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Photofuel - Biocatalytic solar fuels for sustainable mobility in Europe

Deliverable D3.6

Identification of optimal strategies for waste utilisation and recycle

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Summary

Having reviewed the full range of biochemical and thermochemical processes, evaluating harvesting, pre-treatment and operational costs as well as product yields, we identified hydrothermal liquefaction (HTL) as the most promising method for processing wastewater into biofuel. HTL is a process that converts algae into biocrude, which can then be upgraded into sustainable third generation biofuels by hydrotreatment. Recently, there has numerous studies published on the HTL of microalgae; however, most are conceptual or conducted in batch reactors, which are not applicable to large-scale industrial production.

Some of the notable benefits to using HTL include; the ability to process wastewater continuously rather than in batch; processing wet biomass thereby removing costs associated with dewatering and drying; destroying all GMM material during the process; using water as the catalyst; and recycling nutrient present within the aqueous phase. Having identified HTL as the best wastewater process, we conducted a series of experiments with the aim to i), assemble and run a continous flow-through HTL process on algal feeds ii), determine the effect of temperature and residence time (RT) on product yield and composition and iii), perform an ASPEN model simulation to evaluate the energy recovery and define the operating conditions for optimised energy recovery.

We investigated HTL for the microalgae *Chlamydomonas reinhardtii*, *Nannochloropsis* sp. and *Scenedesmus almeriensis*; using an algal feed concentration of 0.4, 1.5 and 0.8 wt%, respectively. Unfortunately, as the HTL continuous flow-through reactor was newly setup, we had no prior knowledge of optimal biomass loads; as such the biocrude yields for *C. reinhardtii* were below a detectable level and are therefore not present here. In addition, due to insufficient biomass available for the other project strains, we used *Nannochloropsis* sp. and *Scenedesmus almeriensis* cultures for HTL processing. We included a co-solvent, cyclohexane (10% of the total flowrate), to aid in oil extraction, and which also helped prevent algal blockages in the backpressure regulator. We performed a series of experiments using a reactor temperature ranging between 300-350 °C, with a RT of 20-60 s. After drying, the biocrude was analysed with thermogravimetry (TGA) and chromatography, while the aqueous phase was analysed with TOC to calculate yields.

A higher reactor temperature improved the boiling point distribution, making biocrude more comparable to crude oil (TGA). In addition, different compositions were obtained with cyclisation occuring at temperatures above 350°C (GC-MS). The maximum biocrude yield (26%) for *S. almeriensis* was obtained at 350 °C with a 30 s RT. The maximum biocrude yield (38%) for *Nannochloropsis* sp. was obtained at 380 °C with the same RT. Under these process conditions, and with a flowrate of 2 mL/min, steady-state biocrude yield was achieved after 10 minutes. Char production was constant with temperature, but increased with RT; an observation, which underlines the advantage of a faster, flow-through HTL system over batch runs, which would otherwise lead to a great fraction of char. ASPEN simulations show that low temperature decreases the energy recovery of biocrude yield, yet increases the energy recovery from the waste water.

Compared to other thermal conversion processes, such as pyrolysis, HTL has no drying costs. This is highlighted by the biocrude produced via HTL (39 MJ/kg) having a higher High Heating Value (HHV) compared to pyrolysis oil (33.5 MJ/kg). We found that the continuous HTL system was most efficient when combining a high heating rate within a short reaction time, underlining the need for inexpensive continuous flow-through processing.

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