

Hydrothermal Carbonization of Oat in a Lab-Scale Batch Reactor

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Biomass as feedstock for renewable energy and biomaterials production is of great importance to tackle energy, economic and environmental issues. Biomass can be processed in several ways depending on its composition, moisture content and availability. Hydrothermal Carbonization (HTC) is one possible option to deal with the biomass streams. In this study, oat was processed in a lab-scale stirred-batch HTC reactor to evaluate the effect of reaction temperature and residence time on the composition and yield of hydrochar obtained during the process. The results demonstrate that these operating parameters strongly affect the characteristics and the amount of the hydrochar produced. The results indicate that the increasing of the HTC severity conditions produces an enrichment of hydrochar in carbon content up to 72.8%. On the other hand, the hydrochar yield decreases from 0.85 to 0.56 g/g as the severity factor increases from 0.11 to 0.37.

1. Introduction

Biomass has gained an essential role in the last decades as renewable energy feedstock due to energy, economic and environmental concerns. Among the many available thermochemical processes, Hydrothermal Carbonization (HTC) converts wet biomass into hydrochar by carbonization reactions at relatively low temperatures, usually in the range 180-250 °C (Wang et al., 2018), absence of oxygen and Sub-Critical Water conditions, under saturation pressure for several hours, as reported by Funke and Ziegler (2010). The HTC process is convenient when biomass is wet since it can carbonize substrate with a water content up to 90% by weight without drying the substrate as a pre-treatment, an expensive and long process, as shown in Mastellone (2020) and Zhung et al. (2022). Water is a good medium both for heat transfer and storage processes, enhancing the efficiency of heat transfer during the preheating process and at the same time avoiding local overheating, which can occur because of the exothermal reactions which take place during hydrothermal carbonization (Wang et al., 2018). Hydrolysis is a crucial step in generating reactive intermediates for subsequent conversions. Then, hydrothermal processes, specifically dehydration and decarboxylation, take place eliminating the hydroxyl and carboxyl groups in biochemical components. Dehydration and decarboxylation increase the coalification degrees by lowering the H/C and O/C atomic ratios in the solid products (Toufiq et al., 2016).

The HTC phase products are solid, liquid and gases. Generally, the liquid and gas products have received limited attention in literature. These by-products need more detailed analysis for a deeper understanding of the whole hydrothermal process in relation to the hydrochar formation. The liquid products can generally be treated by wet oxidation (Toufiq et al., 2016 and De la Rubia et al., 2018) or recovered for production of biogas (methane) and fertilizer, as detailed in Pagés-Díaz et al. (2020), Mau et al. (2019) and Huang et al. (2018). In particular, the post-treatment process is essential to the wastewater and hydrochar for phosphorus and nitrogen recovering (Huang et al., 2018 and Guo et al., 2016).

The yield of these products is strongly affected by the process conditions, such as reaction temperature, reactor pressure, water/biomass ratio, and feedstock composition, as shown in Zaccariello et al. (2020).

On the other hand, the solid product, hydrochar, can be used to obtain products such as solid fuels, activated carbon, carbon-based catalysts and other useful carbonaceous materials, and it can also be used as boost for biogas production (Zaccariello et al., 2020). Possible uses of HC can be soil amendant, environmental absorber, dry solid fuel (Ischia et al., 2021).

The aqueous fraction is rich in organic acids and Hydroxy-methyl-furfural showing high value of total organic carbon (TOC). The handling and disposal of this liquid may outweigh the advantages of the HTC process from economic and environmental point of view. The combination of aqueous-phase recirculation and its use as a fertilizer can be a valid method to reuse the liquid phase and return nutrients to support plant growth, thus increasing the HTC efficiency and economic feasibility.

Oat represents an important cereal with high yield production and good grain quality. It has been chosen as a reference matter for the experimental tests since it could be representative of non-lignocellulosic agro-food waste biomass, and for its large availability, fixed composition and easiness of finding.

In this paper, the impact of the reaction temperature and residence time on the composition, calorific value and yield of hydrochar produced from HTC of oat is evaluated.

