Sustainable Aviation Fuel (SAF) from liquefaction

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John Holladay,[1] Zia Haq[2]

[1]Pacific Northwest National Laboratory

[2] U.S. DOE, Bioenergy Technologies Office

Special thanks to Karthi Ramasamy, Beau Hoffman, Mike Thorson, Justin Billing, Josh Heyne, Steve Csonka

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

In November 2020, PNNL facilitated an international workshop on HTL for SAF production

Present an overview of findings

- Quick overview of HTL
- Details from the workshop – research opportunities
- Examples of pilot and demonstrations
- Conclusions

Take home message

- HTL has high promise
- Roughly 20% of fuel in SAF range
- Four areas of "research opportunities"

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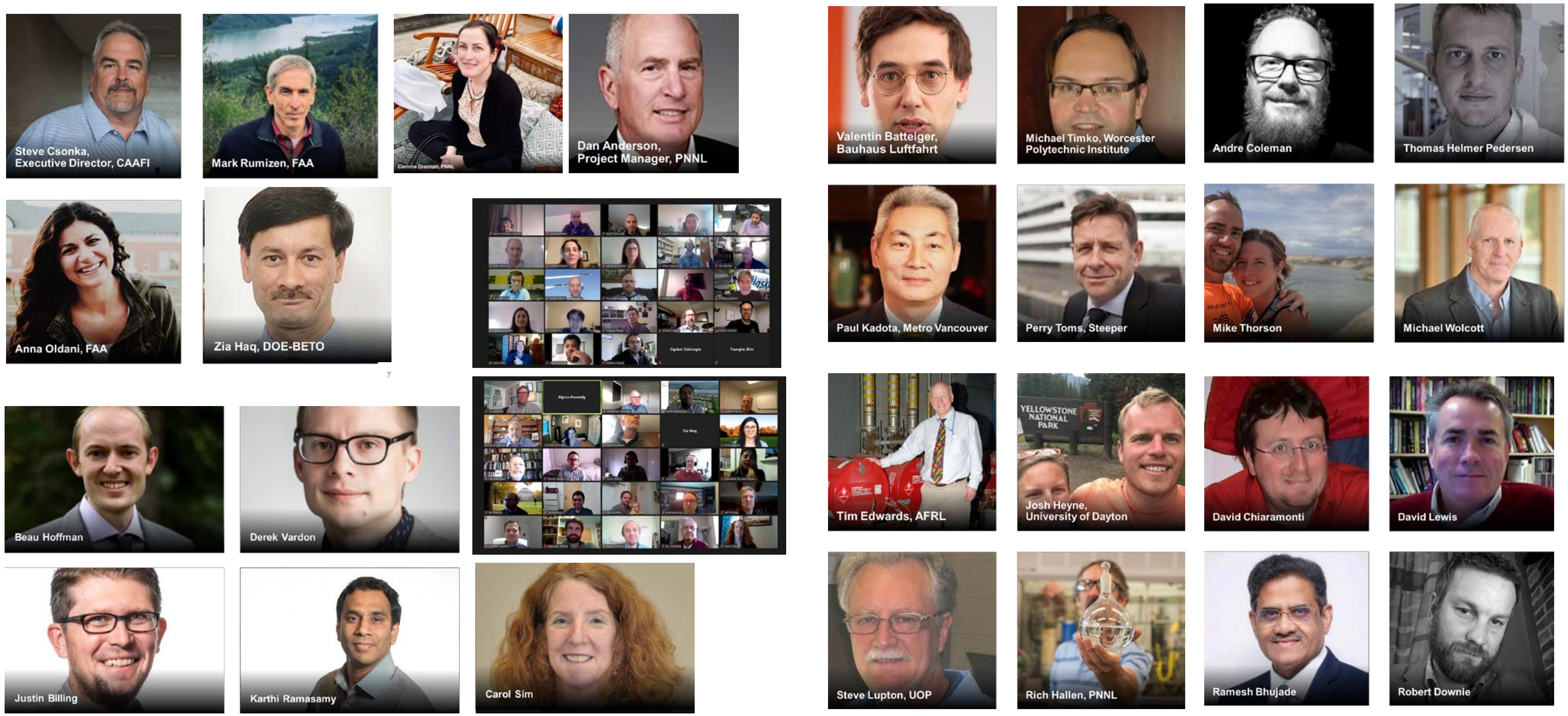
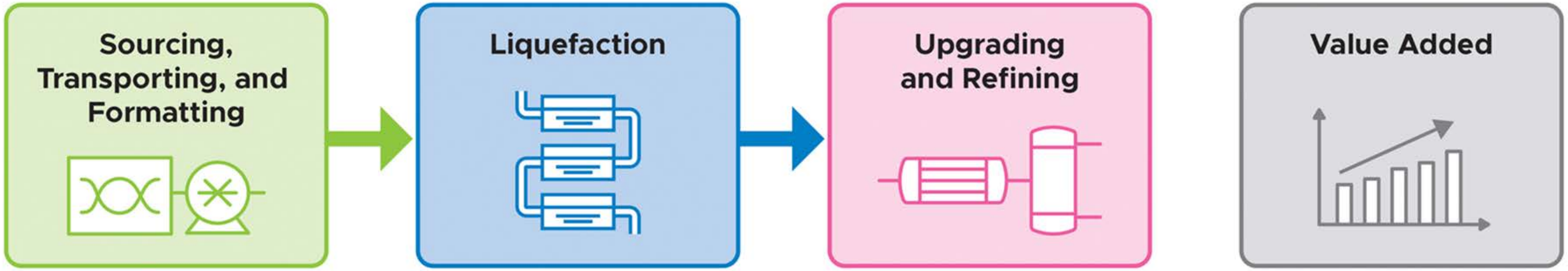
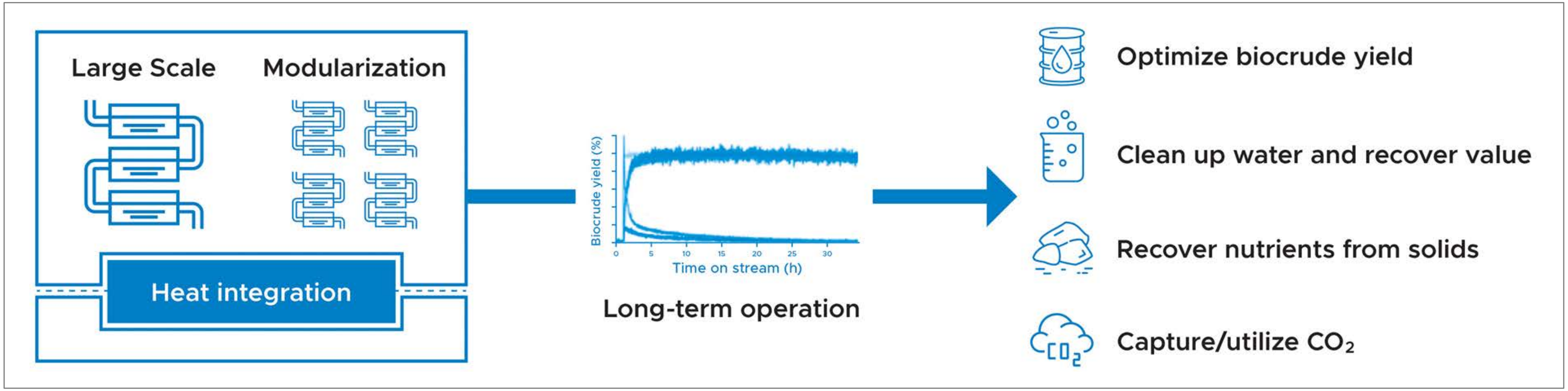
We thank those who organized and participated in the workshop



Quick overview of HTL



Hydrothermal liquefaction is a means to convert wet carbon streams to biocrude oil

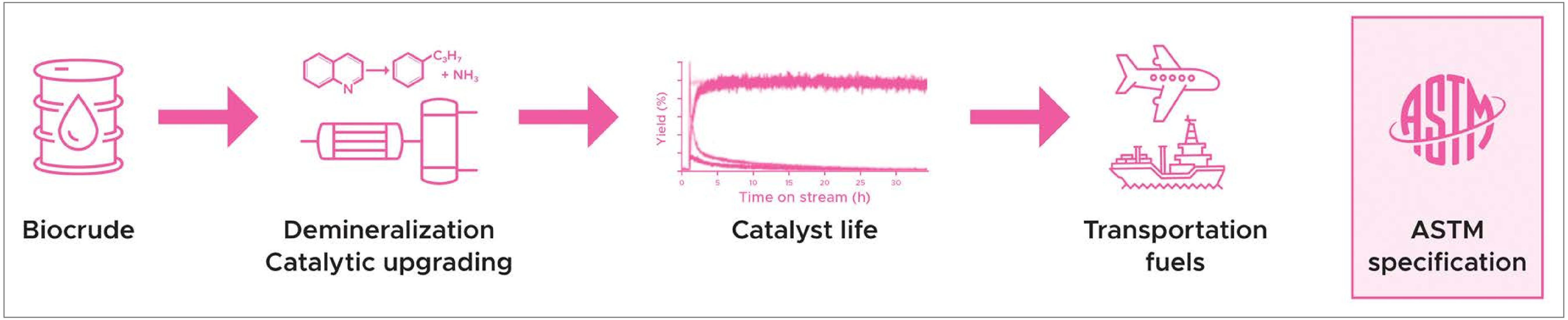


- Heat and pressure (300-350 ºC, 16-22 MPa, 10-20 min)
- Produces a biocrude oil, thermally stable
- Biocrude can be upgraded to fuels, rich in diesel
- Need to optimize value from other HTL streams (aqueous, solids, gasses)

HTL expands feedstock from classical biomass to low-cost carbon-waste streams

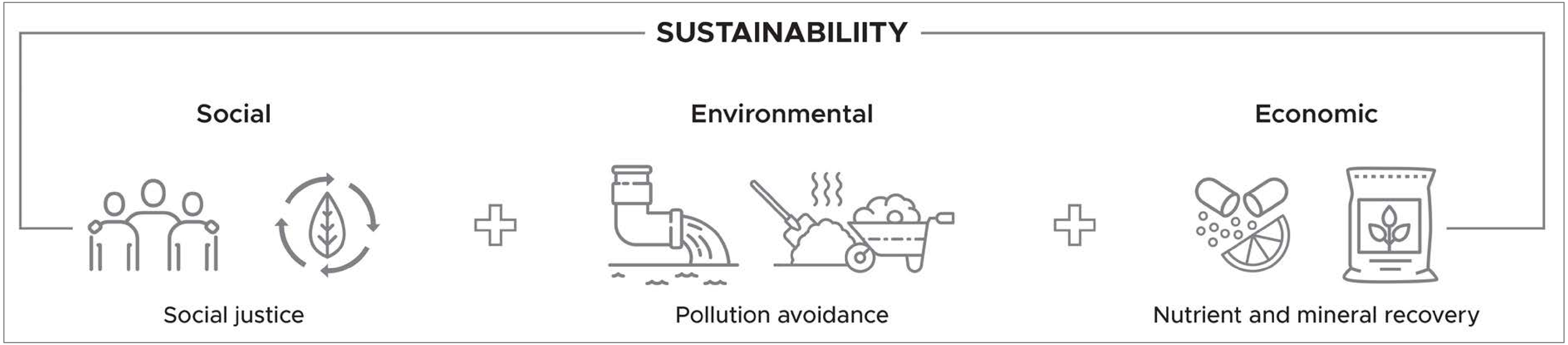
- Municipal wastewater sludge, food waste, manures
- Classical biomass can be added as a mixture (or as the primary feed)
- Feedstock changes the composition of the biocrude

The biocrude can be upgraded to produce transportation fuels



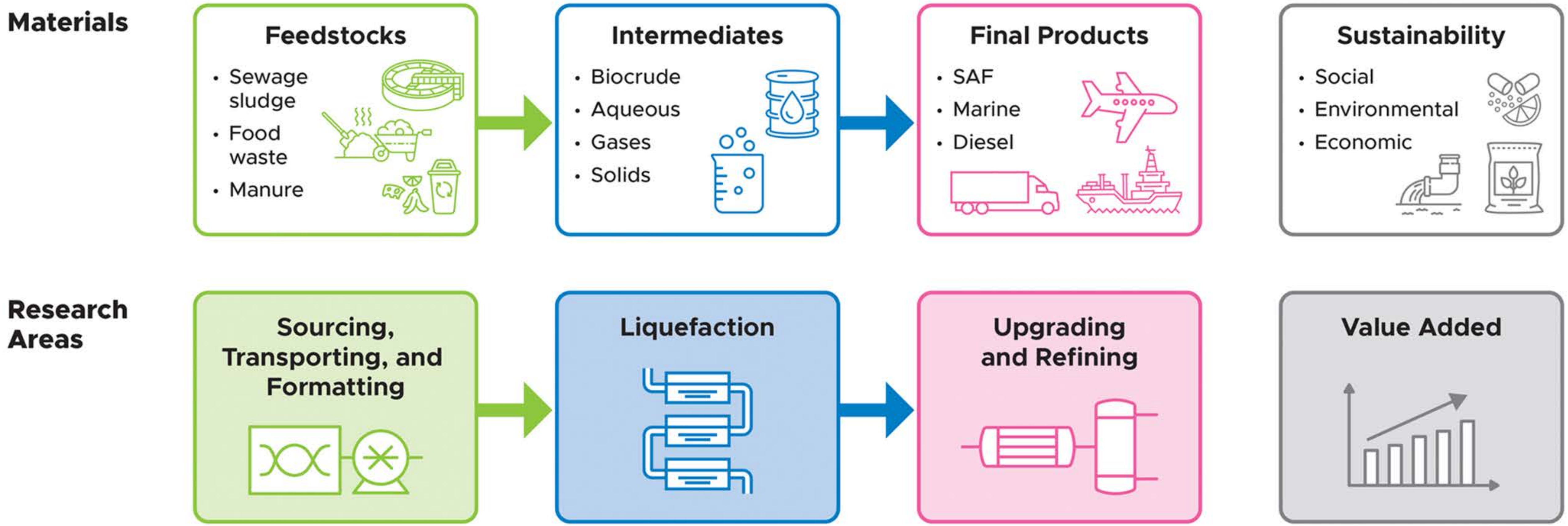
- Co-processing in petroleum refineries, risk
- Hydrotreating, the biocrude removes O and N
- Fractionated into gasoline, diesel, and jet fuel

Valuing the economic services of treating carbon waste needs to be fully understood



- Social justice
- Pollution avoidance
- Economic services of cleaning up carbon sources

Hydrothermal liquefaction provides a means to convert wet carbon-rich waste into biocrude oil

