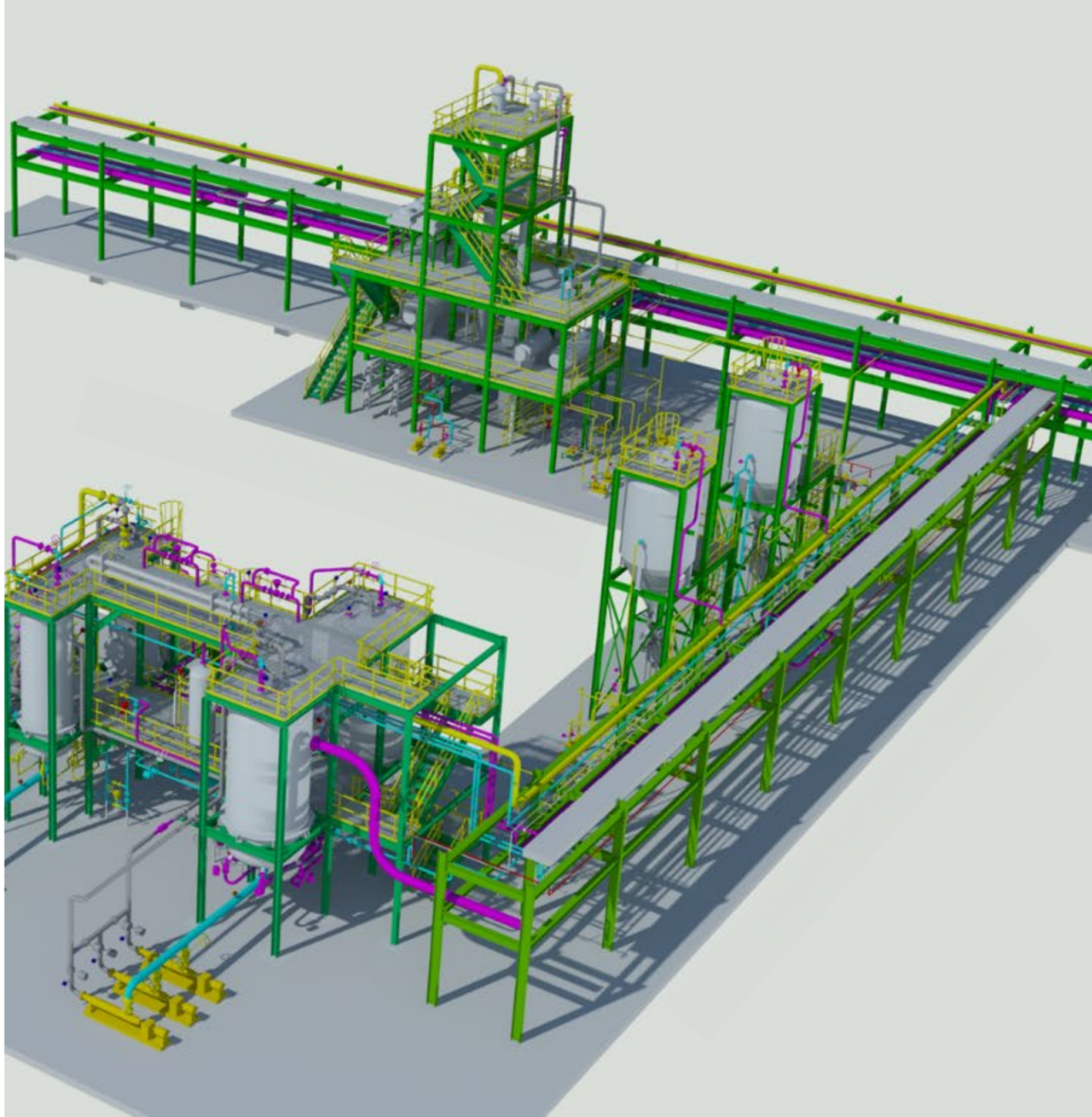
Pacific Northwest
NATIONAL LABORATORY

Re-imagining Hydrothermal Liquefaction (HTL) for Reliability

Uriah Kilgore

Mike Thorson

Pacific Northwest National Laboratory



Hydrothermal Liquefaction
A pathway to fuel from sewage sludge

HTL Plant

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

HTL Biocrude

Stable biocrude
60% C-yield
Gravity-separable
Thermally stable

Hydrotreater

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

Hydrocarbon blendstock (Diesel, Jet, Naptha)

Fuel Blendstocks
(95%+ C-yield)
Predominantly high cetane diesel (70%)

- HTL is conceptually simple (i.e., heated pipe)
  - Can accept a diverse range of wet feedstocks (no drying!)
- HTL results in high carbon yields to liquid hydrocarbons (up to 60%)
- HTL produces a gravity-separable, stable biocrude with low oxygen content (5–15 %)

Fuels create a new potential value proposition for organic wet wastes

Example: 100 dry tons/day

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

~8,500 gallons fuel from HTL

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

$4.00/gal

Costs of sludge disposal will grow as regulations increase

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

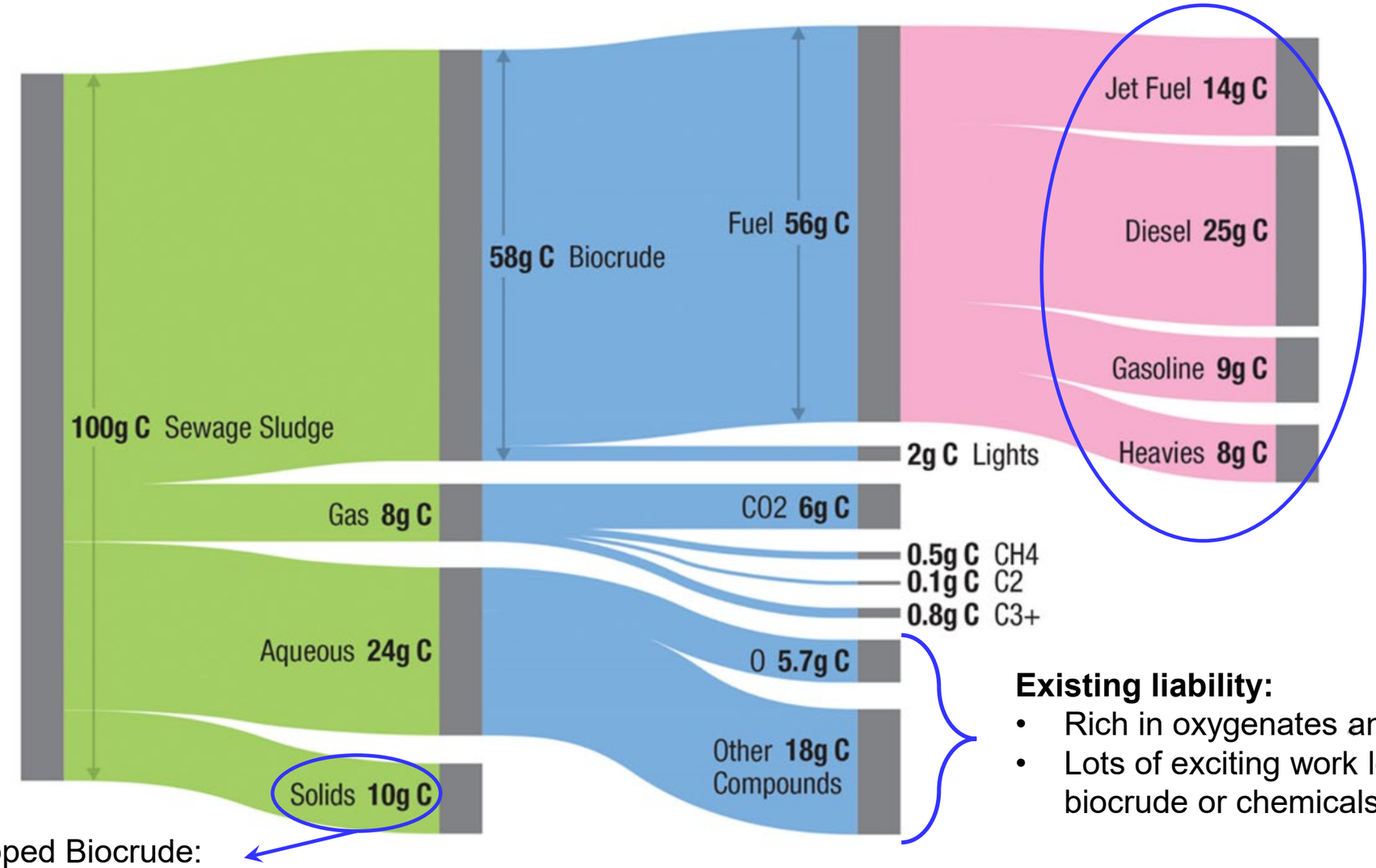
Sludge used as crop fertilizer has contaminated soil, water, crops and cattle, forcing farmers to quit

