

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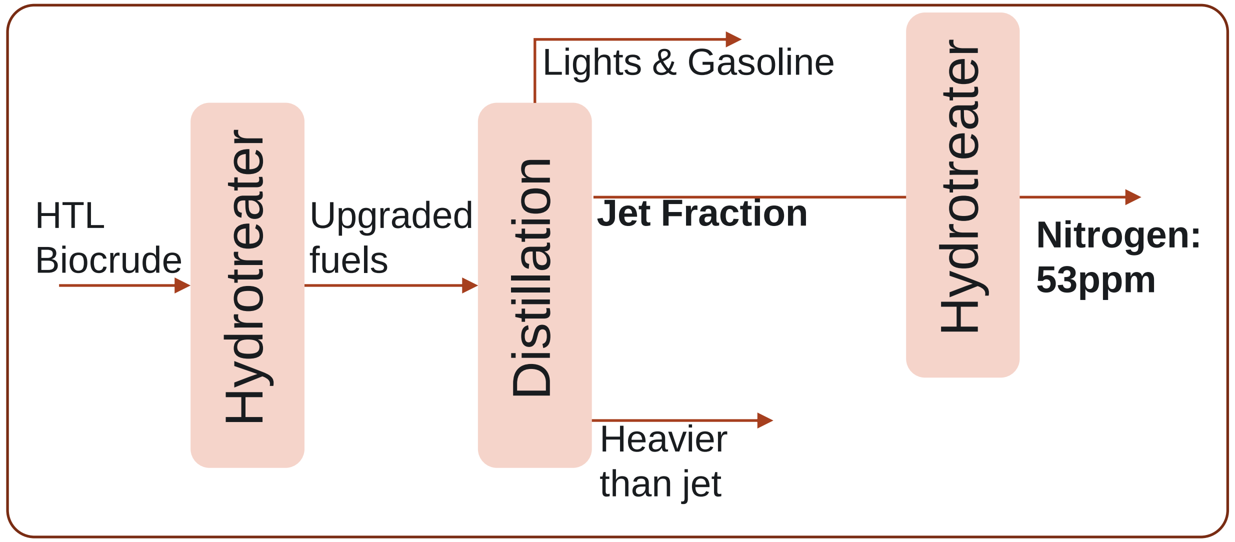
[+] 2ppm N is the project goal based on the level achieved via other SAF pathways

