Hydrothermal Carbonization of Biomass: Design of a Batch Reactor and Preliminary Experimental Results

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Hydrothermal carbonization (HTC) is a thermochemical conversion process through which it is possible to directly treat a wet organic substrate with reduced process efforts. The main interesting product obtainable by HTC is the so-called "hydrochar", that is a solid enriched in carbon and with chemical characteristics comparable to those of fossil coals.

The interest aroused by HTC stems from the fact that it represents an effective alternative to the common treatments for wet biomass, i.e. composting and anaerobic digestion. In fact, if compared to these conventional processes, HTC has several advantages: it is faster, it is not affected by inhibiting or toxic substances and, finally, the process produces a solid fraction exploitable in different fields: energy production, soil improvement, raw material for high added value applications.

Thus, a batch reactor ($V_{reactor}$: 50 mL; P_{design}: 140 bar; T_{design}: 300 °C) was designed and constructed to investigate the HTC process. At first, the scheme of the equipment (P&I) and its main characteristics are detailed. Then, preliminary experimental tests and relevant analyses are addressed.

HTC experimental runs were performed with two different substrates: a model mixture of water and sugar and a mixture of water and grape seeds, which represent a by-product of the wine-making industry. For the first time in the literature, HTC data on these two kinds of substrates are reported.

The substrates and the hydrochar were analyzed (chemical and thermal characterization). Preliminary data on the effect of process conditions (temperature and residence time) on process yields ($kg_{hydrochar}/kg_{dry\ feed}$) and on hydrochar carbon content ($kg_{carbon}/kg_{hydrochar}$) were obtained. Moreover, based on the analytical data, a van Krevelen diagram was constructed for the HTC of both sugar and grape seeds.

1. Introduction

Waste biomass with a significant moisture content (e.g. the organic fraction of municipal solid waste, sewage sludge, agro-industrial wastes) is nowadays treated through anaerobic digestion or composting. Composting is less and less utilized because of the bad-smell released and the difficulties in finding large-scale compost users. Anaerobic digestion allows energy recovery and seems at the moment the preferred choice. Nevertheless, anaerobic digestion has relevant drawbacks too, in particular the management of the digestate. On the other hand, traditional thermochemical processes (combustion, air gasification, pyrolysis) can be applied to this kind of wet waste biomass only after a severe drying-up pre-treatment which makes the whole process unsustainable from an energy point of view.

HTC can represent the solution to the above mentioned problems. HTC consists in reacting substrates in a liquid water environment in order to obtain a carbon-rich solid fraction (hydrochar). Hydrochar can be utilized in co-combustion with low-rank fossil coals, which can be a very effective and economically feasible way to exploit biomass for energy production (Libra et al., 2011). A recent literature review (Basso et al., 2013) highlighted other possible uses of the hydrochar: it can be utilized as soil amendment, as precursor for activated carbon, for the generation of nano-structured materials, as a catalyst and for CO_2 sorption and sequestration.

The whole amount of water initially present within the HTC reactor is normally found after the process, and during HTC some organic compounds dissolve in it (Funke and Ziegler, 2010). HTC produces a small amount of gas, which is mainly composed of CO_2 with traces of CO.

The HTC process operates in a temperature range between 180 °C and 250 °C and with residence times from one to several hours. The pressure is a variable which depends on the temperature. As a matter of fact, at the beginning of the process its value equals that of the vapour pressure of water (1.0-4.0 MPa according to the operating temperature) and most water remains in the liquid state. Under these conditions, water behaves as a catalyst and a reactant for organic compounds and it is a good solvent for polar compounds. Moreover, the transport properties of water are enhanced, allowing a homogeneous distribution of temperature within the whole volume of the reactor.

Such mild process conditions could be applied without the need to resort to high-tech plants, as it would be the case for the close-related process referred to as supercritical water gasification (SCWG) (Fiori et al., 2012a). In order to provide indicative values of the severe process conditions required by SCWG, it seems worth mentioning that Myréen et al. (2011) performed SCWG experimental tests at temperatures of 600-700 °C and pressure of 25 MPa, and Freitas and Guirardello (2013) modeled SCWG at temperatures and pressures in the range 430-830 °C and 24-30 MPa, respectively.