Value of fuel may be more valuable than the service provided:

- Potential for credits
- Long-term demand for liquid fuels (after other sectors are decarbonized)

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

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



Fuel testing critical

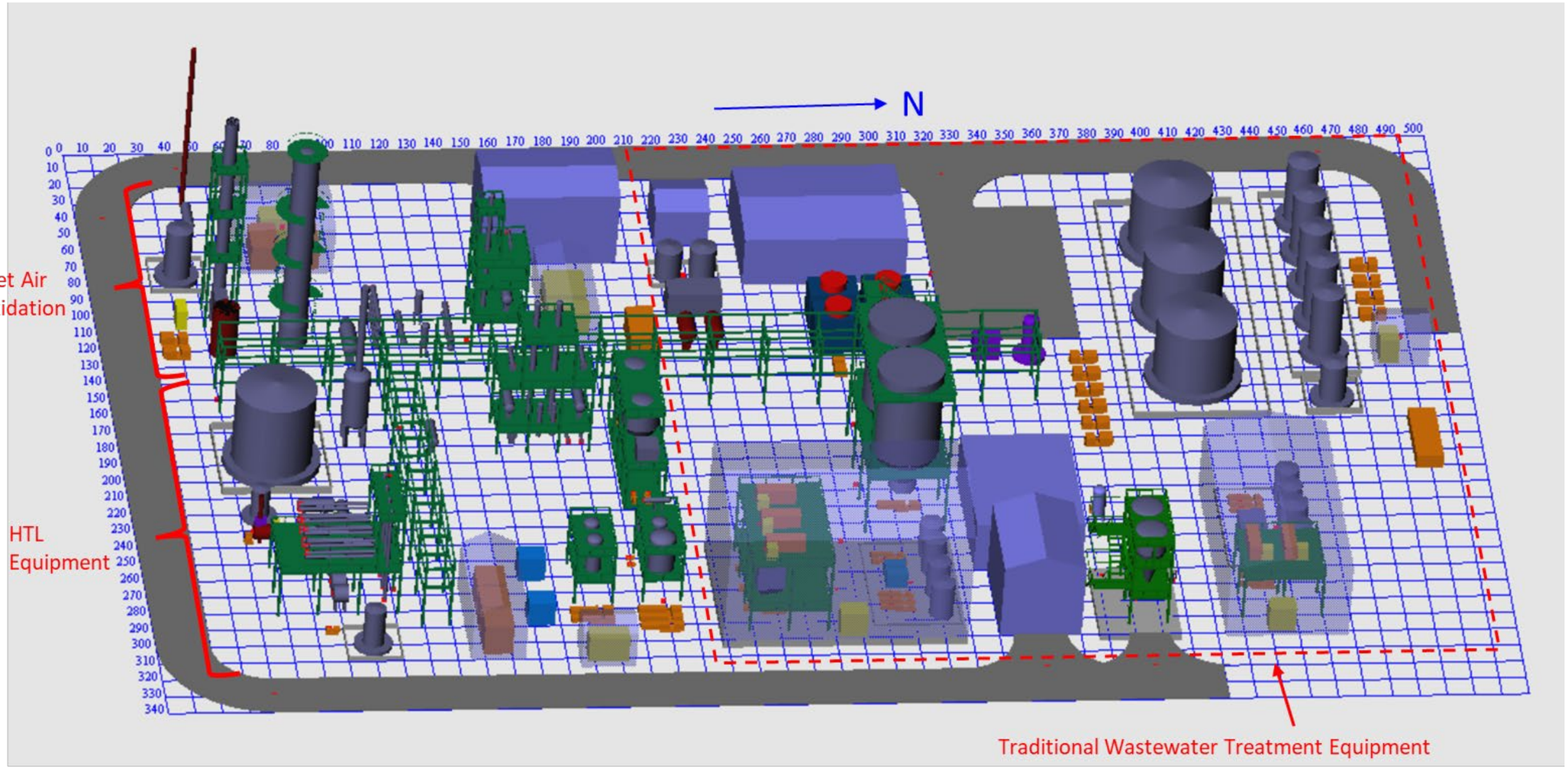
Existing liability:

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

Includes trapped Biocrude: Opportunity for extraction

*This analysis based on carbon basis

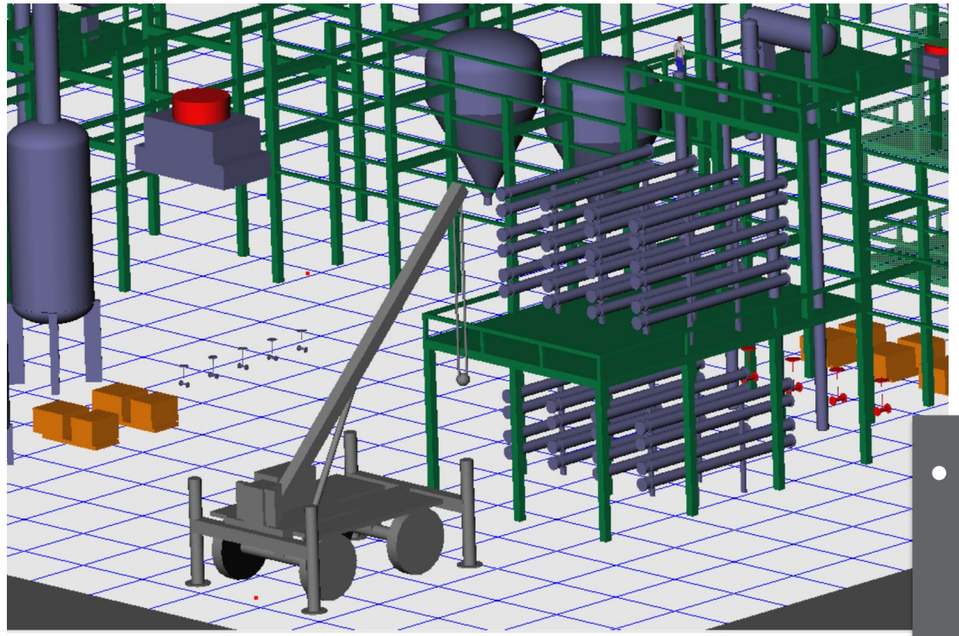
Basic engineering to identify scale-up challenges



Design helps us look at potential commercial embodiment

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

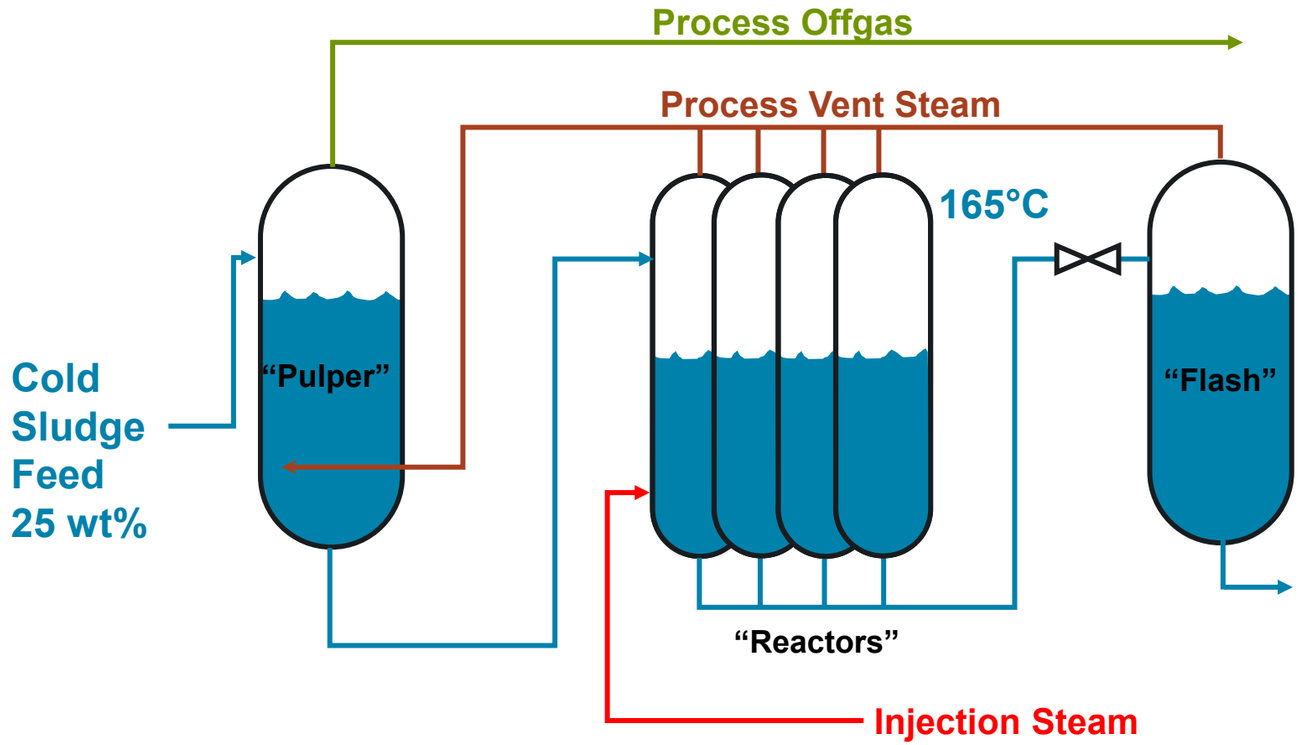
- **Fouling may challenge operability of commercial plants**
- **Can a commercial design minimize use of heat exchangers & "hot spots" ?**

