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Feedstock blending as a strategy for hydrothermal liquefaction: lipid-rich scum from primary sedimentation and wastewater sludge

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Lipid-Rich Scum and Wastewater Sludge

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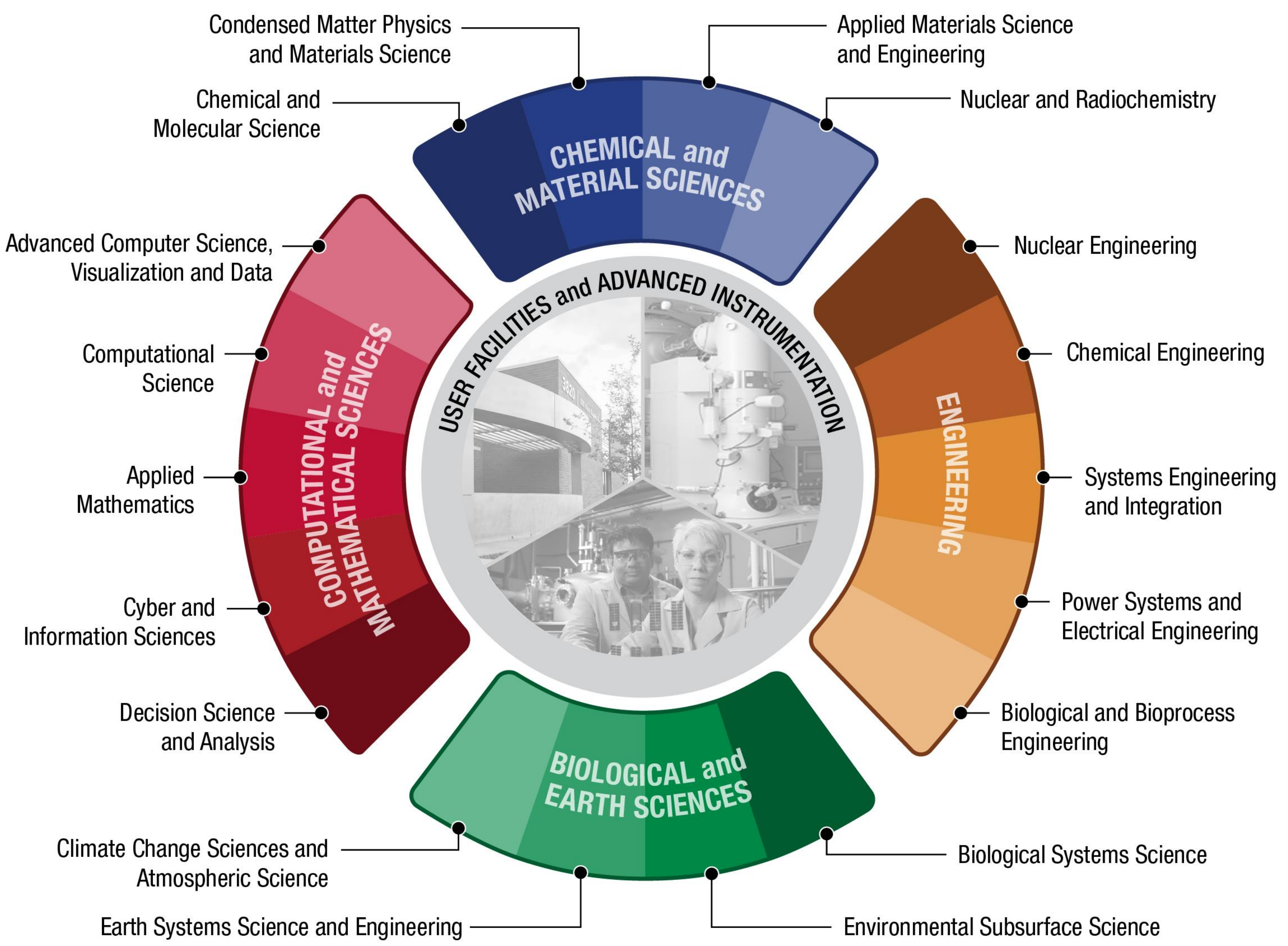
PNNL is 1 of 17 DOE **national laboratories**

A powerful combination of capabilities



Bioproducts, Sciences & Engineering Laboratory (BSEL)

