Pacific Northwest
NATIONAL LABORATORY

Feedstock Impacts for HTL of Organic Wet Wastes

Mike Thorson

Pacific Northwest National Laboratory

U.S. DEPARTMENT OF ENERGY BATTELLE

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

Value of HTL for sewage sludge is disposal

Cost of disposal[1]:
$40,000 – $80,000

$2.30-4.70/gal of fuel produced

200 dry tons

→

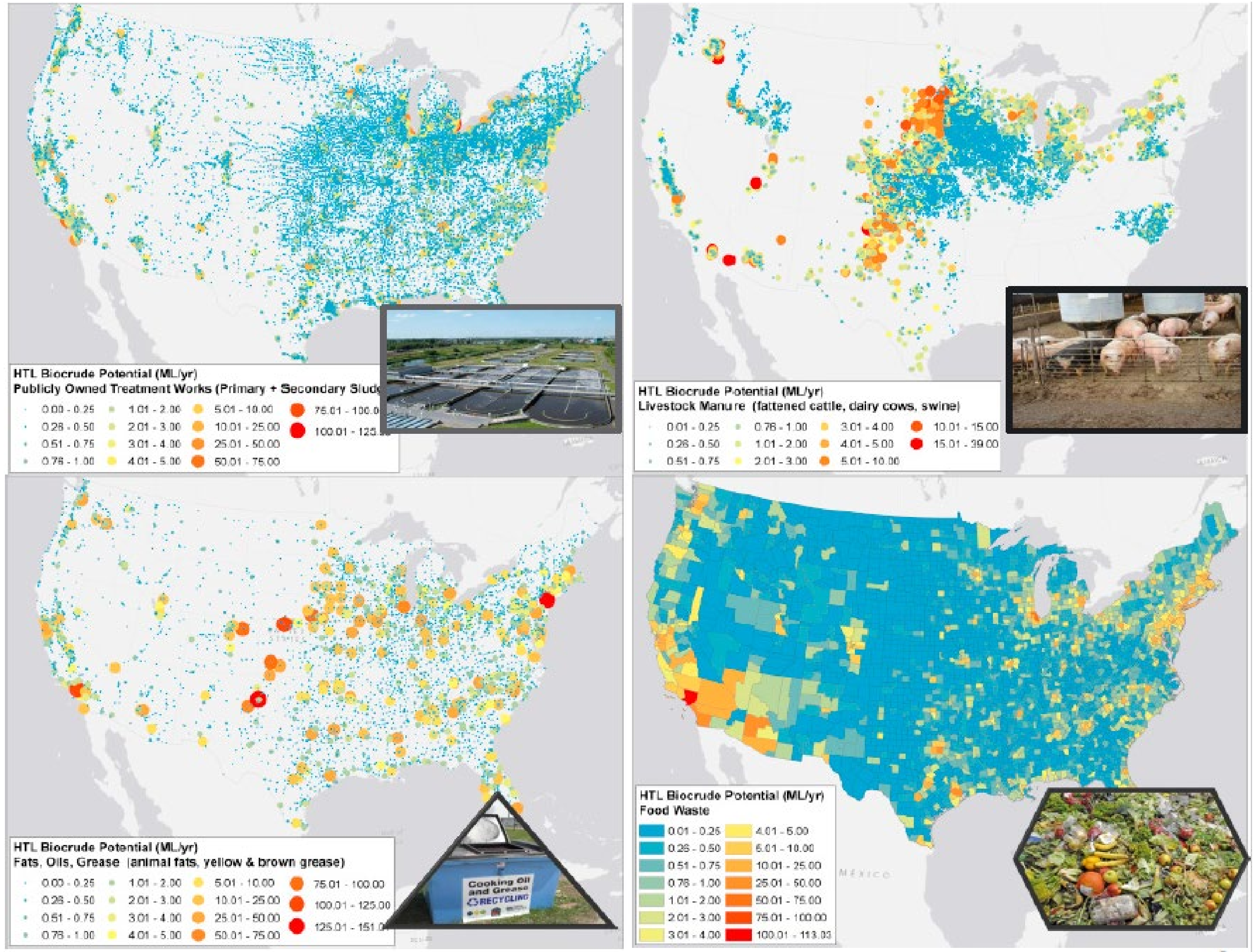
~17,000 gallons fuel

Value of fuel[2]:
~$34,000 - $51,000

$2-3/gal

[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

Wet Waste HTL of Organic Wet Wastes



It Works!

- Sewage sludge provides HTL biocrude yield and quality comparable to expensive algae feedstock
- Catalytic upgrading results in a high yield to distillate (~70%) and good cetane number (~60)

It's Cheap!

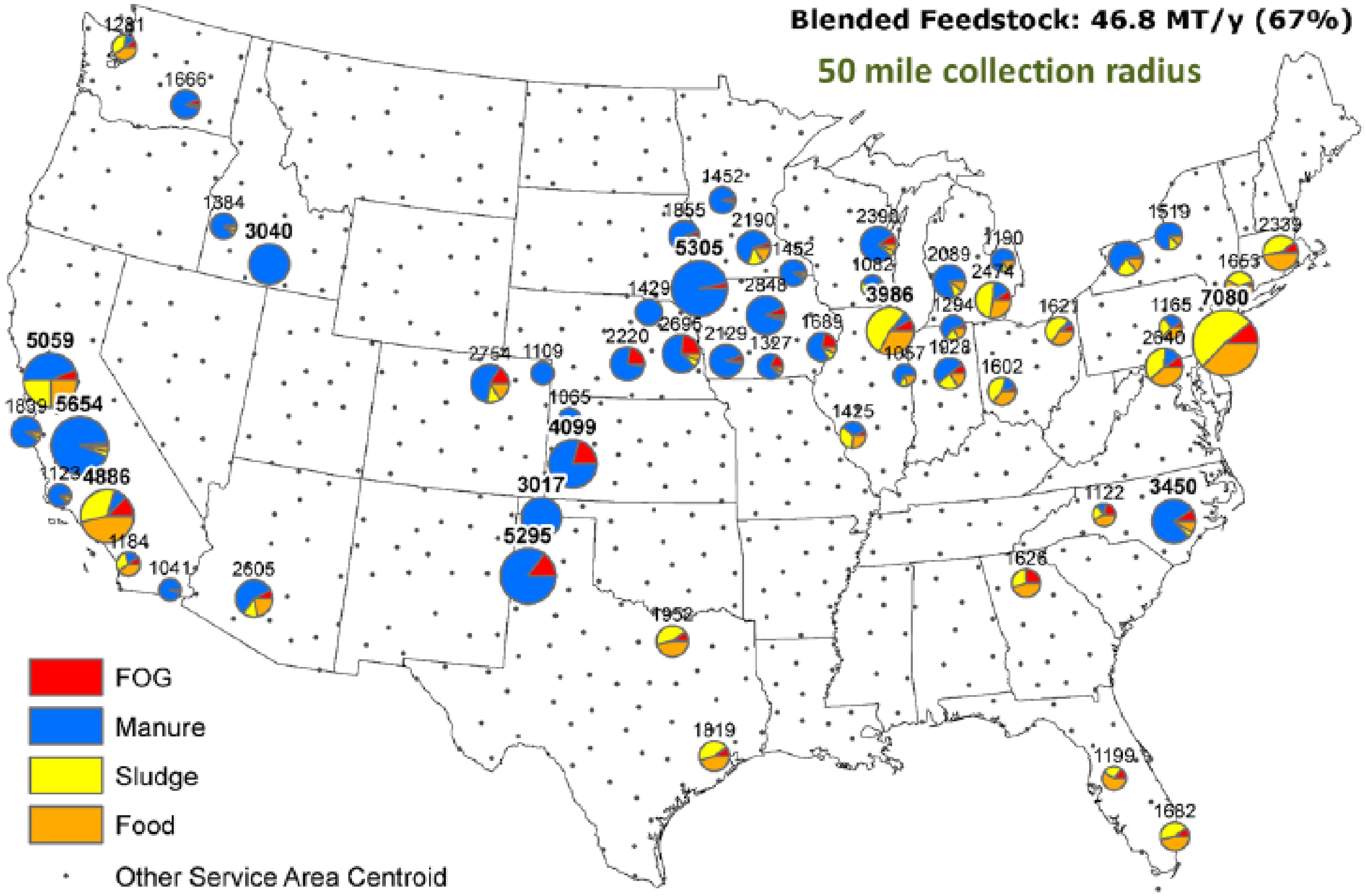
- Thermochemical conversion is highly sensitive to **feedstock cost**
- **Sludge disposal costs** represent 45-65% of WWTP operating expenses
- Wastewater treatment **infrastructure is aging**

It's the Right Thing to Do!

