IOWA STATE UNIVERSITY
Bioeconomy Institute

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Autothermal Hydrothermal Liquefaction

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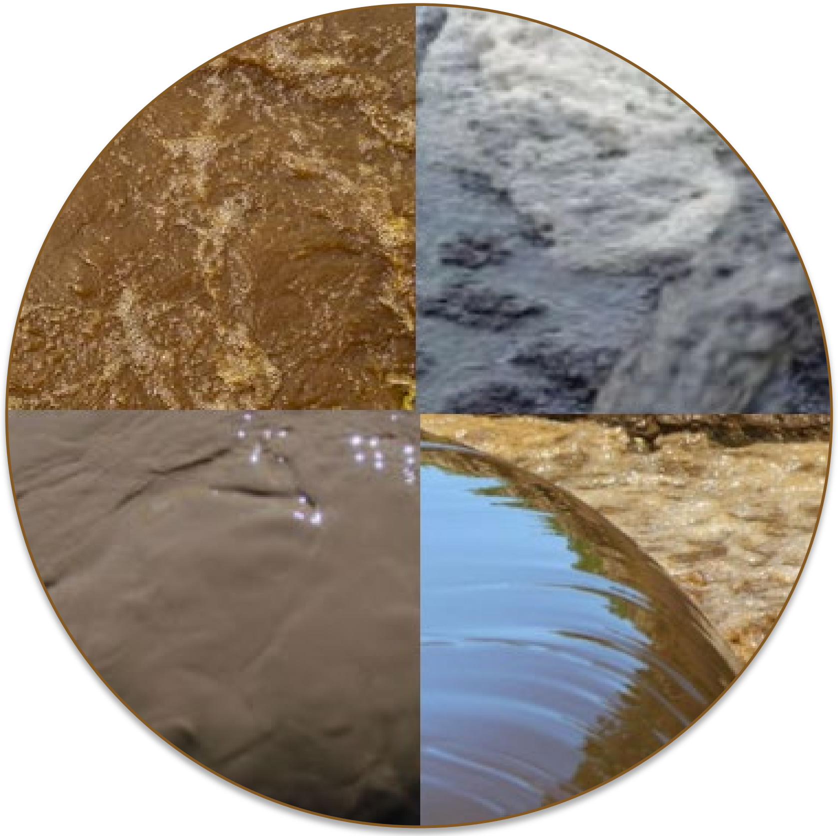
The conversion of organic waste into advanced fuels through Hydrothermal Liquefaction (HTL) is a promising route

- Management of waste has become increasingly difficult with population growth.

- The US alone generates 77.17 MM Tons of wet waste annually, with 41 MM Tons from animal waste having $5.7 \times 10^{11} MJ$ inherent energy content[1].

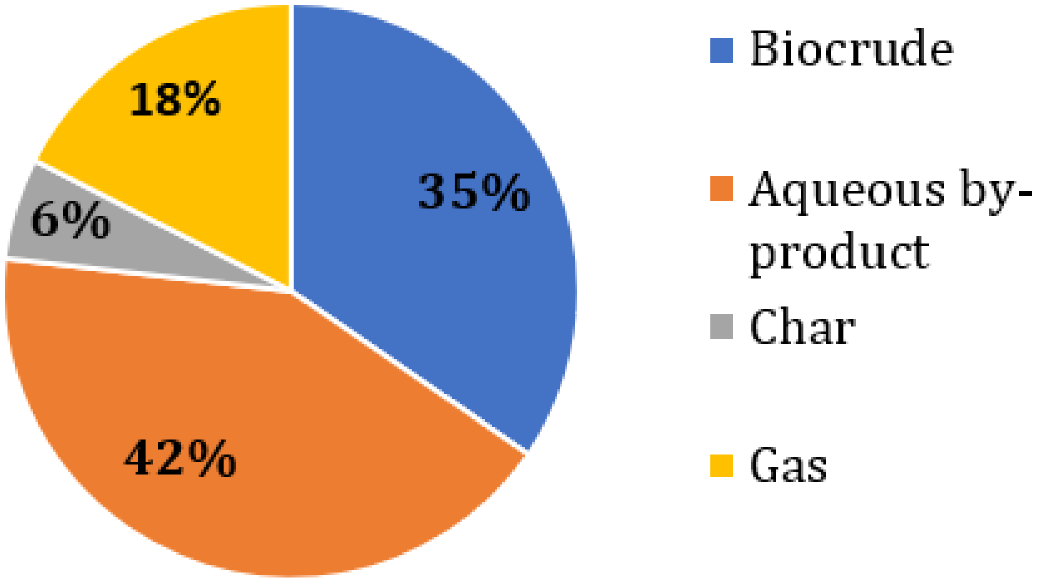
- HTL can process these wet wastes to produce biofuels.