A research partnership with WSU

- Science and engineering of converting biomass—agricultural and forest residues, industrial waste streams—into novel energy sources including jet fuel
- Developing technologies to transform low-value biomass into value-added chemicals for products from plastics to pharmaceuticals
- Built in partnership with Washington State University on nearby WSU Tri-Cities campus to allow collaborative research
- High bay permits scale-up of biomass conversion processes

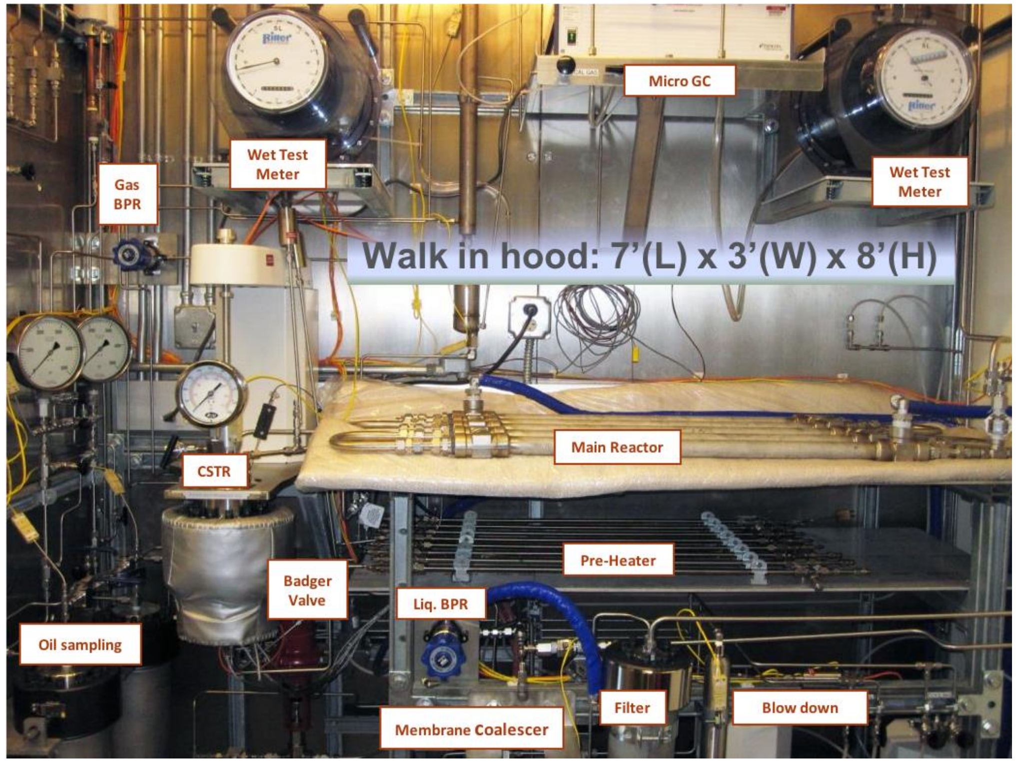
What is HTL and why does it matter?

Hydrothermal liquefaction (HTL) is…

the thermochemical conversion of biomass in a hot, pressurized water environment for sufficient time to break down the solid biopolymer structures to predominantly liquid components

It matters because…

- HTL is a conceptually simple (i.e., heated pipe), scalable, and robust continuous process that can accept a diverse range of wet waste feedstocks (no drying!)
- HTL results in high carbon yields to liquid hydrocarbons (up to 60%)
- HTL produces a gravity-separable biocrude with low oxygen content (5–15 %) that can be upgraded in a single stage hydrotreater



Bench-scale continuous HTL system

HTL Conditions
Temp: 330-350°C
Pressure: 2900 psig
t_{res}: 10-30 min

Hydrotreating Conditions
Temp: 400°C
Pressure: 1500 psig H_2
Sulfided NiMo on Al

Wet biomass material (sludge, manure, algae) → Stable biocrude oil (up to 60% C-yield) → Fuel Blendstocks (95%+ C-yield)

By the numbers

Since 2010, PNNL has performed 137 bench-scale continuous HTL tests, (typical test: 12-15 h)

- 63 lignocellulosic tests
- 53 algae tests
- 21 wet waste tests

Since 2017, PNNL has performed 5 engineering-scale tests in the MHTLS (photo), the longest test lasting 85 hours

Modular Hydrothermal Liquefaction System (MHTLS) at PNNL

Why process sewage sludge?