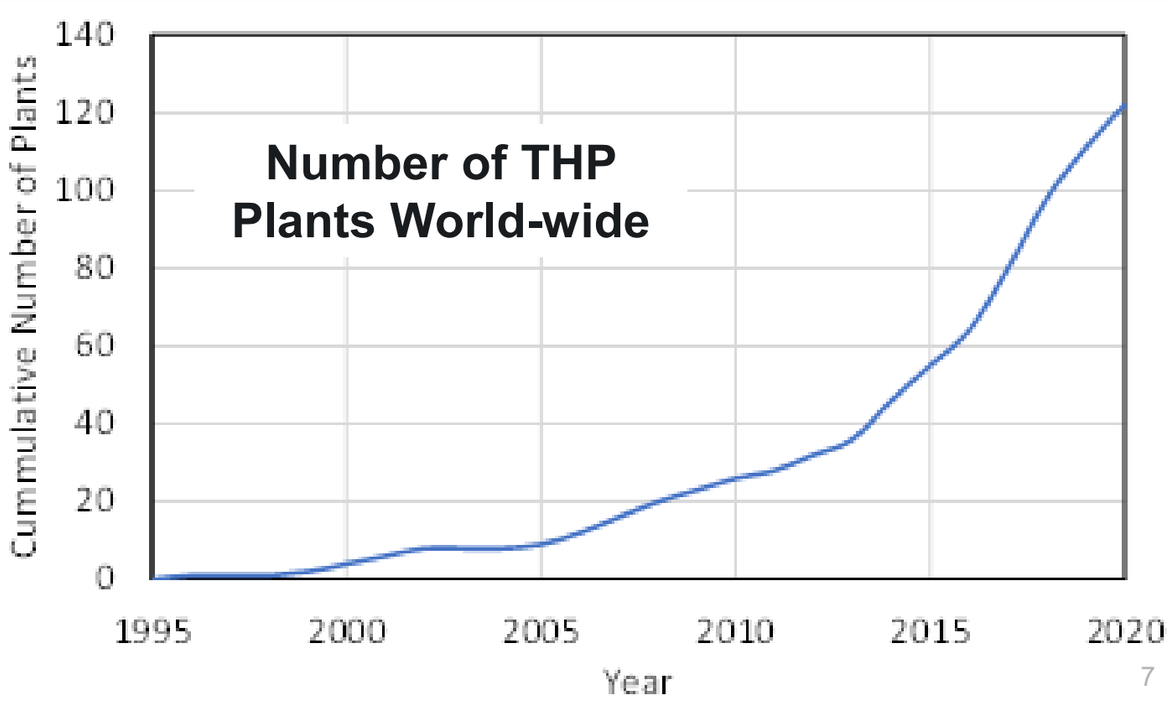
Waste-water treatment plants might have the solution!

- Thermal Hydrolysis is operationally robust because it has no heat exchangers
  - Significant growth within WRRF community
- Decades of experience has proven process vent steam heating is reliable and safe

Why Thermal Hydrolysis?:

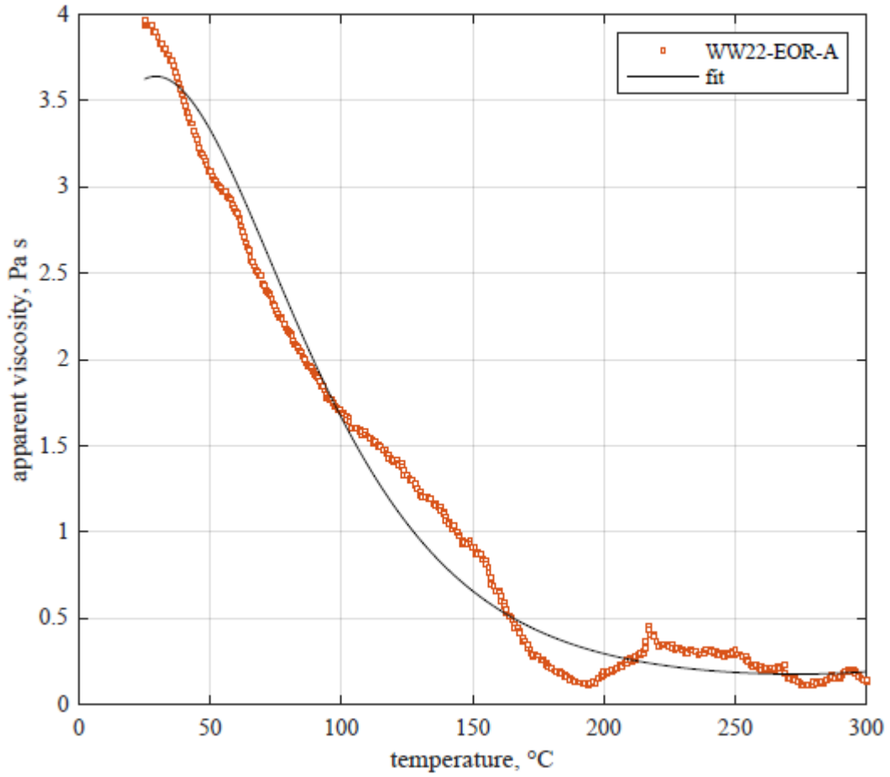
1) It works!
2) It covers the range of HTL's low pressure heat exchanger
3) It uses HTL feed
4) WRRF's embrace it
5) It is scalable

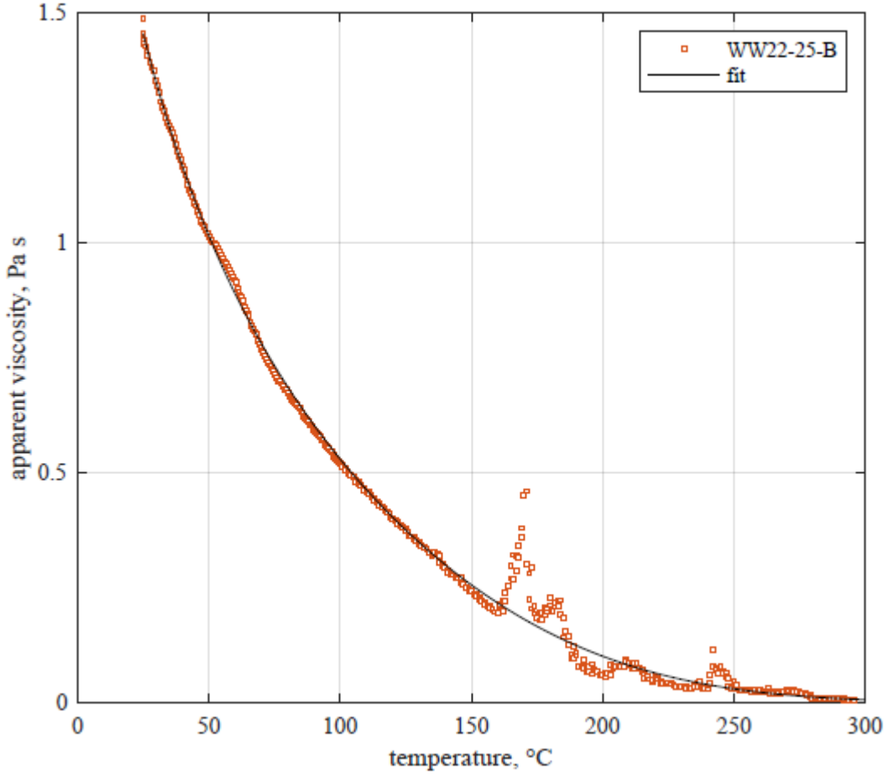




Rheological changes in sludge

- Rapid drop in viscosity (non-reversible) with increasing temperature
- Example rheology curves of two sludge samples:



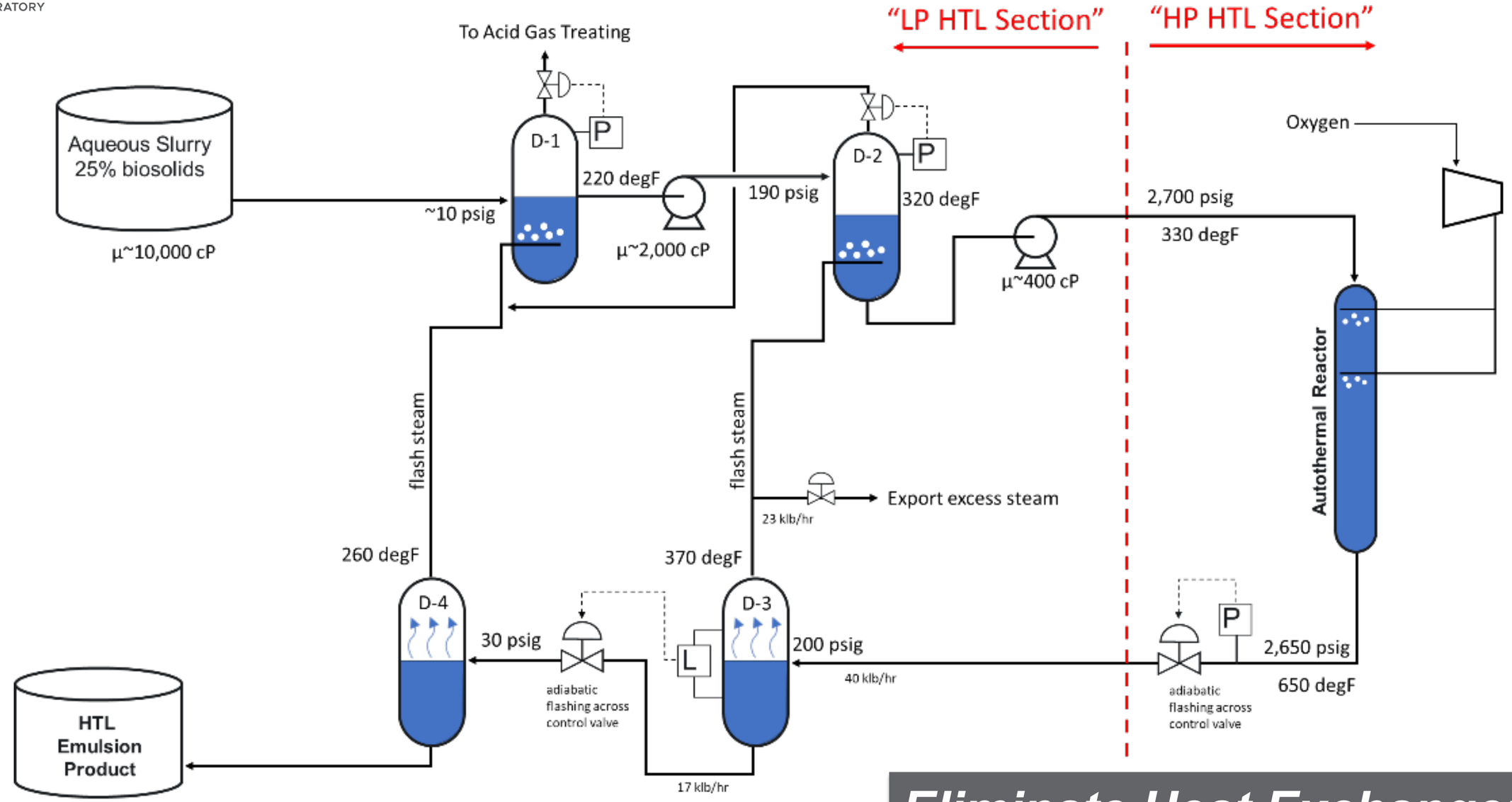


Rheological changes in sludge

Before heat cycling

After heat cycling

HTL with flash steam heating

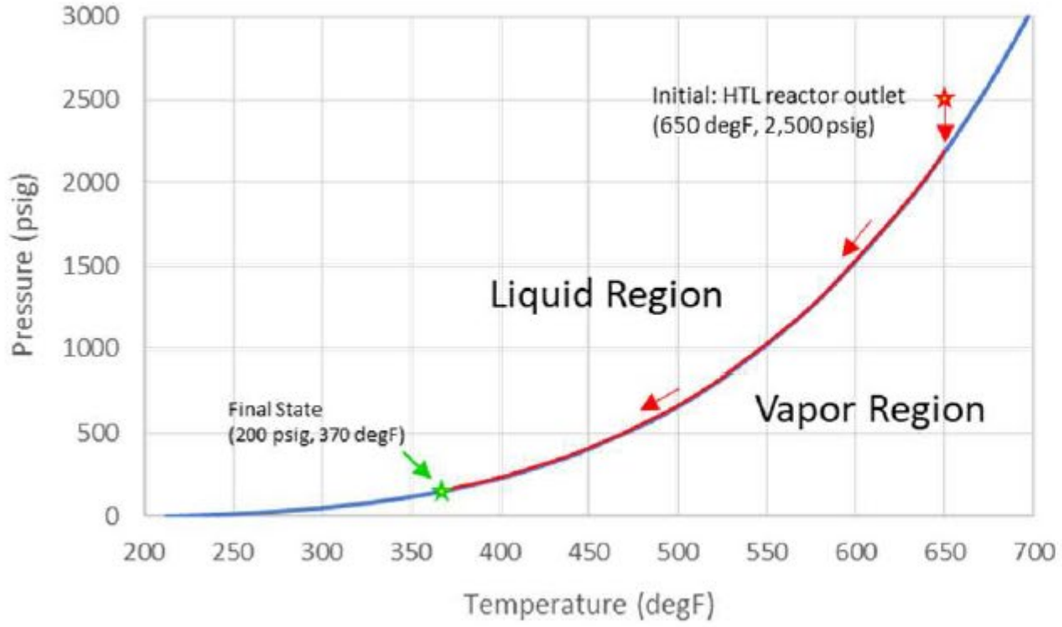


Eliminate Heat Exchangers

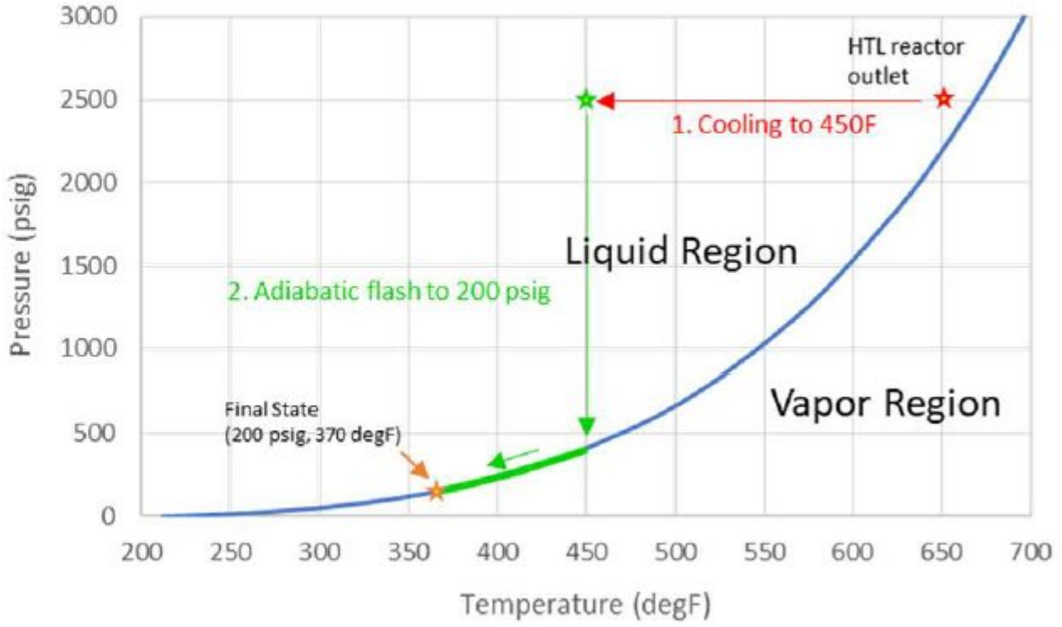
Visualization of Steam Flashing on Vapor/Liquid phase diagram

