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Nannochloropsis Hydrothermal Carbonization for Hydrochar Production

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Hydrothermal carbonization (HTC) is a hydrothermal treatment that converts various types of high moisture biomass into hydrochar. Several operational parameters must be considered, such as temperature, reaction time, biomass/water ratio and initial pressure, which ultimately affect the performance of the process. One of the main advantages of HTC is the possibility to use wet feedstock, which promotes the decrease of the operational energy cost. In this work, Nannochloropsis microalgae was tested for the production of hydrochar. A Batch reactor was used, initially pressurized with 20 bars of nitrogen. A 2^k factorial design was used to plan the experiments, with three different factors tested at two different levels: temperature (160-190 ºC), reaction time (30-45 min) and biomass/water ratio (1/10-1/15 w/w). Four different products were obtained: solid fraction (hydrochar), aqueous and gas phases, and an insignificant amount of bio-oil. The gas collected was analyzed by the gas chromatograph to determine the compounds and the mass produced. All the other products were separated by vacuum filtration and decantation, and then weighed to calculate the corresponding product yield. The results indicate that the HTC process is suitable for processing biomass with high moisture content. The reaction temperature was a key parameter that significantly decreased the hydrochar yield, resulting in a higher production of the other products. The effects of reaction time on the hydrochar yield depend on the biomass/water ratio. Overall, HTC process produced a carbon-rich solid and a small amount of gaseous products mainly composed of carbon dioxide.

1. Introduction

Microalgae are unicellular aquatic organisms that contain chlorophyll and are capable of converting sunlight, water and carbon dioxide into metabolites and chemicals through photosynthesis. Microalgal biomass is characterized as a biomass rich in carbohydrate, lipid and protein components (Brindhadevi et al., 2021). Some of the advantages that make algal biomass an interesting potential source of renewable energy are the high growth rate and energy conversion efficiency, the resilience to grow in diverse environmental conditions and the high carbon dioxide consumption. However, there are high production costs associated with the cultivation, harvesting and separation of algae (Elliot, 2016). The organic compounds of microalgal biomass can be easily converted into valuable products. Furthermore, the high moisture content of this biomass significantly reduces the operational energy costs and facilitates the decomposition and conversion of the microalgae (Chen et al., 2020). Hydrothermal carbonization (HTC) is a thermochemical process in which the feedstock is decomposed in a pressurized system under compressed water, at relatively low temperatures (180-250 °C) and at elevated pressures (20-100 bar). To achieve an optimal HTC process, several parameters, such as temperature, reaction time, initial pressure and biomass/water ratio need to be considered (Nizamuddin et al., 2017) to improve the evaluation of hydrothermal decomposition. The main objective of the HTC process is to obtain hydrochar over the other end products, such as aqueous and gas phases. It is known that the percentages of these final products and, consequently, their chemical composition are highly dependent on the type of biomass species as well as on the operational parameters of the HTC process. This is due to the fact that several types of reactions take place during the process, such as hydrolysis, dehydration, decarboxylation, decomposition, polymerization, aromatization, isomerization and condensation (Śliz et al., 2022).

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Hydrochar is a solid carbonaceous material containing high levels of carbon, oxygen, hydrogen and nitrogen and low levels of sulphur content. Hydrochar can have several applications mainly due to its stable morphology and carbon-rich structure. Some examples of these applications are the usability as a fuel, catalyst, an adsorbent or even application on soil (Wang et al., 2018). The hydrochar application on soil is particularly promising due to its potential to mitigate climate change, to control and remediate environmental pollution, to store energy and to increase soil fertility (Islam et al., 2021). The aqueous fraction is a processed water that may contain various organic chemicals and nutrients, including soluble minerals and micronutrients (Kbns et al., 2020). These nutrients are chemical substances that can be essential for biomass cultivation purposes and for increasing soil fertility. The gas fraction is typically composed of high levels of carbon dioxide and small amounts of hydrocarbons derived from a large series of cleavage chain reactions (Mikusińska et al., 2023). Carbon dioxide can be captured from the gas, stored and used to accelerate the growth of the biomass species or to be converted into energy for thermochemical processes. During the HTC process, an unexpectedly small mass of bio-oil can be produced. However, bio-oil can be used as a fuel in boilers, engines or turbines for heat and power generation. Separation of the products is necessary in order to analyze each of them separately. The most common method of separating these products is by vacuum filtration and decantation. A centrifuge can also be used to increase the efficiency of product separation (Zhong et al., 2022). In the chemical treatments of biomass, an experimental design can be used to plan the experiments and to increase the quality of the information obtained at the end (Leardi, 2009). It is also a reliable way to observe the interaction between the different parameters or factors in order to obtain a better understating of how a specific process works and to determine the optimal levels for each one. The main objective of this work is to study the production of hydrochar by hydrothermal carbonization using a species of microalgae called Nannochloropsis, initially freeze-dried. A factorial design was planned to improve the quality of this work. Furthermore, the study of the effect of each different HTC parameter (temperature, reaction time and biomass/water ratio) on the production of hydrochar is fundamental to increase the review information about this hydrothermal treatment.