1. Biofuels and Bioproducts from wet and gaseous waste streams: challenges and opportunities. US DOE BETO (2017)

Hydrothermal Liquefaction (HTL)

- Subcritical: 250 – 374 °C and 5 – 22 MPa
- Supercritical: 375 – 480 °C and 24 – 34 MPa
- Typical feedstocks: Woody biomass, algae, swine manure, digestate, sewage sludge, food wastes, etc. [1]
- HTL uses water as the process medium



Product distribution of HTL of a dry biomass feedstock[2]

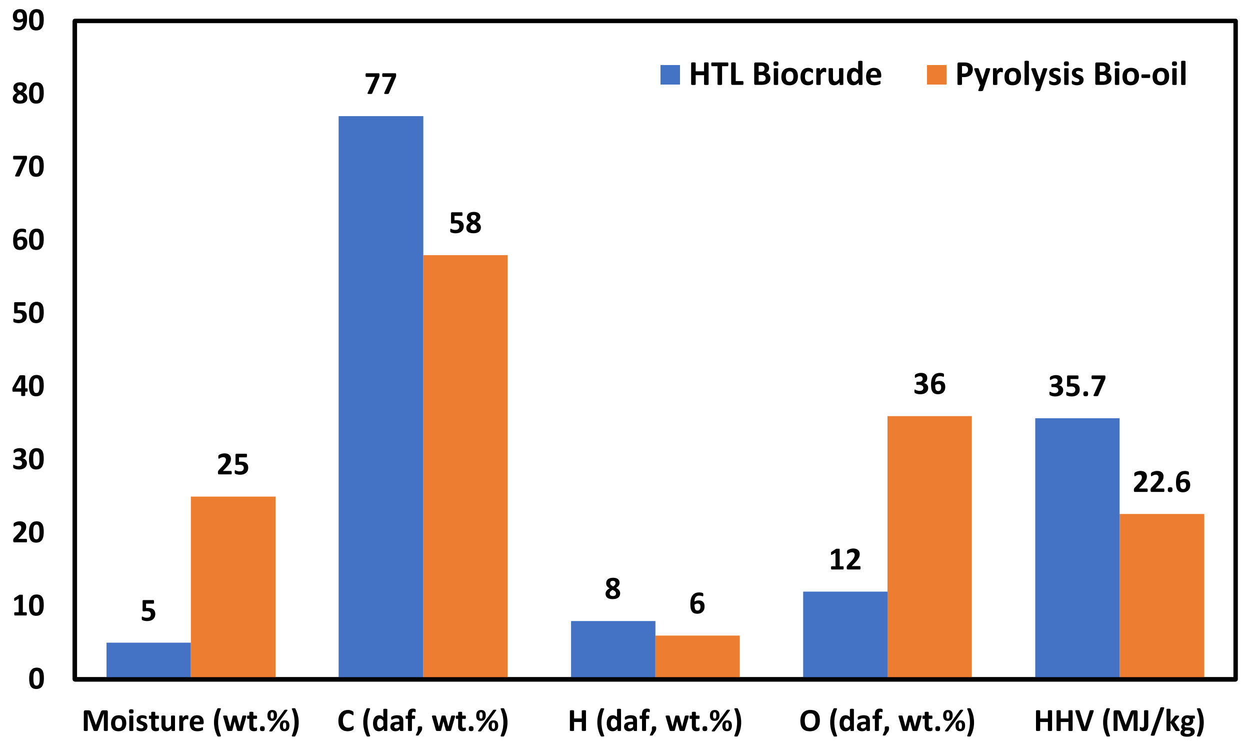
1. Thomsen, L. B. S., Anastasakis, K., & Biller, P. (2022). Wet oxidation of aqueous phase from hydrothermal liquefaction of sewage sludge. *Water Research*, *209*, 117863.
2. Tews, I. J.; Zhu, Y.; Drennan, C.; Elliott, D. C.; Snowden-Swan, L. J.; Onarheim, K.; Solantausta, Y.; Beckman, D. Biomass Direct Liquefaction Options. TechnoEconomic and Life Cycle Assessment; Pacific Northwest National Lab.(PNNL), Richland, WA (United States), 2014.

HTL offers significant advantages over other thermochemical conversion technologies

- The high-pressure condition prevents a phase change, hence avoiding large enthalpic energy requirements

- Biocrude from HTL have improved qualities:
  - Lower oxygen
  - Lower moisture content and
  - Higher heating value (HHV)

HTL/Pyrolysis Liquid Products Comparison



*daf – dry ash-free basis

Dimitriadis, A., & Bezergianni, S. (2017). Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: A state of the art review. *Renewable and Sustainable Energy Reviews*, *68*, 113-125

Major barriers to HTL commercial viability

- Char and coke formation[1]
- High-pressure feeding systems[2]
- Heat and Mass Transfer[3]

