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Hydrothermal Liquefaction of Microalgae for the Production of Biocrude and Value-added Chemicals

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Hydrothermal liquefaction (HTL) is a thermochemical process used to convert biomass with high moisture content, like lignocellulosic material and aquatic biomass, into biocrude and value-added chemicals. It occurs in water subcritical conditions. The main advantages in relation to other thermochemical processes is the possibility of using wet biomass, avoiding the high cost of drying processes. The microalgae tested grew in a fertilizer industry effluent. Growing microalgae has a significant cost in the production process of liquid biofuels. Thus, the use of industrial effluents has economic and environmental advantages. Effluents from fertilizers industries are rich in different forms of nitrogen that can be assimilated by growing microalgae. HTL is dependent on experimental conditions, namely temperature, reaction time and biomass/water ratio. Reaction temperatures from 300 to 350 °C and biomass ratio from 1/5 to 1/20 were studied. Four product fractions were obtained: gases, aqueous and organic (biocrude) fractions and solid. All these fractions were characterized. The main components in biocrude were long chain hydrocarbons and aromatic ring type structures like phenols or nitrogen heterocyclics such as indole or pyrrole. The increases in the reaction temperature decreased the water-soluble products, increasing the other products yields. However, the biocrude yield increased with temperature until 325 ºC, and then decreased slightly at 350 ºC (from 56 % to 48 %, dry basis). This paper will analyse the effect of operation conditions on biocrude yield and composition to select the best conditions for microalgae conversion into biofuels or valuable chemicals.

1. Introduction

Reducing GHG (greenhouse gas) emissions in the transport sector can be achieved without significant changes to existing infrastructure by increasing the use of renewable resources in current fuel production. In this way, the increased use of biofuels has the potential to help solve the environmental and sustainability problems associated with the current use of petroleum-based fuels. Among the most promising biofuels are second-generation biofuels, produced from lignocellulosic biomass, woody crops, agricultural residues and waste, and third-generation biofuels, produced from non-terrestrial organisms such as algae and yeast (Kargbo et al., 2021). These new generation biofuels do not have the disadvantages associated with the first generation and are, therefore, the most favourable for future applications as a liquid fuel for transport sector. Algae are one of the most promising third-generation raw materials. The term “algae” describes a diverse group of aquatic photosynthetic organisms that includes more than 72,500 species. Larger multicellular organisms are called macroalgae and make up about 20 % of all algae species. The remaining 80 % are known as microalgae, that is, single-celled algae species (Brindhadevi et al., 2021). Recently, interest in algal biomass production has grown in Europe. According to the EU Science Hub, various macro- and microalgae are currently produced in more than 144 facilities located in 15 EU Member States.
HTL technology takes advantage of significant differences in the physical properties of water under subcritical conditions. Essentially, the main advantages of HTL can be summarized as follows. it converts biomasses with high moisture contents, avoiding the use of dehydration and drying procedures and, therefore, is a technology especially suitable for microalgae. It minimizes unwanted side reactions as the solvent dilutes the concentration