If properly designed, the HTC of wet waste biomass could be adopted by both public and private actors (for example: civil waste-water treatment plants, waste management companies, businesses producing large amount of agro-industrial waste).

Based on previous results on gasification with supercritical and subcritical water (Castello et al., 2013) and for the interesting perspectives, it has been decided to investigate and test the HTC process.

2. Materials and methods

2.1 Experimental apparatus

A HTC experimental apparatus was designed and constructed at the Department of Civil, Environmental and Mechanical Engineering of the University of Trento (Italy), consisting of a stainless steel (AISI 316) batch reactor with an internal volume of about 50 mL. Figure 1 shows the piping and instrumentation diagram (P&ID) of the experimental system and a design drawing of the HTC flanged reactor; Figure 2 shows a picture of the apparatus.

Two pipes of 2 mm internal diameter are connected to the reactor flanged cover. At the ends of the pipes, two needle valves are positioned, V1 and V2. Through V1, an inert gas (N_2) can be fluxed inside the reactor to purge it from the presence of air; V2 is used to exit the gaseous products, which are formed during the HTC process, at the end of the process. On the left pipe, a pressure transmitter (PT) and a pressure gauge (PI) are placed. For safety reasons, a rupture disc is positioned in the pipe upstream the PI. Moreover, a water bath is foreseen on the left pipe to avoid that hot fluids from the reactor could come into contact with the PT or the PI. A thermocouple (TT) is embedded inside the reactor, passing through the reactor flanged cover. Both the thermocouple and the pressure transmitter send data to the HTC controller, which provides temperature and pressure data to a temperature indicator and recorder (TIR) and to a pressure recorder (PR), respectively. The HTC controller (TIC) is also connected to a band heater, in order to heat the reactor and to hold its temperature at the desired set point.
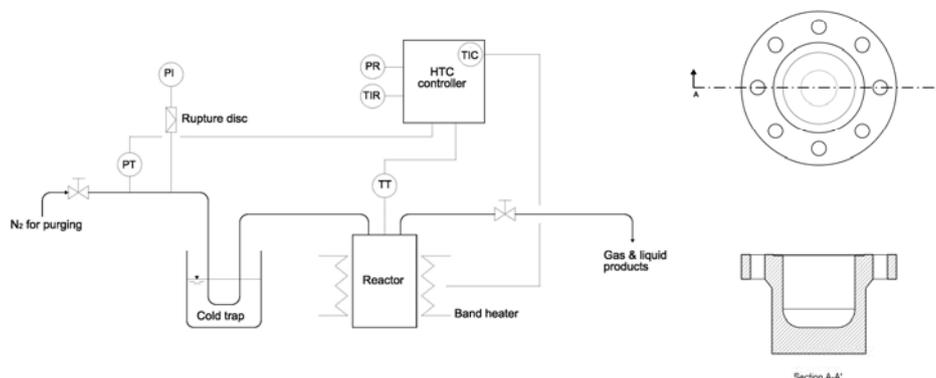

Figure 1: P&I diagram of the experimental apparatus and details of the reactor
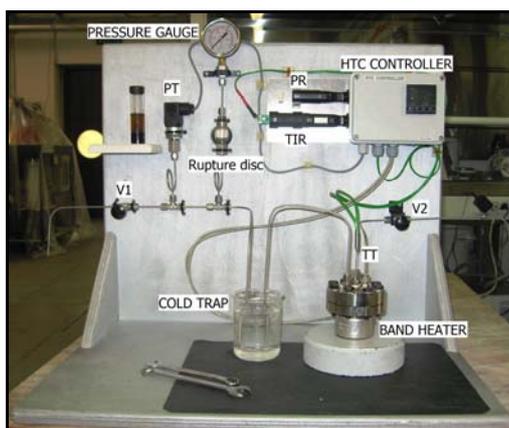
Figure 2: Experimental apparatus

The seal of the HTC reactor is realized through a copper gasket, housed between the reactor flange and the flanged cover.