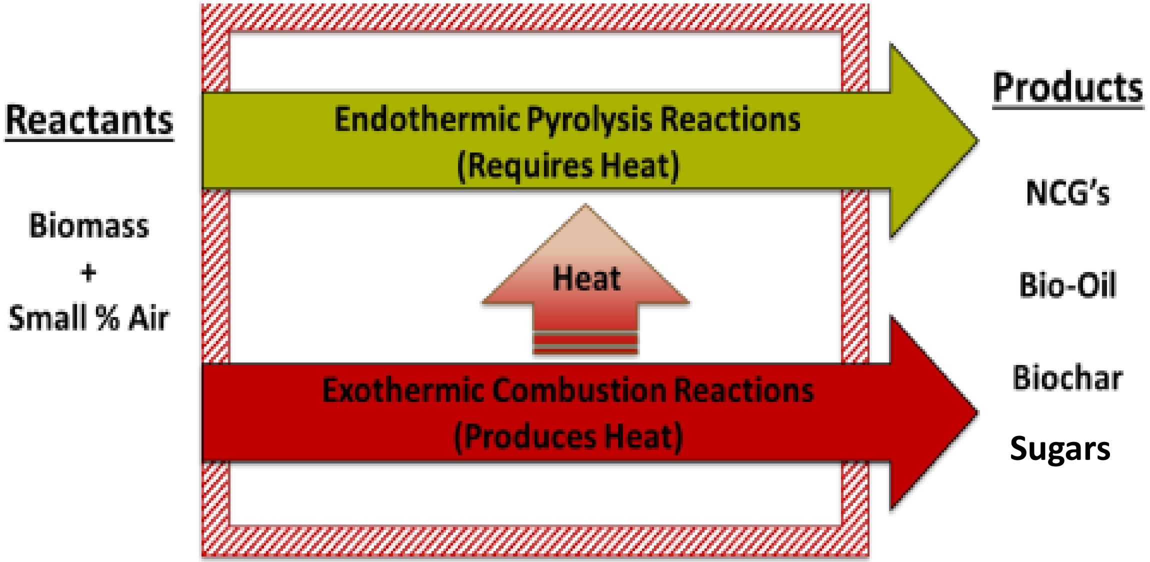
1. D. Lachos-Perez, P. César Torres-Mayanga, E. R. Abaide, G. L. Zabot, and F. De Castilhos, “Hydrothermal carbonization and Liquefaction: differences, progress, challenges, and opportunities,” *Bioresource Technology*, vol. 343. Elsevier, p. 126084, Jan. 01, 2022. doi: 10.1016/j.biortech.2021.126084.
2. D. C. Elliott, P. Biller, A. B. Ross, A. J. Schmidt, and S. B. Jones, “Hydrothermal liquefaction of biomass: Developments from batch to continuous process,” *Bioresour. Technol.*, vol. 178, pp. 147–156, 2015, doi: 10.1016/j.biortech.2014.09.132.
3. C. Hognon, F. Delrue, and G. Boissonnet, “Energetic and economic evaluation of Chlamydomonas reinhardtii hydrothermal liquefaction and pyrolysis through thermochemical models,” *Energy*, vol. 93, pp. 31–40, Dec. 2015, doi: 10.1016/J.ENERGY.2015.09.021.

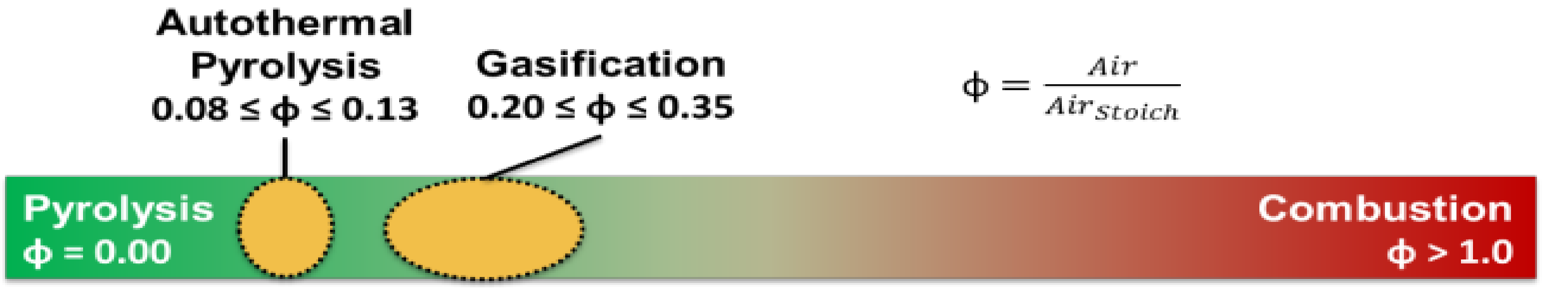
Autothermal operation could overcome the heat transfer bottleneck of HTL

- Exothermic reaction within reactor provides energy for endothermic HTL reaction

- Demonstrated at Iowa State University for pyrolysis through partial oxidation
  - The valuable heavy ends are preserved
  - Process intensification of three-fold achieved