It Works!

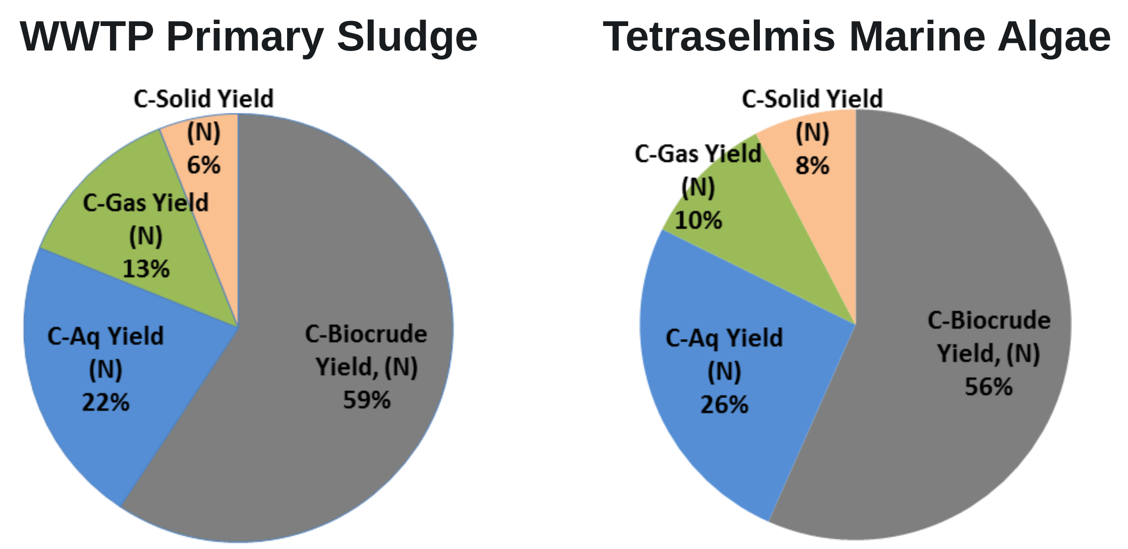
- Sludge HTL biocrude yield and quality comparable to microalgae
- Catalytic upgrading results in a high yield to distillate and good cetane

It's Cheap!

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

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



Normalized carbon yield on a dry, ash-free basis

←Design Case PNNL-27186

Water Environ. Res. **90**, 329 (2018) →

What are the benefits of blended feedstocks and co-liquefaction?

- We have some ideas, but we’ve only just begun to test the possibilities!

1. Expand the resource base to **increase the scale** of distributed HTL conversion units and thereby reduce the cost of producing biocrude.

A bigger piece of the pie!