2. Materials and Methods

A microalgal biomass named Nannochloropsis was selected to study the production of hydrochar by HTC. The Nannochloropsis chemical composition was determined in order to observe its potential to produce a carbon-rich solid fraction. A 0.16 L Parr Instruments Batch reactor pressurized with nitrogen (N_2) was used to study the production of hydrochar. The nitrogen is used to maintain an inert atmosphere within the reactor. During the experiment, the feedstock is agitated by an oscillating system incorporated into the furnace. The total mass of the feedstock was 77 g, including the water content. A factorial design was used in these experiments, with three different factors tested at two different levels: temperature (160-190 ºC), reaction time (30-45 min) and biomass/water ratio (1/10-1/15 w/w). To increase the reproducibility of the factorial design, each experiment was repeated once. Therefore, a total number of 16 experiments were performed (23x2). In all experiments, the initial pressure was approximately 290 psi, which is equivalent to 20 bar. At the end of each experiment, the reactor was cooled down to room temperature. The gas fraction was then collected in a bag sample and analyzed in a GC-FID-TCD (Gas Chromatography – Flame Ionization Detector and Thermal Conductivity Detector) in order to determine its composition and the mass of gas produced. The liquid and solid fraction were then separated by vacuum filtration. The reactor was cleaned with 2 mL of cyclohexane per 1 g of feedstock and the liquid phase was decanted to assess if any bio-oil was produced. The collected bio-oil mixed with cyclohexane was then dried using a nitrogen steam. Finally, the liquid phase was distilled and weighed, and the solid fraction was dried at 105 °C, until the solid mass stabilized, and also weighed to calculate the product yield. An elemental analysis of the solid fraction was made to determine the carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and oxygen (O) content. The experimental design is shown in table 1. The 2^3 factorial design helps to study the edges of the cube of the experimental design. Therefore, the levels of each factor must be coded as -1 and 1 for low and high values, respectively.

Table 1: Experiment plan

Number	Experiment	Temperature	Reaction time	Biomass/H_2O ratio
1	160:30:1/15	-1	-1	-1
2	190:30:1/15	1	-1	-1
3	160:45:1/15	-1	1	-1
4	190:45:1/15	1	1	-1
5	160:30:1/10	-1	-1	1
6	190:30:1/10	1	-1	1
7	160:45:1/10	-1	1	1
8	190:45:1/10	1	1	1

3. Results and Discussion

According to table 2, Nannochloropsis biomass contains more than 50 % of carbon content, in which around 7.5 % is fixed carbon. This result is particularly promising as carbon components are needed to produce hydrochar.

Table 2: Nannochloropsis chemical composition

	Carbon	Hydrogen	Nitrogen	Chlorine	Sulfur	Volatile matter	Ash
Dry base (w/w) %	55.7	7.2	8.8	0.55	0.58	84.9	7.6

Regarding the obtained elemental analysis of the different hydrochar (table 3), an increase in carbon and hydrogen content was observed up to 3.68 to 11.34 % and 0.68 to 2.14 %, respectively, compared to the feedstock. However, this increase in carbon content was not verified in experiment 7 (160:45:1/10). Similar results were observed by Castro et al., 2021, in which the author also verified an increase in C and H content of the hydrochar followed by a decrease in N, S and O content after the hydrothermal treatment of microalgal biomass. Overall, the change of reaction temperature from 160 to 190 °C increased the carbon content and decreased the oxygen content of the hydrochar in all experiments. In fact, the carbon content increased from 3.01 to 10.79 % and the oxygen content decreased from 1.51 to 9.06 %. According to the literature, the reaction temperature may increase the chain of reactions, including dehydration and decarboxylation, that occur during the process. These reactions lead to the removal of carboxyl and hydroxyl groups, which may eventually reduce the O/C and H/C ratios of the hydrochar (Romano et al., 2023).