Anaerobic digestion (AD): many positives yet it is slow and requires solids disposal
Land application: PPCP, PFAS, regulation, consumer distaste
Landfilling: CO_2/CH_4 release, loss of nutrients (N, P)
Incineration: energy intensive, requires CH_4 for combustion

Pacific Northwest NATIONAL LABORATORY

Within a 50-mile radius, wet carbon waste can be blended for treatment



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

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

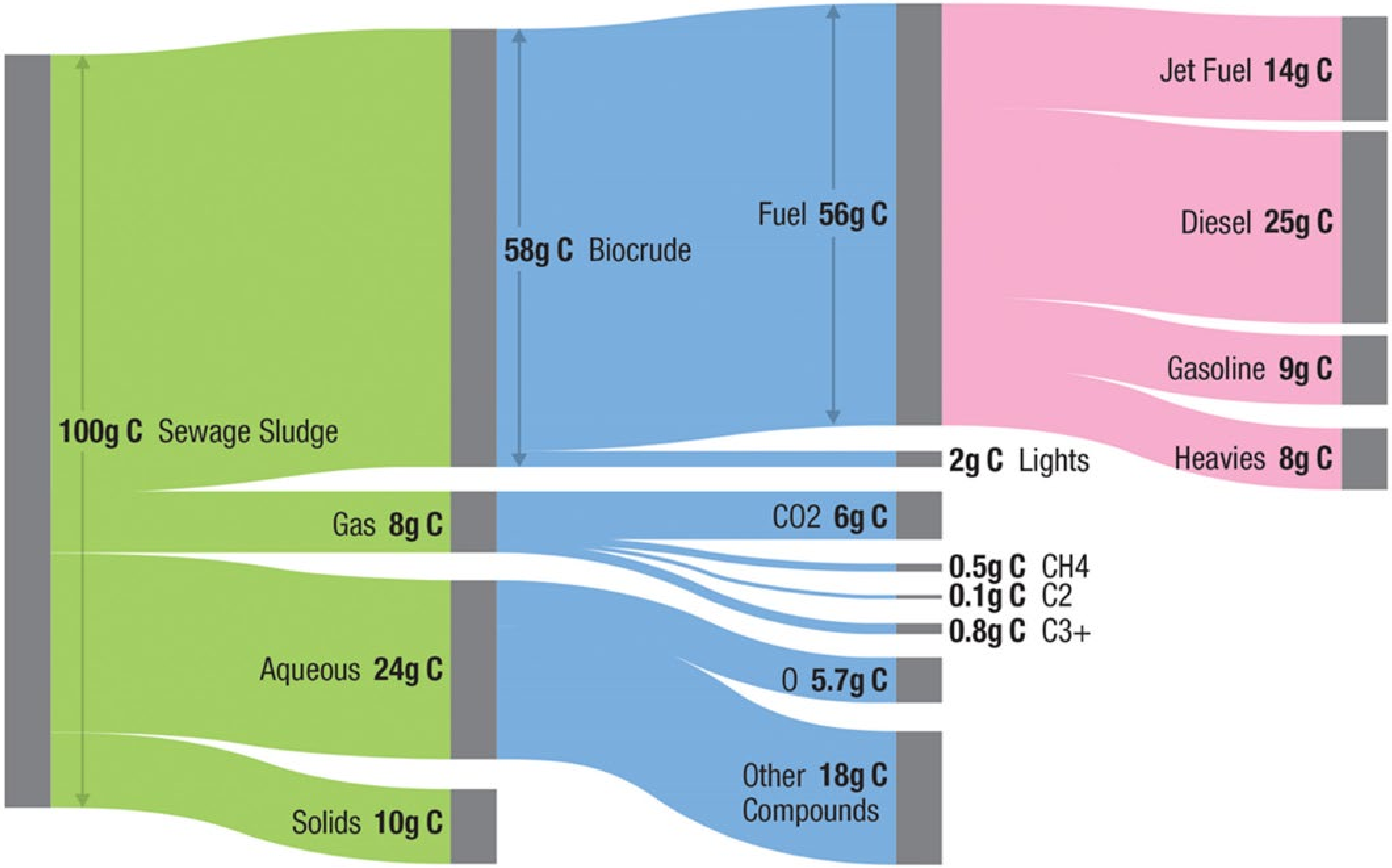
Points

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

The carbon yield to fuels is among the highest in bioprocessing: Sewage Sludge Example

Typical yields of HTL from wet wastes

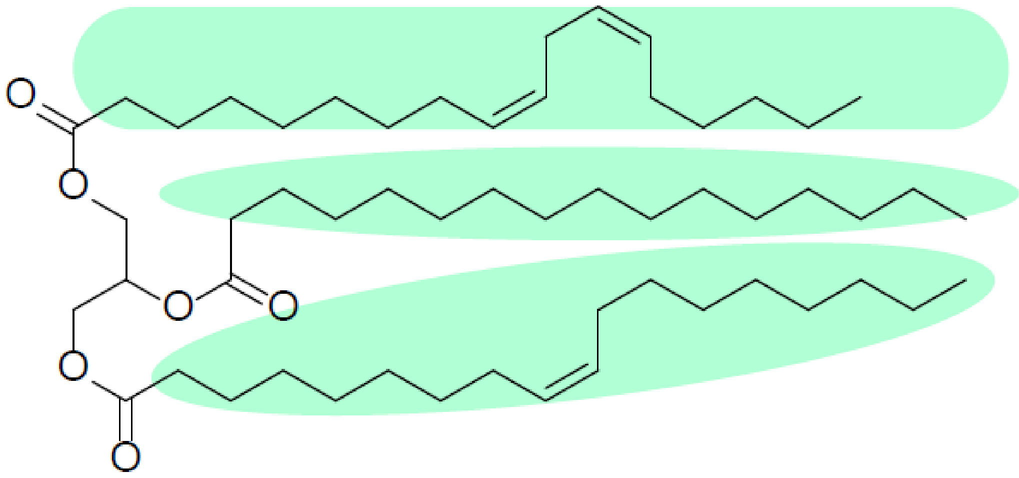
- ~60% to biocrude
- Biocrude is stable
- Rich in diesel hydrocarbons