2. Materials and Method

2.1 Experimental apparatus and procedure

The lab-scale HTC apparatus used for the experimental tests (Figure 1) is composed of three main sections, a reactor, a heat exchanger and a condenser. The HTC reactor is a 3-litres stirred-batch reactor made of AISI 316L. It is heated-up by two electric heating elements of 1.2 kW each. The temperature is guaranteed by a control loop using a type K thermocouple (TT1) connected to the reactor bottom, a comparator for the set-point temperature and the voltage controller for tuning the current into the resistance. A 3 cm thick insulating layer of glass wool was used to minimize the reactor heat dissipation.

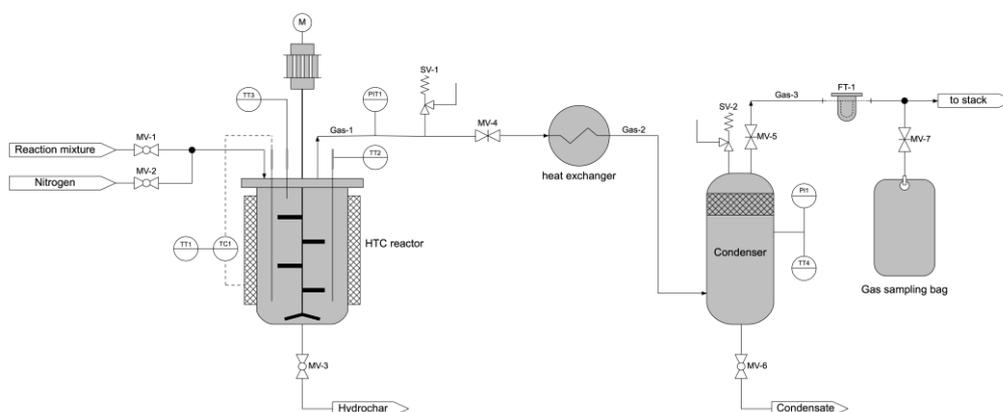


Figure 1: Schematic illustration of the bench-scale HTC apparatus

For each HTC test, dried oat is mixed with water to obtain a reaction mixture with a defined water/dry oat ratio (R). The R value is obtained by using Eq(1):

$$R = \frac{W_{H_2O}}{W_{oat\ dried}} \quad (1)$$

with W_{H_2O} the mass of the added water and $W_{oat\ dried}$ the mass of the dried oat.

The reaction mixture is placed into the reactor, keeping about 10% of the total reactor volume as empty head space. After that, the filled reactor is flushed with nitrogen to remove oxygen from the head space of the reactor. The reactor is heated immediately after its filling with the reaction mixture and flushing with nitrogen. The advancement of the process leads to the formation of the HTC products (hydrochar, bio-oil and gas).

Once the set-point reaction time is reached, the electric power is switched off and the gas vent valve is open. The hot vapours coming from the reactor are cooled down by the water-cooled shell and tube heat exchanger. Then, the cooled gas reaches the 60-litres condenser where the separation of permanent gases from the condensed liquid occurs. The gas is sampled in tedlar bags from the condenser by using a suction pump, and subsequently analyzed with an Agilent 490 micro gas chromatograph.