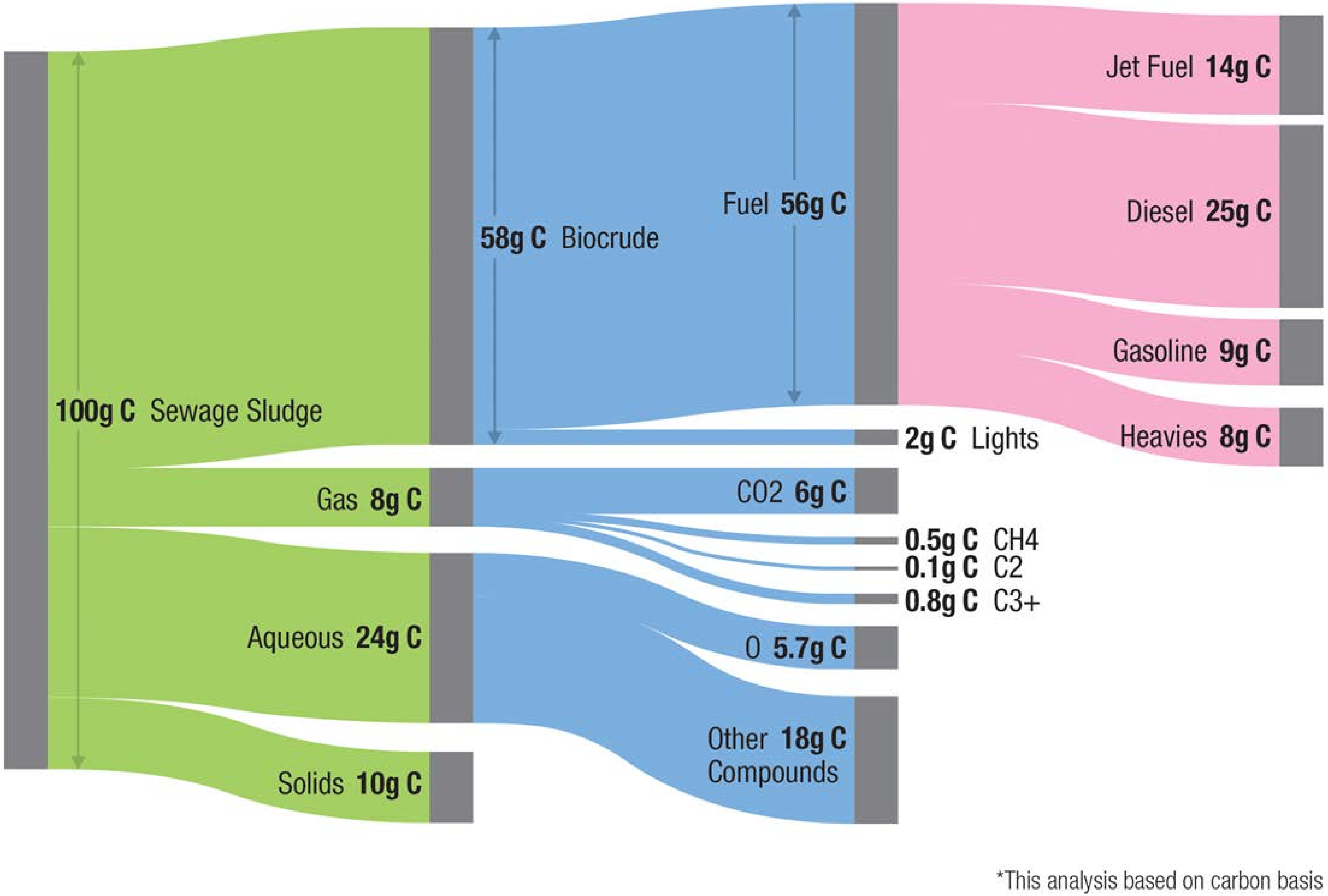


Details from the workshop

The carbon yield to fuels is among the highest in bioprocessing

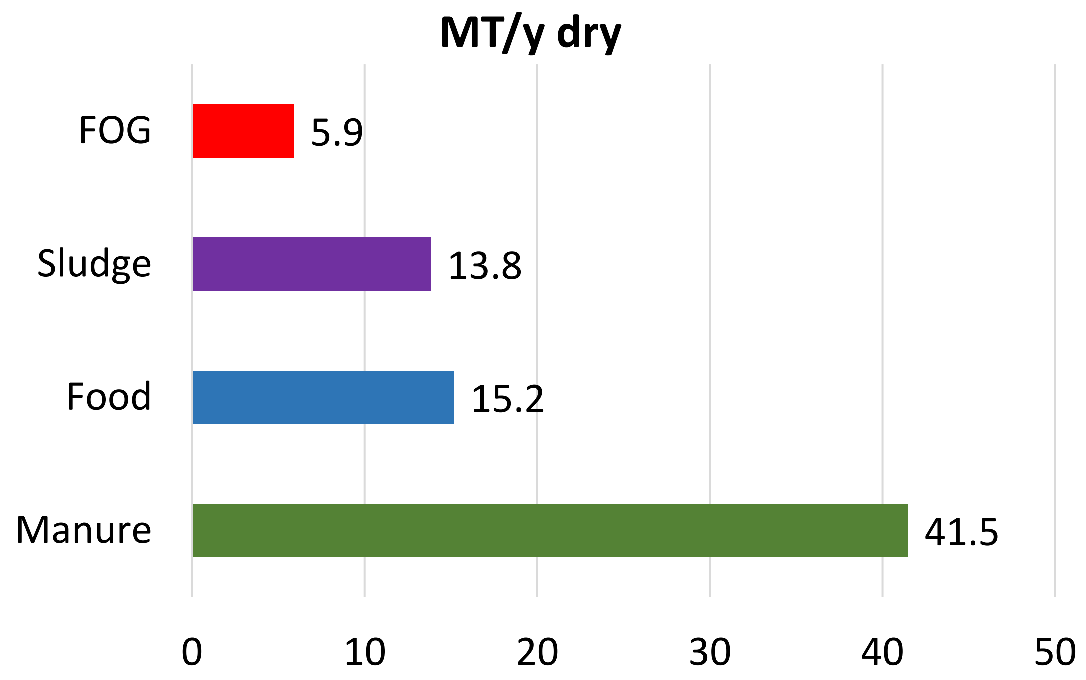
Typical

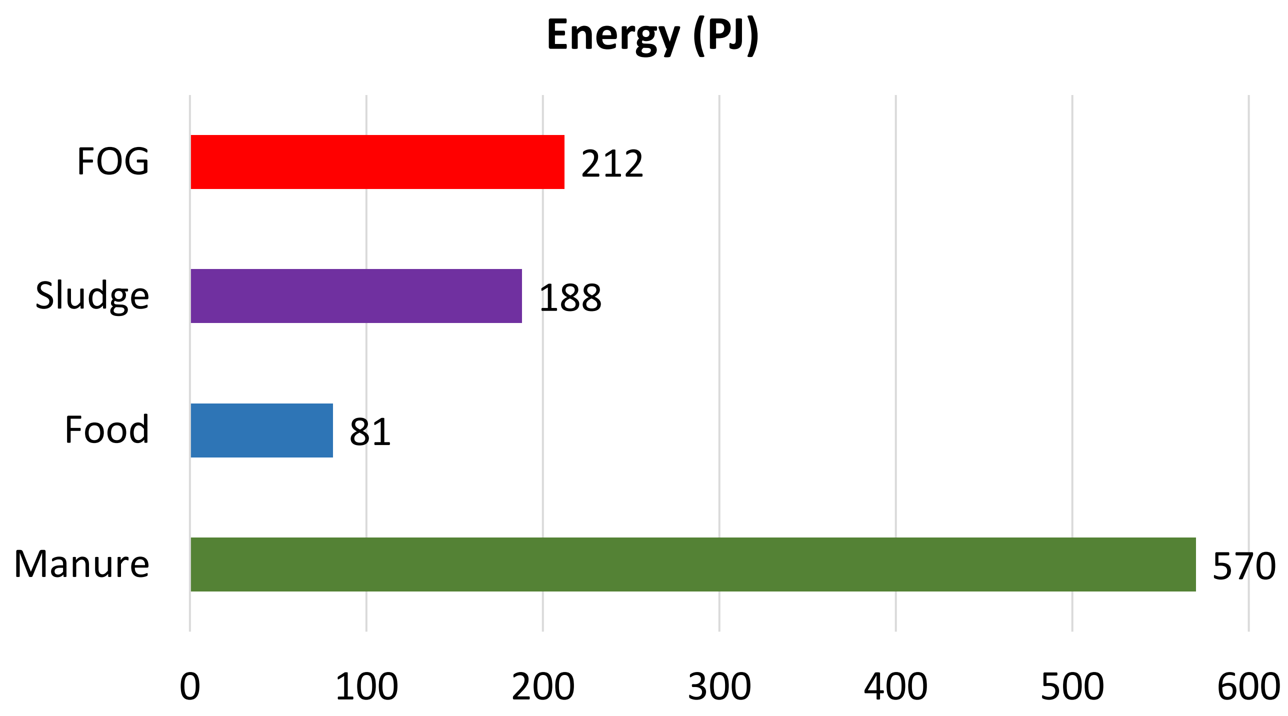
- 58% to biocrude
- Biocrude is stable
- Rich in diesel hydrocarbons



* Solids have the highest level of uncertainty

Accessible municipal sludge, manure, food waste, and FOG could provide ~ 6 B gallons of biocrude (CONUS*)

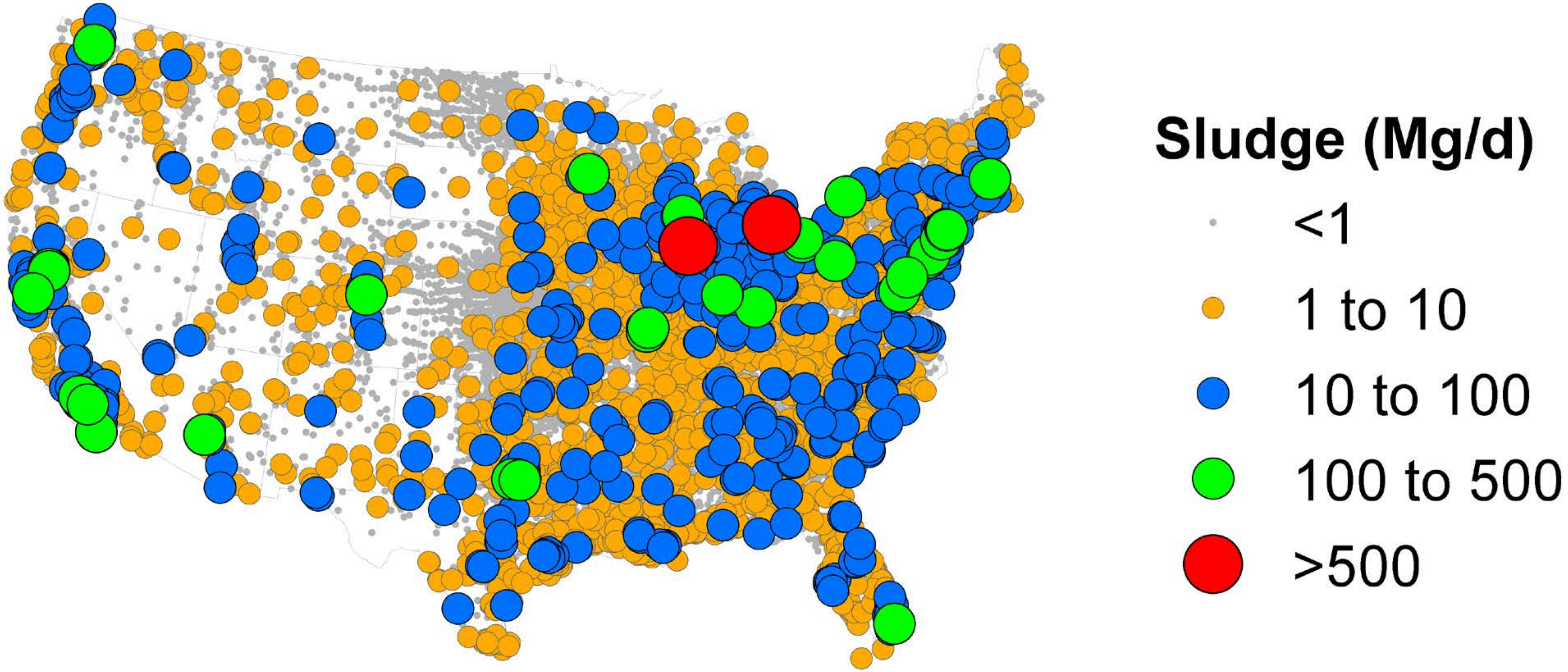




- Greater than 70% of waste can be aggregated (50 mi radius) with a capacity of 1000 dry tons/day (TPD)
- Promising economic performance down to 5 TPD
- 76 MMT/y dry waste at 56,000 sites
- 5.6 Bgal/y biocrude potential

*CONUS – Continental United States

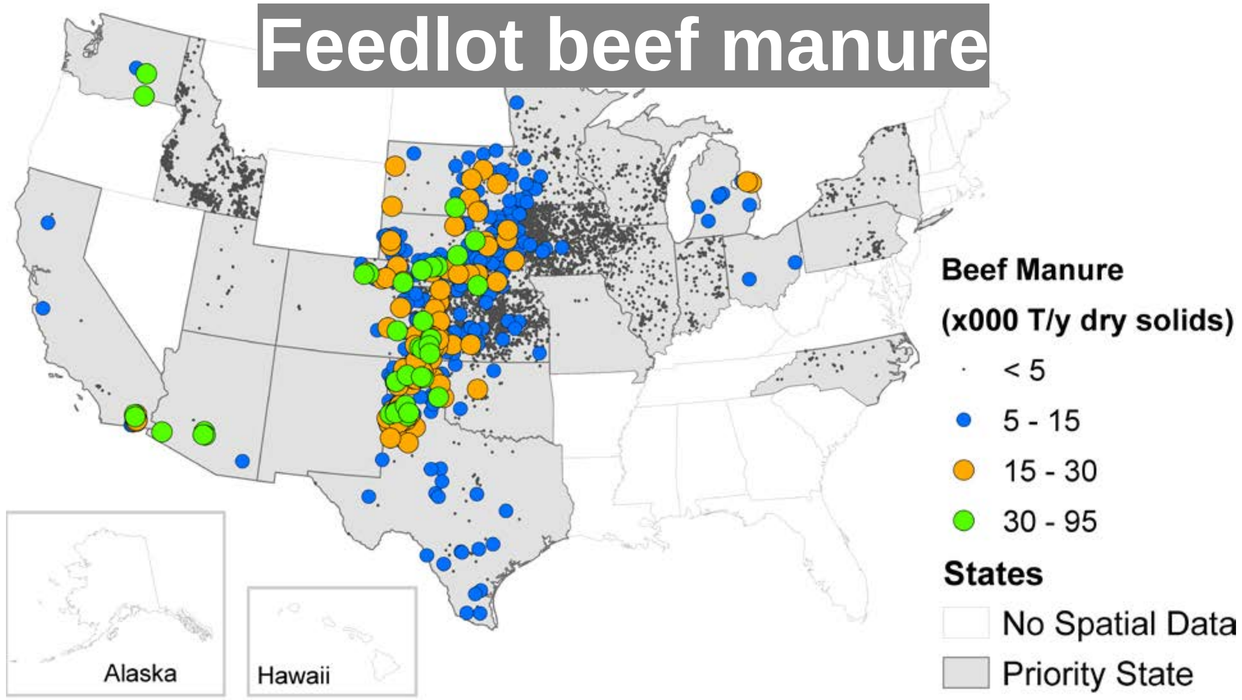
The wet resources are widely dispersed, with municipal sludge centered in urban areas