2.2 Experimental campaign and procedure

The experiments presented in this work were aimed at obtaining information on both the yield ($kg_{hydrochar}/kg_{dry\ feed}$) and the carbon content ($kg_{carbon}/kg_{hydrochar}$) of the hydrochar produced, by varying the temperature and the residence time of the HTC process. Thus, experimental runs were conducted at three different residence times (1, 3 and 8 h) and three different temperatures (180, 220 and 250 °C).

Two organic substrates were tested: white refined sugar and grape seeds. The former allowed to conduct experiments with an initial homogenous liquid phase, while the latter can be of practical interest, since grape seeds represent a high moisture by-product of the wine-making industry and a waste from distilleries (Fiori et al., 2012b). Because of the relatively modest interest in the HTC of sugar, in this case tests were executed only at 220 °C for the three residence times. HTC of sugar was done mainly for comparative purposes in respect to the HTC of grape seeds.

The performed tests are reported in Table 1.

Table 1: Scheme of the experimental tests performed in the present work

Sugar (220 °C)	Grape seeds (180 °C)	Grape seeds (220 °C)	Grape seeds (250 °C)
1 h	1 h	1 h	1 h
3 h	3 h	3 h	3 h
8 h	8 h	8 h	8 h

The substrate to water ratio ($kg_{dry\ substrate}/kg_{water}$) was kept equal to 0.3 for all the experiments.

Substrate and deionised water were accurately weighted and loaded into the reactor. The reactor was then closed and an inert gas (N_2) was fluxed through the system for about 5 min, to purge it from air. The reactor was then heated up by means of the band heater: around 20-25 min were required to reach the desired set point starting from an initial temperature of about 20 °C. The quite relevant duration of the heat-up phase was due to the lack of thermal insulation of the reactor. However, this phase was much shorter if compared to the residence times in the reactor. The residence time was measured starting from the instant when the TIC indicated the desired set-point value. At the end of the experiment, the reactor was quenched through a massive stainless steel disc at -30 °C, which was positioned below the reactor. Quenching was helped by blowing compressed air over the reactor walls. This operation took 15-20 min, depending on the process temperature. The quenching was stopped when TIC indicated 26 °C.

Once the system had been cooled down, valve V2 was opened in order to evacuate the gas formed during the reaction. Once atmospheric pressure had been reached, the reactor was opened. Its content was then filtered and both liquid and solid products were collected. The wet spent filter and the reactor, both presenting some remaining solids, were put in an oven at 105 °C for at least 8 h. After drying, the filter and the reactor were weighted. The hydrochar yield was then determined in terms of amount of obtained solid with respect to the amount of substrate initially loaded into the reactor ($kg_{hydrochar}/kg_{dry\ feed}$).

The carbonized solid residue (hydrochar) was finally stored in vials, before chemical characterization through ultimate analysis and thermal characterization. The ultimate analysis was carried out according to (UNI EN 15104, 2011). The determination of the amount of ashes in grape seeds was performed according to (UNI EN 14775, 2010); ash content in hydrochar was calculated based on hydrochar yields (Table 2) and assuming that the amount of ashes remained unvaried during HTC. The heating values were measured according to (UNI EN 14918, 2010).

An indication of the gas formed during the HTC reaction was given by the value of the reactor residual pressure, in particular by the pressure value read after reactor quenching.

3. Results and discussion

Tables 2 and 3 show the hydrochar yields obtained during this first experimental campaign, respectively for grape seeds and sugar.

Table 2: Hydrochar yields as a function of reaction temperature and residence time: grape seeds

Temperature (°C)	Residence time (h)		
	1	3	8
180	80.3 %	78.7 %	77.0 %
220	73.8 %	68.9%	67.7 %
250	67.2 %	63.9 %	62.3 %

Table 3: Hydrochar yields as a function of residence time: sugar

Temperature (°C)	Residence time (h)		
	1	3	8
220	55.7 %	52.5 %	47.5 %

As it was expected, the amount of hydrochar resulting from the HTC process decreased with the increase of both of temperature and residence time. In the operating ranges investigated, the hydrochar yield was more affected by a variation in temperature than by a variation in residence time. The decrease in hydrochar yields was accompanied by an increase in the reactor residual pressure (data not shown): the lower the hydrochar production, the higher the gas production. This behaviour is in agreement with other results available in the literature (Castello et al., 2013).