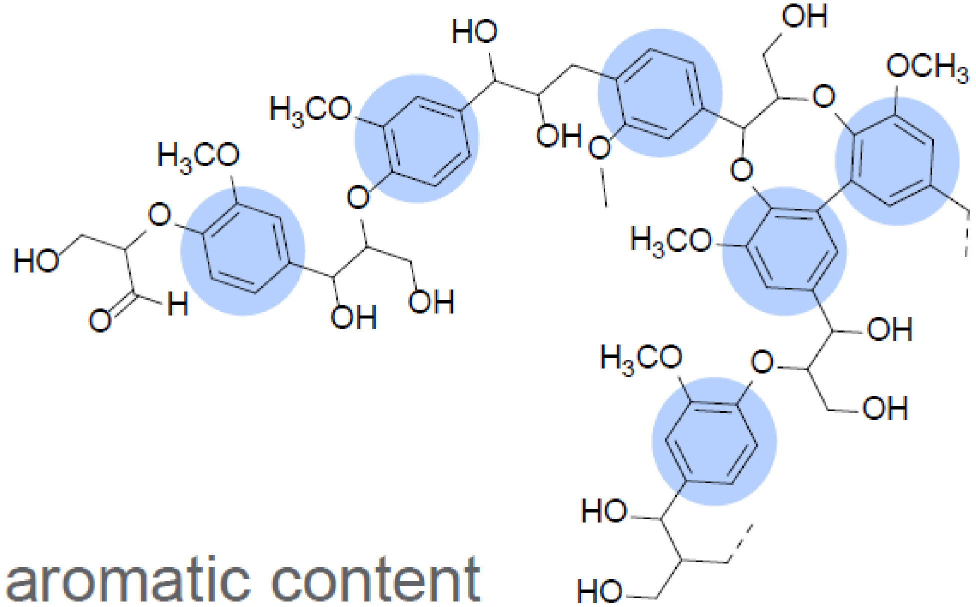
*This analysis based on carbon basis

Pacific Northwest
NATIONAL LABORATORY

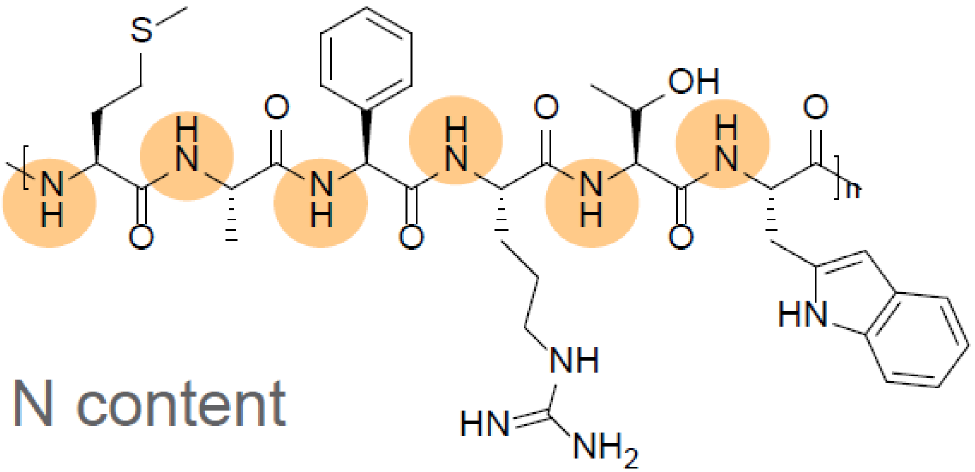
Feedstock impacts the biocrude: Hydrocarbon type, N content, % aromatic content



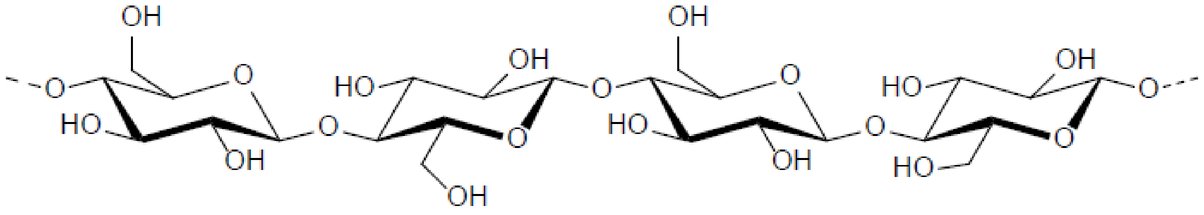
Fats –
increased long n-alkane (cetane)