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


HTL Biocrude

Hydrotreater

Upgraded fuels

Distillation

Lights & Gasoline

Jet Fraction

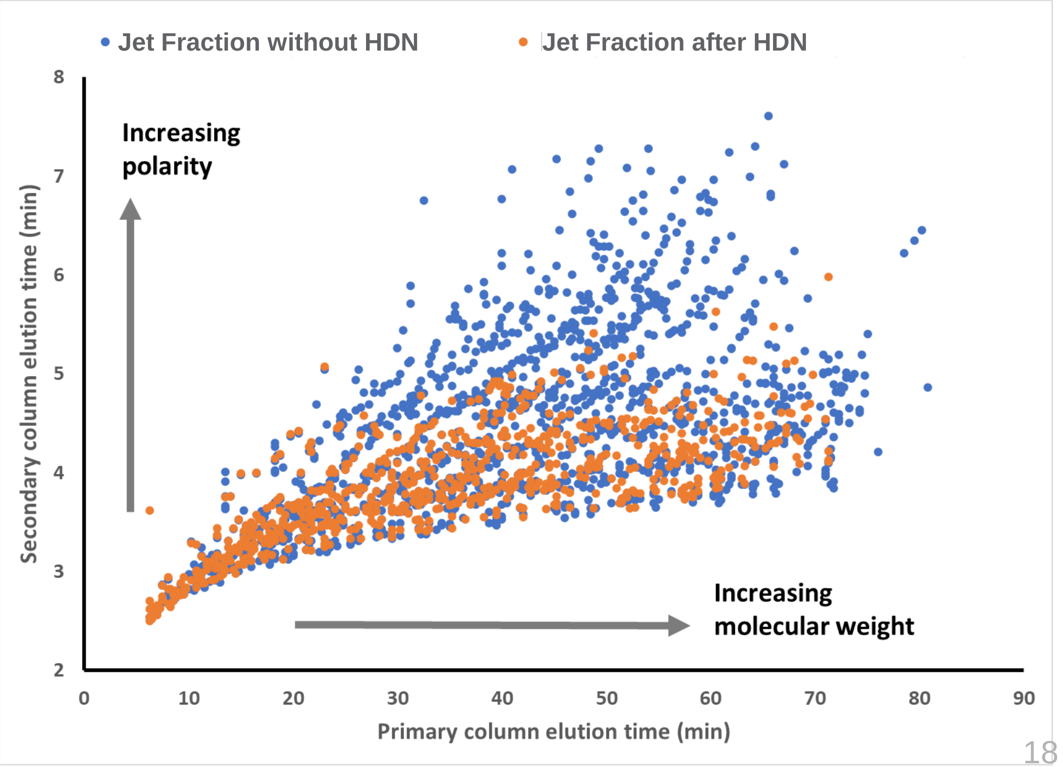
Heavier than jet

Hydrotreater

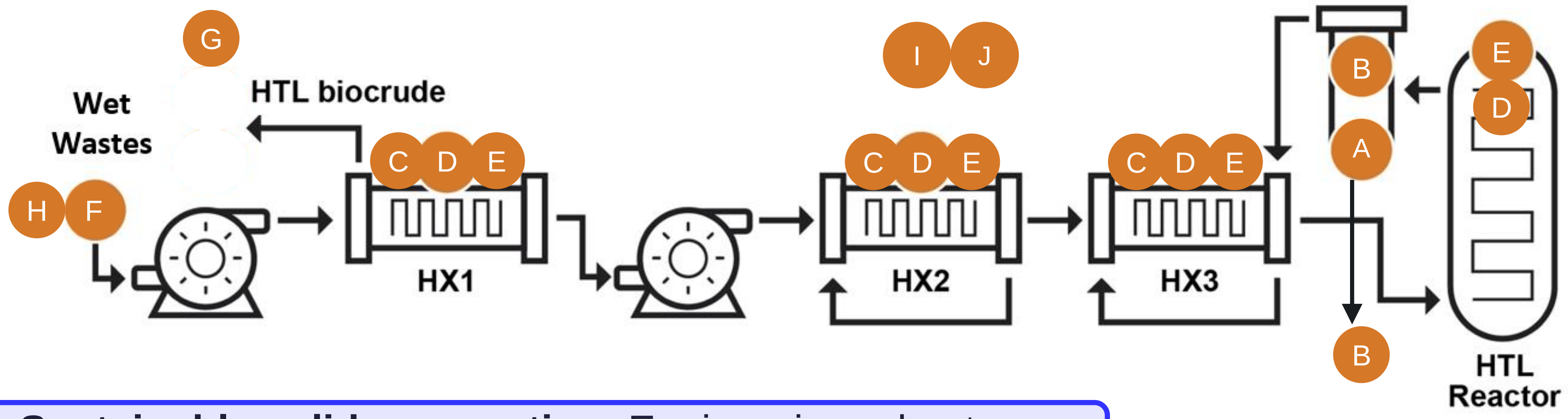
Nitrogen: 53ppm

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



Key Research underway at PNNL to Accelerate Successful Commercial Deployment



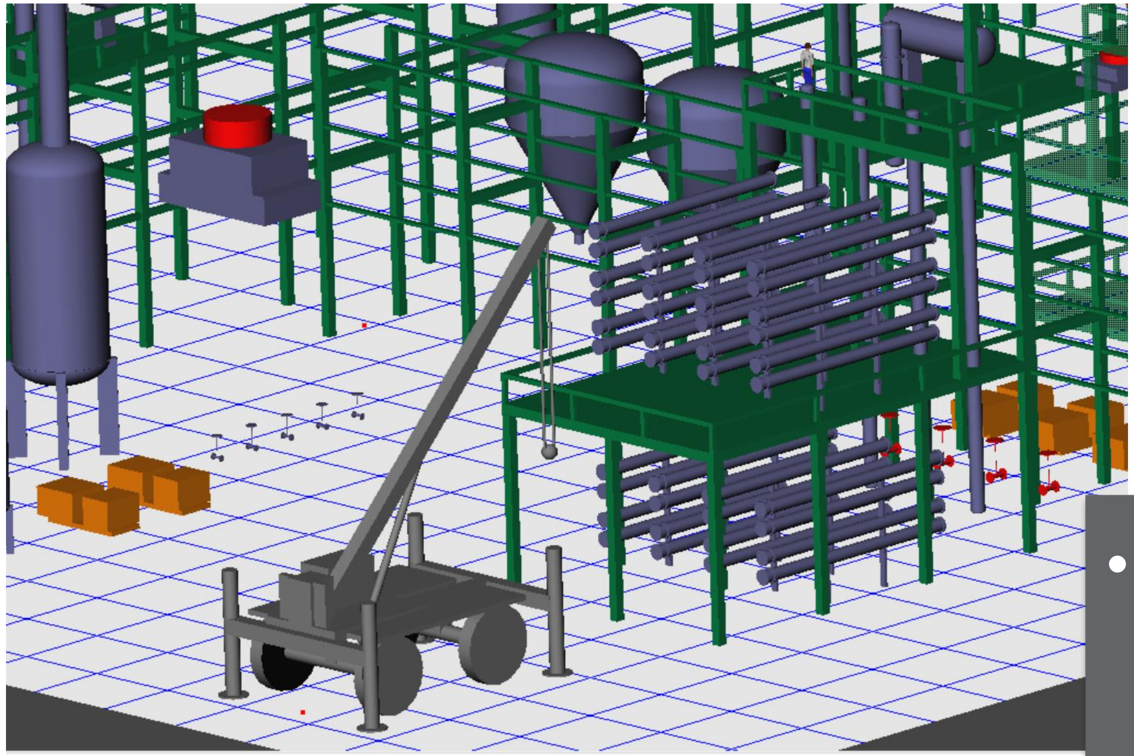
A. **Sustainable solids separation:** Engineering robustness
B. **Solids disposal:** Ensure end of life solution for solids
C. **Improved HX:** Lower cost heat exchangers
D. **Sustainable HTL Operations:** Quantify fouling
E. **Reactor Plugging:** Sustainable operations w/o plugging
F. **Strategic Feedstocks:** Evaluate strategic wet-wastes
G. **Aqueous treatment:** Enable sustainable recycle
H. **Low-grade feedstocks:** Develop pathways for opportunity feedstocks and de-grid feedstock
I. **Scale up testing:** Campaigns in MHTLS
J. **Corrosion:** Material of construction compatibility