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of products at relatively low temperatures; typically, occurs at lower temperatures than fast pyrolysis resulting in higher energy efficiency. It allows for total biomass processing (not just lipids, for example). It results, in addition to other products, in an aqueous phase from which essential nutrients for microalgae growth can be separated and recycled. Usually, bio-oil obtained from microalgae HTL has higher nitrogen (5 – 8 %) and oxygen (10 – 15 %) contents compared to crude oil (Lu et al., 2021). This chemical profile leads to bio-oils having generally negative combustible properties, including high acidity, humidity and corrosivity, poor combustion performance and low H/C ratio, which makes their direct application as a liquid fuel for transport difficult (diesel and aviation fuel). Therefore, upgrading bio-oil is a necessary step to overcome these limitations and improve its stability and fuel properties. The most used upgrading techniques include phase separation (to reduce the water content), hydrotreatment (to reduce the viscosity, nitrogen, and sulphur content), hydrodeoxygenation (to reduce the oxygen content), esterification (to reduce the acidity), water and catalytic cracking (to improve the H/C ratio and cetane number) and emulsification (to prevent phase separation) (Kazemi et al., 2019). HTL is an emerging technology for the liquefaction of biomass that uses hot compressed water at high temperatures and pressures, between 250 – 380 °C and 5 – 20 MPa, respectively (Mathimani and Mallick, 2019). This hydrothermal processing involves a series of complex, multi-step chemical reactions that are driven by the combined action of thermal energy, high pressure, and the hydrolytic attack on the most susceptible bonds of the biomolecules that make up the biomass. This conversion results in a series of products, including a hydrochar, an aqueous phase, a gas phase, and an oil phase analogous to crude oil. In addition to bio-oil, HTL's products also include gases, solids and an aqueous phase and the valorisation of these by-products can represent a perfect combination with the concept of circular bioeconomy. For example, the gas phase is mostly composed of CO_2 and can be used to grow microalgae. The solid phase, also known as hydrochar, can be incorporated into asphalt or mortar formulations, as an adsorbent for gas or wastewater remediation or as a biofertilizer., The water-soluble products (aqueous phase) mainly include organic acids and nutrients and can be recirculated in the HTL process itself, used as a microalgae growth medium or even as a substrate in anaerobic digestion (Vieira de Mendonça et al., 2021). Two of the parameters that most influence the HTL process are the reaction temperature and the water/biomass ratio. The main aim of this work was to stablish the values of these two parameters to increase the biocrude yields and its quality. The novelty of this study is to use real industrial effluents from a fertilizer industry, decreasing the cost in the production process of liquid biofuels.

2. Materials and methods

The HTL tests were performed in 0.16 L batch reactors, built in Hastelloy C276 by Parr Instruments, with a controller device connected to both the pressure gauge and the thermocouple. Firstly, the feedstock was placed inside the reactor and closed, afterwards it was cleaned with N_2 to maintain an inert atmosphere inside the reactor. The reactor was heated by an oven that has an oscillation system to provide agitation. The two operation parameters studied were: temperature, and biomass/water ratio. The temperatures tested were, 300 ºC, 325 ºC, and 350 ºC. The biomass/water ratios were 1/20, 1/10, and 1/5 (w/w), which are equivalent to solids concentrations of 4.8 %, 9.1 % and 16.6 % (w/w). The reactor always operated with 77 g of material (biomass+water). So, when the biomass/water ratio was 1/20, 3.7 g of biomass and 73.3 g of water were added; while for the 1/5 ratio, 12.8 g of biomass and 64.2 g of water were added. Before the beginning of each test, the autoclave was purged and then pressurized with nitrogen gas (N_2), to guarantee that the operating pressure was within the desired range. To ensure that the pressure reaches the needed value at the test temperature (130 - 170 bar), initial pressures were determined from preliminary tests. The higher the test temperature, the lower the initial pressure since pressure increase as a function of temperature. However, the increase in pressure as a function of temperature does not occur linearly. At the end of each test, the reactor was cooled in an ice bath until it reached room temperature for the collection of the products. After cooling, the gas products were measured and collected for the GC-FID-TCD (Gas chromatography – Flame Ionization Detector - Thermal Conductivity Detector) analysis. Then the reactor was opened, and the products were separated accordingly with process presented in Figure. 1. The bio-oil was characterized by GC/MS (Gas chromatography – Mass Spectrometry). The tests were carried out in a completely randomized design (CRD), with two repetitions for each treatment. The feedstock used was a microalgae grown in a fertilizer industry effluent. Growing microalgae has a significant cost in the production process of liquid biofuels. Thus, the use of industrial effluents has economic and environmental advantages. Effluents from fertilizers industries are rich in different forms of nitrogen that can be assimilated by microalgae. The characterization of the feedstock is presented in Table 1. Different HTL tests were performed to assess the influence of the biomass/water ratio and of the reaction temperature in the product yields and quality. The reaction time was always settled to 30 minutes. In Table 2 are listed the tests performed.