Table 3: Hydrochar elemental chemical composition

	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen
160:30:1/15	61.60	8.30	6.88	0.44	22.78
190:30:1/15	66.57	9.02	4.79	0.32	19.31
160:45:1/15	62.34	8.65	6.41	0.43	22.19
190:45:1/15	67.04	9.34	4.80	0.30	18.52
160:30:1/10	59.38	8.17	6.89	0.48	25.09
190:30:1/10	62.39	7.88	5.59	0.56	23.59
160:45:1/10	55.38	8.71	6.12	0.44	29.36
190:45:1/10	66.16	8.86	4.48	< 0.2	20.31

The chemical composition of the gas fraction was essential to calculate the mass yield of this product. In general, the gas products were mainly composed of carbon dioxide (table 4). These results show that a significant amount of oxygen, which was not present in the solid fraction, can be converted into carbon dioxide. This is due to the excessive amount of energy supplied to the decomposition process during the HTC treatment.

Table 4: General gas chemical composition

	Carbon dioxide	Hydrocarbons
(v/v) %	76.81-100	0-23.19

Figure 1 shows that the lower temperature (160 °C) increased the solid yield from 12.02 to 24.79 % and decreased the aqueous yield from 2.18 to 24.21 %. This degree of change was more pronounced when a biomass/water ratio of 1/10 was tested. Wilk et al., 2021, also reported that higher temperatures reduced the mass yield of the hydrochar. Furthermore, no bio-oil production was observed. In fact, only 1 to 2.57 % of bio-oil was produced in three experiments tested at the higher temperature (190 °C). According to the results, up to 24 psi of gaseous compounds were produced, resulting in a gas product yield of 1.09 to 10.27 %. It was also found that the temperature increased the gas production by 0.59 to 8.83 %. This value was significant when the combination of a reaction time of 30 min and biomass/water ratio of 1/15 was tested. This fact may be caused by a higher decomposition of the material, which leads to a decrease in the volatile matter of the hydrochar and, therefore, in the O/C and H/C ratio (Song et al., 2022). Increasing the reaction time resulted in an increase (4.42 to 5.81 %) or decrease (3.82 to 11.42 %) in the solid yield, depending on the value of the biomass/water ratio (1/15 or 1/10). These results were not as significantly different when compared with the change in temperature. In fact, several authors, including Hejna et al., 2022, also observed that the effect of increasing the temperature was more significant than the increase in the reaction time. The biomass/water ratio parameter essentially decreased the solid yield from 0.38 to 8.62 %, except for the temperature of 160 °C and reaction time of 30 min, which resulted in a significant increase in solid yield of 12.40 %.

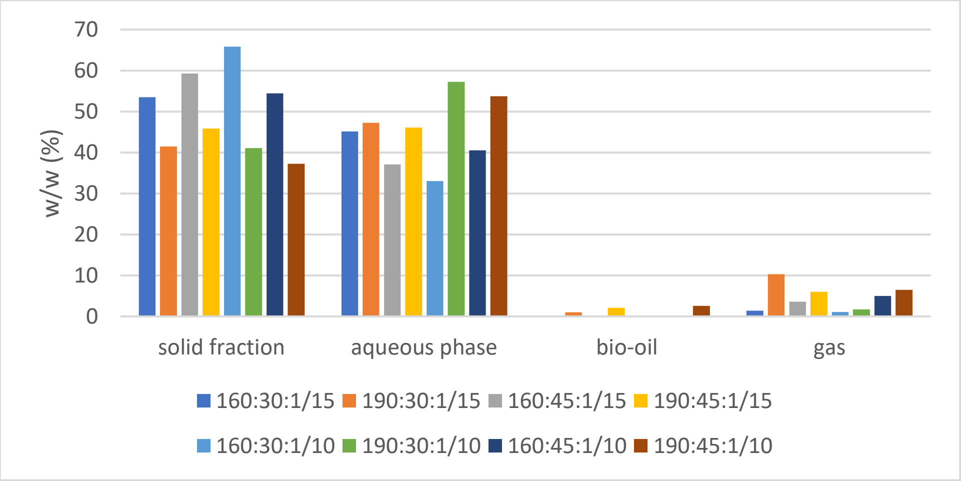

Figure 1: Effect of the different combination of parameters (temperature:reaction time:biomass/water ratio) on products yield.

Figure 3 shows that for a biomass/water ratio of 1/10, the combination of the lower temperature and reaction time produced the highest solid yield (65.86 %) and the combination of the highest temperature and reaction time produced the lowest solid yield (37.24 %). These results are indeed in agreement with the literature. In fact, the reaction time can decrease the hydrochar yield (Patel et al., 2021), due to the higher continuity of the decomposition reactions. However, this phenomenon was not observed when the biomass/water ratio of 1/15 was tested (figure 2). In this case, the reaction time behaved in the opposite direction, increasing the solid yield, as can also be observed in figure 1. This interaction may indicate that less feedstock mass or more water content, which acts as a solvent, can potentially lead to a chain of secondary reactions such as polymerization. Furthermore, the range between the maximum and minimum solid yield obtained was higher for biomass/water ratio of 1/10 (28.62 %) compared to 1/15 (17.82 %), resulting in less conservative results.