Skaggs et al. (2018)
doi: 10.1016/j.rser.2017.09.107

Renewable and Sustainable Energy Reviews 82 (2018) 2640–2651

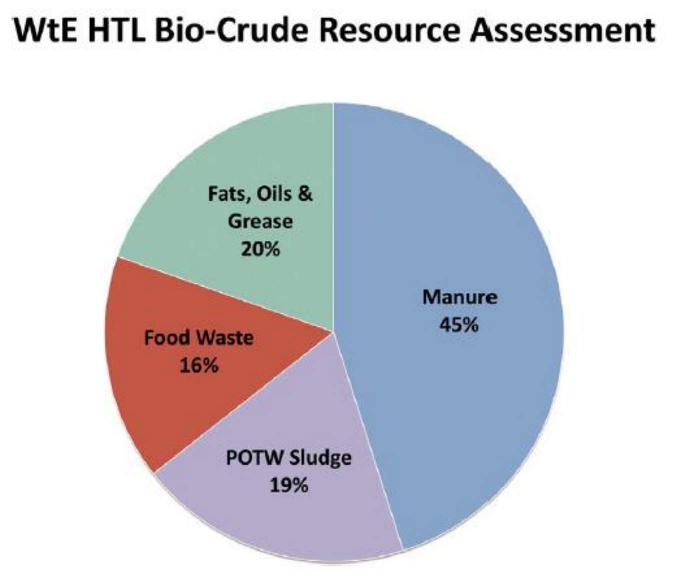
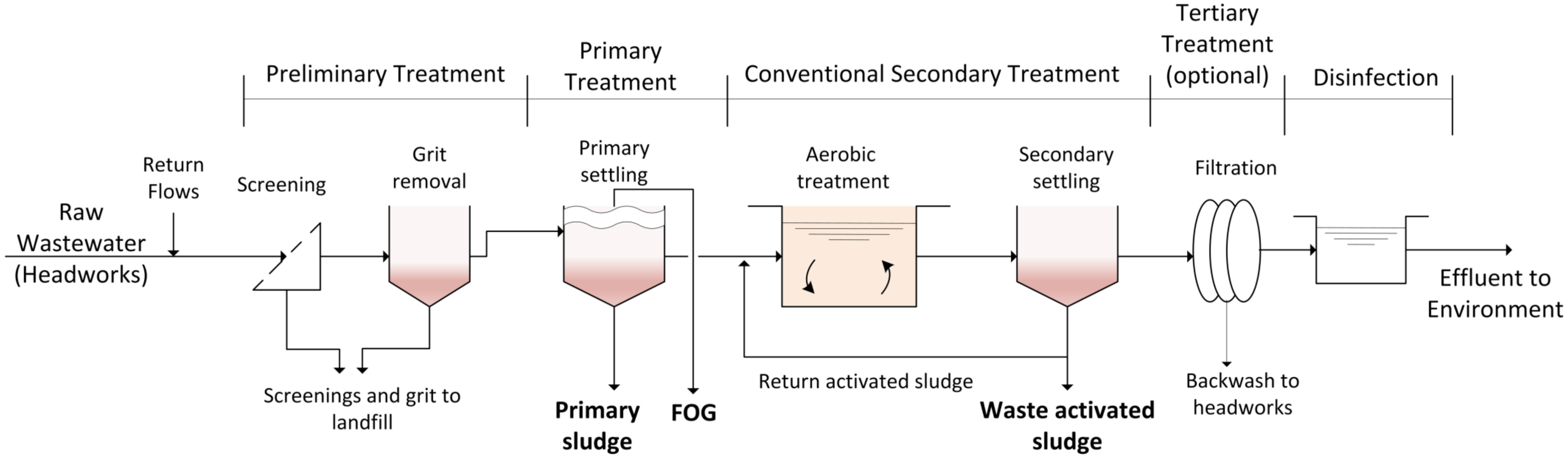


Fig. 6. Total fractions of unconstrained resource availability for major waste feedstocks groups converted to bio-crude oil.

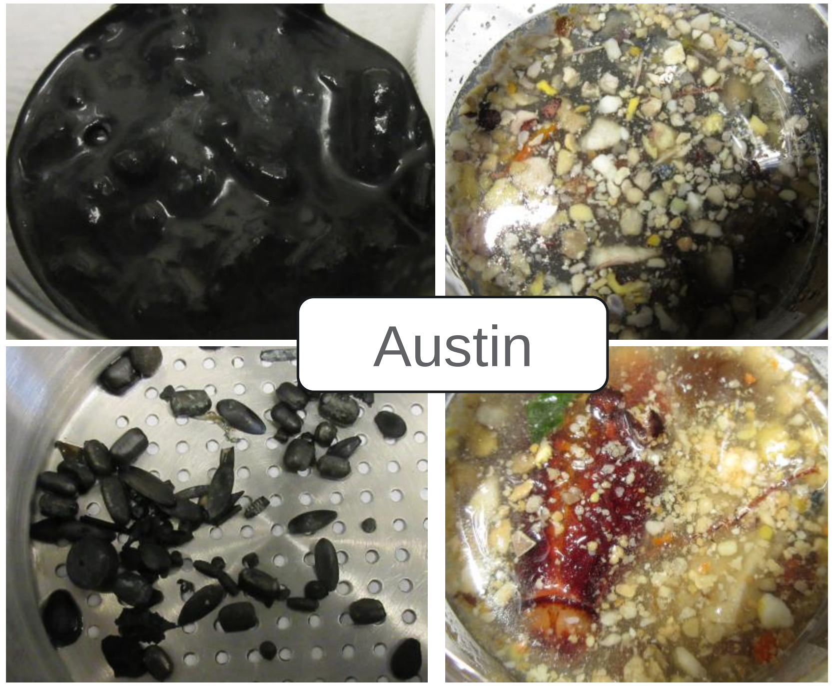
2. Complementary physical and biochemical properties may lead to synergistic chemical reactions increasing biocrude yield and quality.
3. Blends may also aid dewatering, enable onsite storage, or improve slurry pumpability.