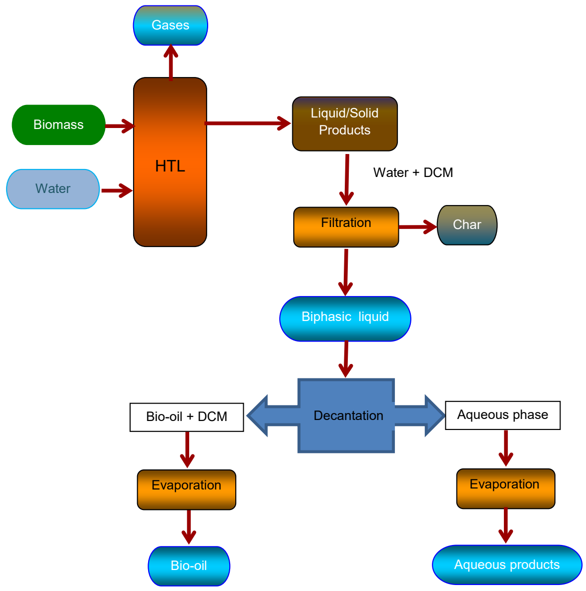

Figure 1: Scheme of the process

Table 1: Microalgae characterization

	Results		Method
	As received	Dry base (105ºC)	
Moisture % (w/w)	89.1±0.8		EN ISO 18134-1:2015
Ashes % (w/w)	2.7±0.3	24.5±1.8	ISO 18122:2015
Volatile matter % (w/w)	7.4±0.6	68.4±0.5	ISO 18123:2015
Chlorine % (w/w) Cl	<0.01	<0.11	ISO 16994
Sulphur % (w/w) S	0.07	0.62	ISO 16994
Carbon % (w/w) C	4.6	42.4	ISO 16948
Hydrogen % (w/w) H	0.48	4.4	ISO 16948
Nitrogen % (w/w) N	0.83	7.7	ISO 16948
HHV % (kJ/kg) (High Heating Value)	$2.1x10^3$	$19.4x10^3$	ISO 18125
LHV % (kJ/kg) (Low Heating Value)		$18.4x10^3$	ISO 18125

Table 2: Experimental conditions used in the HTL experimental tests

	Experimental parameters		
Test	Temperature (ºC)	biomass/water ratio (w/w)	Pressure at room temperature (bar)
1	300	1/10	49
2	325	1/10	38
3	350	1/10	7
4	325	1/5	38
5	325	1/20	38

3. Results and discussion

3.1 Product yields

The first experimental parameter assessed was the reaction temperature. The influence of temperature on the bio-oil yield of the HTL and of other thermochemical processes, relates to the reactions that dominate in a certain range of temperatures. In the HTL process the ionic characteristics of water vary with temperature, and so, a series of reactions are favored in different temperature ranges (Couto et al., 2018). This parameter was varied between 300 ºC and 350 ºC. When the temperature reached the value previously settled the reactor was kept at that temperature for 30 minutes before being rapidly cooled down. The biomass/water ratio was maintained at 1/10. The four products yield was determined to enable the identification of losses in the separation process. These losses were relatively low and are mainly due to the stage of solvent evaporation because some volatile compounds can be lost (Couto et al., 2018).
As shown in Figure 2, at the lowest temperature tested the product produced at a higher percentage was the water-soluble products, but this tendency has changed at higher temperatures, being the bio-oil the one produced at higher amounts. So, with the increase in the reaction temperature an increase in the gas and solid fractions and a decrease in the aqueous phase were observed. The bio-oil yield increased with temperature until 325 ºC, and then decreased slightly at 350 ºC (from 56 % to 48 %, dry basis). Similar results were obtained in other studies of micro and microalgae. Chen et al. (2014) observed similar tendency when comparing the results obtained at 300 ºC and 320 ºC for the HTL of biomass cultivated in effluent.