Autothermal Reactor System





$$\phi = \frac{Air}{Air_{Stoich}}$$

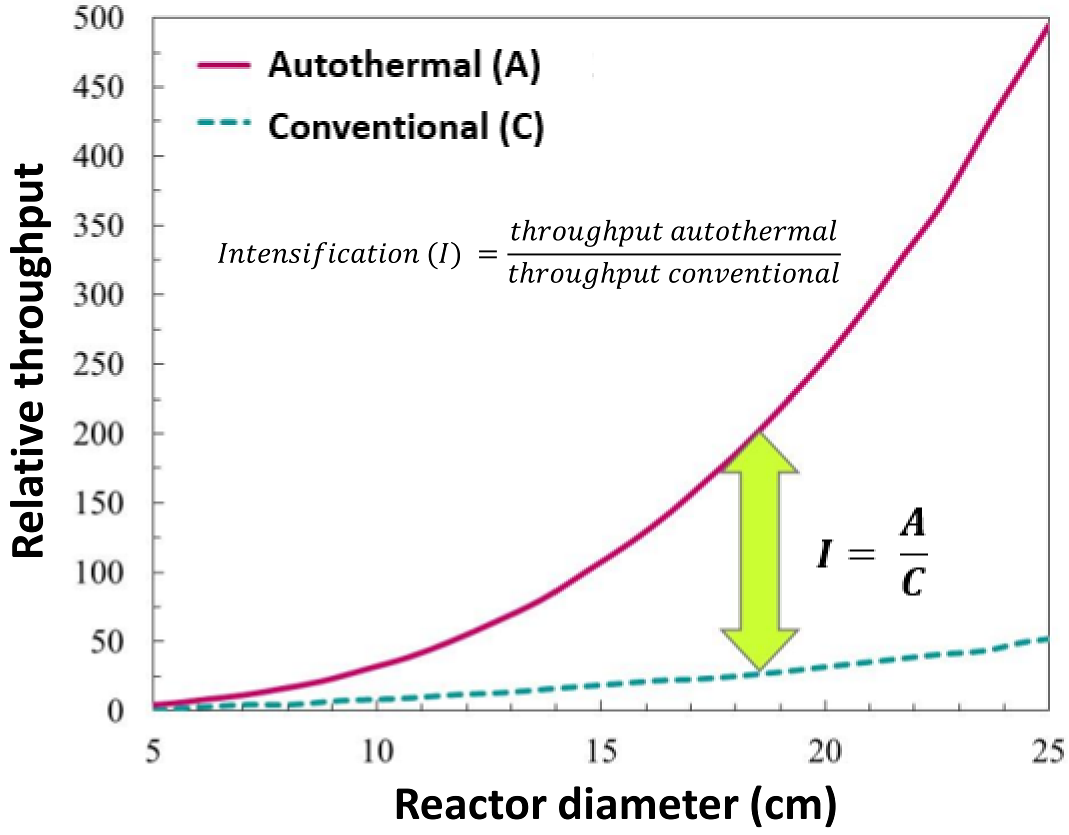
As the system size increases, the impact of heat transfer limitations becomes more pronounced

- For a first-order chemical reaction in a tubular reactor, the diameter D (m) for which heat transfer becomes rate limiting is given by:

$$D > \frac{4h(T_w - T_{rx})}{k_c C_A |\Delta H_{rx}|}$$

- Accordingly, the maximum diameter of a tubular HTL reactor is only 0.064 m, illustrating the challenges of heating a commercial-scale HTL reactor

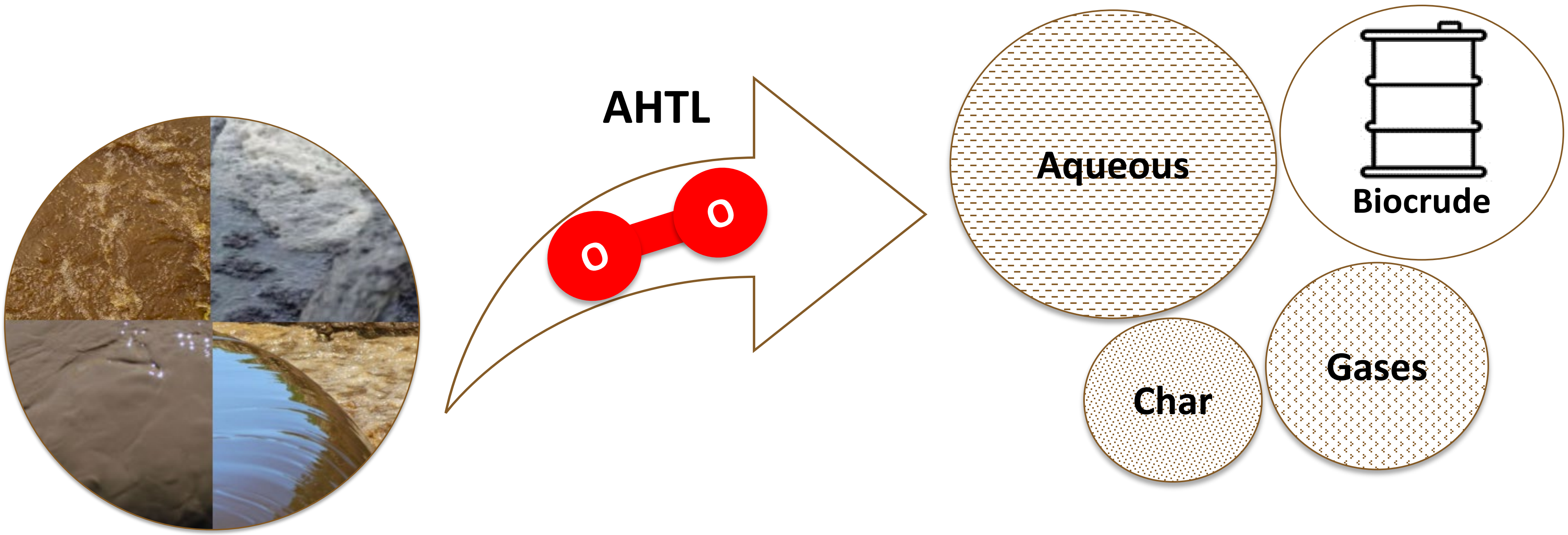
Throughput vs Reactor Size[1]