When comparing the two different substrates, the hydrochar yield from sugar was much lower than the one from grape seeds. The reactivity of sugar was much greater than that of grape seeds, as it should be expected considering the different nature of the substrates. Moreover, it is worth underlining the different kinetics paths of the hydrochar produced by the two substrates. According to Karayıldırım et al. (2008), the solid phase can be formed through a solid-solid conversion or, alternatively, by polymerization of intermediates dissolved in water, which previously evolved from the biomass. In the former case the carbon particles are referred as "char", in the latter case they are referred as "coke" (Karayıldırım et al., 2008). Hydrochar from grape seeds mainly consisted of carbonised seeds (char), as it was evident by visual observation. Conversely, hydrochar from sugar was actually coke, deriving from the polymerization and subsequent segregation of liquid molecules originated by the degradation of sugar.

Table 4 shows the ultimate analysis and the heating values (HHV_{meas} and LHV_{meas}) of the original substrates and of the hydrochar produced by HTC.

In Table 4, each sample is identified by an alphanumeric code in which the first number indicates the residence time in hours, the letter indicates the substrate (G: grape seeds, S: sugar) and the following number indicates the temperature of the process (e.g. 1G180 denotes a hydrochar obtained from grape seeds treated for 1 h at 180 °C).

Both high heating value (HHV) and low heating value (LHV) increased as a result of the process. Averaging the various values, the HHV and the LHV of the hydrochar produced from grape seeds are about 20 % greater than the HHV and the LHV of the original substrate. With the same approach, the HHV and the LHV of the hydrochar produced from sugar are, respectively, 52 % and 60 % greater than the HHV and the LHV of the original sugar.

In Table 4 the higher heating values (HHV_{calc}) calculated through the formula proposed by Gaur and Reed (1998) are also reported, along with the error among the measured and calculated data (M=HHV_{meas}; C=HHV_{calc}). It is noteworthy that the HHV_{calc} for milder HTC conditions (i.e. 1G180, 3G180, 8G180, 1G220,

3G220, 1S220 and 3S220) are lower than the HHV$_{meas}$, while for more severe conditions (i.e. 8G220, 1G250, 3G250, 8G250 and 8S220) the calculated values result greater than the measured ones.

Table 4: Ultimate analysis, higher and lower heating values of substrates and hydrochar

Sample	C (%)	H (%)	N (%)	O (%)	Ash (%)	HHV$_{meas}$ (MJ/kg)	LHV$_{meas}$ (MJ/kg)	HHV$_{calc}$ (MJ/kg)	(M-C)/M (%)
Grape seeds	*54.40*	*6.60*	*1.60*	*34.20*	*3.20*	*23.584*	*22.189*	*23.140*	*1.88*
1G180	60.24	6.62	1.32	27.84	3.98	26.459	25.053	25.848	2.31
3G180	60.60	6.50	1.40	27.43	4.07	26.825	25.439	25.871	3.56
8G180	62.30	6.80	1.40	25.35	4.15	28.028	26.584	27.032	3.55
1G220	63.40	6.70	1.60	23.96	4.34	27.944	26.524	27.434	1.82
3G220	63.60	6.40	1.60	23.75	4.65	28.498	27.148	27.166	4.68
8G220	68.40	6.70	1.90	18.28	4.72	28.307	26.893	29.755	-5.12
1G250	66.50	6.40	1.80	20.54	4.76	26.163	24.798	28.505	-8.95
3G250	69.50	6.60	1.90	16.99	5.01	29.866	28.464	30.148	-0.94
8G250	70.70	6.50	2.00	15.66	5.14	29.878	28.504	30.582	-2.36
Sugar	*41.31*	*6.39*	*0.04*	*52.26*	*-*	*16.648*	*15.292*	*16.546*	*0.61*
1S220	64.80	4.40	0.10	30.70	-	25.369	24.432	24.630	2.91
3S220	65.70	4.40	0.10	29.80	-	25.210	24.287	25.038	0.68
8S220	67.50	4.50	0.10	27.90	-	25.456	24.502	25.980	-2.06

The results of the ultimate analysis allow stating that:
- the carbon enrichment of the hydrochar produced from sugar was much higher than the one from grape seeds (60 % and 20 %, respectively);
- hydrochar from sugar contained 30 % less hydrogen than sugar, while grape seeds and hydrochar from grape seeds contained practically the same percentage of hydrogen;
- hydrochar from sugar contained 45 % less oxygen than sugar, while, on average, hydrochar from grape seeds contained 35 % less oxygen than grape seeds.