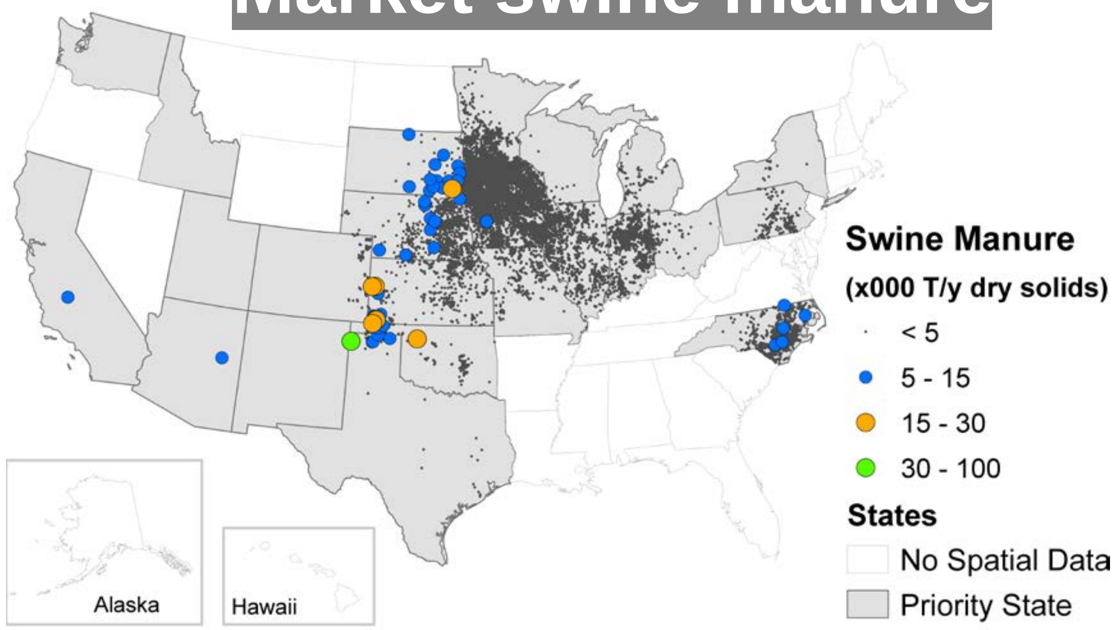
Site-specific inventory of untreated sludge production at >15,000 municipal wastewater treatment plants (WWTPs) in the US

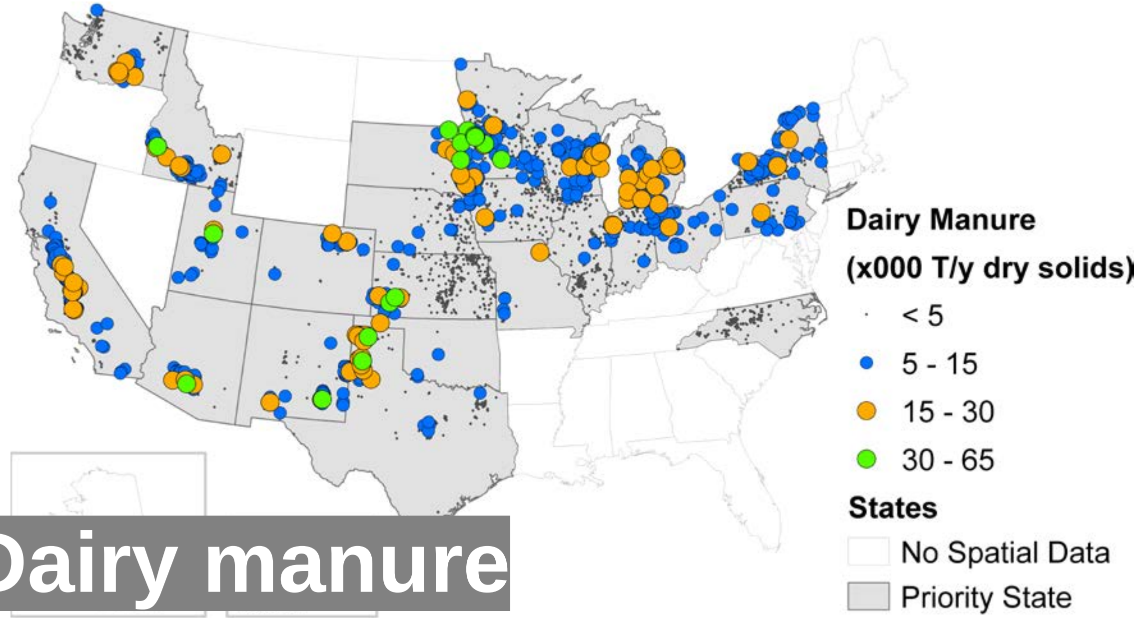
Manures are dispersed in rural areas

Feedlot beef manure



Market swine manure

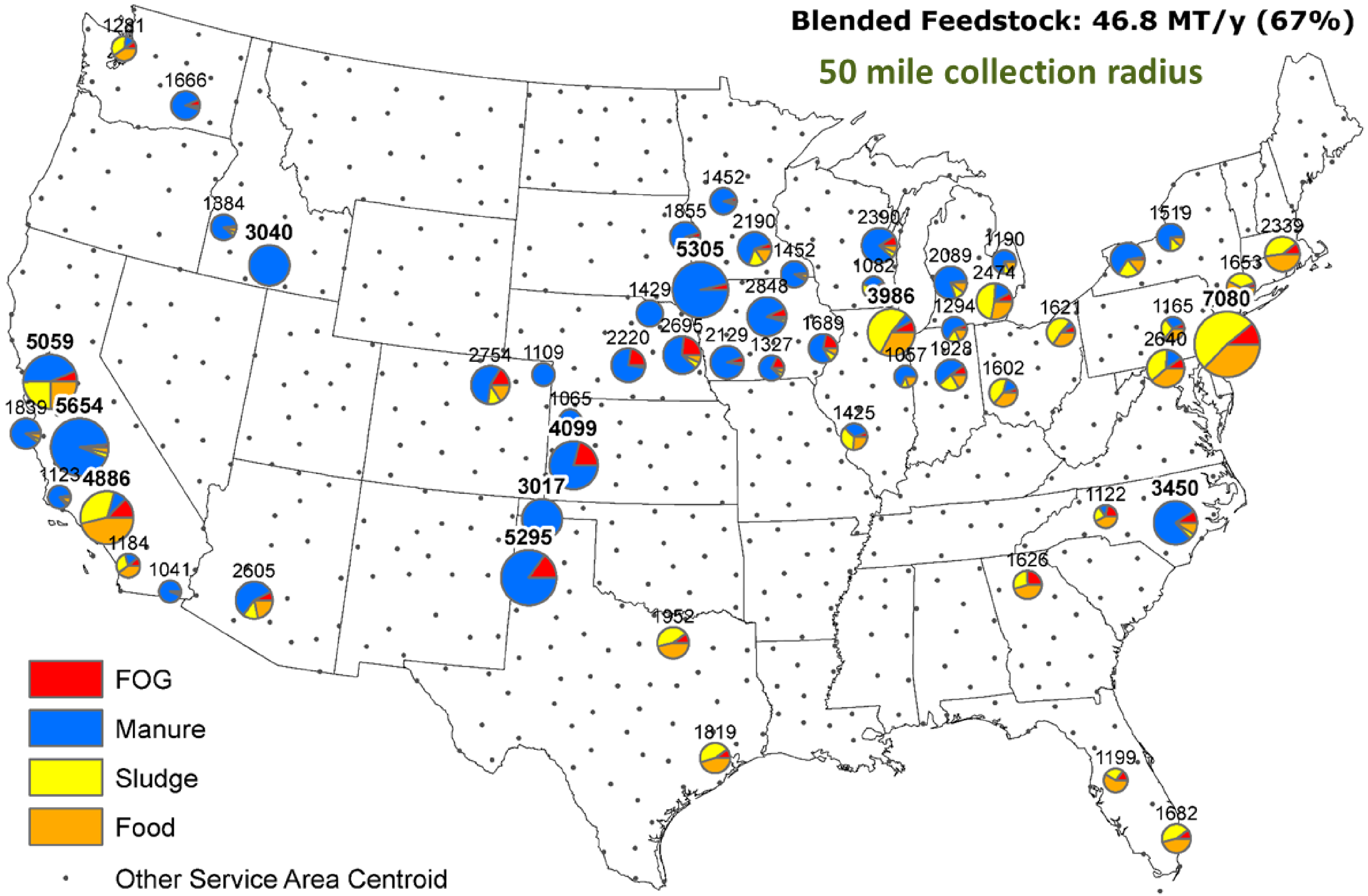




Dairy manure

Site-specific inventory of confined manure production at >32,000 feedlot beef, dairy, and market swine operations

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

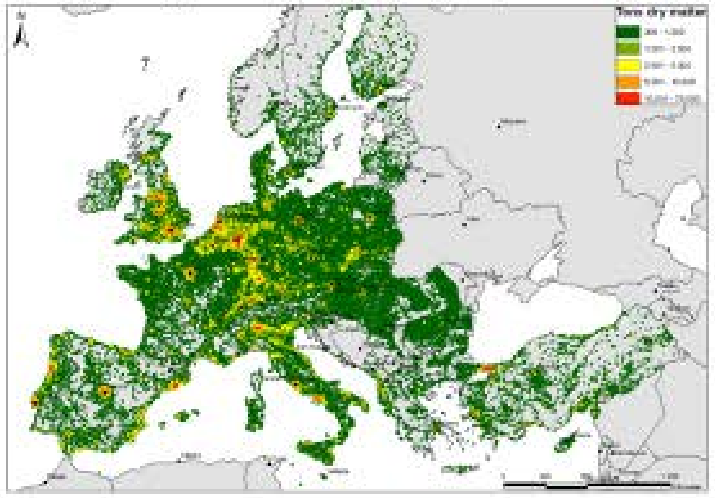
Europe has similar resource assessments

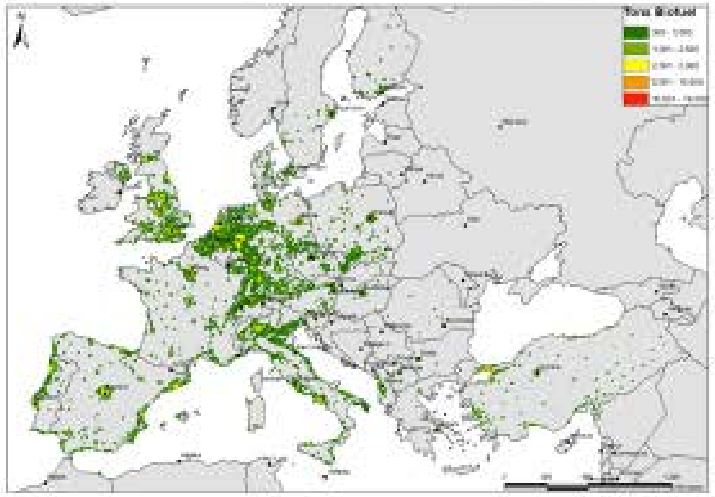
HTL feedstock potentials, wastes and residues in EU

- *Spatial analysis of residue and waste availability in Europe*
- *Feedstock density maps available for:*
  - Animal excretions (cattle, pigs, poultry), agricultural by-products (straws, sugar beet leaves, corn stover), sewage sludge, biowastes
- *Conversion to biofuels potentials (yield model)*
- *Theoretical fuel production potentials*
  - Agricultural by-products: 26-29 Mt
  - Animal excretions: 10-26 Mt
  - Sewage sludge: 3 Mt
  - Biowastes: 1.5 Mt

Potentials refer to mixture of liquid hydrocarbons!

