

Hydrothermal Liquefaction of microalgae targeting bio-crude oil production

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Microalgae hydrothermal liquefaction (HTL) emerges as a cutting-edge approach to sustainable biofuel production, offering a promising solution to meet increasing global energy demands while addressing environmental issues. This advanced technology involves exposing microalgae biomass to elevated temperatures and pressures in a water-rich environment, leading to the conversion of the algae into a versatile liquid biofuel. Microalgae, minute photosynthetic organisms known for their adaptability and rapid lipid accumulation, prove to be an ideal raw material for HTL as they are cultivated in an aqueous environment. During the process, intricate organic compounds within the microalgae cells undergo thermochemical reactions, resulting in a liquid biocrude that can be refined into biofuels like biodiesel and renewable diesel. The appeal of microalgae HTL lies in its efficiency, scalability, and potential to simultaneously tackle energy security and environmental sustainability challenges, contributing to the pursuit of a greener and more sustainable energy landscape. So, in the present study, the hydrothermal liquefaction of two different microalgae strains (*Chlorella Vulgaris* and *Chlorella Sorokiniana*) was examined.

The research conducted a comparative analysis of the Hydrothermal Liquefaction (HTL) process on the two microalgae strains, focusing on both bio-crude oil yield and properties. The initial phase of the study involved optimizing the process for each biomass type to achieve maximum oil production. This optimization was carried out by assessing two key parameters: temperature and residence time. Temperature variations from 280° to 350°C and residence times ranging from 5 to 60 minutes were examined. Also, in order to examine the potential synergistic effect of the two parameters, a parameter called Severity was used from literature. The experimental procedure took place at the Centre for Research & Technology Hellas (CERTH) using a bench-top, batch, high-pressure stirred reactor with a 250 mL internal vessel volume (Parr 4576A). The reactor features a J-type thermowell for heating and a U-type cooling coil for temperature control. Each run involved loading 10g of feedstock (at a 1/10 biomass/solvent ratio) and 100 mL of deionized water into the reactor, followed by sealing and purging with compressed nitrogen to eliminate inert air. The reactor inlets were then pressurized to 30bar with nitrogen to establish an inert atmosphere, heated according to specified conditions, and subsequently cooled to ambient temperature.

Hydrothermal liquefaction of biomass results in solid, liquid, and gas products due to biomass decomposition. During reactor decompression, a gas sample is collected in a tedlar bag for GC-FID analysis. Solid and liquid product collection begins with vacuum filtration of the mixture in a Buchner funnel equipped with filter paper. The liquid stream collected represents the aqueous phase product, containing the applied solvent and liquefied water-soluble organic molecules. The remaining viscous mixture on the filter paper is rinsed with 300-500 mL of acetone to separate the bio-crude oil from solids (solid residue), which is collected in the Buchner flask. The remaining solids are dried overnight and weighed, while the organic mixture with acetone undergoes rotary evaporation at 40°C under reduced pressure to obtain the final bio-crude oil product and extract the used acetone, as illustrated in the accompanying figure 1.