1. R. C. Brown, "Process Intensification through Directly Coupled Autothermal Operation of Chemical Reactors," *Joule*, vol. 4, no. 11, pp. 2268–2289, 2020, doi: 10.1016/j.joule.2020.09.006.

Hypotheses

- The addition of molecular oxygen (as air) decreases external energy demand for HTL
- Oxygen will preferentially react with organic compounds dissolved in aqueous phase compared to water-insoluble fraction (biocrude)

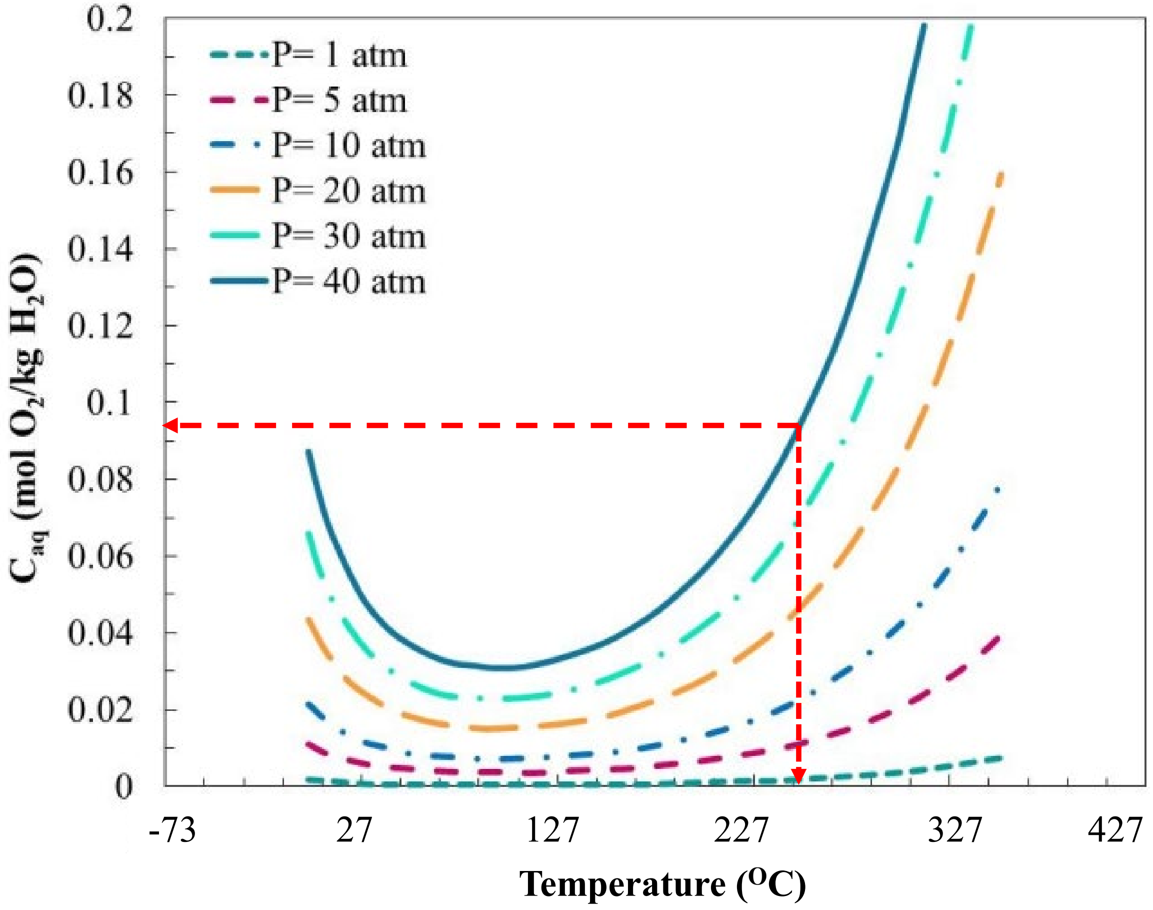


Dissolving oxygen in the aqueous phase

- Mass transfer of oxygen to the aqueous phase will depend on oxygen saturation pressure and effect of mixing on $k_L a$