Sewage sludge: Theoretical feedstock potential



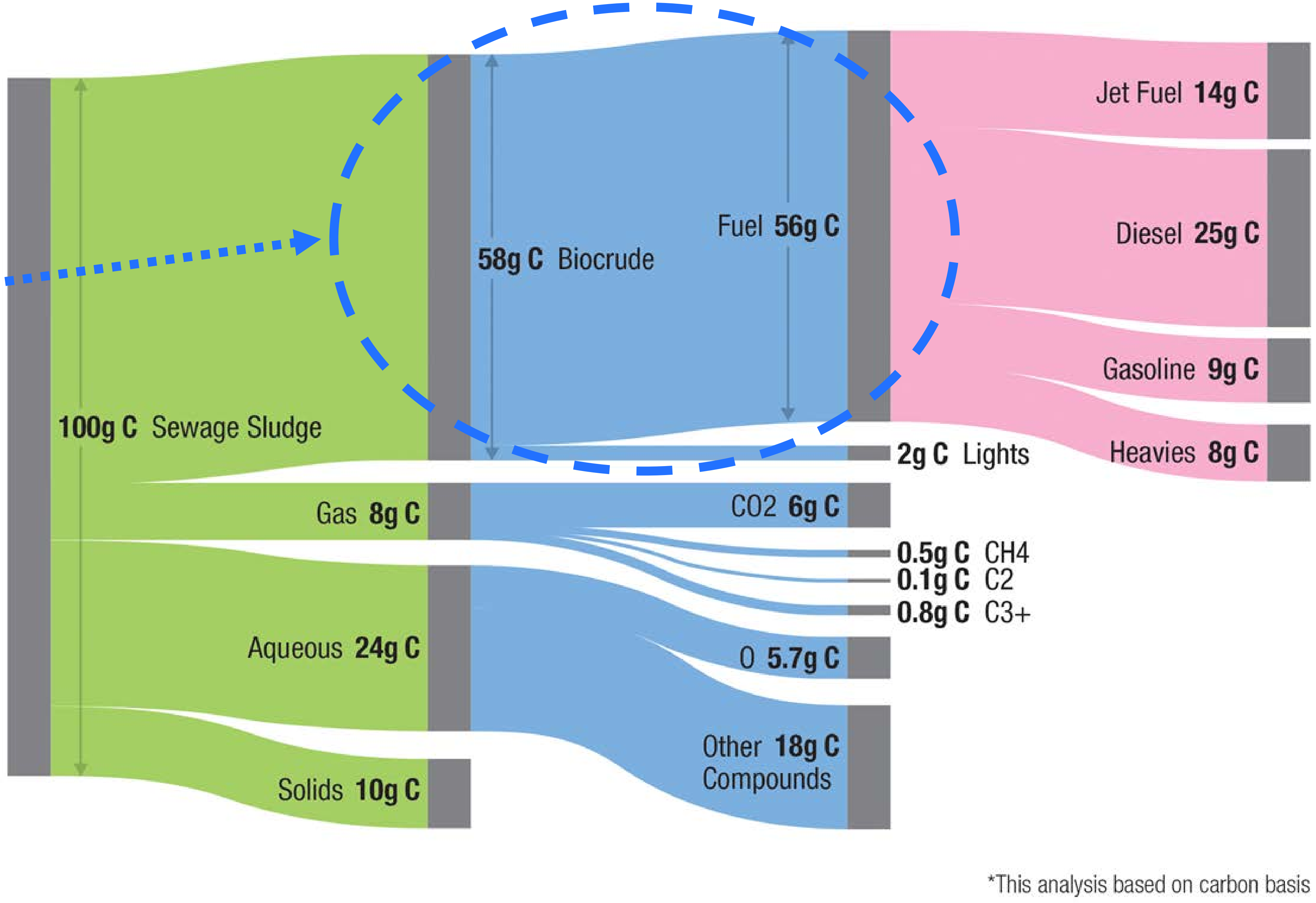


Sewage sludge: Biofuel potential

DBFZ

HyFlexFuel

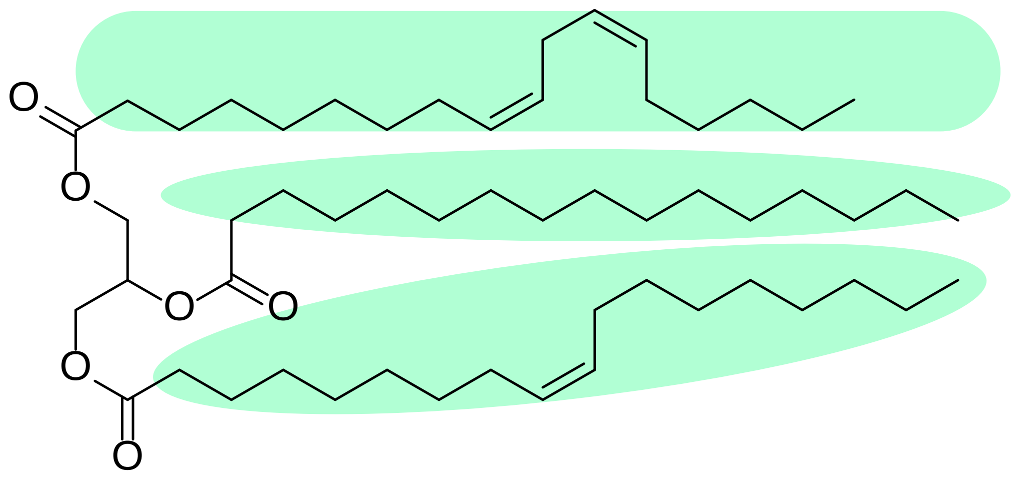
Biocrude and jet fuel from wet waste



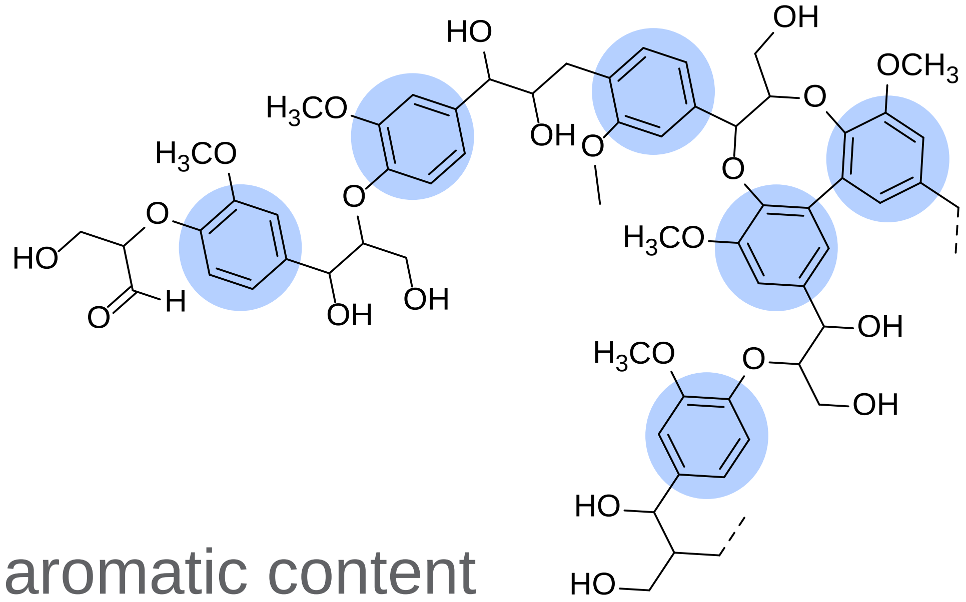
Typical

- 58% to biocrude
- Biocrude is stable
- Rich in diesel hydrocarbons

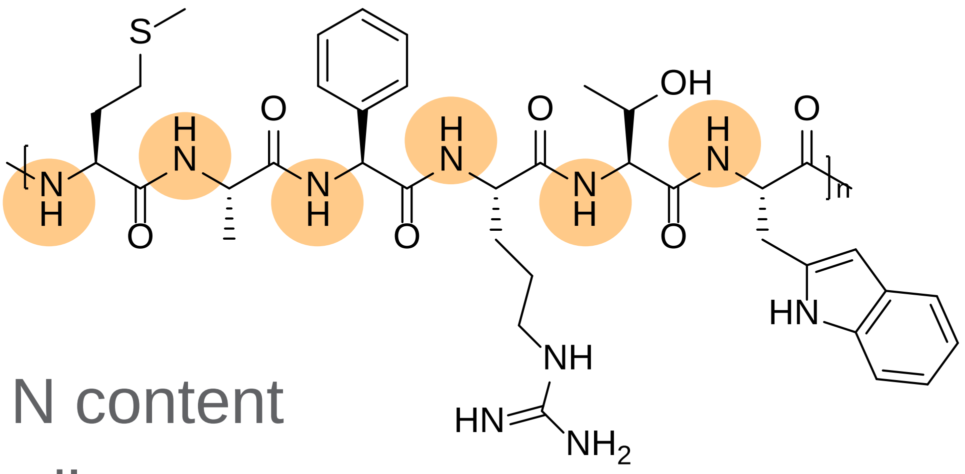
Feedstock has an impact on the biocrude in terms of hydrocarbon type, N content, and aromatic content



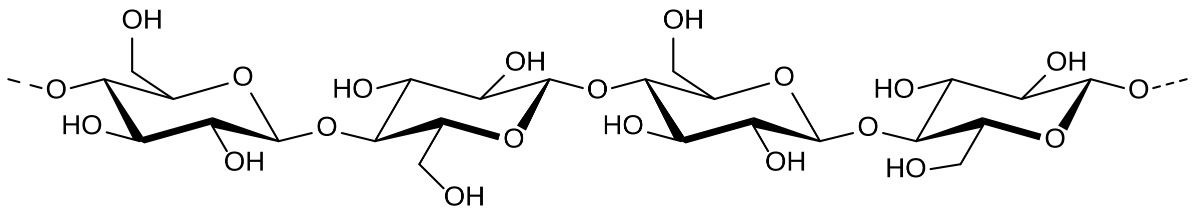
Fats –
increased long n-alkane (cetane)



Lignin –
increased aromatic content



Protein –
- increased N content
- does form oil



Short C length with many O

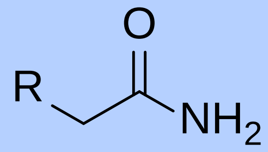
Cellulose –
- increased C to aqueous phase
- does form oil (Maillard reaction with protein)

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

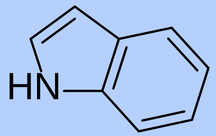
	O%	N%	S%	TAN*
Petroleum*	0.5	0.1-2	0.05 - 6	0.2 - 5
Biocrude				
Sludge	8	4	1	65
Chlorella	4	6	1	53
Pine	10	0	0.01	53

* 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)

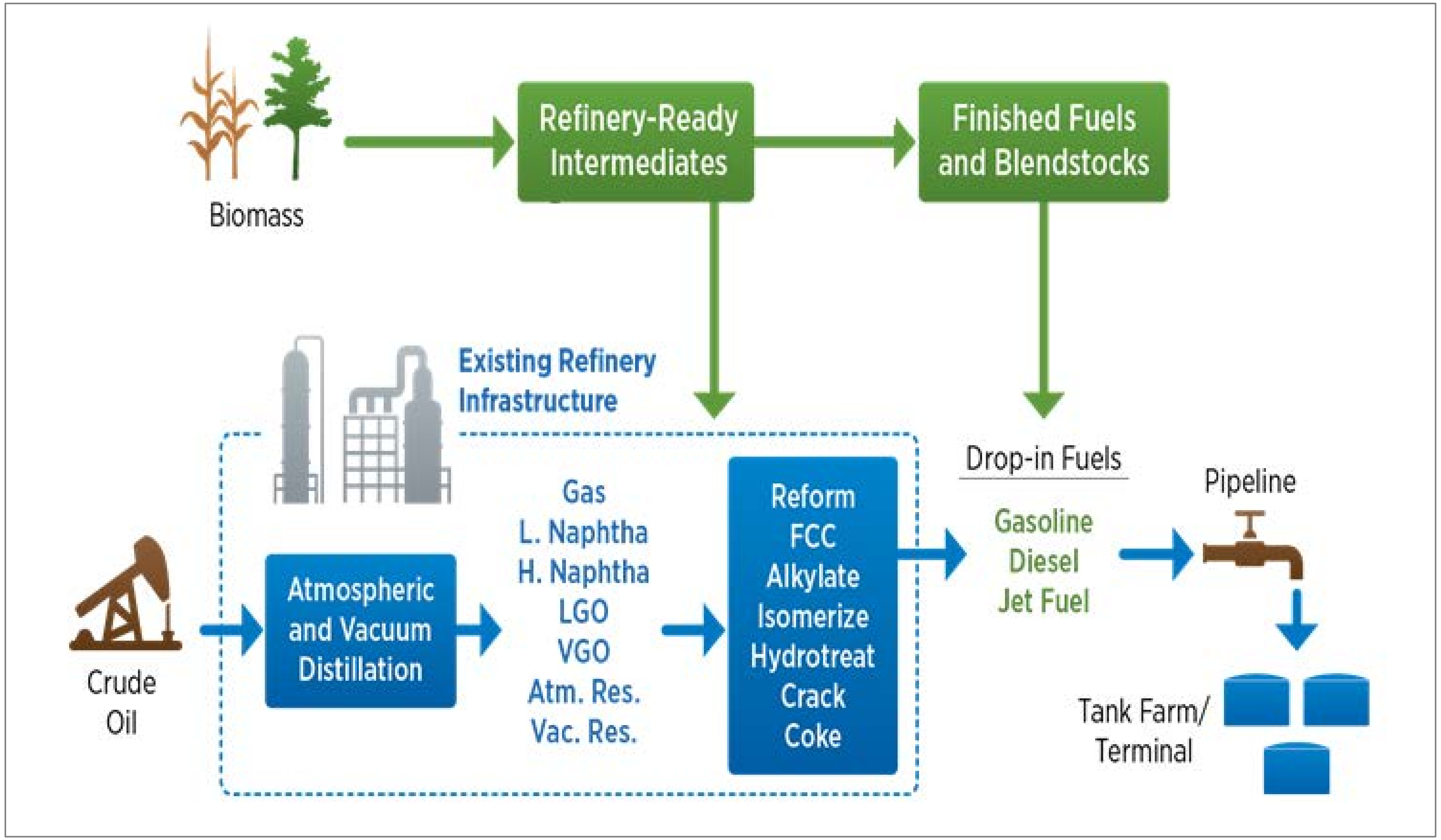
- N content is an issue if cracking is needed (cracking catalysts have acidic sites)
- The heteroatom content is outside of what refiners are comfortable, so they dilute

*TAN = Total acid number

Today two alternative feedstocks have ASTM D1655 approval for co-refining, yet little product is jet fuel

Co-refining

- Interesting to refiners
- Two feedstocks are approved at 5% renewable blend
    - Vegetable oils
    - Fischer-Tropsch liquids
- Little product from co-refining goes into the jet fraction



Upgrading biocrude from wet waste yields 20% in the jet range, more could be produced if heavies were cracked

Biocrude upgrading challenges

- Poisoning of catalyst (alkali, Fe…)
- Increasing jet fraction (cracking)
- Improving low temperature properties, diesel (isomerization)
- Processing of heavier oil (>350 °C)

Biocrude upgrading achievement

- Achieved 2000 h on untreated biocrude
- Biocrude from municipal sludge, food waste

Jet fuel properties met

- Viscosity (-40°C, -20°C)
- Density (15°C and 22°C)
- Flash point
- Heat of combustion (HOC)
- DCN

Properties to monitor

- Freeze-point (high n-alkane content)
- Stability (trace N content)

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Initial testing of HTL SAF from wet sludge is promising

University of Dayton HEAT Lab

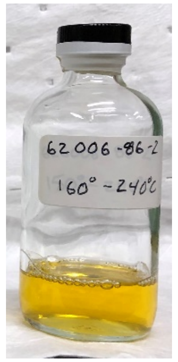
- Composed of well distributed carbon numbers and a range of hydrocarbon types
- Likely to provide adequate blend properties for Jet A
- Initial swell testing with fluorosilicone o-ring material suggests acceptable swelling behavior of neat HTL products
- Impact of nitrogen content on thermal stability and other items need to be investigated
- Prescreening of HTL fuels with blends of wet waste and wood or other biomass sources is needed

