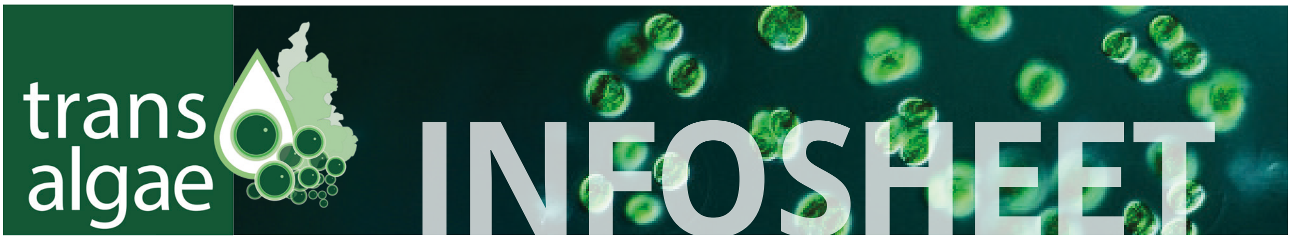

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Hydrothermal Liquefaction, HTL

Hydrothermal liquefaction (HTL) is a feasible technique to treat large amount of wet algae biomass or other biomass feedstocks and produce a biocrude similar to fossil oil. It can then be further processed an used as a gasoline or diesel drop-in fuel. In TransAlgae, HTL of both micro- and macroalgae will be tested.

HOW DOES HTL WORKS?

As temperature of water increases under pressure (see Fig. 1), water becomes more reactive and can function as solvent, catalyst and reactant to hydrolyze carbon resources such as coal, lignin and algal biomass near the critical point (374°C, 22.1 MPa).

PRODUCTS AND WASTE STREAMS FROM HTL

The reactions taking place during HTL are hydrolysis and repolymerization, which forms:

- an energy-dense biocrude oil
- a nutrient-rich aqueous-phase
- gas products composed primarily of CO_2
- solid residue or biochar

The conversion of algae to biocrude is shown in Fig. 2. Biocrude mainly consists of unsaturated fatty acids, ketones, aldehydes and various hydrocarbons. In the process, up to 85% of the oxygen contained in biomass can be removed as CO_2 and water. Thus, only about 10% oxygen remains in the biocrude which leads to a high heating value of 35MJ/kg (fossil diesel 42MJ/kg) in comparison to pyrolysis oil with oxygen content 38% and heating value 18MJ/kg. A further process of hydrotreatment and hydrocracking can easily remove the 10% oxygen completely, and finally a drop-in fuel, gasoline or diesel can be produced.

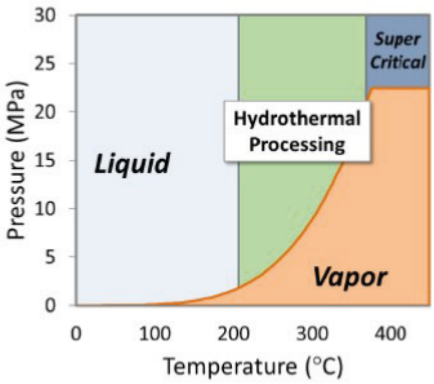

Fig. 1. Water two phase diagram for hydrothermal liquefaction.

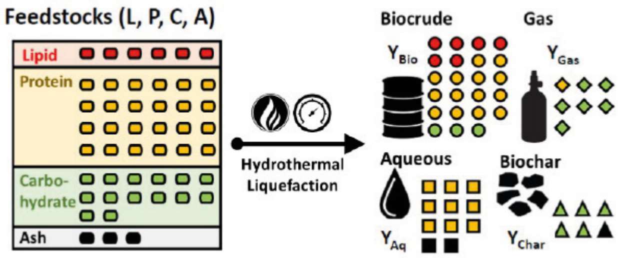

Fig. 2. Hydrothermal conversion of algae to biocrude. The picture shows where different components in the feedstock ends up after a HTL-process.

WHY ALGAE HTL?

Lipid extraction is the most common way to isolate lipids from algae biomass. However, algae with high lipid content are commonly associated with slow growth rates and low biomass productivities due to requirement on nutrient limitation.

For algae with a relatively low lipid content, HTL is a suitable method. HTL processing is applied to whole algae, not just lipid extracts, and as a result higher biodiesel yield have been demonstrated.