The hydrochar produced during the process is taken out by removing the flange from the top of the reactor and then dried and characterized performing ultimate analysis, proximate analysis and thermogravimetric analysis (TGA). The ultimate analysis was carried out processing the dried oat and hydrochar in a LECO CHN/S 628 Analyzer. The proximate analysis provides moisture, volatile matter, fixed carbon, and ash content, while the ultimate analysis gives the fuel composition in terms of its basic elements such as carbon, hydrogen, nitrogen, sulfur, and oxygen (evaluated by difference). In this work, the proximate analysis was performed drying the gross biomass sample in air to 105 °C for 12 h. Then, the dried sample was heated to 950 °C in inert ambient (nitrogen) for 7 minutes to obtain volatile matter (VM), and to 600 °C in air for 4 h to obtain ash amount. Finally, the fixed carbon (FC) that remains after drying and devolatilization was calculated by subtracting the percentage of moisture, volatile matter, and ash from 100%. The TGA provides the percent weight loss as a function of the processing temperature. The thermogravimetric analyses are conducted using about 10 mg of powdered samples inside an alumina crucible heated from 25 to 900 °C at a heating rate of 10 °C/min and a nitrogen flow rate of 50 mL/min. The TGA is carried out using a TA Waters Discovery SDT 650 with simultaneous heat flow measurement (DSC) and weight change (TGA) from ambient to 1500°C. The higher heating value (HHV) of oat and hydrochar was evaluated by means of the correlation proposed by Channiwala and Parikh (2002).

3. Results and Discussion

The HTC tests were carried out using as feedstock a reaction mixture composed of water and oat and varying the reactor temperature and the residence time. Water and oat are mixed in such quantities that a R value equal to 8 is obtained.

Table 1 reports the elemental and proximate analyses on dry basis (db) and the calorific values of the oat utilized for the HTC tests. The carbon content of the oat is about 55%. The second most abundant element is oxygen which amounts to 33.49%. Lower hydrogen, nitrogen and sulphur fractions are found. The proximate analysis shows that the volatile matter (VM) content of oat is about 84% while the ash fraction is quite low (1.54%).

Table 1: Ultimate, proximate analyses and calorific value of the oat

Ultimate analysis					Proximate analysis			Energy content
wt.% d.b.					wt.% d.b.			MJ/kg
C	H	O	N	S	VM	FC	Ash	HHV
55.02	7.53	33.49	2.40	0.02	83.79	14.67	1.54	24.55

The experimental runs were performed at three temperature values: 180°C, 215°C and 250°C and the residence time was varied from 2 to 4 hours (h), while the pressure was autogenous. The reaction mixtures were prepared blending 2.46 kg of distilled water and 0.31 kg of dried oat (R=8). Table 2 reports the operating conditions of the HTC tests. Each tag of the test ID indicates the substrate, the set-point temperature and the reaction time, respectively.

Table 2. Operating parameters of the HTC experimental runs

Test ID	T	t	P
-	°C	h	bar
OAT-180-1	180	1	10.9
OAT-180-2	180	2	11.2
OAT-180-3	180	3	11.8
OAT-180-4	180	4	12.0
OAT-215-2	215	2	32.5
OAT-250-2	250	2	46.4

Table 2 indicates that the autogenous pressure established in the HTC reactor ranges from 11 to 12 bars for the tests carried out at 180°C, while is about 32 and 46 bars in the tests conducted at 215 and 250°C. It is interesting to note how the pressure increases with the reaction time in the tests at 180°C. This indicates that, at the same reaction temperature, oat degrades as the reaction time increases producing more gas, which is largely composed of CO₂ (>98%).

Table 3 lists the results of ultimate and proximate analyses and the calorific value of the hydrochar obtained during the HTC tests. It can be observed that the carbon content is higher than that of the fresh oat (see Table 1), and that it increases as reaction time and temperature rise. Nitrogen and sulphur show a similar trend. Conversely, hydrogen and oxygen decrease as these two operating parameters increase. These results indicate

that the extension of carbonization reactions on the one hand produces an enrichment of hydrochar in carbon, nitrogen and sulphur, on the other hand favours the migration of hydrogen and oxygen in the liquid and gaseous phases. Similar results were obtained by Xiao et al. (2012) and Zaccariello et al. (2021).