- Suddenly reducing the pressure of the hot reactor product produces steam
- Quantity of steam formed can be controlled by varying the final pressure and amount of cooling

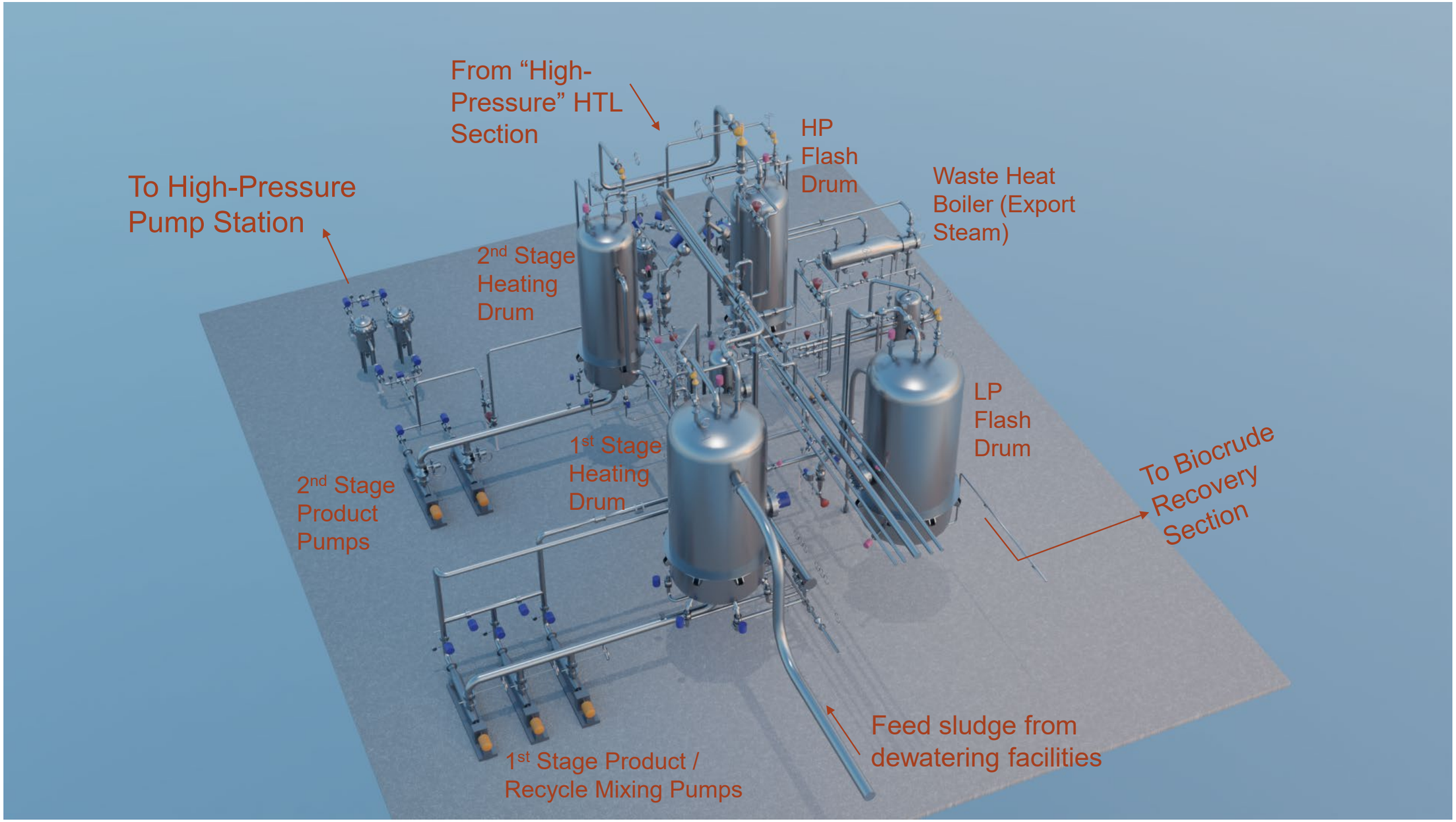
1-step process of reducing the pressure of the HTL product to generate flash steam



2-step process: first cooling the reactor product, then reducing the pressure to generate flash steam



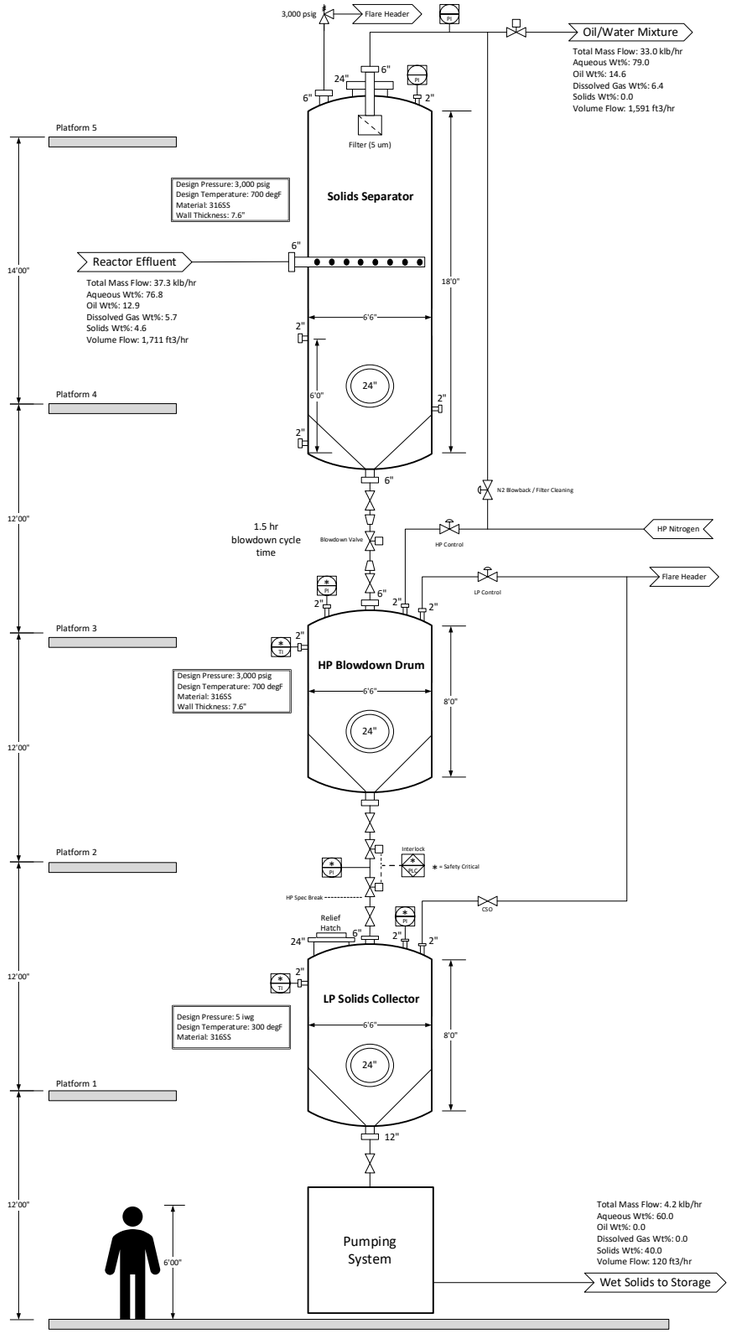
Conceptual implementation of new heat integration



Scaling-Up the Solids Separations

- Operability and safety factors change with process scale.
- We need to design unit operations that are practical at full-scale (i.e. >100 DTPD).
- Need alternative technology for commercial scale deployment:
  - Reliability
    - ✓ Erosion from high velocities
    - ✓ Thermal cycling
    - ✓ Filter plugging
    - ✓ Ability to service online
  - Safety
    - ✓ Leaks with H_2S
    - ✓ High pressure / low pressure segregation
    - ✓ Vessel fatigue / cyclic stresses
    - ✓ Equipment prep requirements