Lignin –
increased aromatic content



Protein –
- increased N content
- does form oil



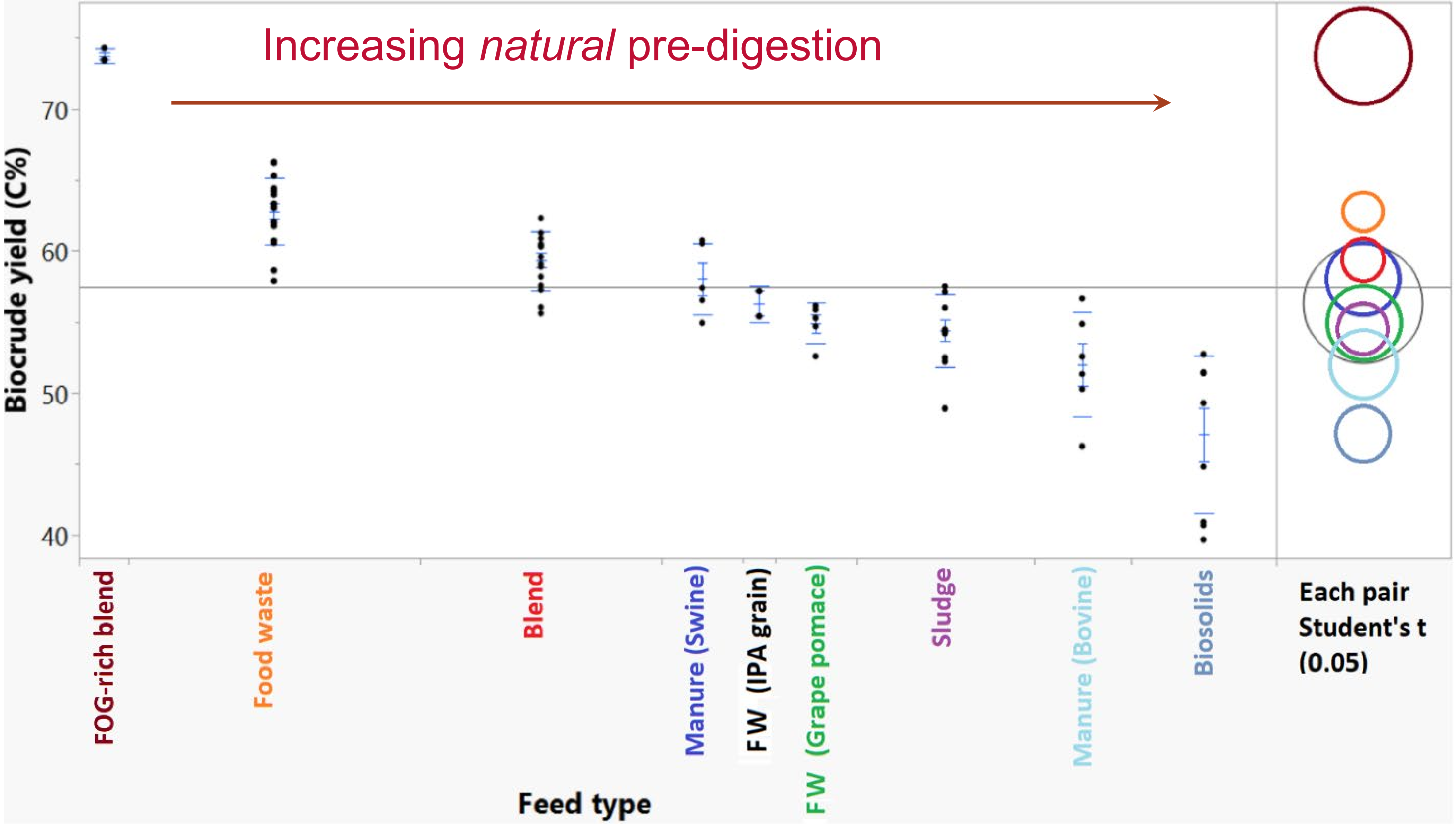
Short C length with many O

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

Statistical analysis of the impact of feedstock on upgrading performance

HTL carbon yields range from 40 to 75% depending on feedstock

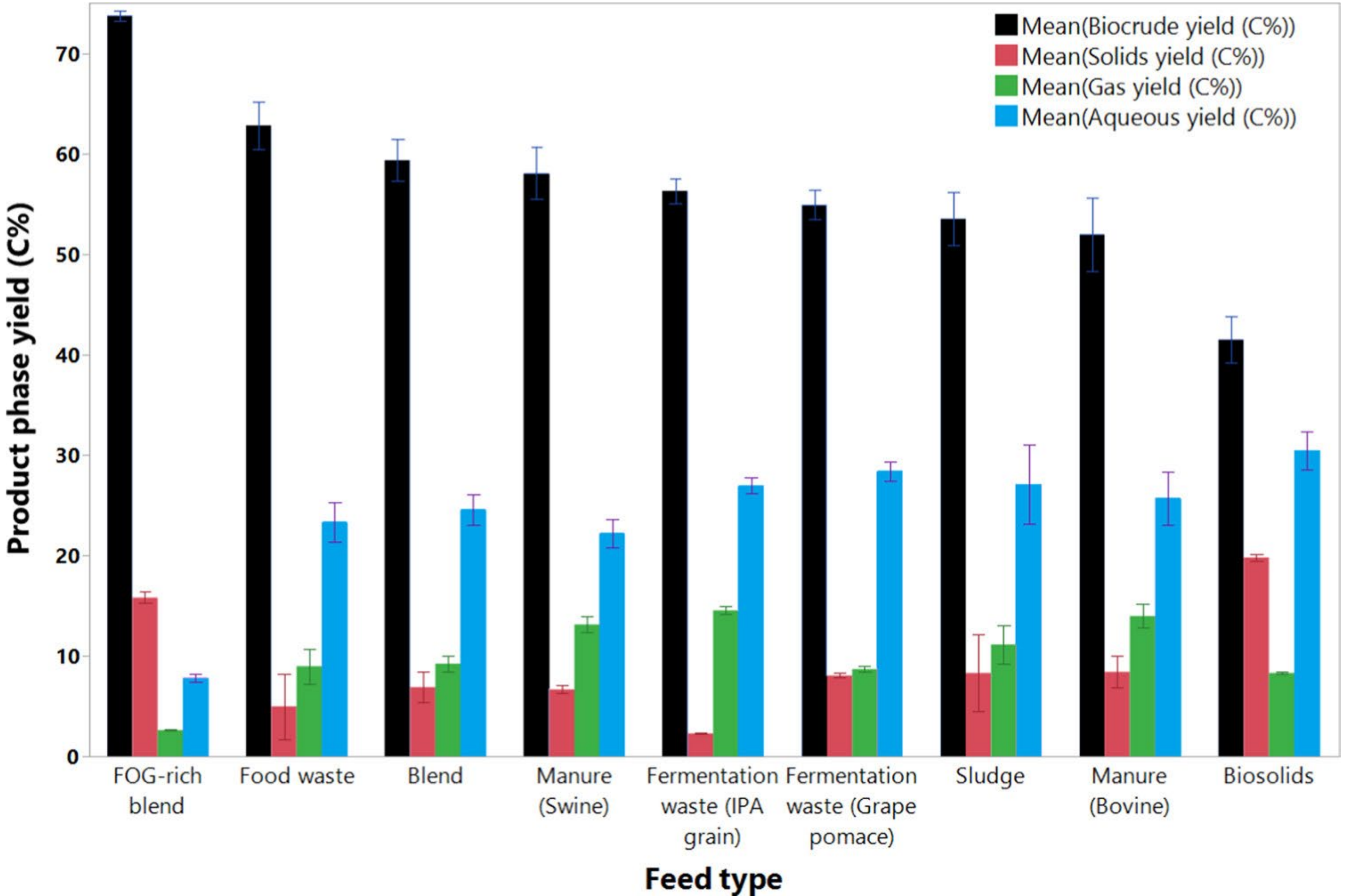
- FOG-rich blends result in high overall yields
- Food waste has higher yield (less losses to the solids stream)
- Increasing *natural* pre-digestion decreases biocrude yield
- Statistically significant differences between feedstock types

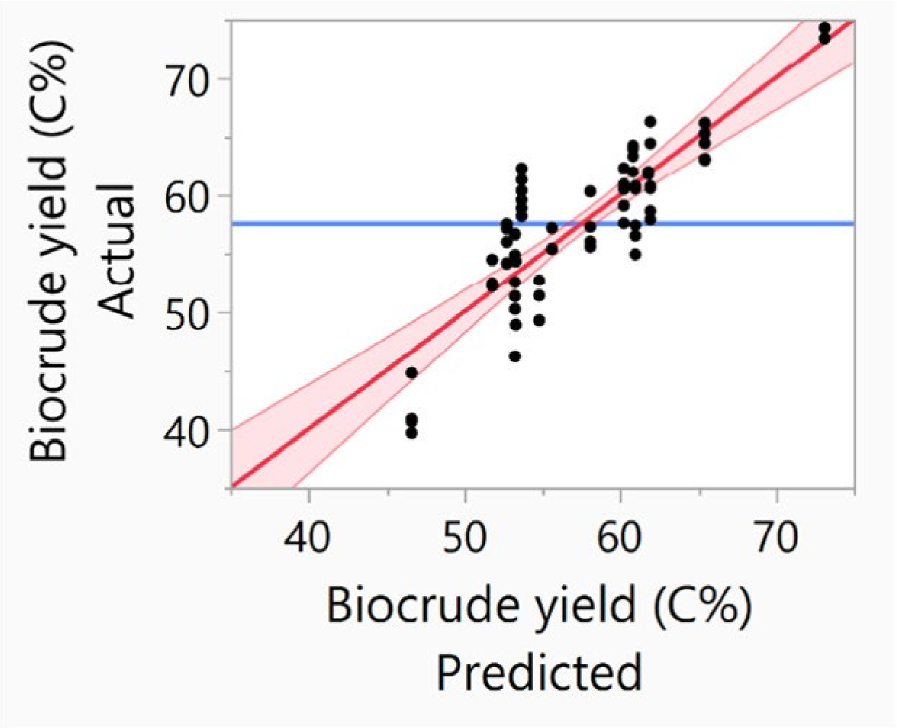


Fat and Ash Significantly Influence Yields

Most significant factors:

- Fat content: direct increase in biocrude
- Ash: Increased carbon lost to the solids





Variable	LogWorth	*p*-value
Feed fat content (wt%)	12.553	$< 1\times10^{-5}$
Feed ash content (wt%)	2.441	3.62×10^{-3}
Feed carbohydrates content (wt%)	1.421	3.793×10^{-2}
Summary of fit		
R^2	0.7405	
R^2 adjusted	0.7285	
RMSE	3.5596	