$$r_m = k_L a\left(C^*_{O_2} - C_{O_{2,L}}\right)$$

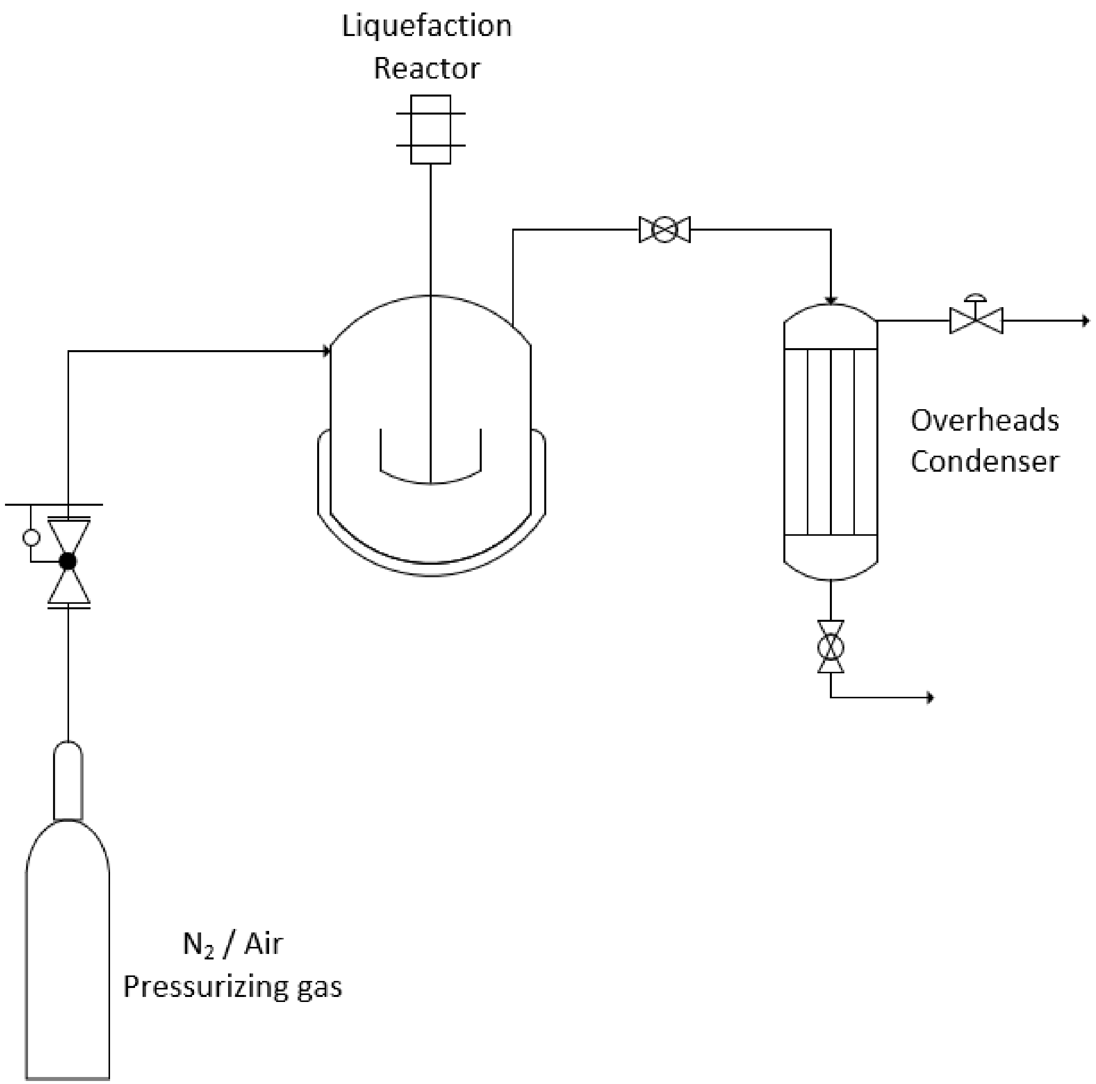
- At typical HTL operating conditions, oxygen is much more soluble in water than at ambient conditions
- Poor solubility of the biocrude fraction in water should protect it against oxidation



C_{aq} is the molal solubility of oxygen in water[1]

1. D. Tromans, “Temperature and pressure dependent solubility of oxygen in water: A thermodynamic analysis,” *Hydrometallurgy*, vol. 48, no. 3, pp. 327–342, 1998, doi: 10.1016/s0304-386x(98)00007-3.