SOT Case – Conceptual Dimensions



Solids separations, a key scale-up uncertainty

Solids separations identified as a key process uncertainty

- Operability and safety needs differ across process scales
- Important considerations: Reliability and safety

INCLINED PLATE SEPARATORS UNDER CONSTRUCTION AT THE HORIZON FROTH TREATMENT FACILITY (PHOTO COURTESY CANADIAN NATURAL RESOURCES)

Scale Down Technology

~100 dry ton/day size

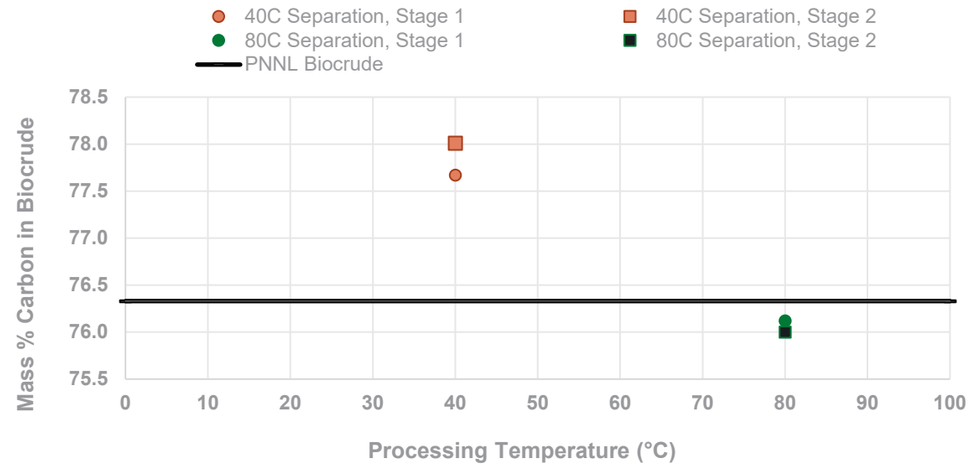
Leveraging oils sands process technology

- Bitumen has similar physical properties to biocrudes
- Commercially implemented by many major oil companies
- Removes solids and improves oil quality

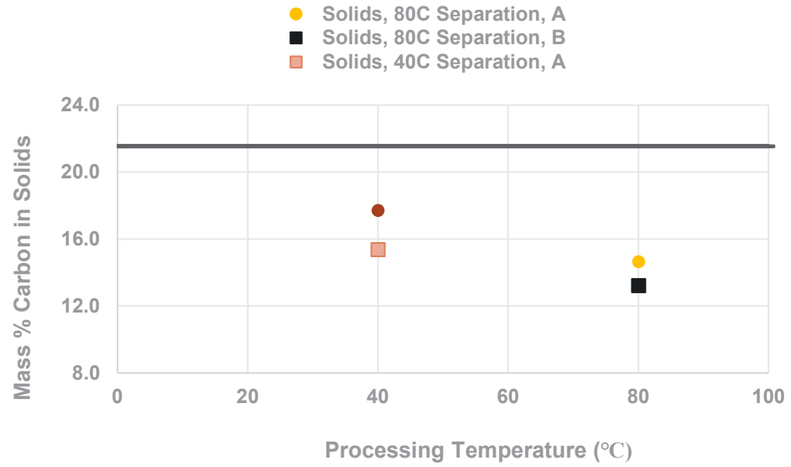
Positive Extraction Results in Bench-scale setup

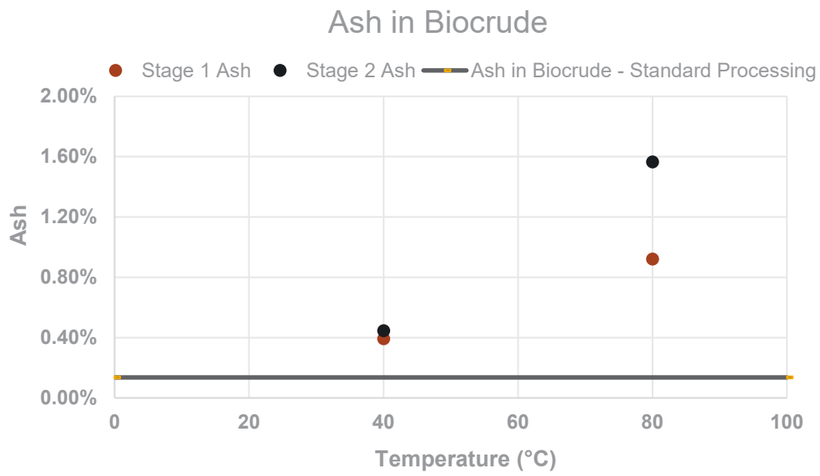
- High removal of solids in extraction process
- Increases overall process biocrude yield (and carbon yield to organic phase)

	Aqueous Phase Mass	Solids Slurry Mass	Solids + Aqueous	Biocrude Mass	Total Mass
Input Mass (g)	240.24	45.02	285.26	15.23	300.49
Mass Recovered or Accounted (g)	249.88	15.31 (as solids)	265.19	16.02	281.21
% Accounted/Recovered			92.96%	105.20%	93.58%

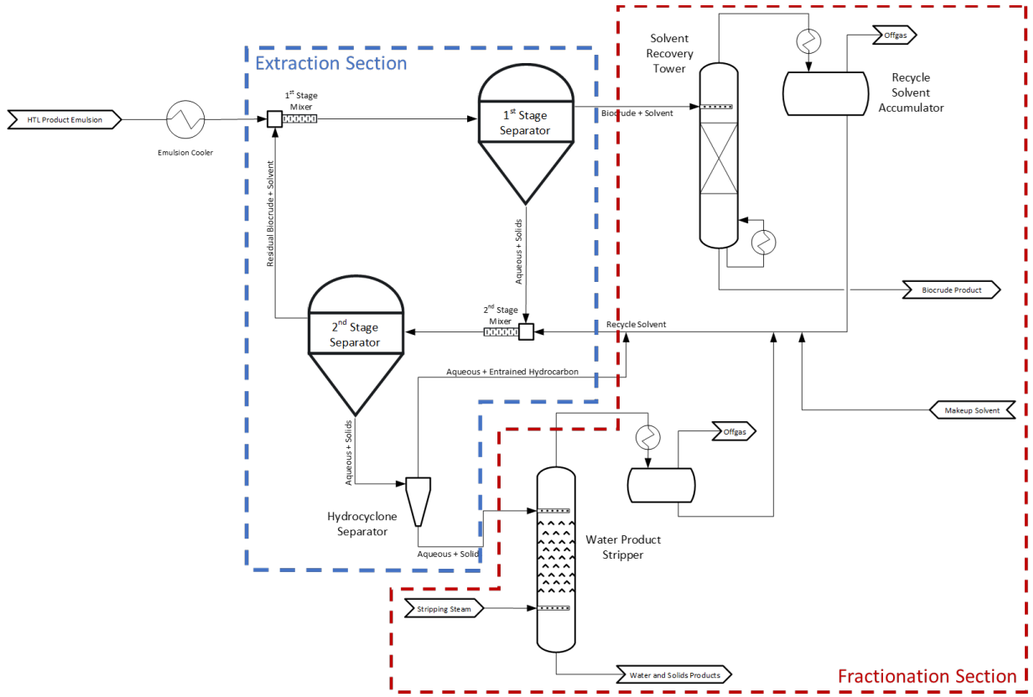


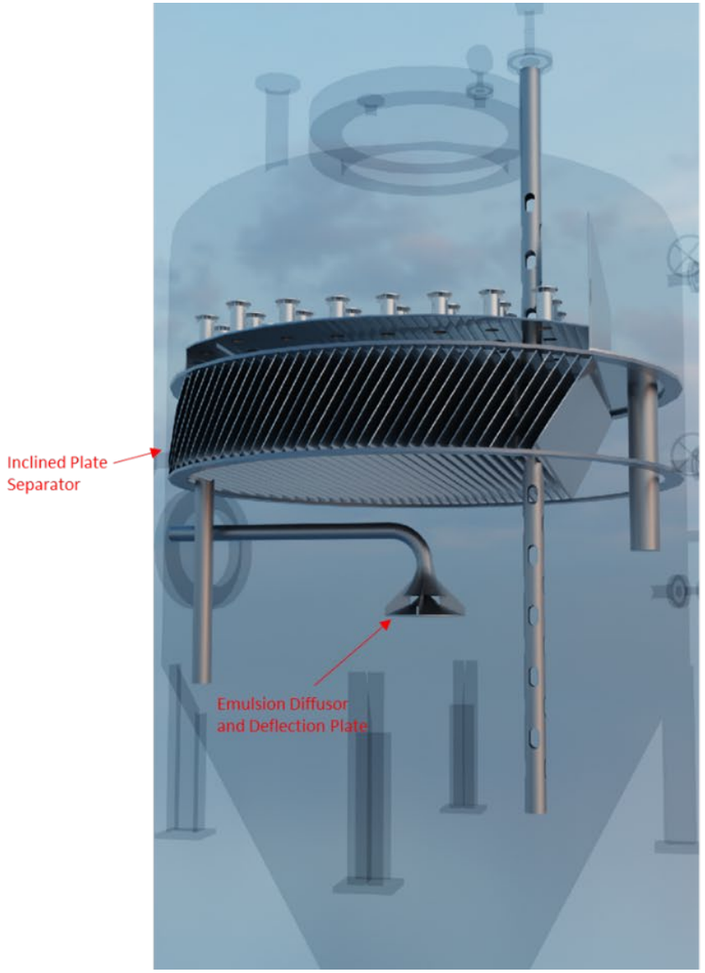
Data displayed in actual, no normalization