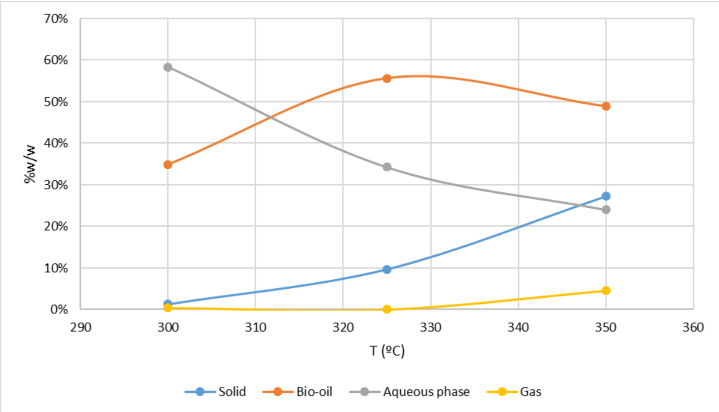

Figure 2: Effect of reaction temperature in product yields (reaction time=30 min; biomass/water ratio= 1/10).

The high increase of the solid fraction with the rise of temperature seems to be at the expense of the aqueous phase. Probably some minerals, only can lead to the formation of compounds soluble in the aqueous phase at lower temperatures, at higher ones most mineral matter of initial biomass remained in the solid phase. Higher temperatures also appear to favor cracking to produce gases and repolymerization reactions to heavy bio-crude oil and solid compounds. The gas fraction increased with the raise of the temperature which seems to indicate that higher temperatures promote the degradation of the biocrude molecules into more volatile compounds, with lower molecular weight that are gases at PTN (Barreiro et al., 2013)). For all the temperatures used, the gas yield was lower than 5 % w/w, and it was composed mainly of CO_2, being the rest small quantities of CH_4, H_2, CO and C_2–C_4 hydrocarbons. The yield of the water-soluble products decreased with the increase of temperature. This reduction is reported in other studies, both for macroalgae and microalgae biomass (Couto et al., 2018).
The other parameter studied was the biomass/water ratio. Three different ratios were used, 1/5, 1/10, and 1/20 (w/w) which corresponded to biomass concentrations of 16.6 %, 9.1 %, and 4.8 %, respectively. The relationship between the biomass/water ratio and bio-oil yield is not clear as no defined tendencies were observed (Figure 3). In the HTL process, the water acts as a catalyst and/or reagent so, it was expected that high concentrations of biomass could compromise the bio-oil production. In the literature, a wide range of results are presented. The differences in the results might be related to the use of biomasses with different compositions in each of the studies, which can lead to different behavior during HTL. However, Biller and Ross (2011) obtained approximately 40 % of bio-oil yields in the HTL of Chlorella sp. and Nannochloropsis sp., using 10 % of biomass concentration, which is near to the value obtained in this study. The solid increased and aqueous phase decreased significantly with the rise of biomass concentration. Probably the amount of water was not enough to promote efficient biomass degradation.

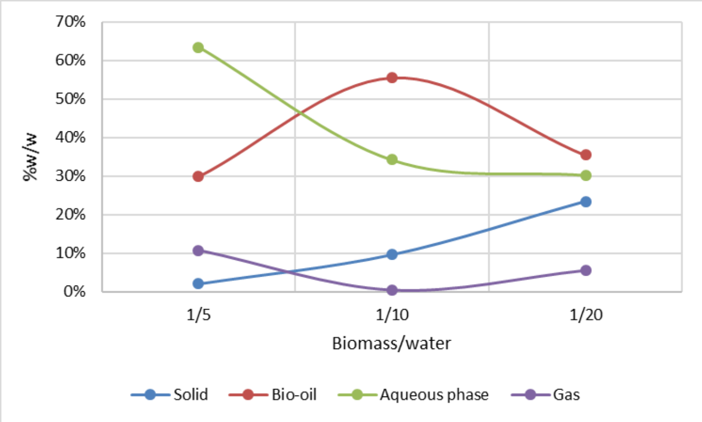

Figure 3: Effect of Biomass/water ratio on product yields (reaction temperature=325ºC; reaction time=30 min)

3.2 Bio-liquid composition

The bio-oil was characterized. Its composition is presented in Figure 4 and Figure 5. It was verified that it is a complex mixture of compounds containing water, hydrocarbons, nitrogen, and oxygenated compounds.