Major focus areas:

- ***Fouling in process***
- ***Solids removal/ disposal***

Reactor fouling, an important consideration

PNNL 2021 HX design:
Use of heat exchangers (like all other HTL designs)



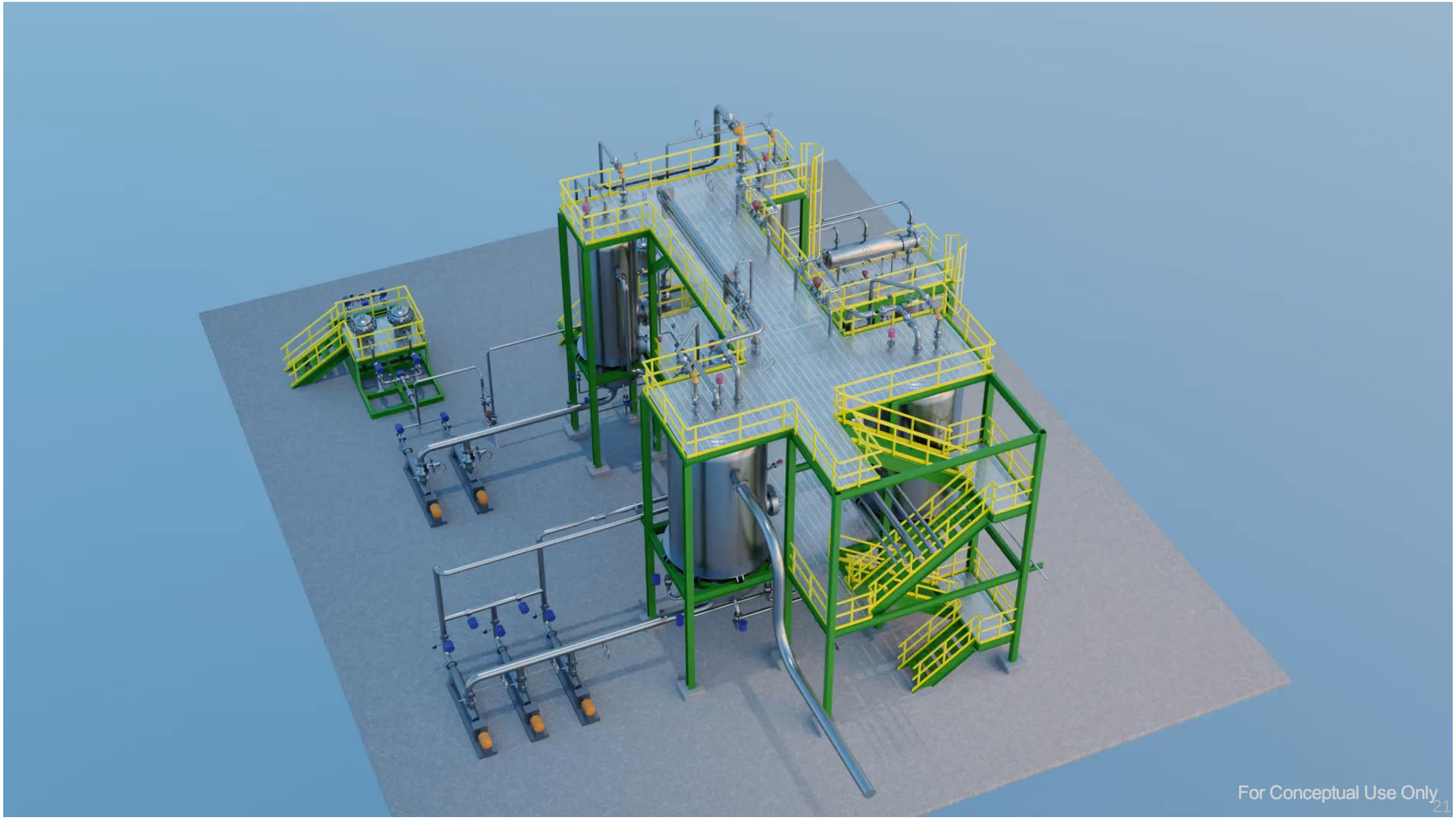
Plug: rich in inorganics

30 unique plugging events (1 - 110 hours TOS)