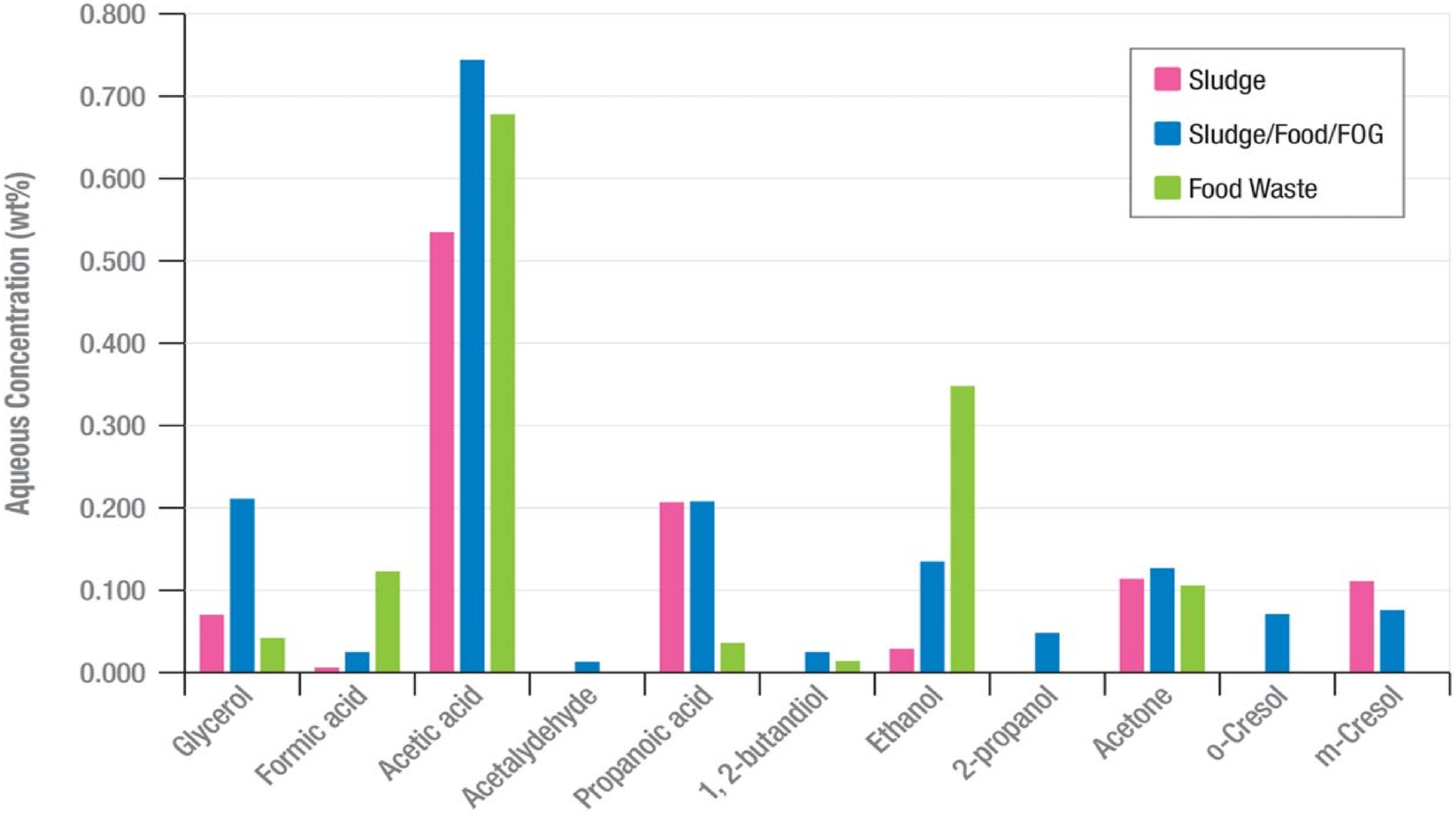
Model equation

Biocrude yield (C%) = 49.9996 + 0.47619 × Feed carbohydrates content (wt%) + 2.06729 × Feed fat content (wt%) – 1.57934 × Feed ash content (wt%)

While 25% of the carbon ends up in the aqueous phase, the product is dilute

Carbon in the aqueous phase

- Acetic acid and other small alcohols, polyols, carbonyls, and phenols
- 2-3% collective concentration

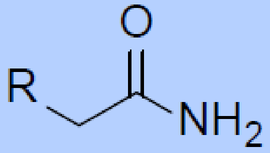


Biocrude has higher O and N content and higher acidity than petroleum crude oil

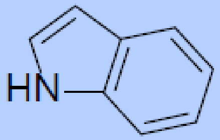
	O%	N%	S%	TAN*
Petroleum*	0.5	0.1-2	0.05 - 6	0.2 - 5
Biocrude				
Sludge	8	4	1	65
Chlorella	4	6	1	53
Pine	10	0	0.01	53

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

Organic N is in two forms



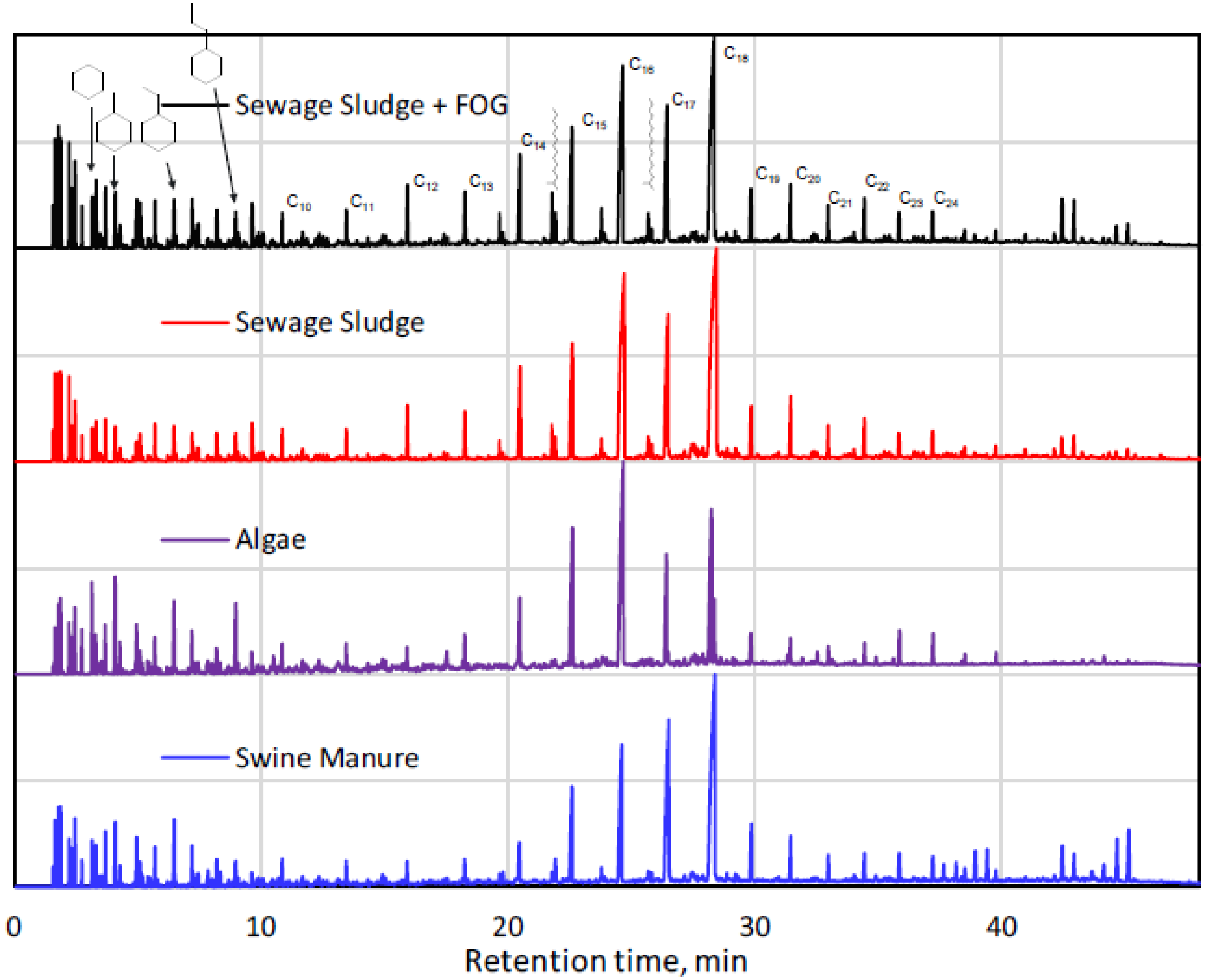
Amides (easily hydrogenated)