Floatable scum is a logical blending choice with wastewater sludge

Typical Wastewater Treatment Process



Samples of Floatable Scum Received at PNNL



How did you choose a blend ratio for floatable scum?

The basis for the blend ratio has three components

1. Resource availability
2. "Signal-to-noise"
3. Processability

Selected target: 20 wt% (daf)

Resource Availability

While scum may only be present at 0.5 to 1.0 wt% of the mass of sludge in a particular WWTP, the average ratio of underutilized fats, oils, and greases (FOG) to sludge is around 20% on a dry basis (see below)

Signal-to-Noise Ratio

We wanted to test a blend ratio that would have a discernable effect (signal)

Processability

The proposed blend was first tested at the 400-mL scale in a blender to assess slurry properties

Table 2-2. Wet Resource Comparison – Annual Utilization and Excess

Wet Resources	Annual Beneficial Utilization (Current) Estimated Resource Availability (MM Dry Tons)	Annual Beneficial Utilization (Current) Inherent Energy Content (Trillion Btu)	Annual Beneficial Utilization (Current) Fuel Equivalent (MM GGE)[2]	Annual Potential Excess[1] Estimated Resource Availability (MM Dry Tons)	Annual Potential Excess[1] Inherent Energy Content (Trillion Btu)	Annual Potential Excess[1] Fuel Equivalent (MM GGE)[2]
Wastewater Residuals	7.12	107.6	927.0	7.70	130.0	1,119.6
Animal Waste	15.00	200.2	1,724.3	26.00	346.9	2,988.7
Food Waste	1.30	27.0	232.9	14.00	291.2	2,508.4
Fats, Oils, and Greases	4.10	147.4	1,269.3	1.95	66.9	576.5
Total	**27.52**	**482.2**	**4,153.5**	**49.65**	**835.0**	**7,193.2**

[1] Unused excess in this definition includes landfilled biosolids and other wet resources.

[2] 116,090 Btu/gal. This does not account for conversion efficiency.

$$\frac{1.95}{1.95 + 7.70} = 20.2\%$$

Source: "Biofuels and Bioproducts from Wet and Gaseous Waste Streams: Challenges and Opportunities." Bioenergy Technologies Office (January 2017)

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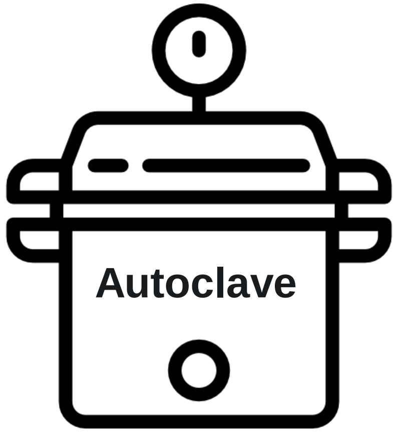
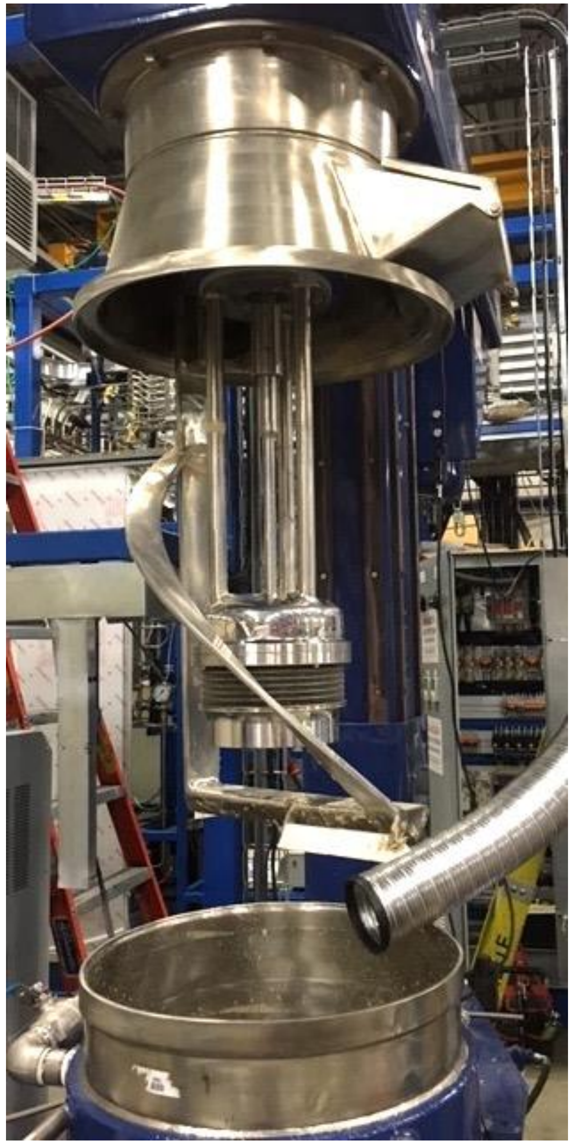
How the sausage is made: feedstock sourcing and immersion milling in the Hockmeyer