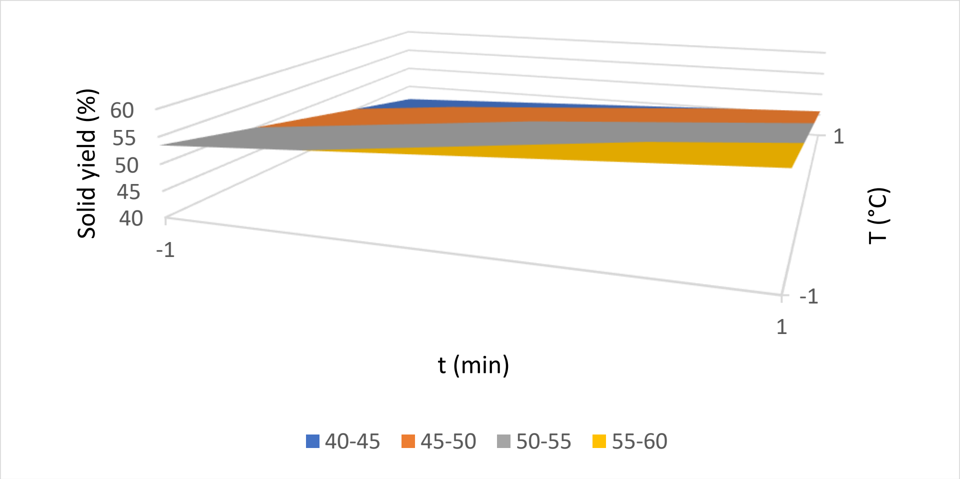

Figure 2: Effect of the temperature and reaction time on solid yield by testing biomass/water ratio of 1/15.

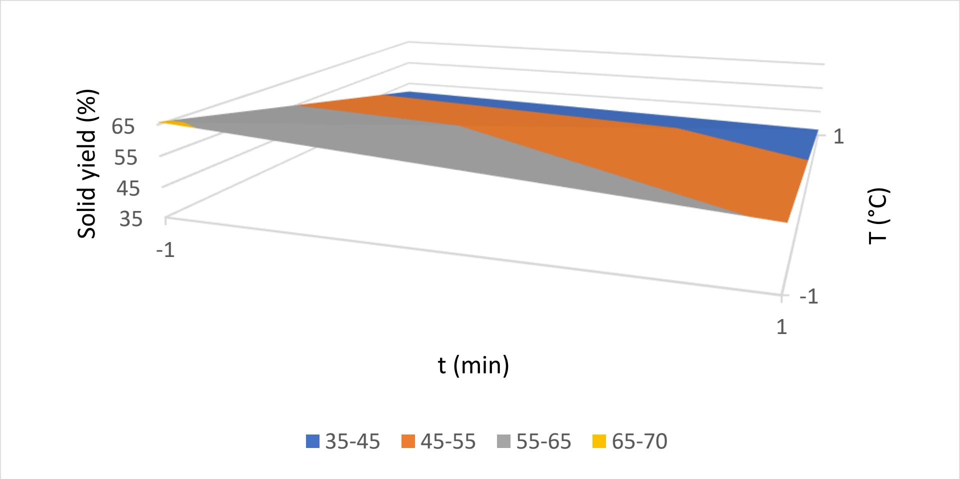

Figure 3: Effect of the temperature and reaction time on solid yield by testing biomass/water ratio of 1/10.

4. Conclusions

HTC is an efficient hydrothermal treatment process for wet biomass to produce hydrochar. In general, hydrochar contains higher carbon content compared to the feedstock. The reaction temperature was a key parameter that significantly affected the hydrochar composition and product yield. Higher temperatures (190 °C) increased the carbon content and improve the quality of the hydrochar. On the other hand, the hydrochar yield decreased, indicating that other types of compounds were formed. In fact, a small amount of bio-oil fraction started to be produced at higher temperatures. In all the experiments, the lower temperature tested (160 °C) resulted in a hydrochar yield of more than 50 %, reducing the yield of the other products. It was also observed that the highest solid yield (65.86 %) and the lowest aqueous and gas phases yields (33.05 and 1.09 %, respectively) were obtained in the 160:30:1/10 experiment. Considering the reaction time, the primary effects were based on the biomass/water value. This interaction between reaction time and biomass/water ratio may explain the importance of feedstock mass input or water content acting as a solvent during the HTC process.

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