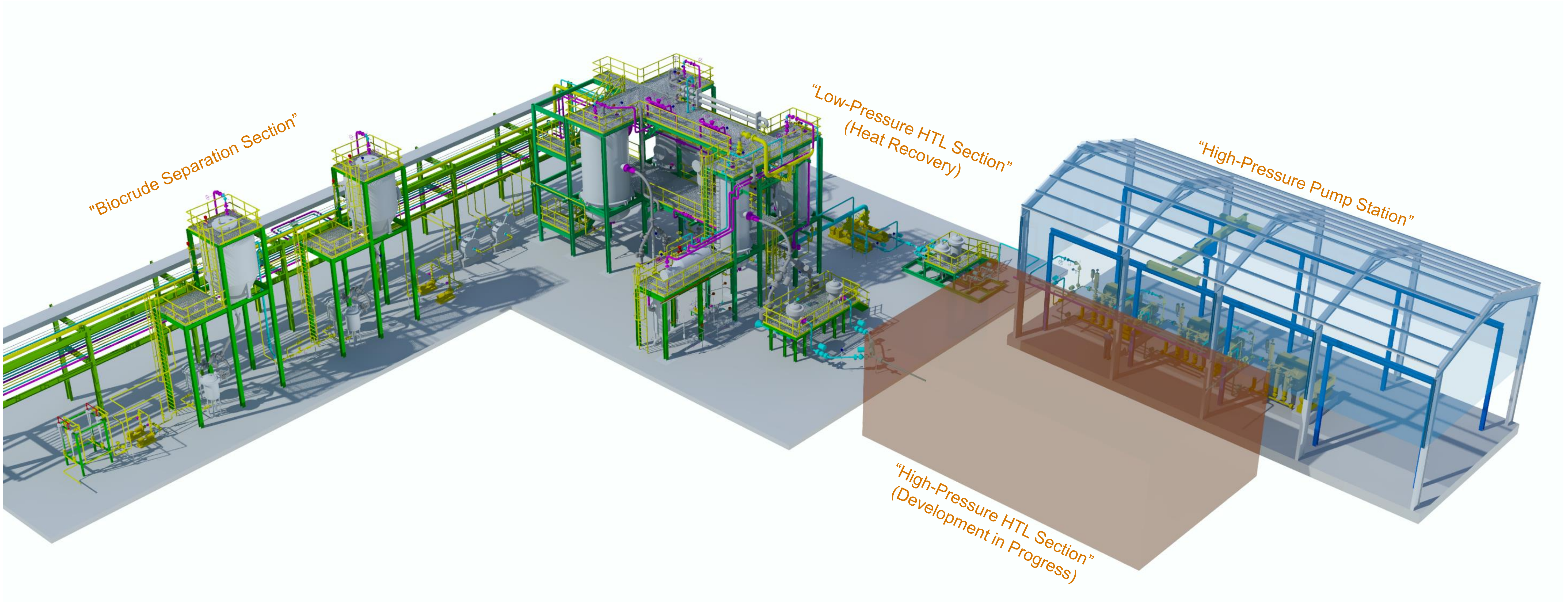
- Frequent plugging in preheater (RT to 215-250°C)
- Hard-plug compositional changes:
  - Reduced C content – up to 40%
  - Increased **Ca**, Fe, Mg, **P**, Si, & **S** content

- ***Fouling expected to hinder operability of commercial plants***
- ***Commercial design should minimize use of heat exchangers & "hot spots"***

Conceptual embodiment of new heat integration approach


For Conceptual Use Only

The Integrated HTL System



HTL is a potentially impactful technology

- Hydrothermal liquefaction solves two challenges:
  - Sustainable aviation fuel
  - Disposal of sludge (Expensive to dispose / Costs ↑ as regulations ↑)
- Significant resource availability (>77 million dry tons/yr)
  - Opportunity for regional process intensification to take advantage of economies of scale
- High quality fuels produced via HTL
- 81% GHG reduction compared to fossil fuels
- Potential for positive story telling (Poop to fuel)

Acknowledgements

- BETO Technology Managers: Beau Hoffman, Ben Simons, Mark Shmorhun

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