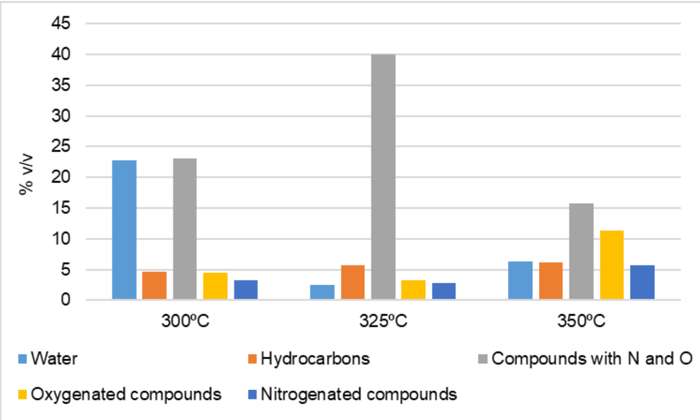

Figure 4: Effect of reaction temperature on bio-oil composition (30 min reaction time; 1/10 biomass/water ratio)

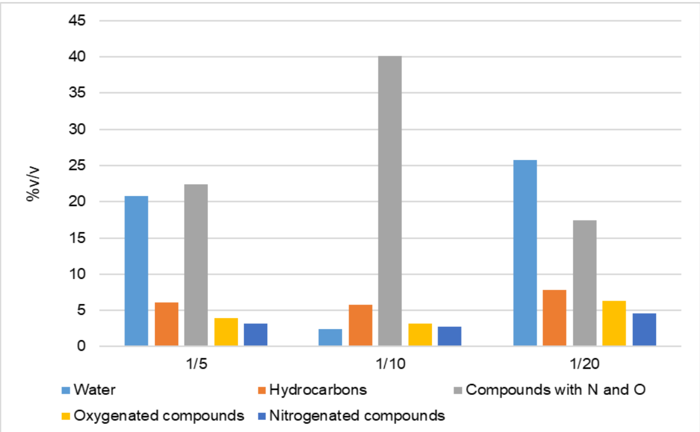

Figure 5: Effect of biomass/water ratio on bio-oil composition (325ºC reaction temperature; 30 min reaction time)

The N balance shows that regardless of the operating conditions used, its content in the bio-oil is significant. These results are reported in other research studies and is the main challenge of the HTL of microalgae. The effect of temperature variation was not clear. Unfortunately, the hydrocarbons concentration was low, of about 5 %, in all the conditions tested, which indicates that further upgrade is needed. The high levels of protein in the biomass justify these results. The high content of water in the bio-oil at the lowest temperature used can be explained by the difficulty of separation of the water of the bio-oil due to its high viscosity. Regarding the effect of biomass/water ratio in liquid composition, the results obtained were similar except for water and compounds with N and O, in which water concentration was much lower and much higher (compounds with N and O) in the tests with 1/10 biomass ratio.

4. Conclusions

HTL is an emerging technology for the liquefaction of microalgae. The product yield and quality depend on the experimental parameters used in the process. The increase in the reaction temperature decreased the water-soluble products, increasing the other products yields. However, the bio-oil yield increased with temperature until 325 ºC, and then decreased slightly at 350 ºC (from 56 % to 48 %, dry basis). Regarding the relationship between the biomass/water ratio and biocrude yield, it was observed a significant increase in the amount of biocrude produced when this ratio was changed from 1/5 to 1/10 but then decreased again. The higher amount observed was of compounds with nitrogen and oxygen The highest value of these compounds (40 %) was obtained at 325 ºC and with a biomass/water ratio of 1/10 (w/w). The N balance shows that regardless the operating conditions used, its content in the bio-oil is significant. Unfortunately, the hydrocarbons concentration was low, of about 5 %, in all the conditions tested, which indicates that further upgrade is needed.

Acknowledgments

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