Wastewater Sludge



Floatable Scum



Hockmeyer HCPS-2.5 Immersion Mill, 15 HP mill, 1.5 HP sweep arm, 32 gal (120 L) batch volume

Hockmeyer Equipment Corporation, Harrison, NJ
www.hockmeyer.com

How does the prepared slurry feed compare to the constituent parts?

	CCCSD Sludge [64.0 kg]	CCCSD Scum [4.5 kg]	Calcu-lated*	Measured Slurry Feed
Solids [wt%]	17.8	62.5	17.6	16.8
Ash [wt%]	16.7	3.4	14.1	17.2
Solids [wt%, daf]	14.8	60.4	15.1	13.9
Lipid [wt%]	6.5	**29.0**	12.1	14.7
Carb [wt%]	37.2	**64.0**	47.6	44.2
Protein [wt%]	36.7	2.5	33.9	21.2
FAMES [mg/g]	137	833	303	259
C16:0 [% of fat]	28.9	26.8		27.7
C18:0 [% of fat]	12.6	3.5		12.5
C18:1 [% of fat]	17.7	38.9		21.5
C18:2 [% of fat]	4.2	5.9		8.1

- Measured solids and ash reasonably close to calculated value, overall a bit dilute
- Batch includes **12.4 kg of water** in addition to sludge and scum, this affects calculated solids concentration
  - Also >1 kg tank heel
- Sludge and scum sample prox analysis on **wet samples** and normalized, slurry feed prox is on **dry sample** (preferred)
- Scum carb content seems high (method: by difference); likely, lipid is low
- Abundant C18 and C16 lipids; changes in lipid profile are qualitatively reasonable

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Results from Scum Blend Bench-Scale HTL Test

- Floatable scum blended at 23 wt% with sludge (dry, ash-free basis)
- **54 L** slurry processed (4 L/h, 17 wt% solids), **4.2 L** of biocrude produced
- Conditions: T=350 °C, P=2900 psig
- **Biocrude mass yield: 50%** with 99% mass balance, 60% C yield with 108% carbon balance
- Compared to 37% biocrude yield for CCCSD sludge only (no scum)
- Biocrude has lower density (0.95 g/cm^3 vs. 0.99 g/cm^3 baseline)

Clockwise from left: autoclaved scum; blended feed as-prepared; liquid-liquid phase separation; bottles of HTL biocrude

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Summary and Concluding Thoughts

- HTL is a promising pathway to liquid fuels from waste biomass
- The simple, robust process can accept a variety of feedstocks individually or as blends to create a greater volume of feedstock
- Floatable scum can be blended into wastewater sludge at up to 20% and increases biocrude yield in direct proportion to the blend ratio
- Yet, the proximate analysis reveals that scum may not be all lipid and suggests more complex interactions than lipid in = lipid out or, perhaps, that the proximate lipid analysis is not ideal for this feedstock and needs further development.

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Acknowledgements

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Bioenergy Technologies Office

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CENTRAL SAN
CENTRAL CONTRA COSTA SANITARY DISTRICT

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- Mike Thorson
- Igor Kutnyakov