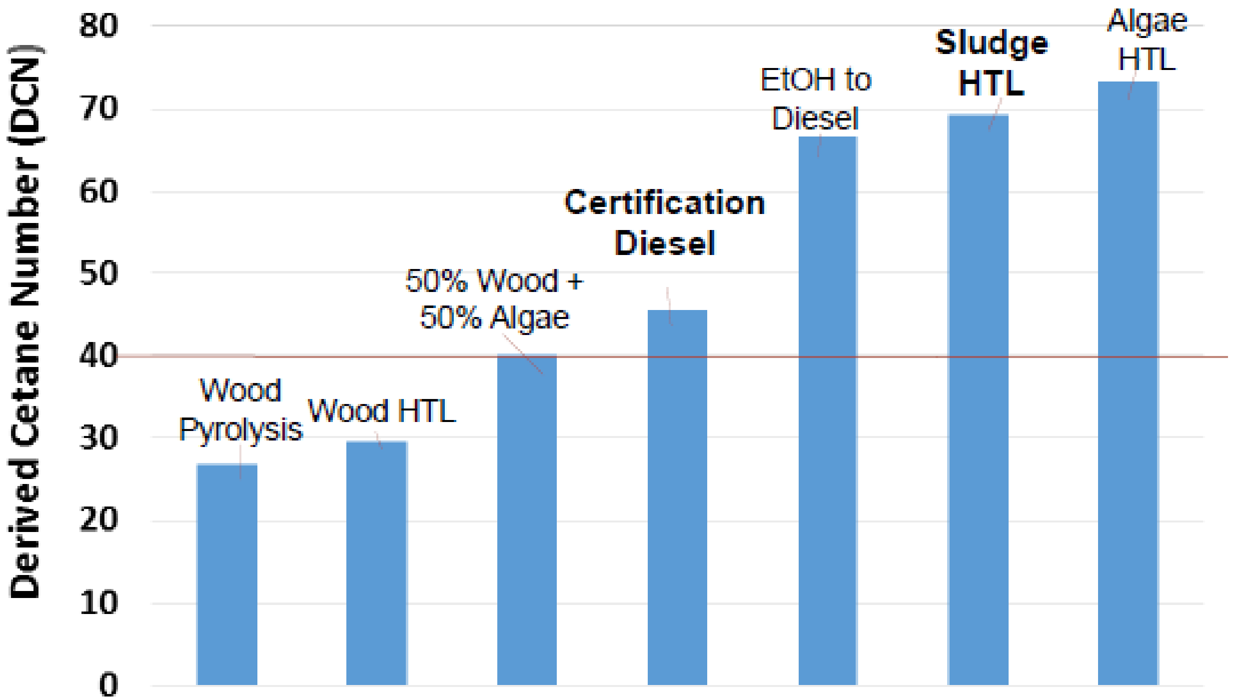
Cyclic amines (more difficult to hydrogenate)

