Valorisation of hydrothermal liquefaction aqueous phase: Process modelling to quantify net energy recovery

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Hydrothermal liquefaction (HTL) is a promising technology for valorising mixed residual organic wastes to produce an energy-dense oil product, which can be refined into chemicals or liquid fuel products. The process is conducted in the presence of supercritical water (250 – 374°C, 4 – 22MPa) and hence eliminates the need for energy-extensive drying of wet biomass feedstocks. During the reaction, water acts both as an acid-base catalyst and solvent to depolymerise, deoxygenate and extract complex biomass compounds into a non-polar oil product which can be separated post-reaction. However, the resulting aqueous phase retains high concentrations of dissolved organic compounds, amounting to up to 50% of the initial carbon in the feedstock. Although some of this aqueous phase may be recycled to the front end of the process to push the reaction equilibrium towards oil production, excess water needs to be fully treated prior to discharge to the environment. Several studies have been published on the treatment of the HTL aqueous phase using different processes, including supercritical gasification, aqueous phase reforming (APR), algae cultivation or anaerobic digestion (AD), with varying success in achieving full removal of the aqueous phase carbon. Among these, AD is particularly attractive as it uses low temperatures, displays higher tolerance to the HTL aqueous phase than algae cultures, and can be integrated with existing industrial processes. For example, we previously studied the liquefaction of a non-digestible solid waste residue ('RDF') recovered from a wet waste recycling facility, before solubilised waste carbon is anaerobically digested into biogas (Okoligwe *et al*, 2022). The HTL reaction of this residue achieved similar carbon recoveries to the oil (32%), solid (31%) and aqueous phase (32%), together with low process gas production (6%), and hence offers a significant opportunity to increase overall energy recovery by using the aqueous phase as additional anaerobic digester feed.

A key consideration for any waste-to-energy process should be its energy recovery efficiency, denoting the energy content of the fuel products, divided by the total energy input to the system (energy content of the feed, natural gas, electricity etc.). HTL requires the heating and cooling of large amounts of water, together with downstream separation, fuel upgrading and water treatment processes. The production of biogas from the aqueous phase could increase the overall energy production from the system, but associated energy and processing costs need to be considered. Previous studies calculated energy yields of up to 85.2% for the HTL of forest residues when combined with supercritical water gasification to produce hydrogen (Magdeldin et al., 2017), while energy recovery from gasification of HTL aqueous phase was two times higher than that achieved using AD (Gerber Van Doren et al., 2017). However, energy requirements for gasification significantly exceed those for AD and involve additional sophisticated processing technologies.
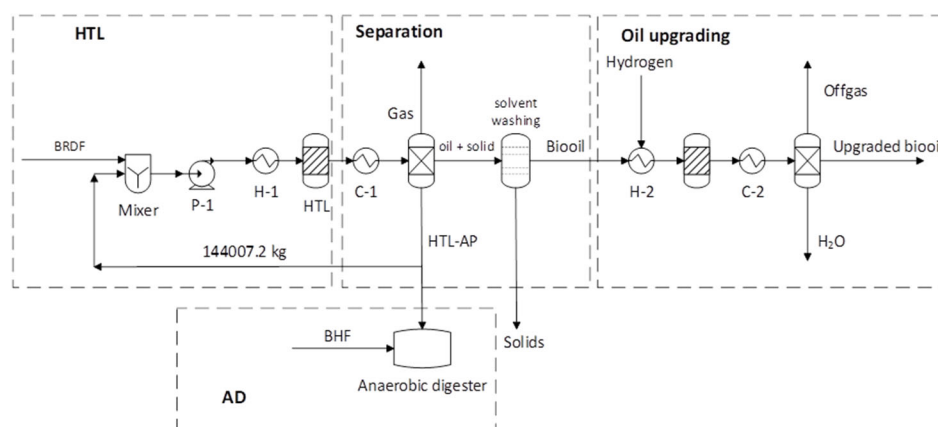

Figure 1. Schematic for integrated HTL-AD process

In this study, we test the aqueous phase from HTL of RDF as potential AD co-feed with the existing hydrolysed organic waste. Combining these results with our previous results of HTL of RDF and literature data for oil upgrading (Ma et al., 2019) we construct a whole-system model of the overall process, including the HTL reaction itself, post-reaction solvent extraction, oil-upgrading and anaerobic digestion, to determine the carbon and