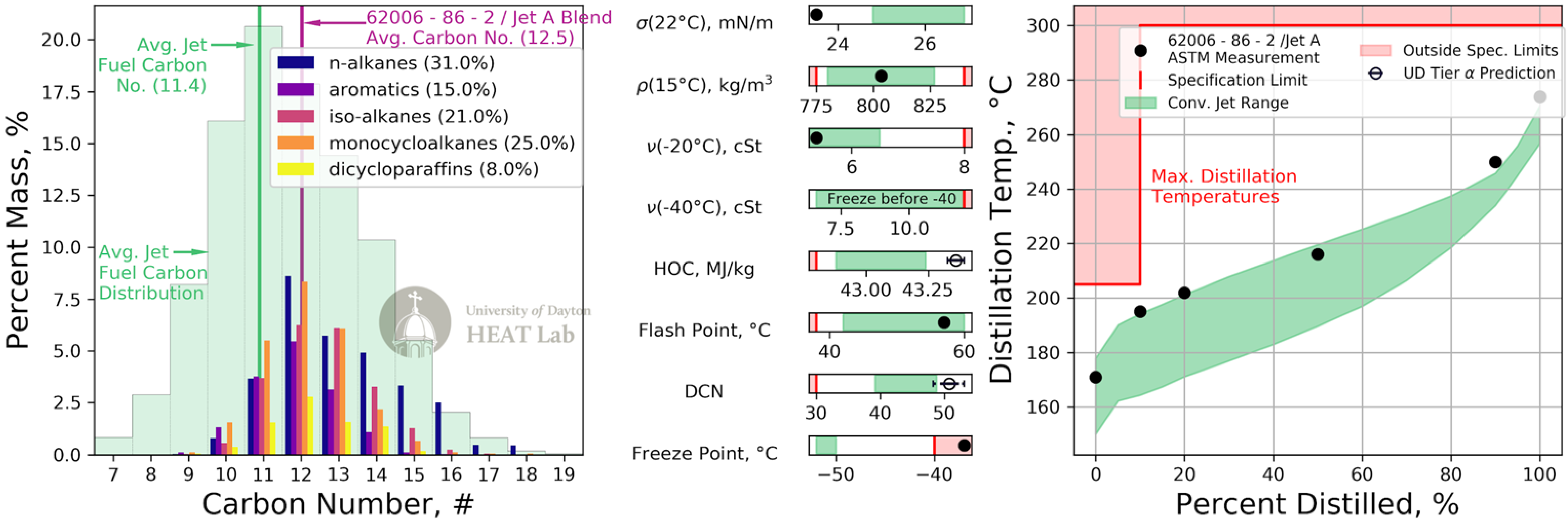
Josh Heyne, University of Dayton

Jet fuel fraction from sewage sludge/FOG is well distributed range of hydrocarbons

Biocrude	Hydrotreating
Sewage Sludge mixed with FOG*	Sulfided NiMo (single stage, 400 °C) Fractionated 160-240 °C

- Likely to provide adequate blend properties for Jet A
- Fuel thermal stability needs to be studied as N content, although low, is higher than Jet A
- N content in fuel 0.3-0.4% (recent)



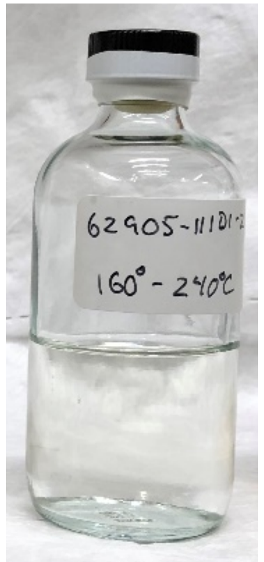


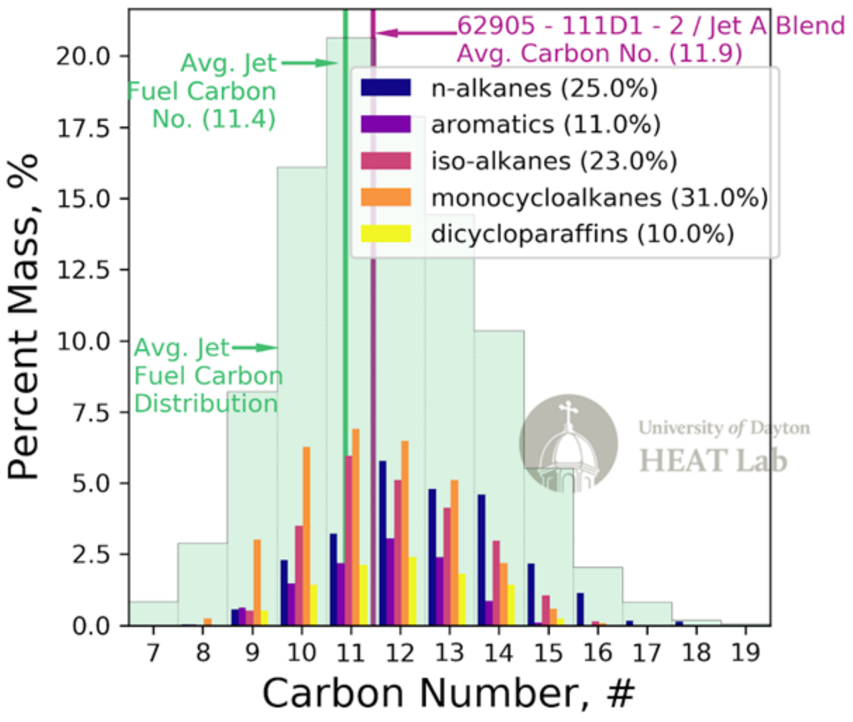
*FOG = fats, oils and greases

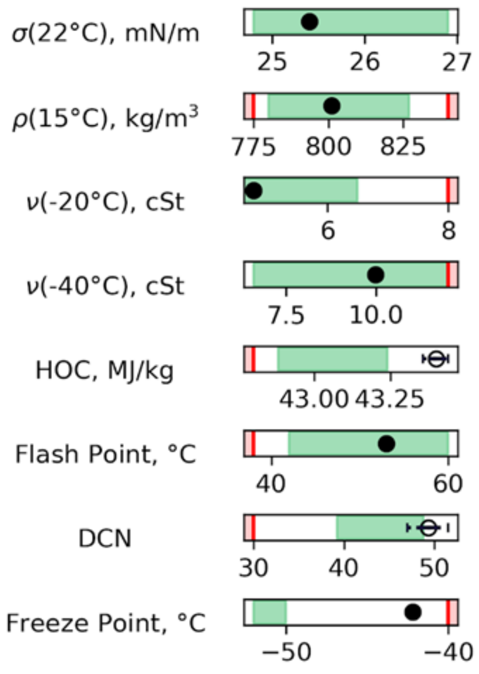
Light hydrotreatment of the jet fraction shifts aromatics to cycloalkanes

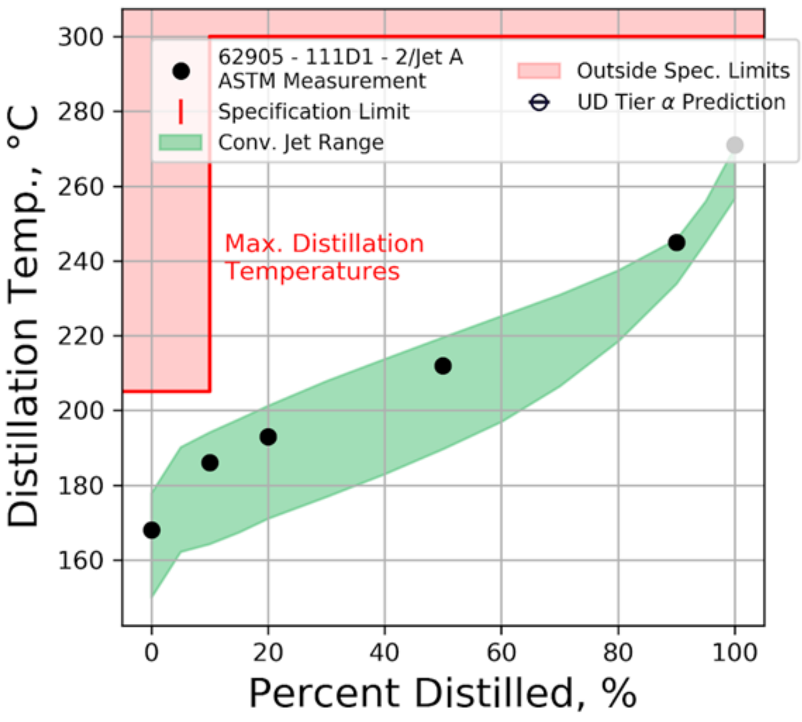
Biocrude	Hydrotreating
	Sulfided NiMo (single stage)
Sewage Sludge + FOG	Fractionated 160-240°C
	Light hydrotreatment using non-sulfided catalyst

- Operability properties are in range
- Initial swell testing with fluorosilicone o-ring material suggests acceptable swelling behavior of neat HTL products
- Hydrocarbon variance similar to Jet A







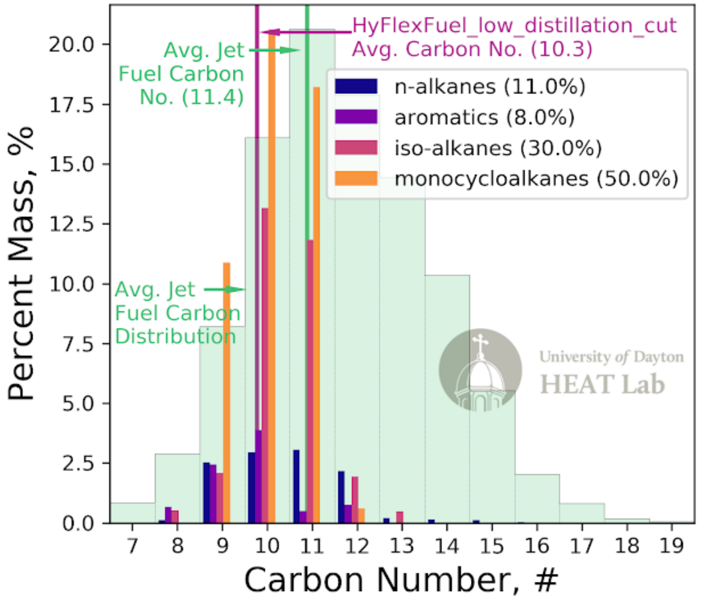


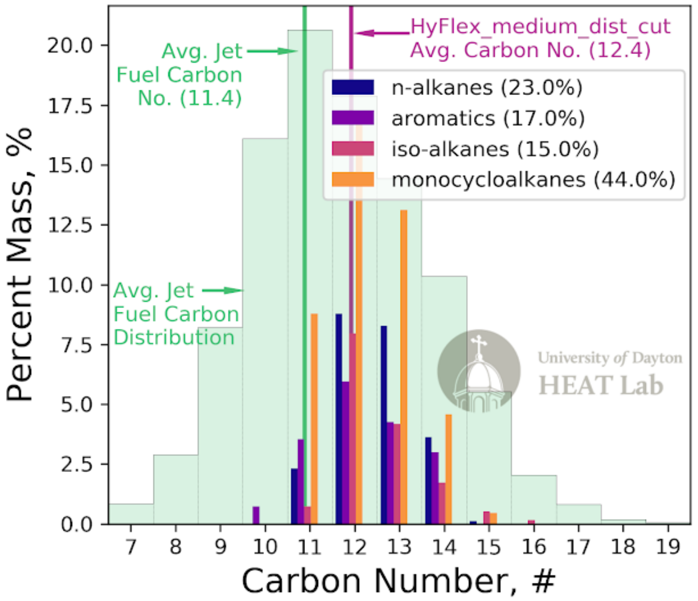
*FOG = fats, oils and greases

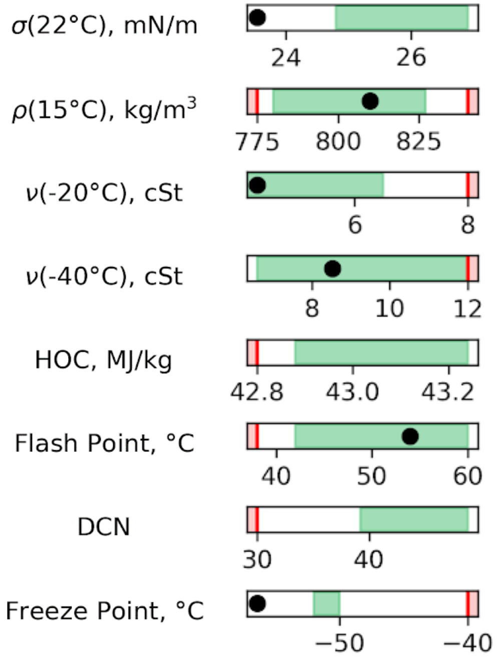
SAF samples from Aalborg (Europe) have similar properties to the U.S. samples

Biocrude	Hydrotreating
Sewage sludge	sulfided NiMo catalysts (4 stages with different catalysts), ranging from 260-400 °C Fractionated 160-240 °C

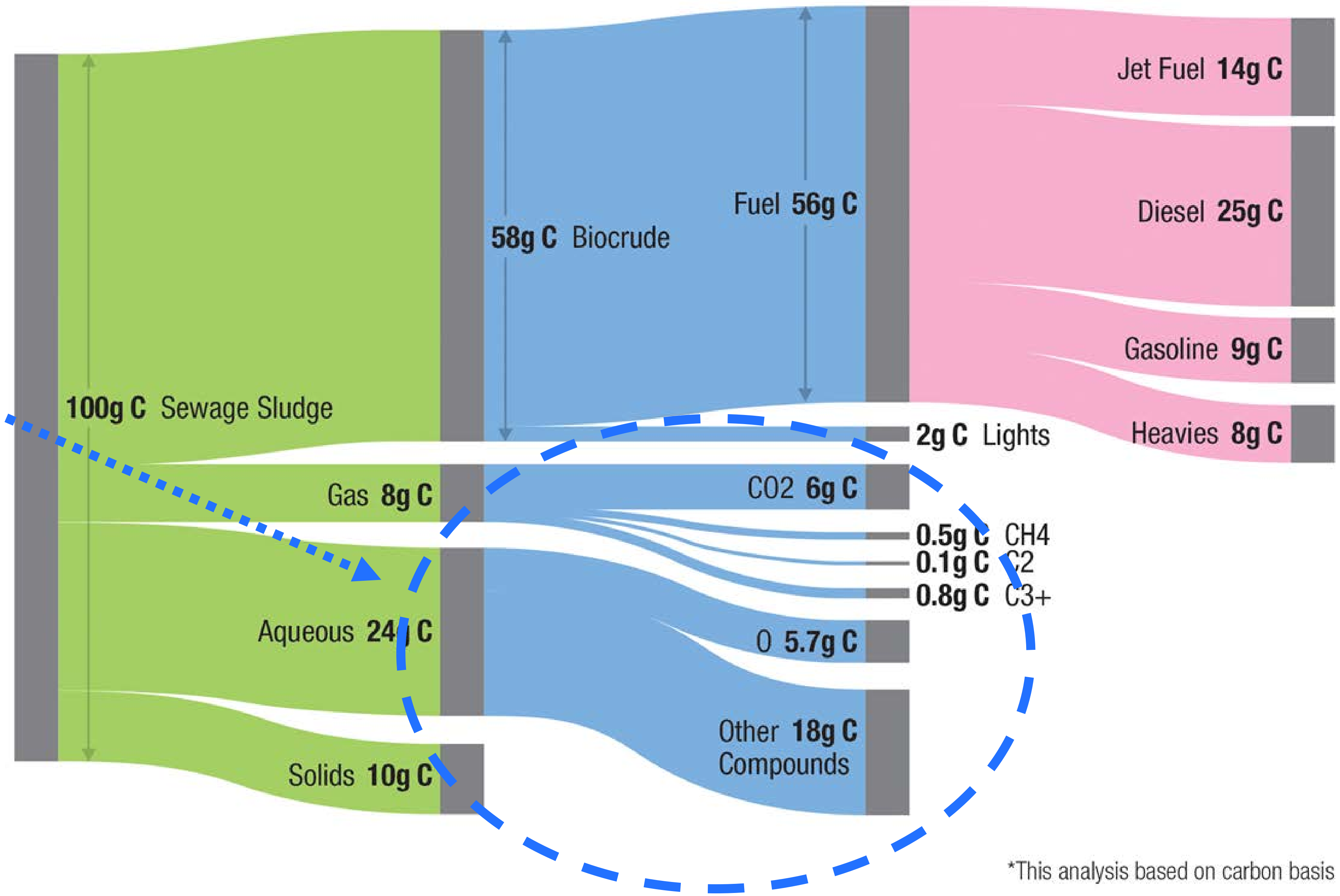
- Similar compositions to PNNL
- Aromatics and high cycloalkane content
- Relatively high n-alkane content
- Bulk properties look promising (Blend of the two GCxGC profiles used for property measurements)