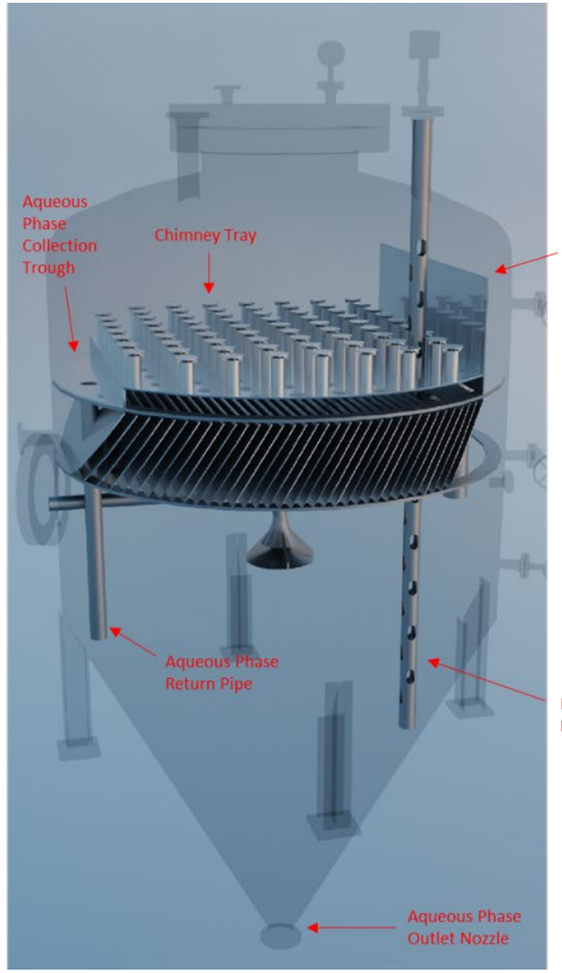




Bench-scale data used to create commercial design







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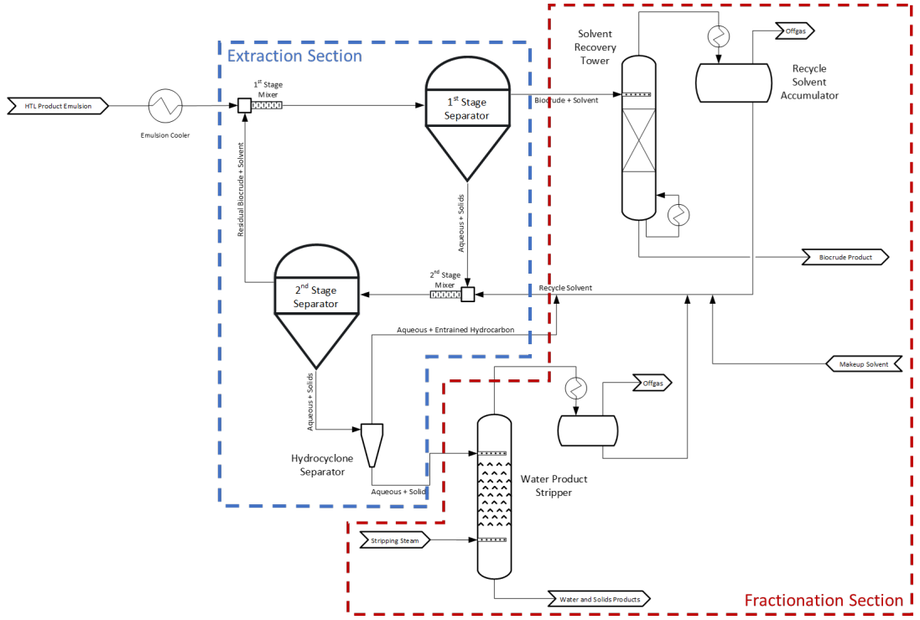
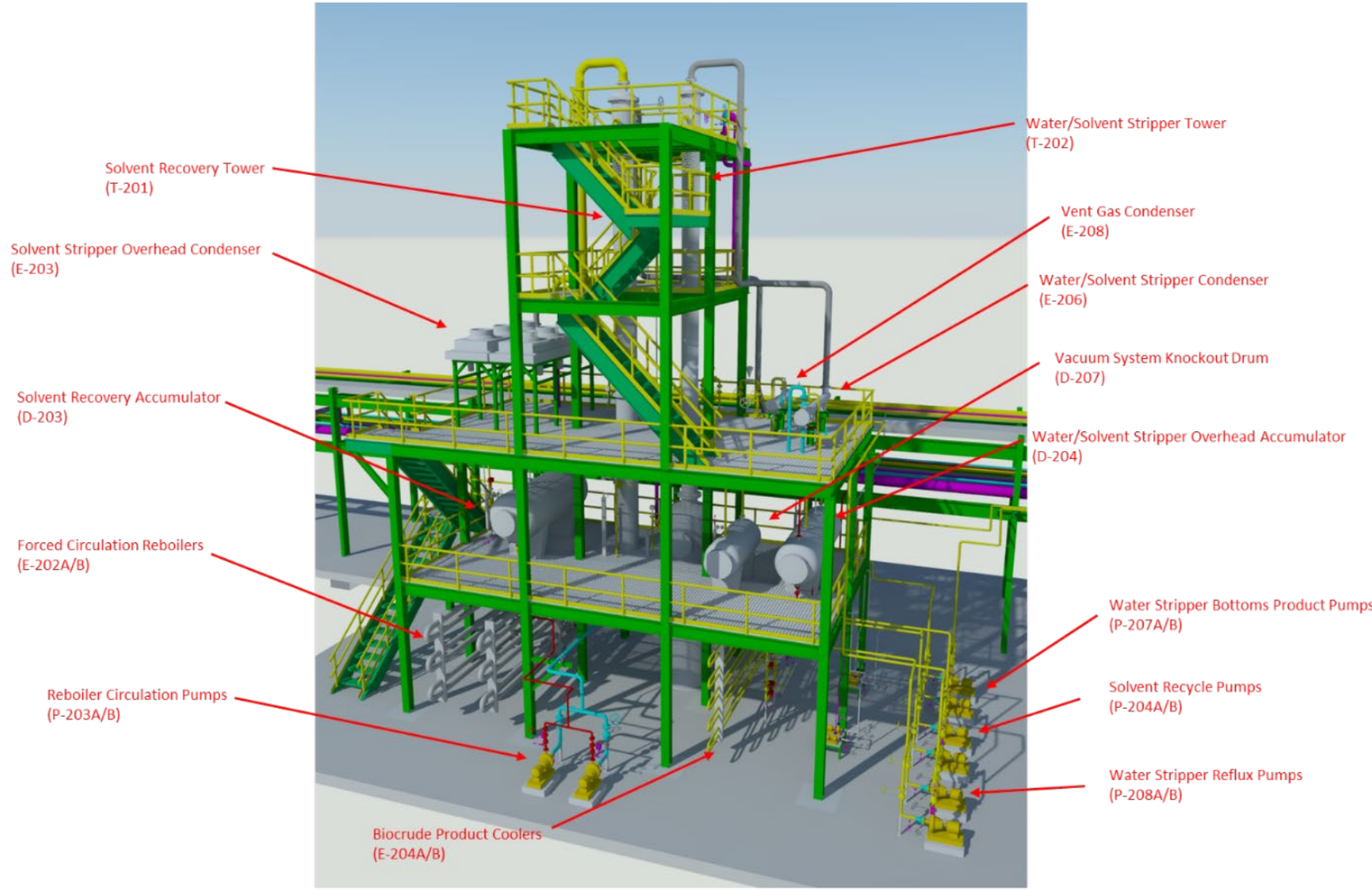
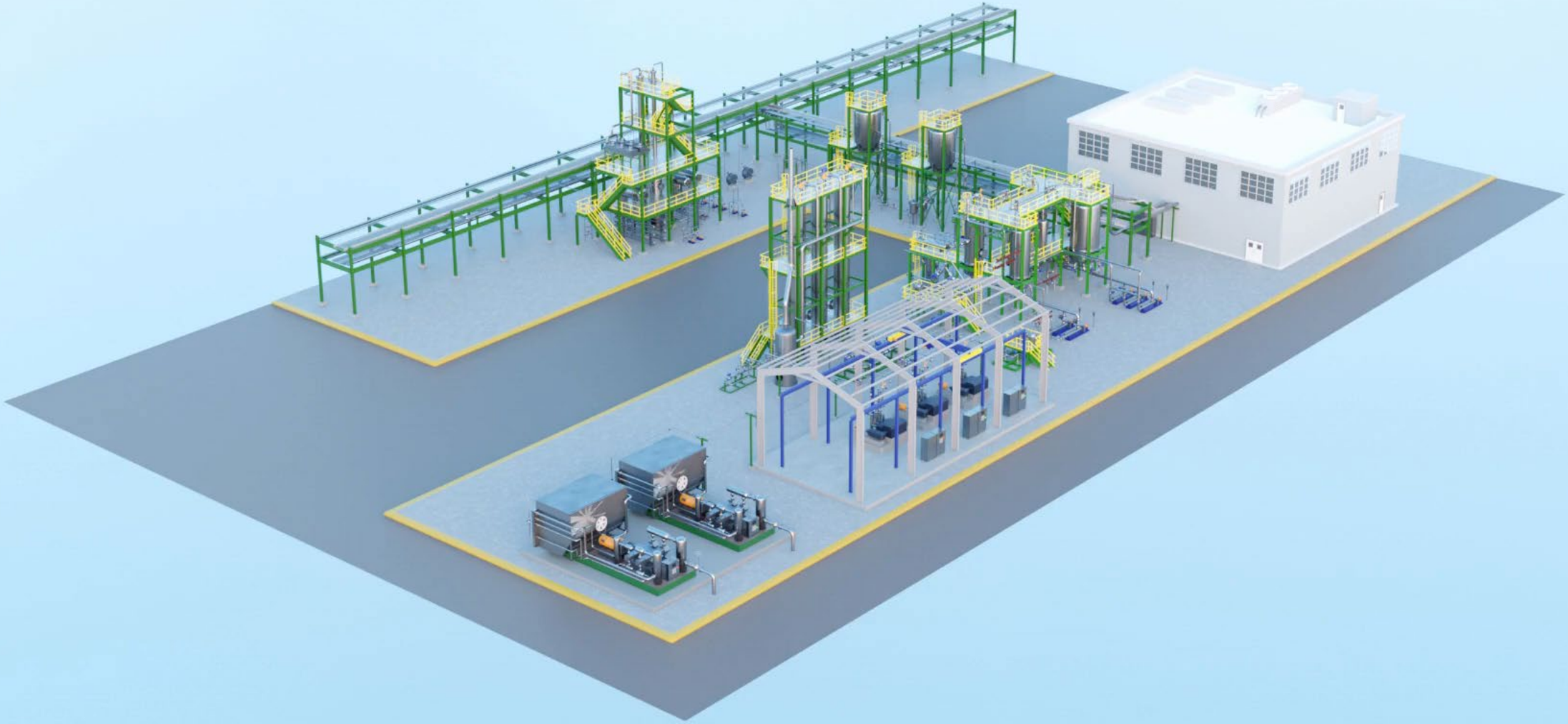