The algae feedstock does not need to be grown under strictly controlled conditions with the intent to maximize the lipid content. A wider range of algae growth scenarios can be considered, including wastewater treatment environment.

Compared to lipid extraction, the energy efficiency can be increased by 50%, freshwater consumption can be reduced by at least 33% and N and P demand by 44%.

In short why HTL on algae is interesting:

- All components can be converted to biocrude with up to 80% yield
- No drying and less dewatering for feedstock
- Energy-dense biocrude to fuels and chemicals
- Nutrient recovery from aqueous phase recycles nitrogen, phosphorus, iron, calcium, magnesium and potassium etc.

FACTORS AFFECTING BIODIESEL YIELD

The HTL product is dependent on both the algal biochemical composition and the reactor operation parameters. Feedstocks richer in lipids (L) give higher biocrude-oil yields than proteins (P) and carbohydrates (C) as expressed in equations below at the temperatures of 280°C and 320°C:

$$Bio\text{-}oil\ Yield\ (wt\%)_{280} = 0.90 \times L + 0.22 \times C + 0.32 \times P$$

$$Bio\text{-}oil\ Yield\ (wt\%)_{320} = 0.96 \times L + 0.30 \times C + 0.43 \times P$$

Temperature

Biocrude is formed in the temperature range of 200-420°C. The yield increases at first with increasing temperature and levels off or decreases with further temperature increase after an optimum temperature between 300 and 370°C due to the competition of two reactions involved in the liquefaction: hydrolysis and repolymerization.

Yield

Biocrude yield decreases at a prolonged residence time, which could be explained by the cracking of biooil or intermediate products to gas and the formation of chars by condensation, cyclization and repolymerization.

Concentration

For microalgae, the algae-to-water ratio can be in the range of 5 to 30%. Too high ratio may limit hydrolysis reaction and reduces the conversion efficiency, and too low ratio is not economic for waste water treatment. The macroalgae needs more extensive processing for size reduction to achieve a pumpable slurry for continuous flow processing. A low concentration macroalgae results in lower biocrude yield due to water solubility of the biocrude.

Heating rate

Slow heating rates usually lead to the formation of char due to secondary reaction. Fast heating rates might increase biocrude yield dramatically up to 80%. This needs more researches to confirm.

pH value

The initial pH plays an important role in the biocrude yield and composition, and in the change of the reaction pathways during HTL process. The final pH of liquefaction is always acidic whether the starting pH is either alkaline or acidic.

Stabilizer

Reducing gas, H_2 and CO, or hydrogen donor such as tetralin, formic acid or organic solvent such as ethanol can be used to stabilize the fragmented products of liquefaction and consequently prevent the residue formation, increase biocrude yield and improve product properties.

Solvent

Water is the most common solvent as it is environmentally benign and the least expensive. Other organic solvents such as methanol and ethanol can also be used, which readily dissolve high molecular products due to lower dielectric constant, and thus improves biocrude yield and composition.

Catalyst

The role of catalyst is mainly to suppress the formation of char, while enhancing the yield of liquid products. Homogeneous catalysts such as Na_2CO_3, KOH and heterogeneous catalyst such as Pt, Ru, zeolite are often used in literature.

ECONOMIC

HTL uses biomass more efficiently but has higher emissions and nutrient requirement as compared to conventional algae oil extraction and biodiesel production pathway.
The feedstock cost is the most significant factor, biodiesel yield is a key variable, and plant scale, feedstock flexibility and internal rate of return are important in the calculation of HTL biodiesel production cost.
Most studies in the literature have been conducted in small scale batch reactors with slow heating rates and long residence times. In order for HTL to be more economically feasible and chemically controllable, continuous reactor system is required for algae HTL commercialization.

CONCLUSION

HTL is today at an early-stage of development, a very promising technology to convert wet biomass such as algae into biodiesel with much higher yield and low cost as compared to algae extraction pathway where only lipid component can be used for biodiesel production.
Compared to pyrolysis, HTL has the potential for producing biooils with better product properties, less oxygen content, much higher heating value and a range of chemicals, but a significant amount of nitrogen is observed in the biocrude.
The HTL product properties and yield depend on algae biochemical composition, operating temperature, biomass-water ratio, residence time, pH value, heating rate, reducing gas, catalyst, reactor design etc..
For commercialization of HTL, continuous reactor system is required. The cost of the feedstock and biodiesel yield are the critical barrier for commercialization. Recycle of the nutrients is a key to sustainable operation.

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