The results of the ultimate analyses are graphically shown in Figure 3. Here, following the same approach as van Krevelen (1950), the diagram reports, for each substrate, the weight ratio between hydrogen and carbon versus the weight ratio between oxygen and carbon. The two large dots (denoted by the labels "GRAPE" and "SUGAR" in the legend) represent the two original substrates. Each triplet identified by the same symbol represents the hydrochar from a substrate that was processed at a specific temperature. The arrows indicate the direction of the increasing time. From Figure 3 it is possible to notice that the carbon content of the solid HTC products is significantly increased for both grape seeds and sugar. For both substrates, increasing the residence time results in an enrichment in the carbon content of the hydrochar produced.
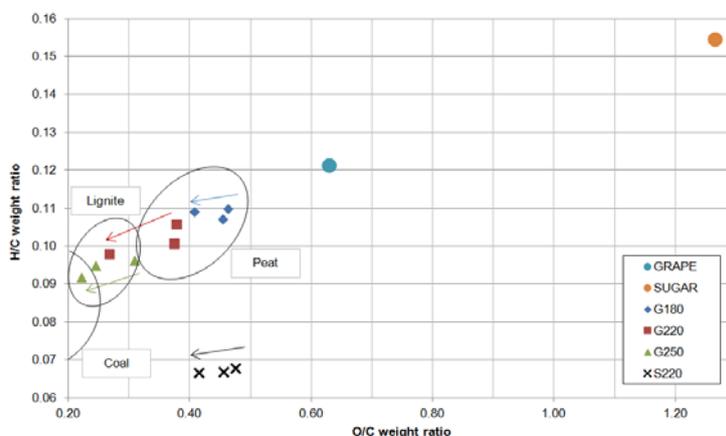

Figure 3: van Krevelen diagram (van Krevelen, 1950) for the HTC of grape seeds and sugar. Both original substrates and hydrochar produced at different temperatures and residence times are reported

In Figure 3 three regions representative of peat, lignite and coal are highlighted. The HTC of grape seeds at 180 °C converted the substrate into a peat-like material. Increasing the temperature to 220 °C allowed obtaining a hydrochar with a composition intermediate between those of peat and lignite. The HTC reaction performed at 250 °C for 8 hours allowed converting grape seeds into a hydrochar resembling coal.

As above mentioned, the hydrochar from sugar was actually "coke" (Karayıldırım et al., 2008) whose composition did not overlap to those of any solid fossil fuels: see Figure 3.

Thus, to exploit the hydrochar for energy purposes, the stronger HTC conditions (high temperatures, long residence times) appear to be the most effective, allowing for the production of a good hydrochar (Figure 3) with high HHV and LHV (Table 4). On the other hand, these conditions imply a lower hydrochar yield (Table 2).

4. Conclusions

In this paper the technical characteristics of a bench-scale batch reactor for HTC of wet biomass were described. The HTC reactor was utilized to perform the carbonization of two substrates (grape seeds and sugar), in order to study the influence of the process conditions (temperature and residence time) on the hydrochar produced. The results, both in terms of hydrochar yield and hydrochar chemical and thermal properties, showed that HTC represents an effective way to obtain a solid product with quite good characteristics as energy vector. In this perspective, high temperatures and long residence times increased the heating values of the hydrochar, although the yields resulted lowered. Thus, further experiments are required to assess the optimal values of the process parameters. In particular, a detailed reaction kinetics study could be useful to optimize the process and thus to obtain its maximum performance. Moreover, a thermal analysis of the whole process is required in view of an actual assessment of the HTC potentiality for large-scale applications.

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