- 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

Upgraded fuel is rich in n-alkanes



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

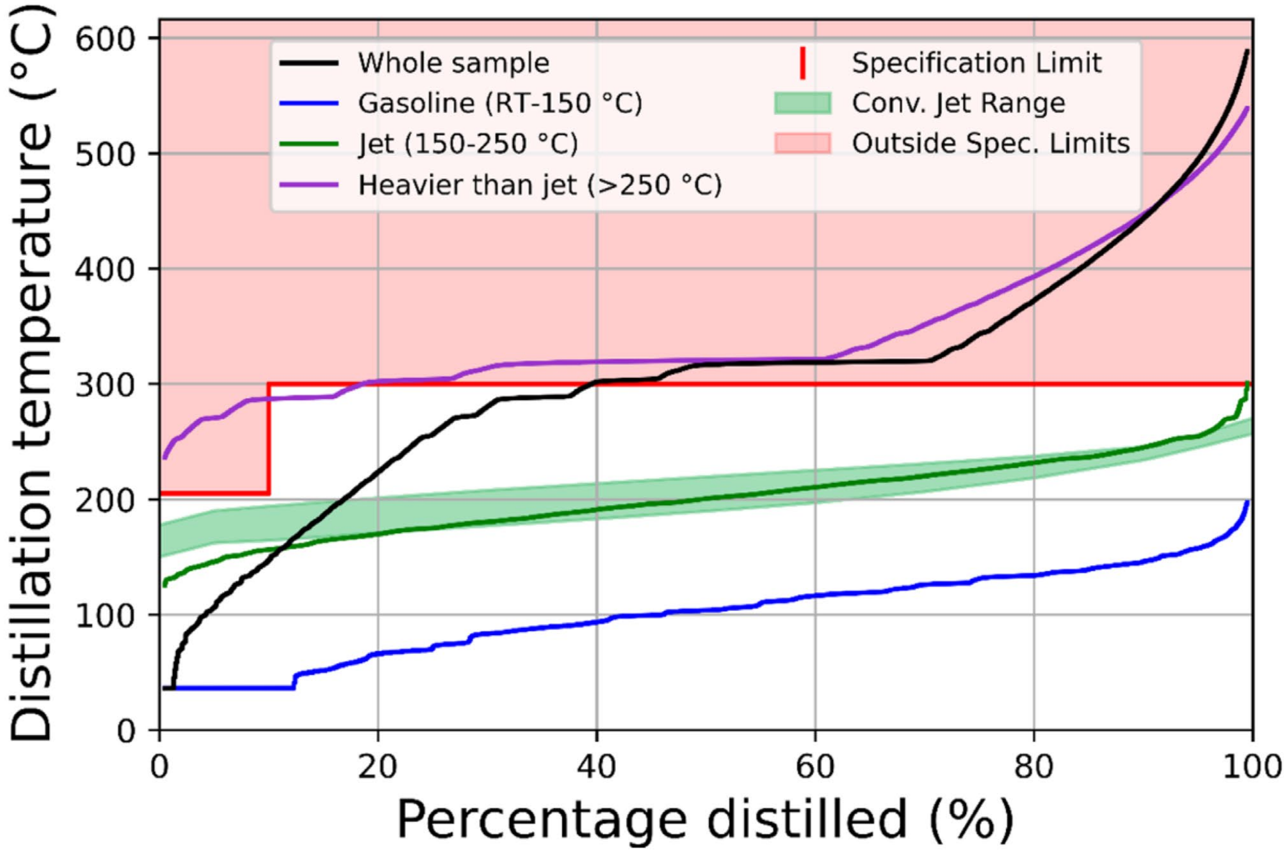


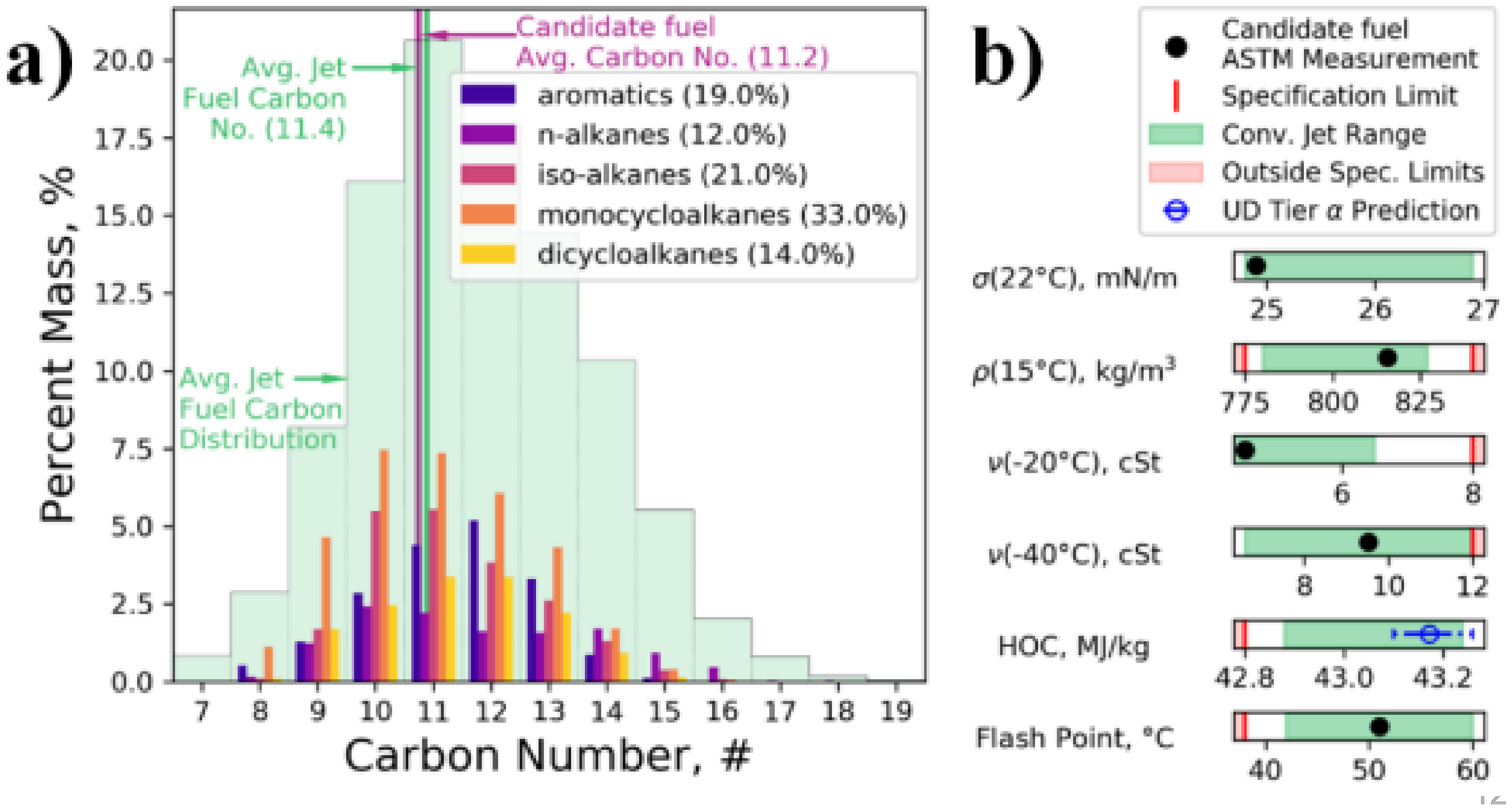
**Analysis by Colorado State University

Pacific Northwest
NATIONAL LABORATORY

High-quality SAF fuel from HTL of wet wastes

- 20-25% of upgraded fuel in jet range
- Similar mix of cycloalkanes, n-alkanes, iso-alkanes, aromatics to traditional jet
- Positive alpha and beta jet fuel properties
- Main concern is the N in the jet fuel

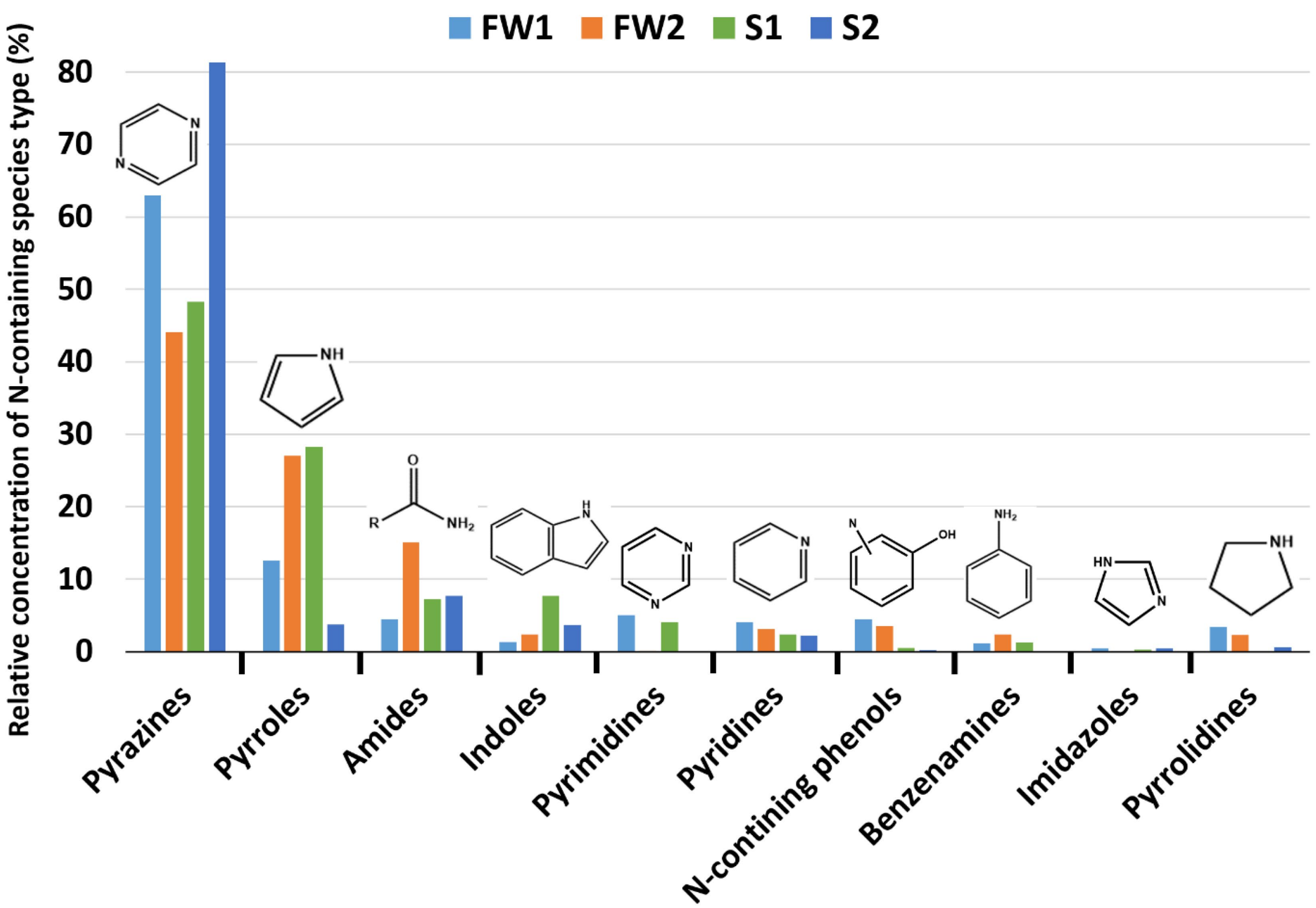




GCxGC MS of the HTL biocrude feed

Biocrude is rich in Pyrazines, pyrroles, amides, indoles, etc.