Need to get value from each HTL fraction



Typical

- Gasses concentrated in CO_2
- Aqueous phase carbon
- Solids

* Highest level of uncertainty

Research opportunities on the solid stream include P recycling and biocrude recovery

Issue

- Solids can either be removed at process temperatures/pressure or after the reactor
- Ash stream is rich in phosphorous and may contain trapped biocrude
- Phosphorus recovery is a concern for the wastewater community
  - Land-applied biosolids can lead to nutrient run-off and ecological harm to surface waters

R&D opportunities

- Phosphorus recovery is an opportunity and benefit of HTL
- Opportunity to recover biocrude trapped on solids

Research opportunities on the aqueous phase can be to recover energy or produce H_2

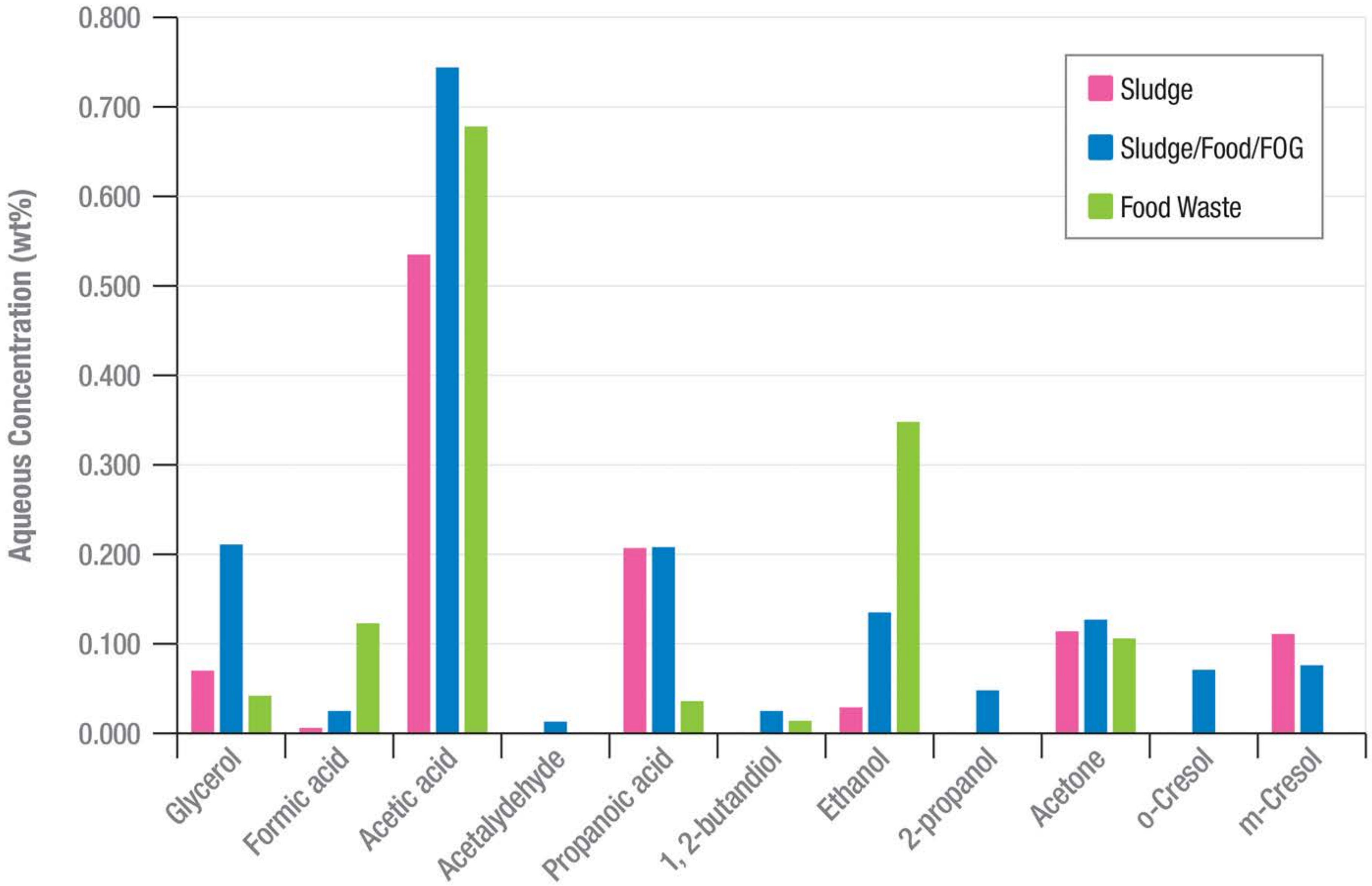
Issue

- One third of carbon is in aqueous phase
  (O-rich, low molecular weight compounds such as carboxylic acids, alcohols, and carbonyls)
- But the compounds are dilute, collective concentration of 2-3%
- Water resource recovery facility (WRRF)
  - interfere with UV sanitation,
  - elevated nitrogen levels can push a wastewater treatment facility beyond their discharge limits
  - or the components of the aqueous stream can interfere with the treatment facilities' other treatment processes.

While one third of the carbon ends up in the aqueous phase, the species are dilute

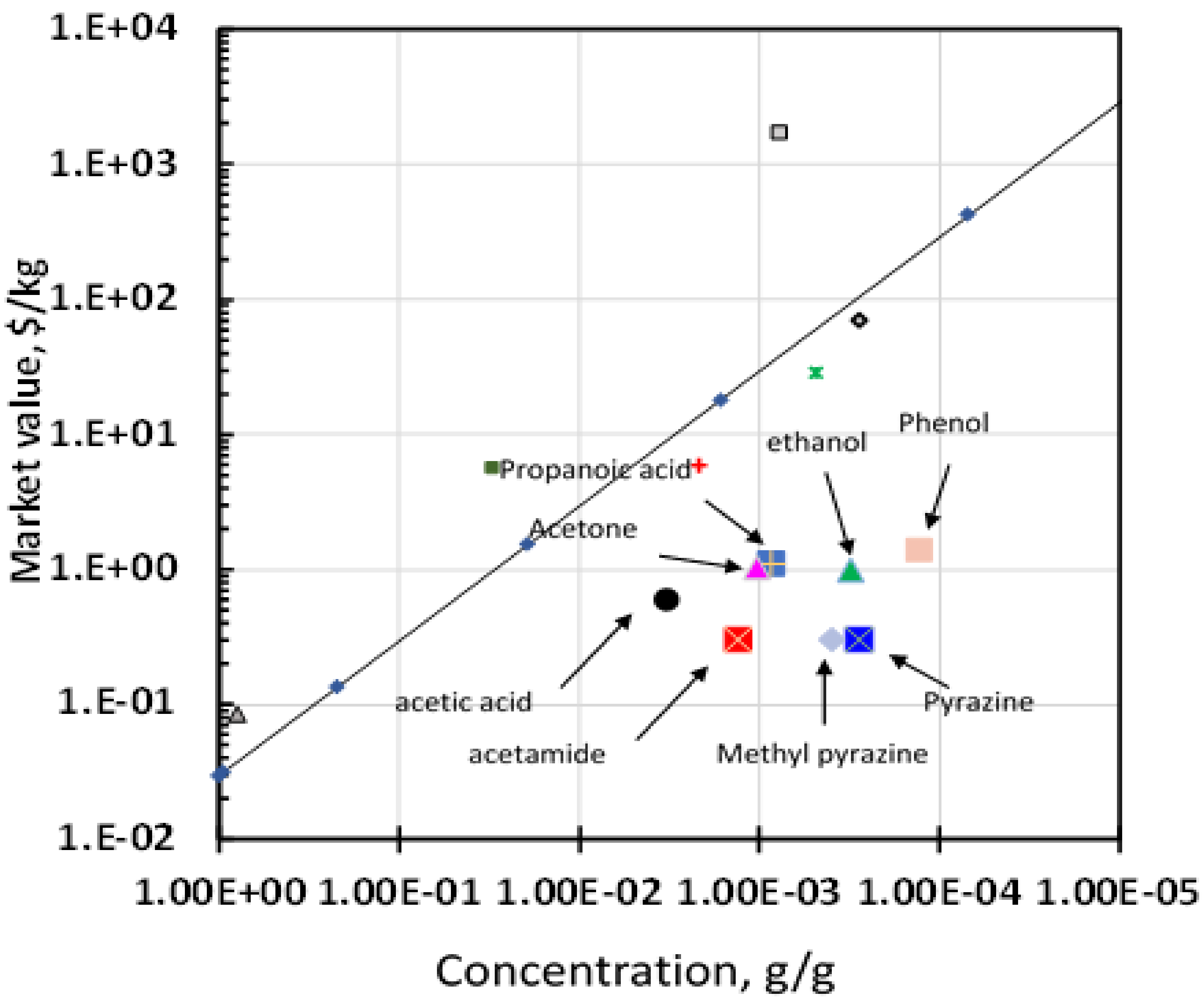
Carbon in the aqueous phase

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



There is not enough value to try to capture components

- C compound concentration is 2-3%
- Purification of individual chemicals is not cost effective (Sherwood plot)



R&D opportunities for the aqueous phase need to be low cost and reduce COD, N, and UV Vis absorbance

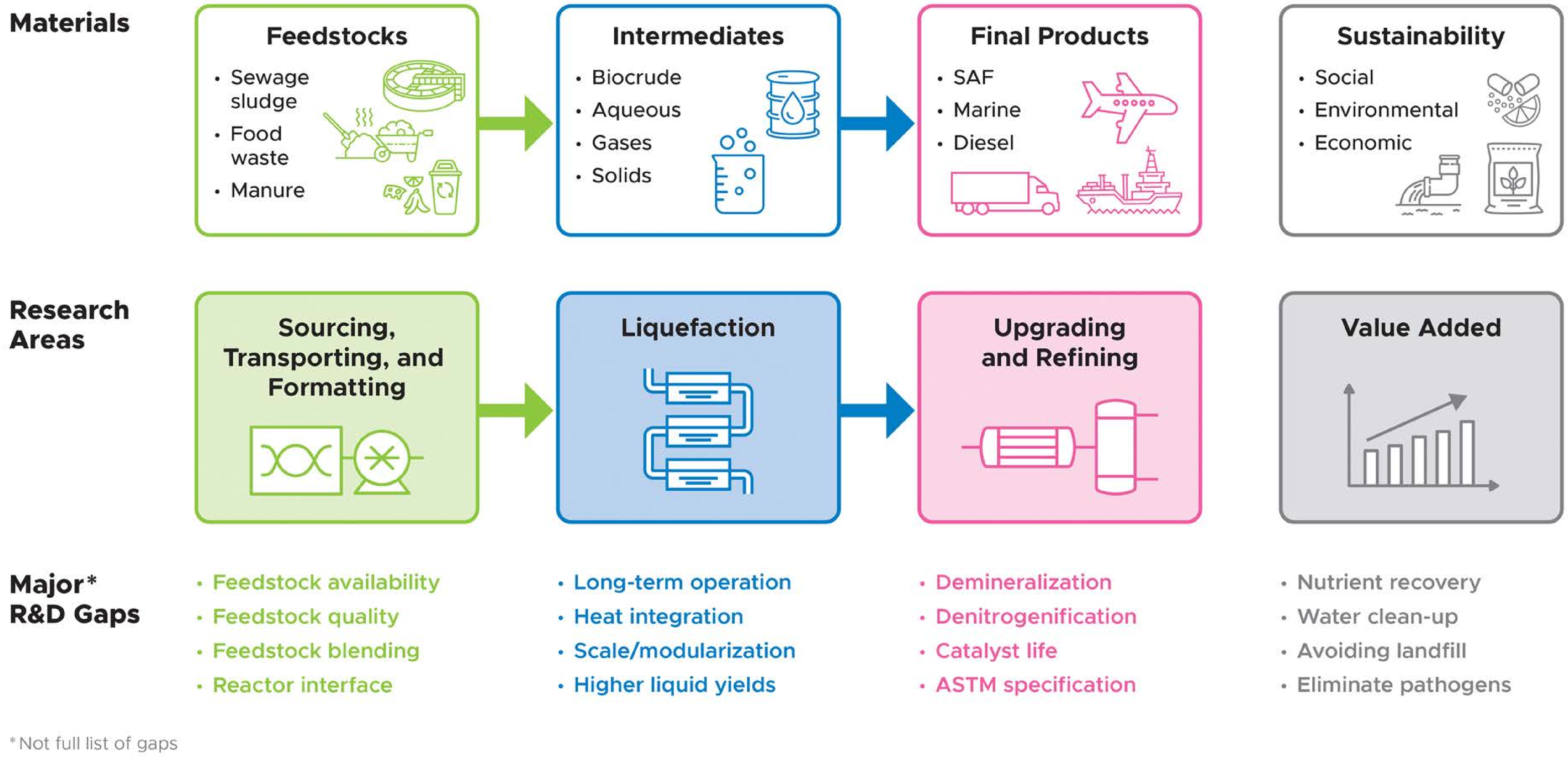
Needs

- low cost
- reduce the chemical oxygen demand (COD) and N content
- reduce the UV Vis absorbance

Options

- Separations
- Biological routes - clean up the stream and generate higher purity products - challenge, inhibitors
- Partial oxidation combined with biological or catalytic conversion
- Thermochemical routes (wet gasification or H_2 production) – challenge, catalyst life (S poisoning)

In conclusion, we have identified critical research opportunities for SAF to jet fuel



* Not full list of gaps

Examples of pilot and demonstrations

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A partial overview of the players in the field include demonstrations and piloting

metrovancouver
SERVICES AND SOLUTIONS FOR A LIVABLE REGION

Reliance
Industries Limited

Licella™
HOLDINGS

steeper
ENERGY

J.J.Richards
& Sons Pty Ltd

Genifuel

SouthernOil

HYPOWERS: Hydrothermal
Processing of Wastewater Solids

MetroVancouver points out the need for water management, understanding opportunity cost

Objectives/questions:

- Can HTL perform better than AD?
- TEA considerations for full scale?