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Thank you

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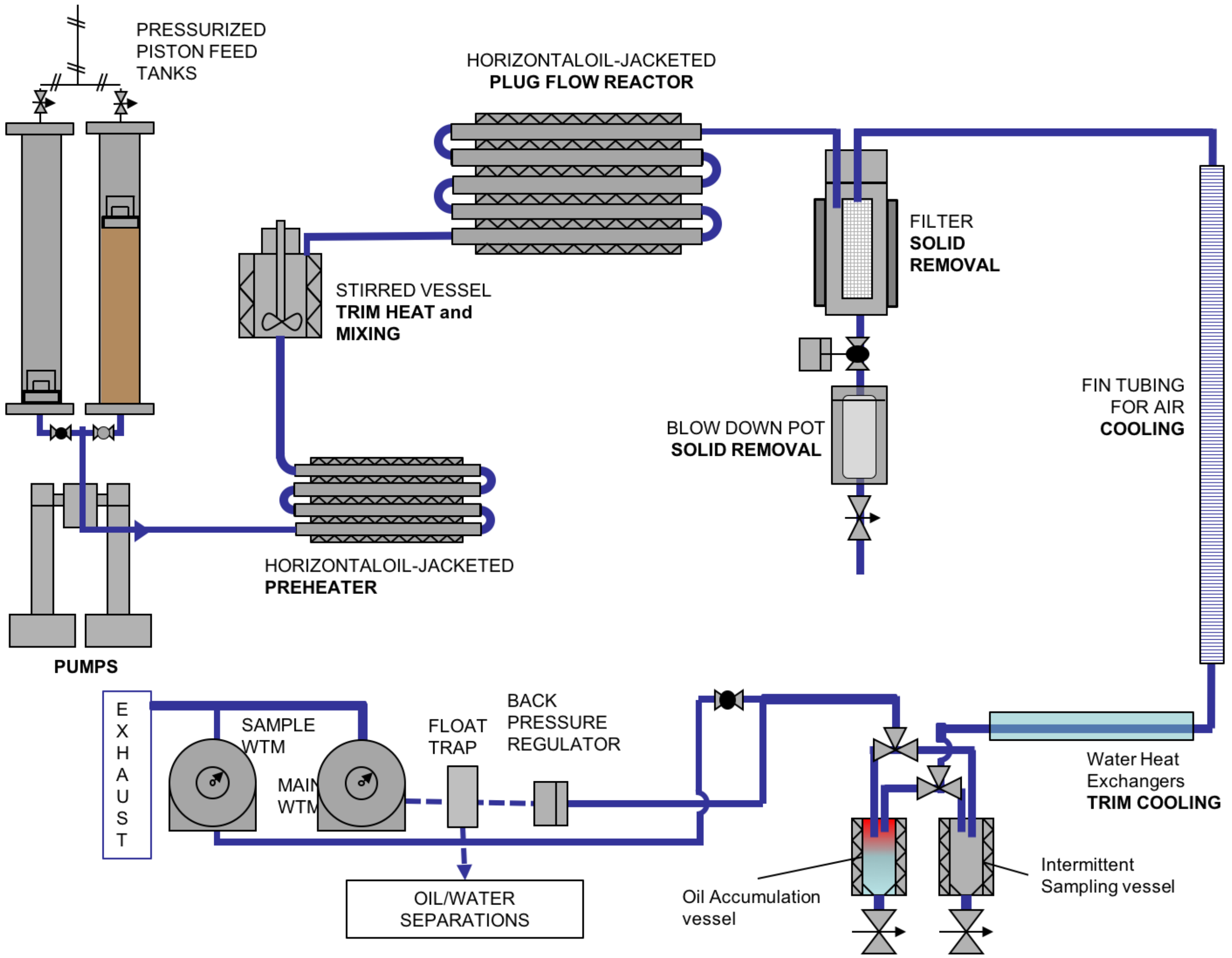
Additional Slides

Acronyms

AD	Anaerobic Digestion
BETO	Bioenergy Technologies Office
CCCSD	Central Contra Costa Sanitary District
DOE	US Department of Energy
FOG	Fats, oils, and greases
HTL	Hydrothermal liquefaction
PPCP	Pharmaceuticals and personal care products
PFAS	Poly- and perfluoro alkyl substances
WWTP	Wastewater treatment plant

Anatomy of a typical HTL run

Bench-scale continuous HTL reactor system



Time Frame	Activity
Day before	Pressure check, flood with water and heat to 250 °C, idle overnight with no flow
05:00	Begin water flow and heat to 350 °C
07:00	Begin feed flow
09:00–14:00	Collect 3 to 7 steady-state product samples
14:00–18:00	Run in continuous product letdown mode for accurate gas flow and concentration data
18:00	Switch to water to flush reactor at temperature
20:00	Start reactor cooling shutdown
21:00	Shutdown
Day after	Vent reactor, clean as needed