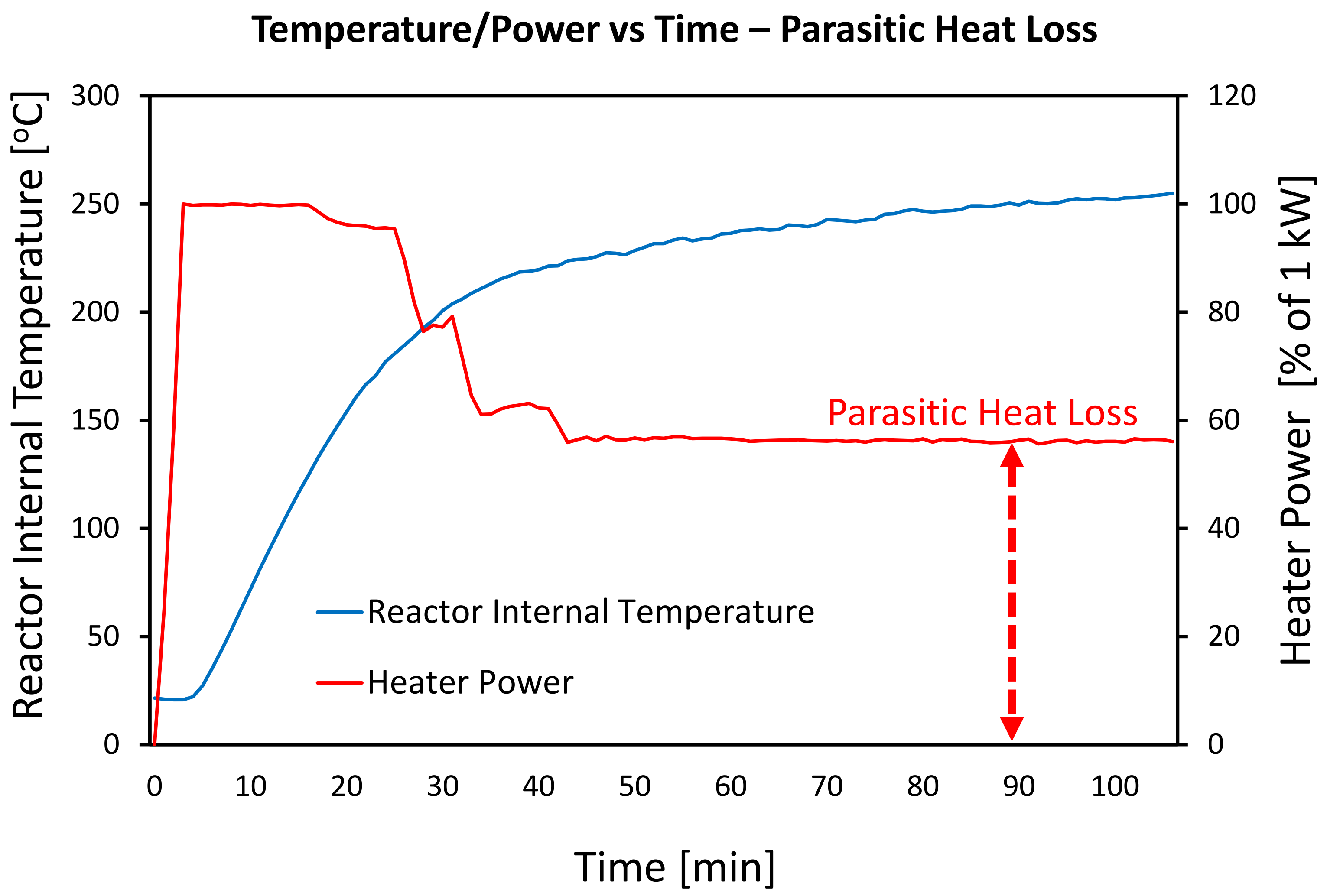
Experimental apparatus



Schematic of apparatus

Close-up of autoclave reactor

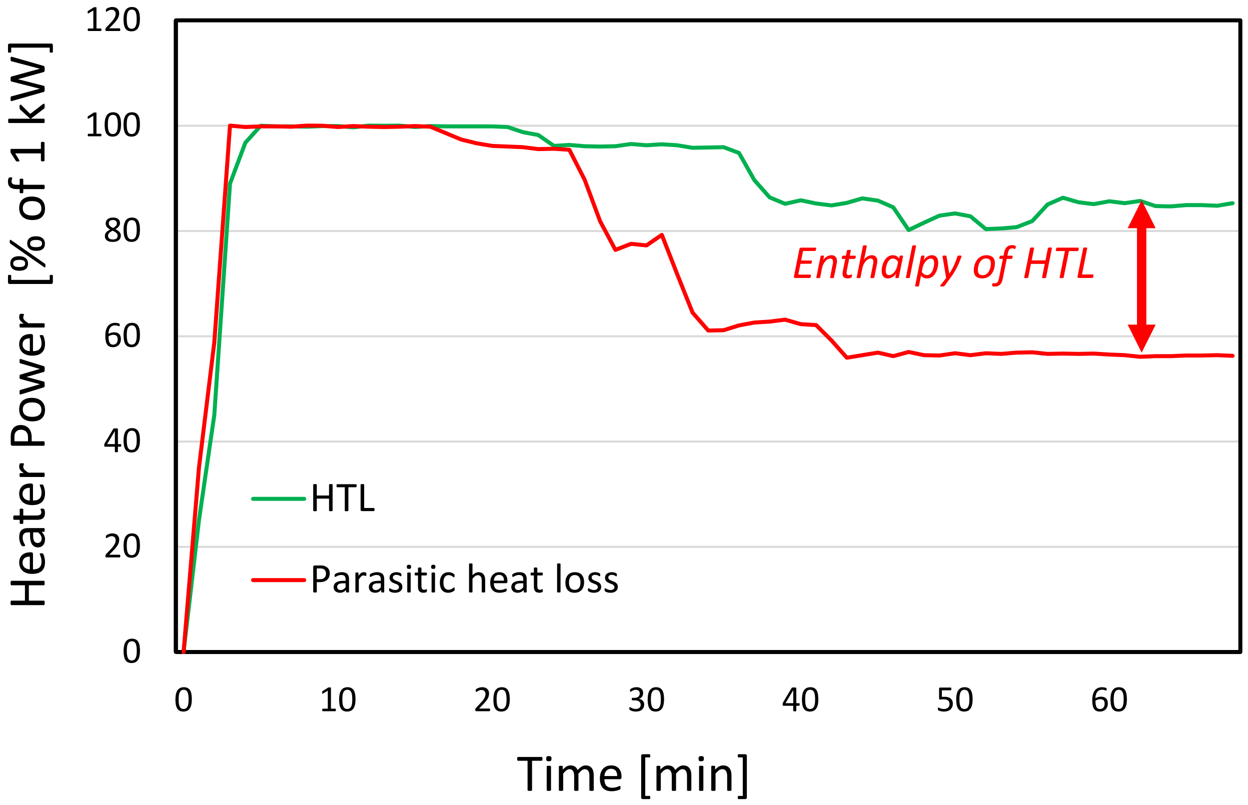
Parasitic heat loss was determined to be 0.56 kW