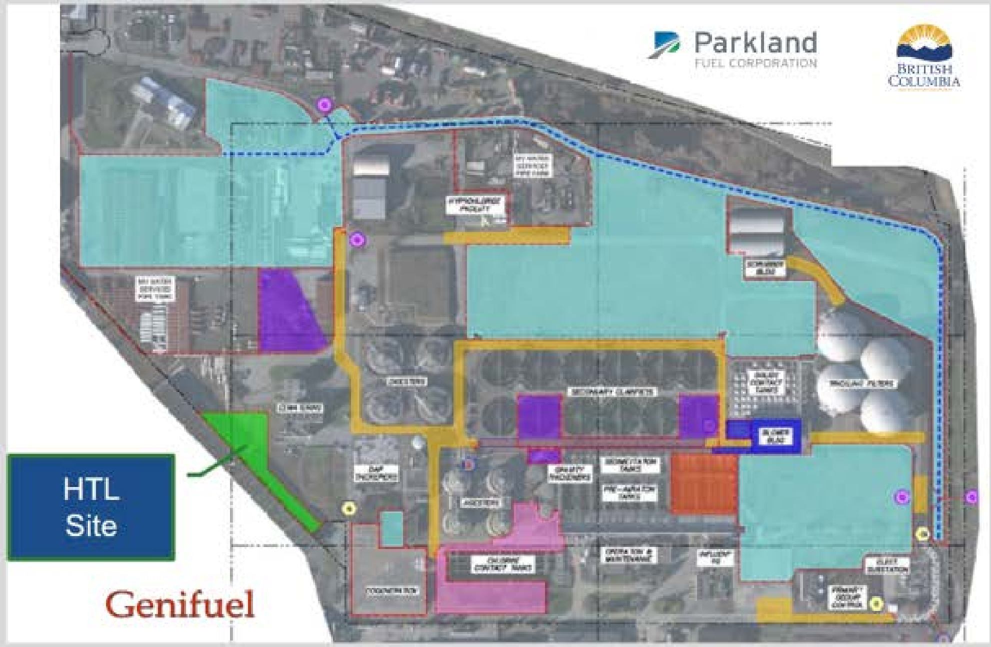
Science needs (Univ. British Columbia)

- Impact of HTL aqueous returned to i) headworks, ii) AD, iii) other?
- Required HTL aqueous pretreatment for i) NH_4^+, ii) phenols, iii) other?
- Required management of HTL precipitate
- Efficient phosphorus recovery or disposal?
- Fate of compounds of environmental concern (e.g. PFAS, other)?

metrovancouver
SERVICES AND SOLUTIONS FOR A LIVABLE REGION

HTL Demonstration at Annacis Facility

- 10 m^3/d Facility
- ~2% of Annacis biomass
- Status:
  - ✓ FEED
  - ➢ Fabrication
  - ➢ Commissioning 2023
- Funding by MV and
  - Parkland; Prov. BC



Paul Kadota

Steeper Energy Norway (wood) and Calgary (sewage sludge) point to H_2 use and links to refining

Questions to be answered:

- Attributes and direct markets for Hydrofaction® Oil
- In situ renewable H_2 for upgrading
- Integration of bio-crude into refineries
- Chemical-linkers that improve compatibility of Hydrofaction® Oil with existing fuels
- Economic pathways to 100% renewable: gasoline, diesel, jet-fuel, marine fuels, and fine chemicals.

Perry Toms

Northern and Southern Oil Refineries (Australia), note capital and operating cost both need to come down

"It is not the return on my investment that I am concerned about; it's the return of my investment" - Will Rogers

- Completed detailed design of a 1t/h HTL process ($7M CAPEX)
- Financial model 16ML/annum, $28M CAPEX
- Feedstock tipping fee $160 – 285/dry tonne

SouthernOil

J.J.Richards & Sons Pty Ltd

David Lewis

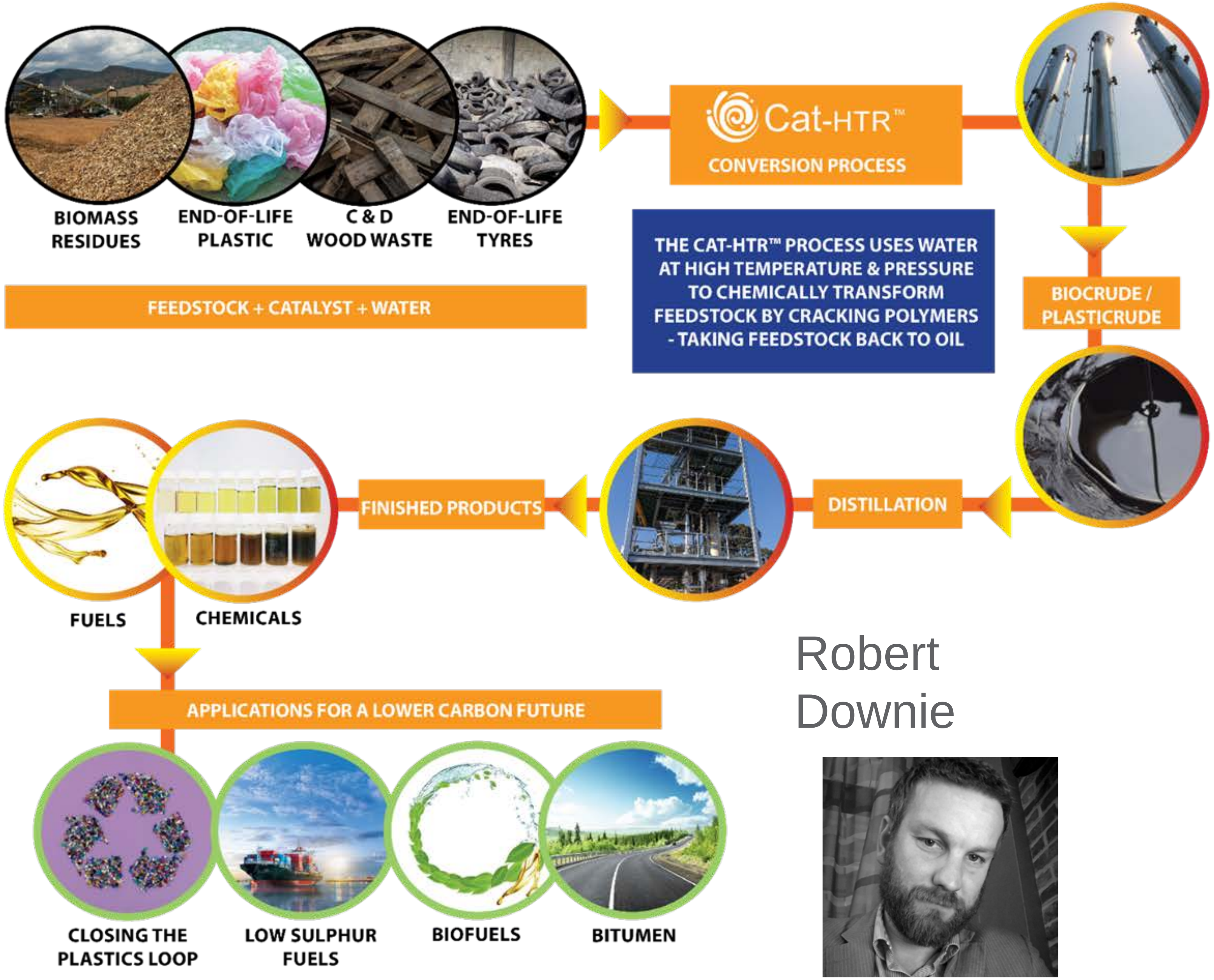
Licella catalytic HTL (Australia, UK and N. America) noted the importance of collaboration

Current focus

- End-of-Life Plastics in the UK with Mura
- Post consumer biomass in North America with Arbios.

Importance of collaboration

- access to large amounts of low-value feedstock without creating bidding wars
- Technology development companies and operational companies require different mindsets.
- Allows for synergies as each company can focus on their core competencies.

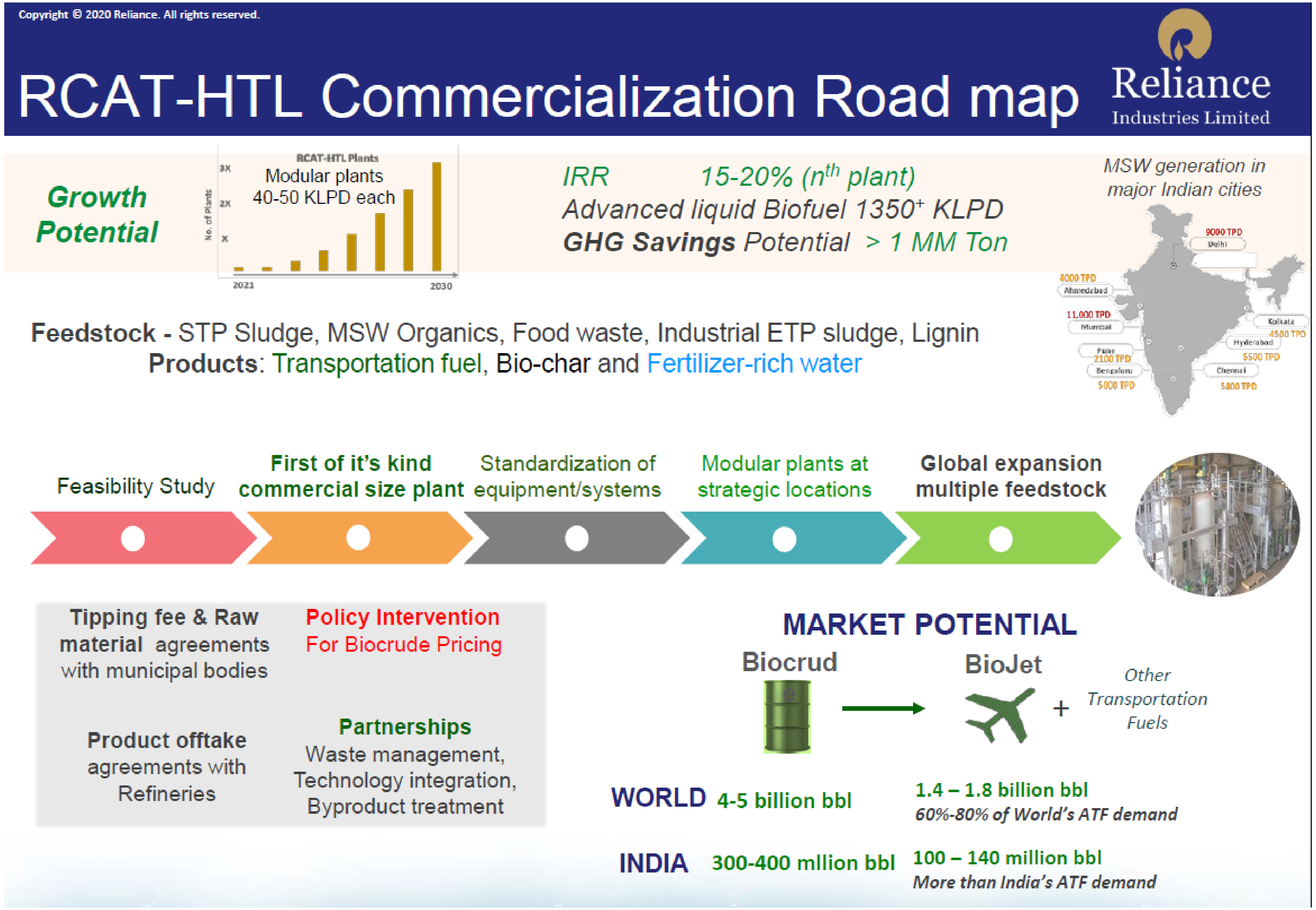


Robert Downie

Reliance (India) point at the need to demonstrate robustness at scale to reduce risk

Next Steps

- Technology and Engineering robustness *at scale*
- Roadmap for Economical viability
- Investor confidence in building “First of it’s kind” precommercial plant



Ramesh Bhujade

Resource: https://ec.europa.eu/energy/sites/ener/files/documents/24._ramesh_bhujade_rileu_indiab2b-_rcat-htl02mar2020.pdf

RE-CORD (Politecnico di Torino) notes the need for co-liquefaction as well as co-refing

Co-Liquefaction

- Enhanced feedstock availability

Water management

- Recycle, Cat HTG, AD, H_2 production

Co-refining

- Stabilization + HDO + co-refining

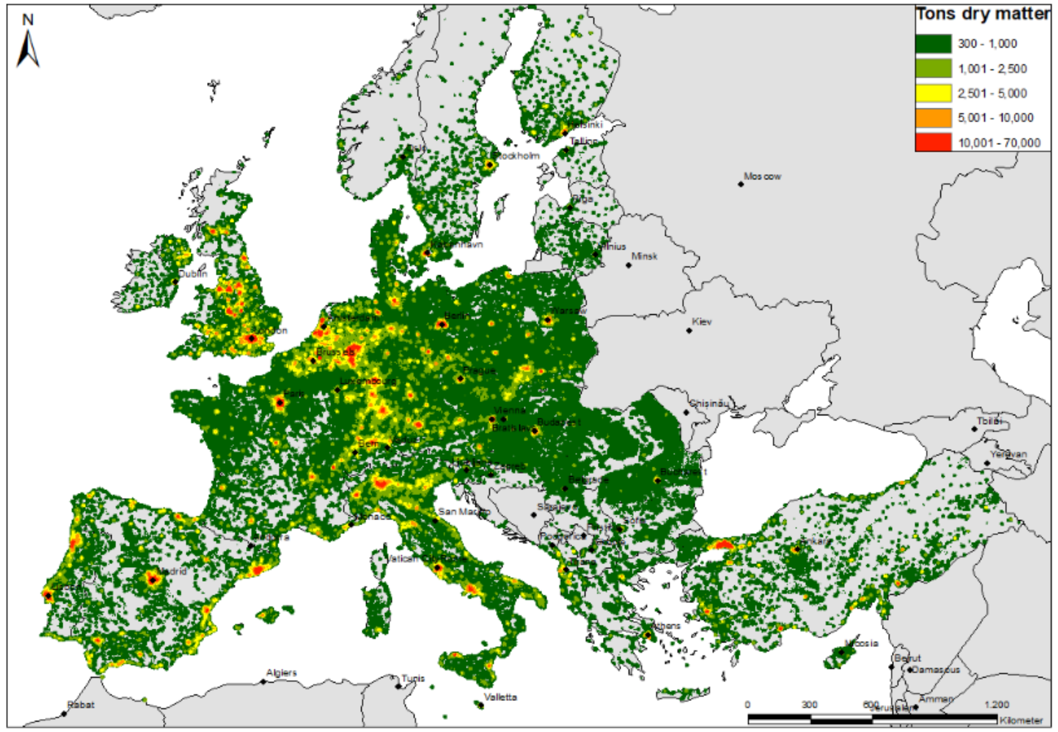
Biocrude sCO_2 fractionation

- extraction yields above 50%, low water and metal content, reduced acidity, moderate oxygen content reduction