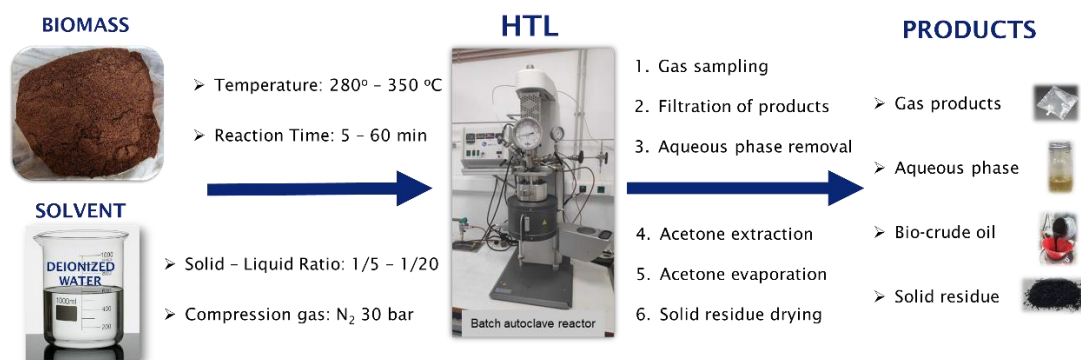


Figure 1. Hydrothermal liquefaction process methodology

According to the results regarding the *Chlorella Vulgaris*, the bio-crude oil yield is increased as the Severity rises to $\text{Log}(R_0) = 8.5$. This can be attributed to the higher rate of liquefaction of lipids and proteins. However, as the severity exceeds the value of 8.5, it seems that secondary cracking reactions are converting the liquid molecules into lighter, gaseous ones. The maximum obtain bio-crude oil yield was $\sim 32.5\text{wt}\%$ at 350°C and 15min. On the other hand, *Chlorella Sorokiniana* trendline was different. As the second biomass was consisted of more carbohydrates and extractives the overall bio-crude oil yield was lower and appeared to alter at two steps. At low severity conditions the yield is relatively low. However, as the temperature gets higher, the oil yield is also higher, but it is stable around values between 7 – 8. The maximum yield was observed at 350°C and 15min but the yield was $28\text{wt}\%$. So, the fact that the lipid was lower seems to decrease the bio-crude oil yield. Regarding the other products, solid residue and aqueous phase product yields tend to decrease as the severity rises which means that they are converted to lighter products as the biomass gets degraded. On the other hand, gas product is increasing along with temperature and residence time increase as the HTL process eventually leads to production of light hydrocarbons.

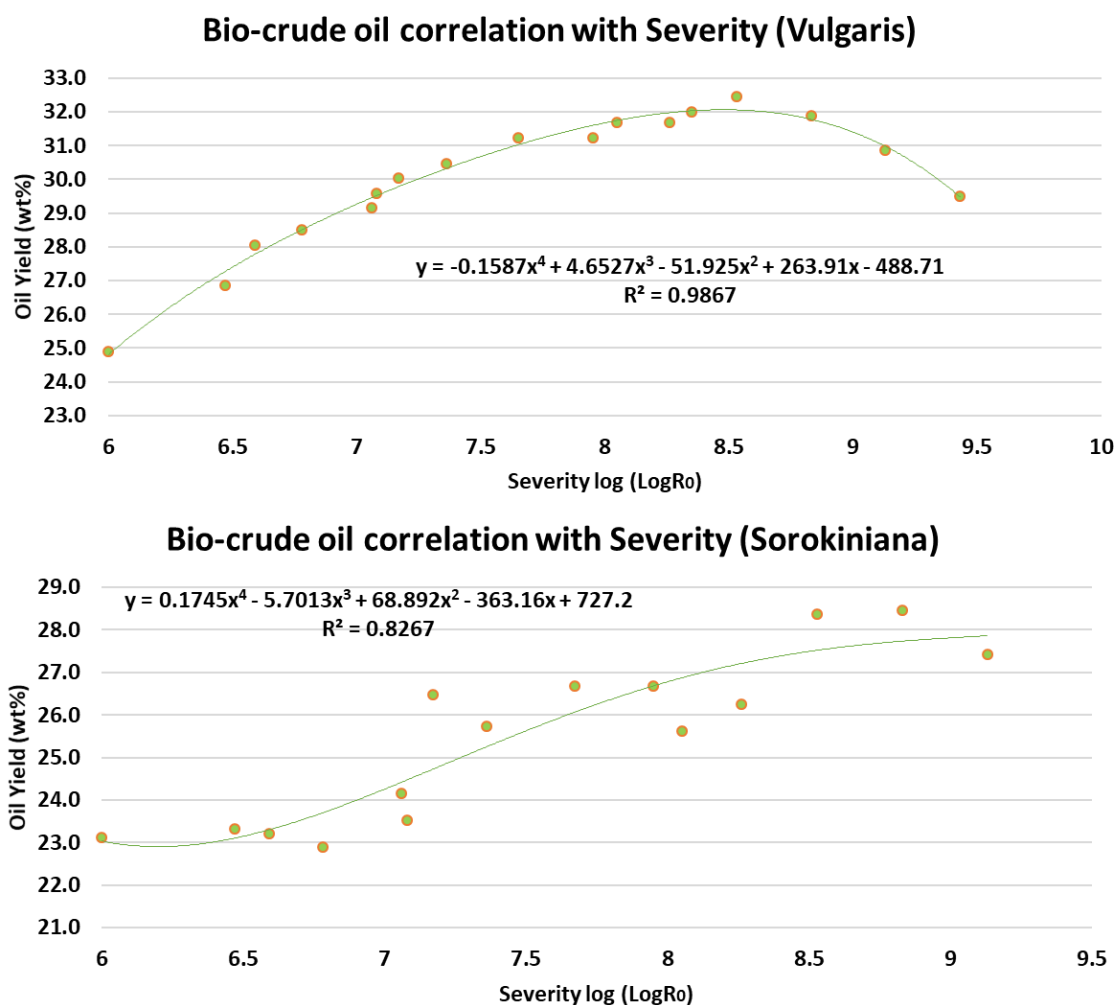


Figure 2. Bio-crude oil yield correlation with Severity factor