energy recovery of the whole system (Figure 1). Finally, we will complete system optimisation and energy integration to determine the maximum net energy recovery.
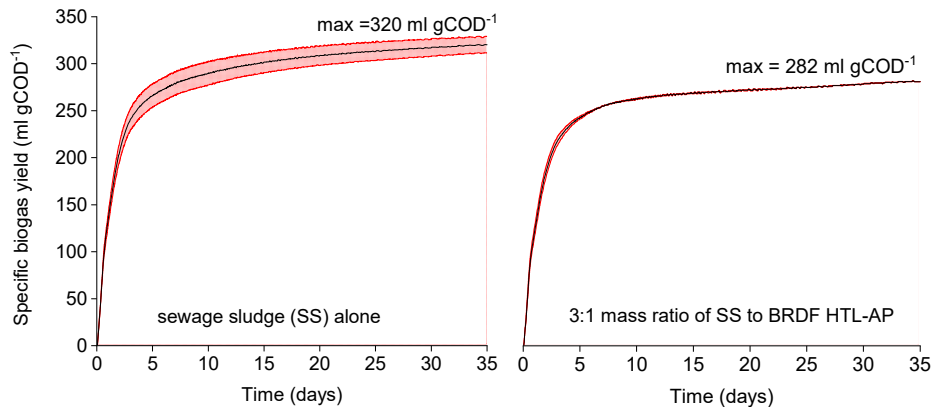

Figure 2. Biomethane yields for co-digestion of RDF aqueous phase with sewage sludge

Biomethane potential tests for mixtures of HTL aqueous phase with the baseline AD feed (sewage sludge) showed increasing levels of inhibition as the HTL aqueous phase ratio was increased (Figure 2). However, the reduction in biogas production (12%) was lower than the aqueous phase loading (25%), indicating utilisation (and hence degradation) of aqueous phase carbon compounds. The 3:1 loading used in these experiments is comparable to the estimated mass ratio of 2.7:1 of existing digester feed to aqueous phase produced, and hence the resulting biogas yields were implemented in our model. Combining HTL flows with the existing wet waste recycling facility for biogas production shows that the oil product represents 21.8% of the total carbon in the feedstock, more than twice the carbon converted into biogas (Figure 3a). This shows the significant potential for using HTL for valorising the non-digestable organic waste fraction and reducing residual solid waste from 58.6% (BRDF) to 20.8% (char).

Energy balance around the process showed an overall energy efficiency of 45.1% (33.4% when excluding biomethane product) comparable to previous literature findings (Figure 3b). However, the current process contains a non-optimised separation process based on a laboratory procedure (e.g. using inefficient solvent extraction for bio-oil recovery) and further increases in biogas production may be achieved after acclimatising AD culture to the aqueous phase culture.

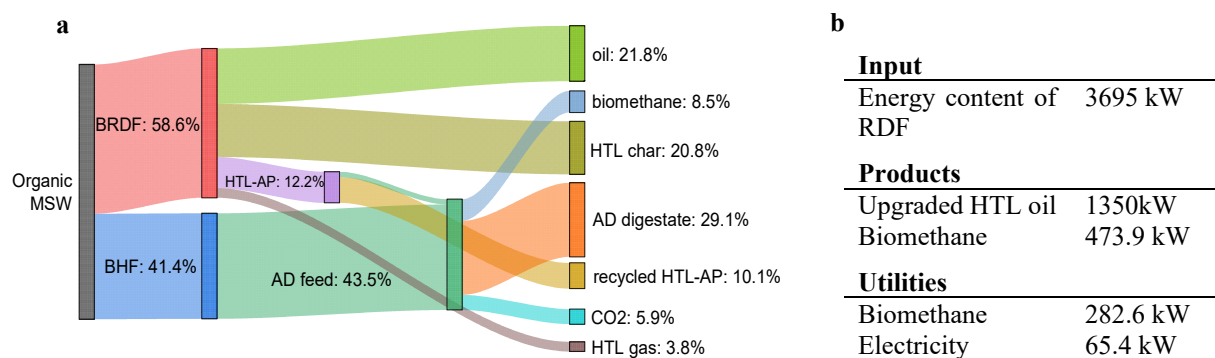| Input	
Energy content of RDF	3695 kW
Products	
Upgraded HTL oil	1350kW
Biomethane	473.9 kW
Utilities	
Biomethane	282.6 kW
Electricity	65.4 kW

Figure 3. a) Carbon distribution for integrated HTL-AD process, b) system energy balance after heat integration

Okoligwe, O., Radu, T., Leaper, M.C., Wagner, J.L., 2022. Characterization of municipal solid waste residues for hydrothermal liquefaction into liquid transportation fuels. Waste Manag. 140, 133–142.

Ma, X., Pang, S., Zhang, R., Xu, Q., 2019. Process simulation and economic evaluation of bio-oil two-stage hydrogenation production. Appl. Sci. 9.

Magdeldin, M., Kohl, T., Järvinen, M., 2017. Techno-economic assessment of the by-products contribution from non-catalytic hydrothermal liquefaction of lignocellulose residues. Energy 137, 679–695.

Gerber Van Doren, L., Posmanik, R., Bicalho, F.A., Tester, J.W., Sills, D.L., 2017. Prospects for energy recovery during hydrothermal and biological processing of waste biomass. Bioresour. Technol. 225, 67–74.