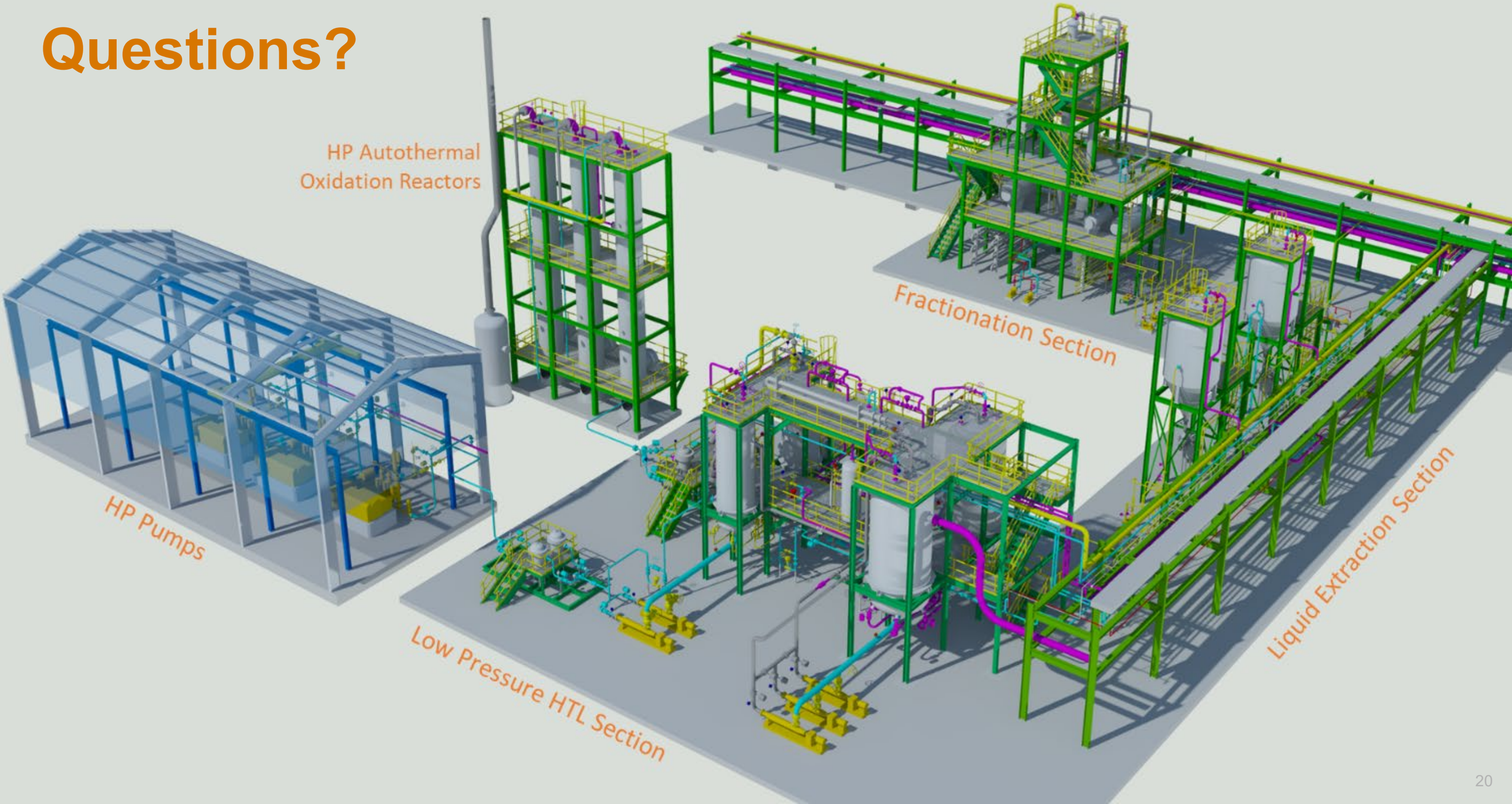




Summary

- HTL provides a unique value proposition for sludge disposal
- HTL operability and reliability will be crucial to any deployment
- Fouling will need to be addressed in commercial designs
  - Steam flashing with autothermal HTL have the potential to eliminate hot spots for fouling
    - ✓ Steam flashing enables heating to ~165°C
    - ✓ Autothermal HTL brings reaction temperature to ~350°C
- Biocrude separations can mimic bitumen processing for oil removal
  - Similar oil properties may justify a similar extraction process

Questions?


HP Autothermal
Oxidation Reactors
Fractionation Section
HP Pumps
Low Pressure HTL Section
Liquid Extraction Section