- Significant amount of the biocrude does not volatize in the column



Challenge for SAF:

Expect the Nitrogen to need to be <10 or <2ppm Nitrogen

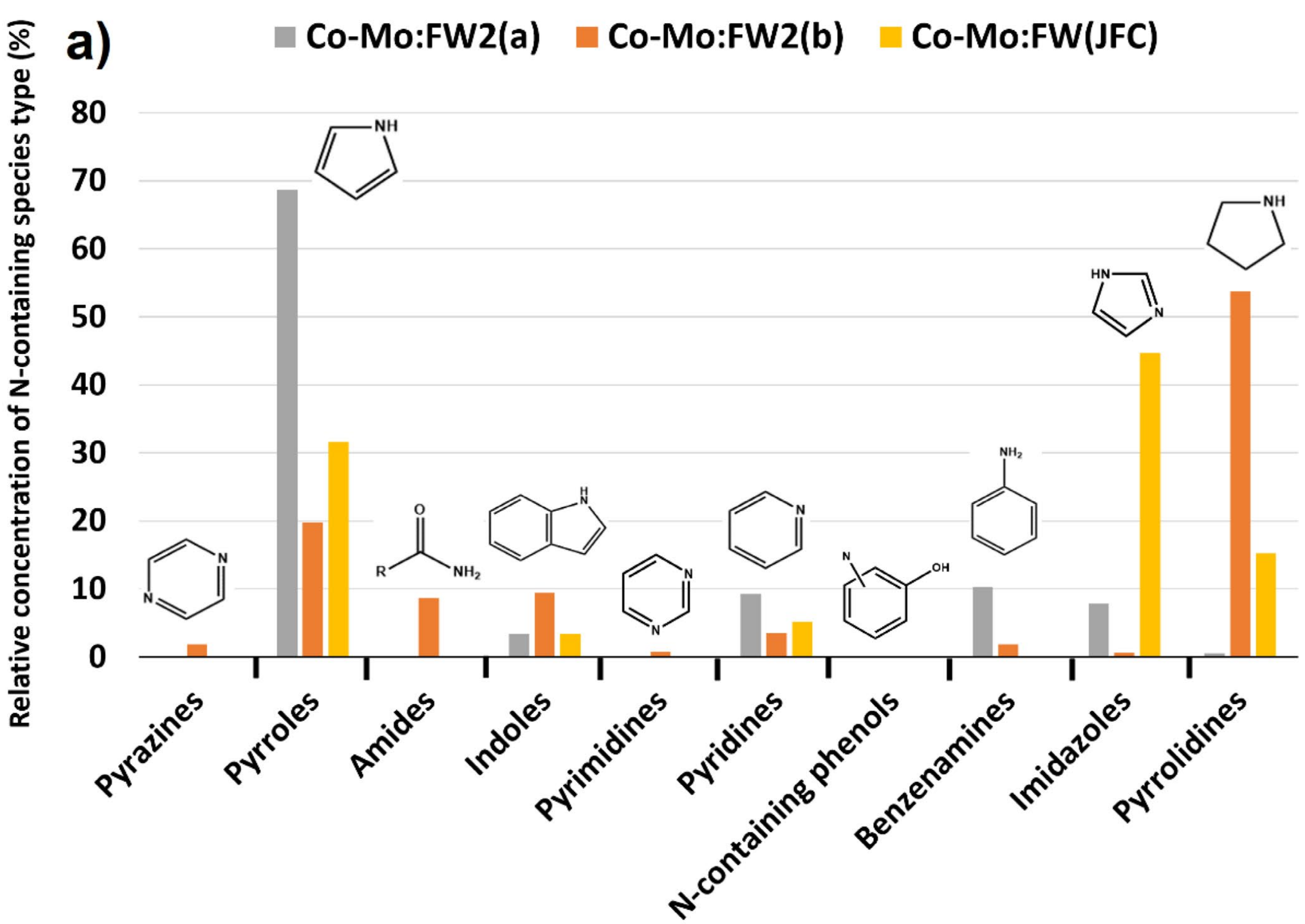
Concern with N-S interactions that can lead to fuel instability issues in engine

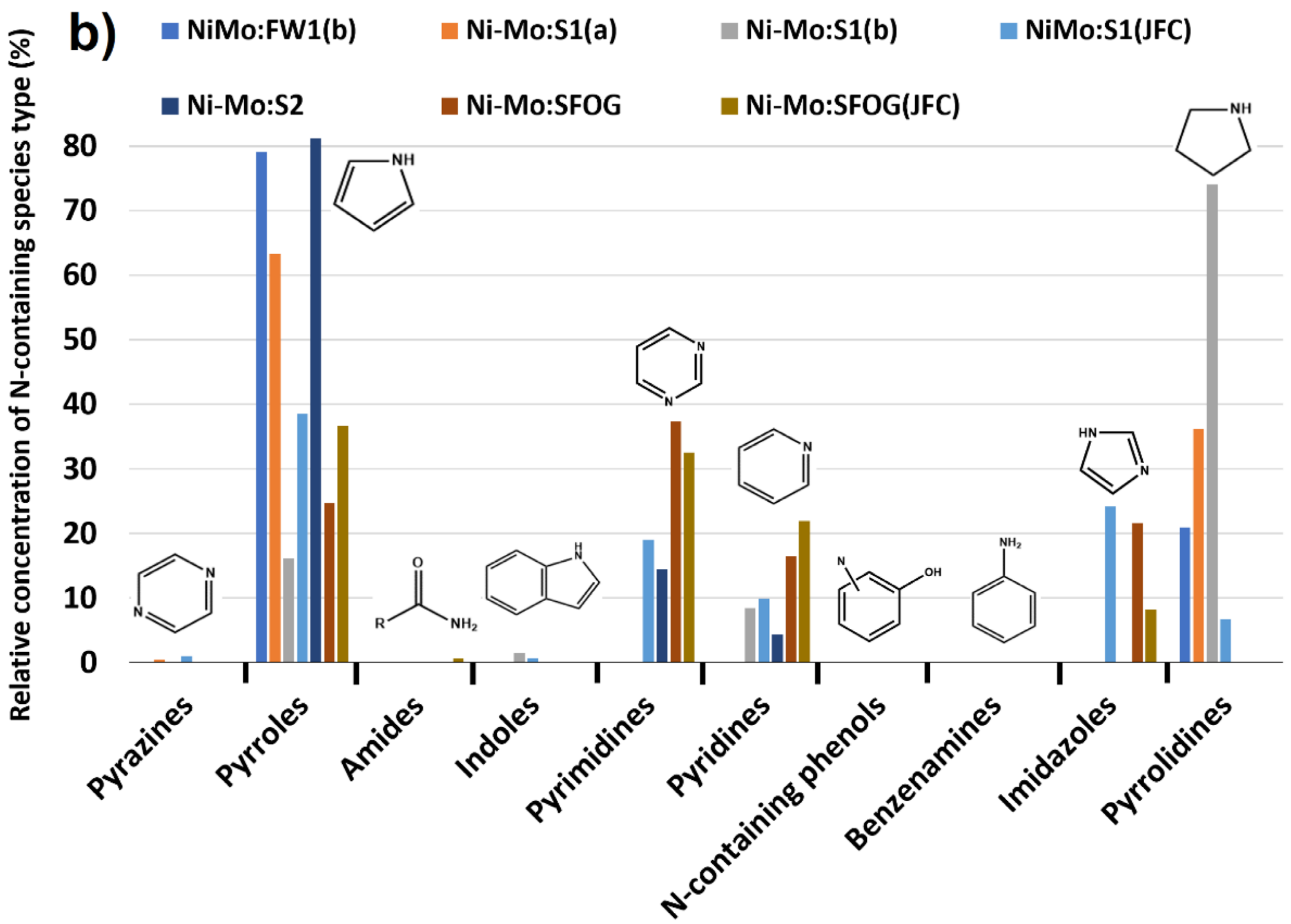
Residual Nitrogen in SAF cut

- Most challenging species to hydrotreat is the Pyrroles, Imidazoles, Pyrrolidines
- Expect further HDN to get to 2ppm N

Typical hydrotreating conditions here:

~400°C
~1500 psi
~0.5hr^{-1} WHSV
Results in ~97% Nitrogen reduction





Key Takeaways

- Primary value proposition for HTL of organic wet wastes is sludge disposal
- Similar HTL performance for organic wet wastes in continuous HTL
  - Fat and ash strongly influence yield
  - Less natural digestion results in higher yields
- Similar biocrude properties for organic wet wastes
- Hydroprocessed biocrude: Rich in n-alkanes for all wet wastes
- Hydrodenitrogenation will be a challenge for SAF
  - Expect a Nitrogen specification of <2ppm or <10ppm

Pacific Northwest NATIONAL LABORATORY

Questions?