Table 3: Ultimate, proximate analyses and calorific value of the hydrochar

Test ID	Ultimate analysis					Proximate analysis			Energy content MJ/kg
	wt.% d.b.					wt.% d.b.			
-	C	H	O	N	S	VM	FC	Ash	HHV
OAT-180-1	56.09	6.76	32.78	2.51	0.05	82.17	16.02	1.81	24.09
OAT-180-2	58.74	6.23	30.02	2.65	0.05	78.33	19.35	2.32	24.66
OAT-180-3	62.74	5.54	26.17	2.96	0.06	68.81	28.66	2.53	25.64
OAT-180-4	64.13	5.21	24.03	3.01	0.06	64.71	32.73	2.56	25.85
OAT-215-2	68.11	4.85	21.60	2.79	0.07	61.53	35.89	2.58	27.17
OAT-250-2	72.83	5.10	16.30	2.96	0.08	57.88	39.39	2.73	29.66

H/C and O/C atomic ratios were computed for the oat and hydrochar produced and analyzed using a Van Krevelen diagram (Figure 2). The results indicate that the H/C and O/C ratios of oat are higher than that of hydrochars produced during the HTC tests and that these decrease as the reaction temperature and residence time increase. This suggests that a rise in severity conditions leads to the generation of hydrochar with higher condensed carbon through the removal of H and O in a coalification-like process (Wang et al., 2018). These findings are corroborated by the increase of the HHV values of the hydrochars with the process severity conditions (Table 3). Van Krevelen diagram can also be used to delineate the pathways of the HTC reactions. Figure 2 reveals that the HTC of oat at lower temperatures (180 °C) is governed by the dehydration reactions while at higher temperatures (215 - 250 °C) predominate decarboxylation reactions.

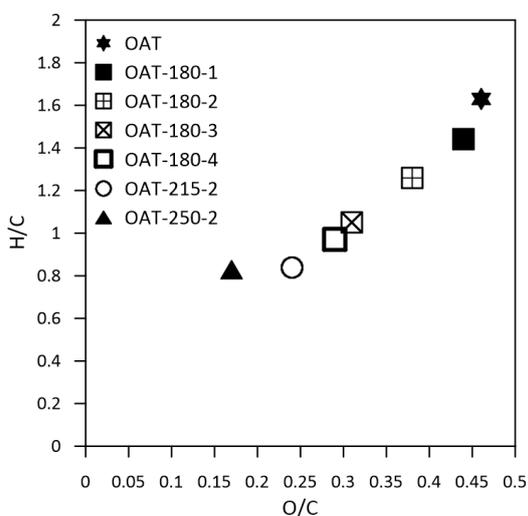


Figure 2: Van Krevelen diagram for oat and hydrochars obtained from the HTC tests

Proximate analysis of hydrochar displays a reduction of VM and an increase of FC. In addition, an increase of HHV up to 20% confirms an enrichment in carbon of hydrochar. As expected, ash content increases due to its refractoriness to the HTC reaction environment.

The results suggest that the carbonization reactions are enhanced by the increasing severity of the operating conditions (i.e., higher residence time and reaction temperature). This suggestion could be confirmed considering the yield of hydrochar obtained during the experimental tests. The yield is an important parameter for evaluating the efficiency of hydrothermal carbonization process. It is calculated as in the following Eq.(2):

$$Y = \frac{W_{hydrochar,dry}}{W_{oat,dry}} \quad (2)$$

where $W_{hydrochar,dry}$ and $W_{oat,dry}$ are the mass of the hydrochar and oat, both dried.

Figure 3 reports the yield of hydrochar as a function of the Severity Factor (SF), which combine the effect of time and temperature of the process. SF is calculated as in the following Eq.(3):

$$SF = 50 \cdot t^{0.2} \cdot \exp\left(-\frac{3500}{T}\right) \quad (3)$$

where t is the reaction time expressed in seconds and T the reaction temperature expressed in kelvin. As expected, the results indicate that the hydrochar yield decreases as the severity of the operating conditions increases. In particular, the HTC test carried out at a SF of 0.11 generated the highest yield of hydrochar (0.85 g/g), while the test conducted at the highest SF value (0.37) showed the lowest yield (0.56 g/g). The greatest mass loss, of about 22%, occurs when SF increases from 0.11 to 0.13. Then, the yield remains almost constant at SF values ranging from 0.13 to 0.23 and decreases of about 7% when SF rises from 0.23 to 0.37.