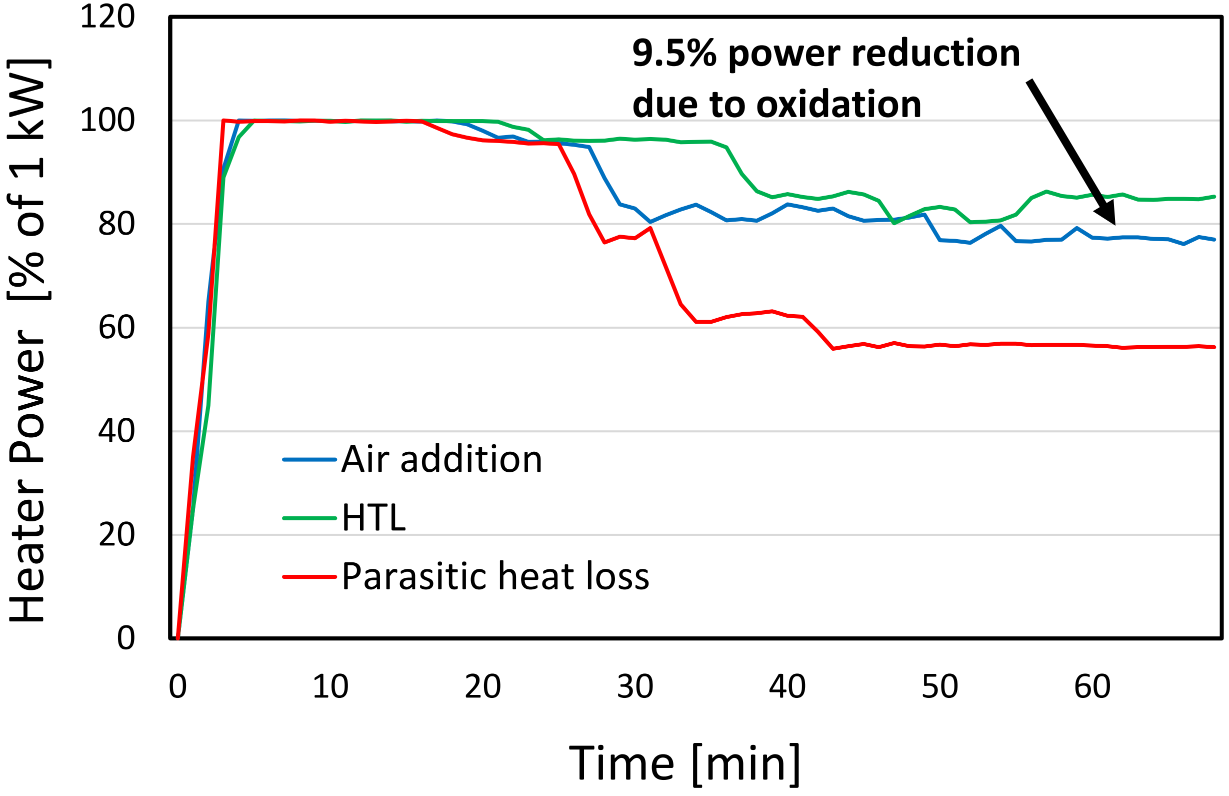
The addition of air leads to a decrease in power requirements for HTL

$$E_{supplied} = \int (P_{HTL} - P_{parasitic}) dt$$

Power curve describing the enthalpy of HTL



Power curve showing the effect of oxidation



Conclusion/Future Work

- In preliminary experiments, a 9.5% reduction in external energy demand was achieved through the injection of oxygen into the HTL reactor.
  - Equivalence ratio was uncertain due to inadequacies in the measurement of oxygen flow rate

- Future work includes:
  - Improvements in instrumentation to accurately measure equivalence ratio
  - Increase energy supplied via partial oxidation reactions
  - Characterize the products of autothermal HTL and compare to products from conventional HTL

Acknowledgements

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