David Chiaramonti

HyFlexFuel note, among other things the need for understanding feedstock supply chain and valorization

- Spatial analysis of residue and waste availability in Europe
- Feedstock density maps
- Energetic valorization of aqueous phase
- Nutrient recovery (phosphates)



HTL pilot reactor at Aarhus University

Valentin Batteiger

PNNL notes the importance of blends (urban and rural), as well as increasing catalyst life in upgrading

Address capital

- 50% of capital cost is in heat exchangers—big opportunity

Feedstock

- blends based on different regions

Co-refining

- refiners question using feed with the N-content of biocrude

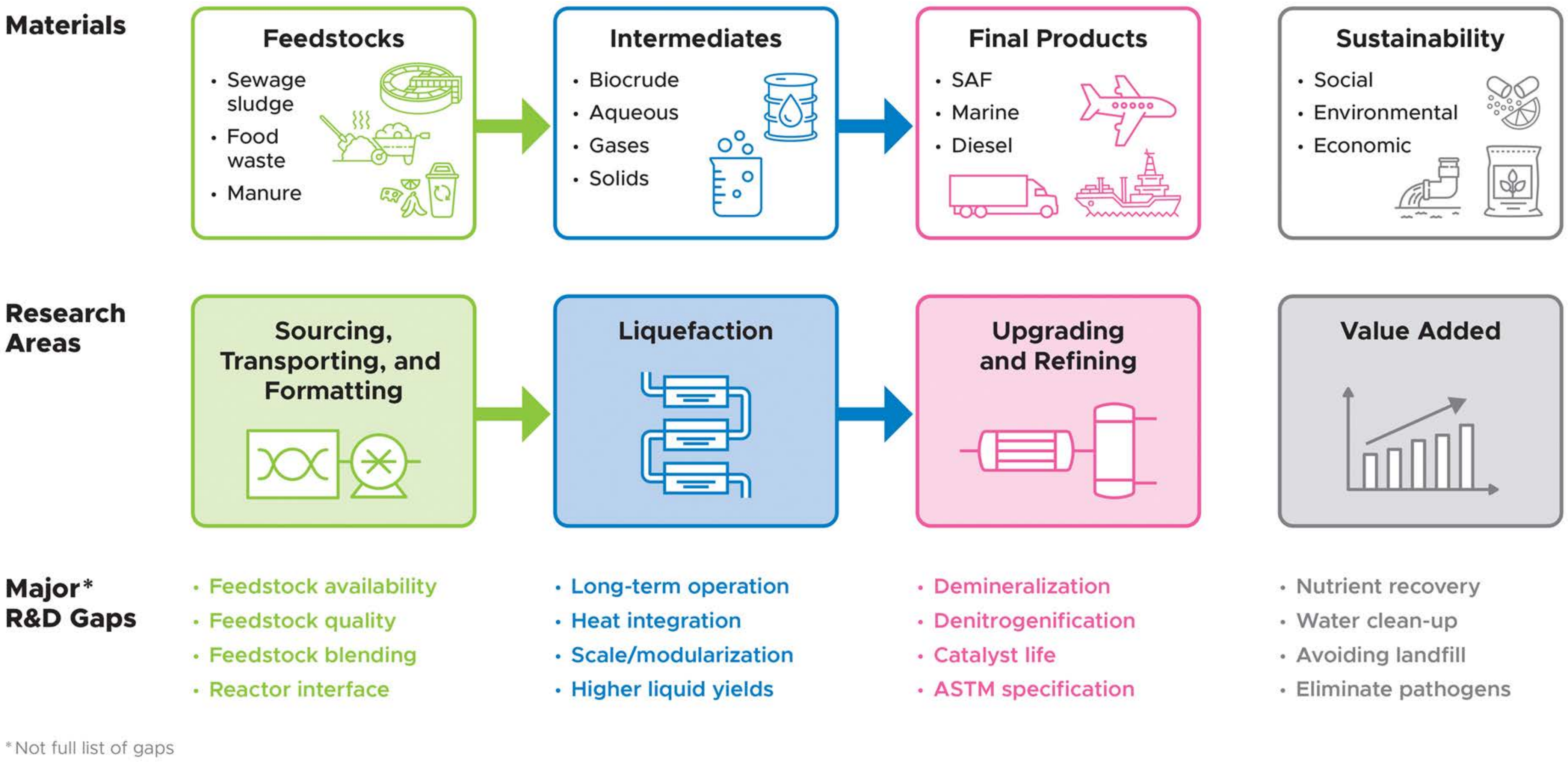
Processing

- Improved HTL efficiency and hydrotreater catalyst life
- greatly improved catalyst life (untreated biocrude)

Current state on upgrading

- Major strides in biocrude upgrading
- Hydrothermal gasification remains a challenge

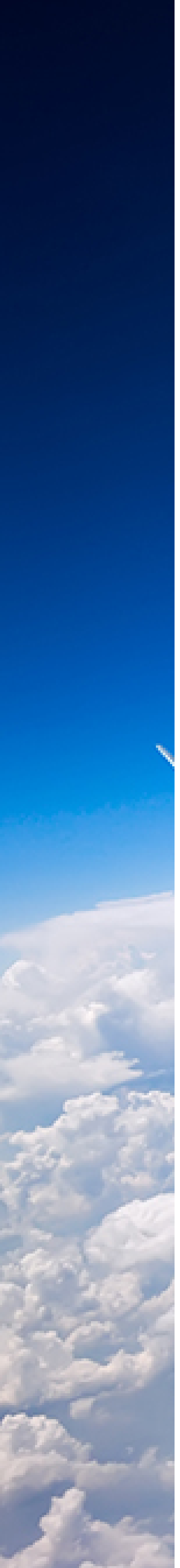
As the next step, we are preparing a roadmap identifying key research opportunities and needs



* Not full list of gaps

Key Results of HTL for Sustainable Aviation Fuels Workshop

- Need to analyze feedstock pre-processing cost to produce uniform quality bio-crude from mixed feedstocks. Feedstock consistency (temporal, seasonal) needs to be analyzed.
- Small decentralized plants could produce bio-crude moved via rail, pipeline, or trucks to processing plant for upgrading and hydro-treatment to finished fuels.
- Aqueous product management, ash removal, and solids removal are key issues. Ability to recover chemicals and dissolved metals from aqueous phase could add to financial viability of project.
- Nitrogen in jet fuel is a key issue. Sewage sludge and waste-water treatment effluent might have high N levels. Interaction between nitrogen and sulfur needs to be better understood.
- Hydrogen requirement for HTL processes needs to be analyzed. Variability of cost and greenhouse gas emissions depends on source of hydrogen.
- Industry needs to produce bio-crude with required specifications on a reliable basis in order to facilitate ASTM approval.
- ASTM Marine diesel could be produced with minimal upgrading of HTL bio-crude. Integration of bio-jet, renewable diesel, and naptha/gasoline in single facility need to be explored.



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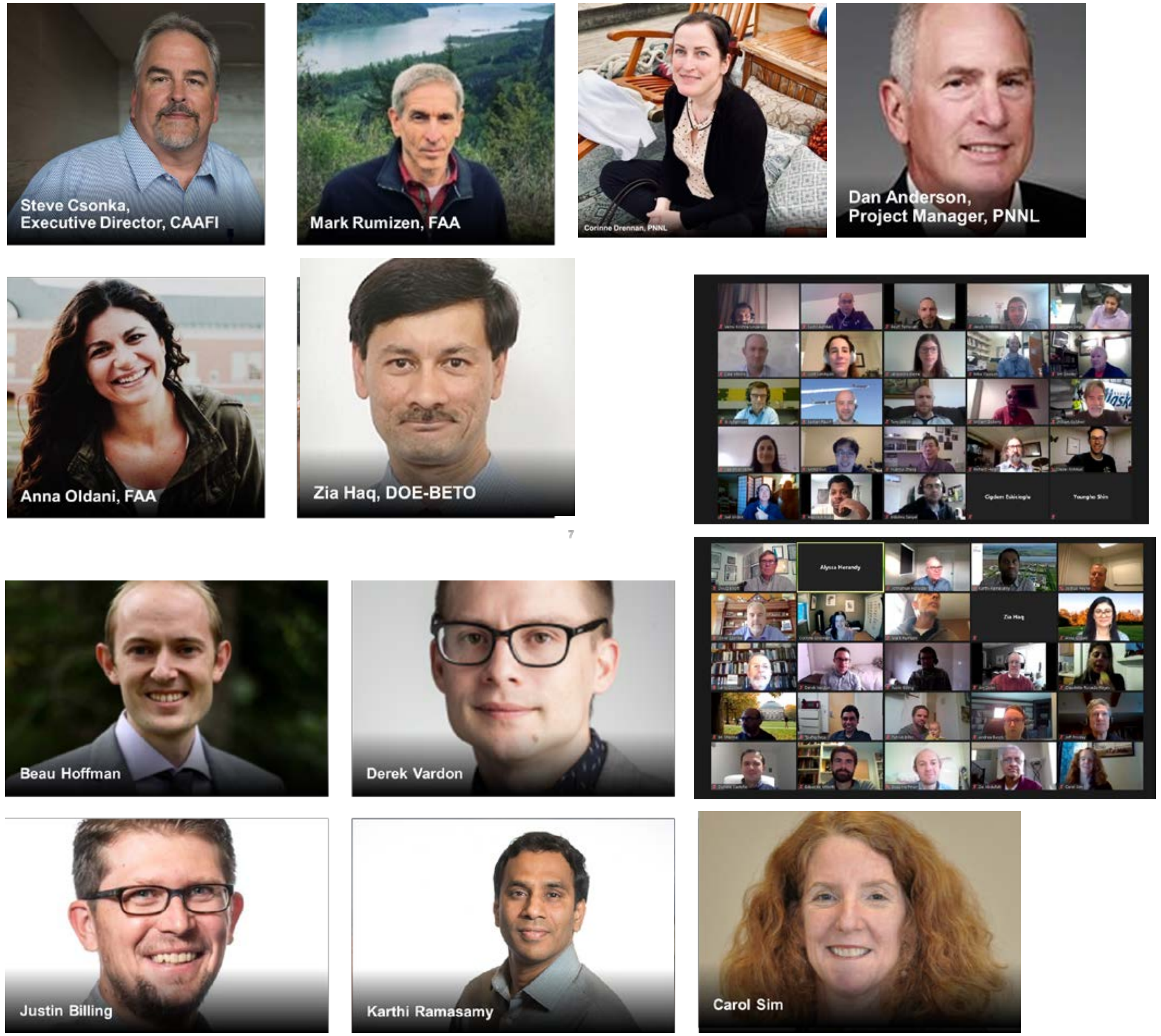
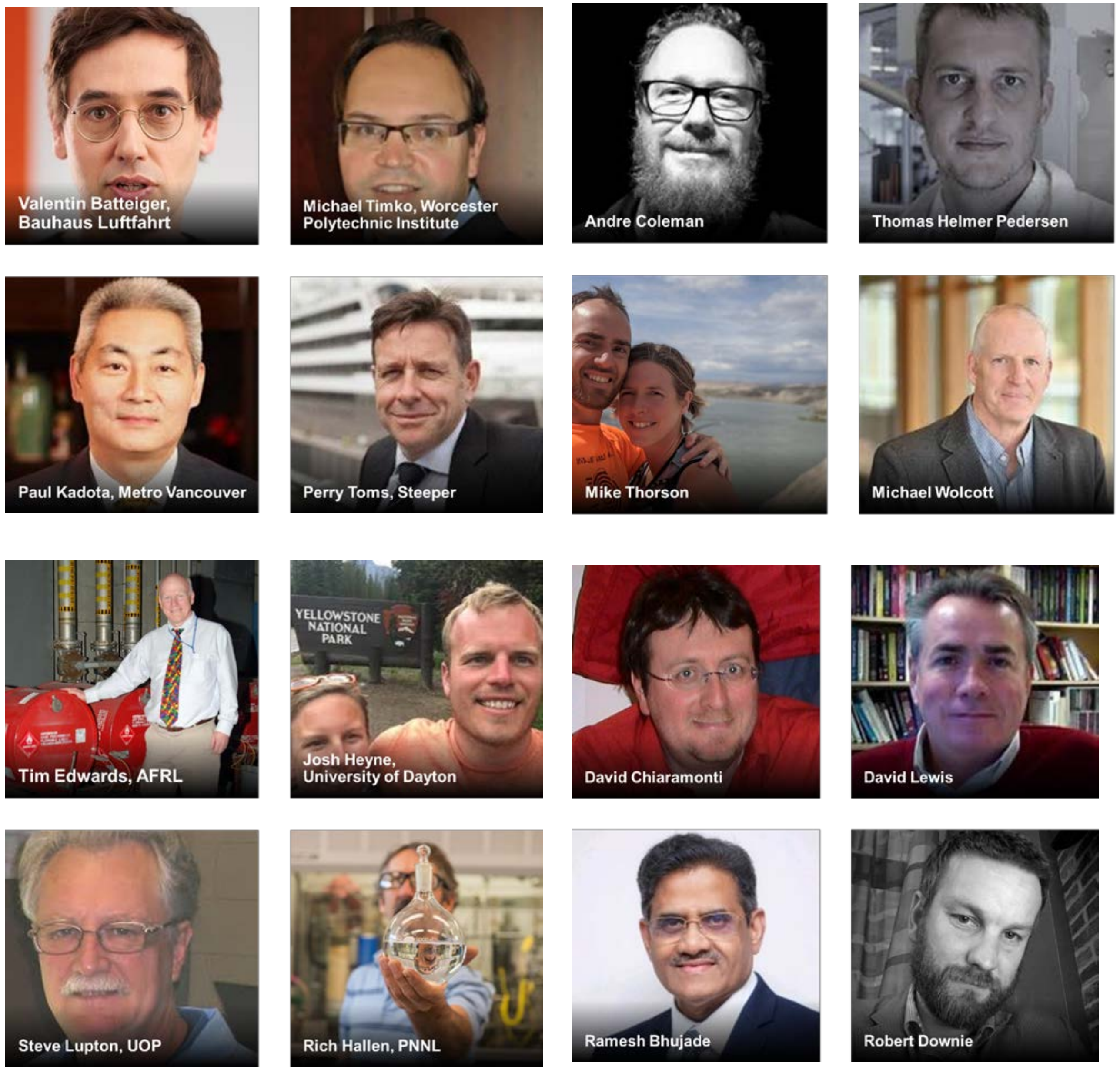
Questions

We thank those who organized and participated in the workshop





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Thank you