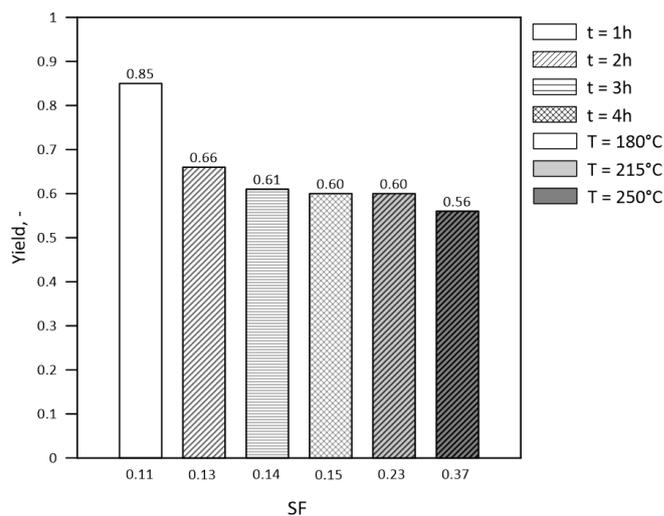


Figure 3: Yield of hydrochar obtained during the experimental runs

Figure 4 displays the results of the percent weight loss (TG Analysis) as a function of the processing temperature of the hydrochar obtained with tests performed at 180, 215 and 250 °C.

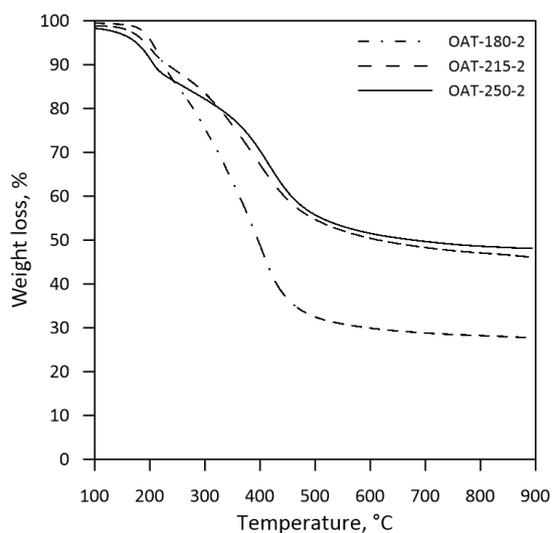


Figure 4: Thermogravimetric analysis (TGA) of the hydrochars with three different processing temperatures

The TGA curves reveals that the hydrochars exhibit two main mass loss stages. The onset temperature of the first stage shifts from 160 to 189 °C as the reaction temperature of the HTC process increased from 180 to 250 °C. Instead, the onset temperature of the second stage changes from 263 to 305 °C with the increase of reaction

temperature. The first mass loss events of the hydrochars are associated to the degradation of the residual labile hemicellulose and cellulose molecules, while the second degradation events are due to the devolatilization of remaining lignin and hydrochar. Moreover, the hydrochar obtained at lower temperatures shows a larger thermal degradation producing a weight loss of about 70%, while the hydrochar produced at 250 °C displays a lower weight loss of about 52%.

4. Conclusions

The role of reaction temperature and residence time on the composition and yield of hydrochar produced from oat is evaluated. The main findings show that these two process parameters severely affect the composition and yield of hydrochar. The results indicate that the extension of carbonization reactions produces an enrichment of hydrochar in carbon, nitrogen and sulphur and favours the migration of hydrogen and oxygen in the liquid and gaseous phases. It is also observed that the hydrochar yield decreases as the severity of the operating conditions increases. The TG analysis shows that the percent weight loss of hydrochar decreases as the HTC reaction temperature raises from 180 to 250 °C; in fact, at low temperatures, the maximum weight loss is of order 70%, whereas at 250 °C the reduction is up to about 50%, confirming that the HTC of oat promotes a more intense polymerization/aromatization process at higher reaction temperatures.

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