Hydrothermal Carbonization of Digestate and Leachate in a Lab-Scale Batch Reactor

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The use of biomass as a feedstock for renewable energy and biomaterials production is gaining increasing attention due to economic and environmental issues. Among all substrates, the organic fraction of municipal solid waste represents a valuable resource for anaerobic digestion facility. This process generates biogas, digestate and leachate. The last two streams are by-products, with potential harmful environmental impact and significant disposal costs. Thus, a proper handling of these biowastes is needed. In the present study, a bench-scale hydrothermal carbonization reactor was operated with two mixtures of digestate and water or leachate varying the residence time and the reaction temperature. The results indicated that aforementioned operating parameters affect the composition and the yield of the obtained hydrochar and that the substitution of water with leachate is technically feasible.

1. Introduction

The world energy demand forecast is expected to rise to about 17,000 Mtoe by 2040 with an increase of 70% compared with 2018 (Exxon, 2019). Therefore, exploitation of many and different efficient alternative renewable energy sources is mandatory (Sharma et al., 2020). Biogas production from the anaerobic digestion (AD) plants is one of the possible pillars to support sustainably the soaring energy demand. In Europe, about 18,000 biogas plants were operating by the end of 2017 (European Biogas Association, 2018).
Among many possible substrates, biomass waste (BW), specifically the organic fraction of municipal solid waste (OFMSW), can represent a valuable resource for AD plants rather than an environmental problem to cope with (Carotenuto et al., 2020). Therefore, the use of BW as a source for renewable energy plants and various biomaterials has gained more and more attention (Hidalgo et al., 2019). Anyway, several issues should be solved to address the existing related environmental impacts.
In fact, in AD facility for biogas production, the energy potential of substrate is not fully exploited, because complex macromolecules do not undergo full biological decomposition (Stobernack et al., 2020). Once the biomass is fed to the digester, then biogas, digestate and leachate are produced as exiting streams at the end of the process (Zaccariello et al., 2020). The last two streams are considered waste, even though digestate could undergo an expensive and time-consuming stabilization process becoming compost.
One of the possible options to deal with the polluting waste streams from AD plants is the Hydrothermal Carbonization (HTC) processing of digestate (Vallejo et al., 2020a). HTC is a thermochemical process via carbonization reactions that converts wet biomass into a carbon-rich material (hydrochar) in Sub-Critical Water (SubCW) conditions. HTC process (Wang et al., 2018) occurs in absence of oxygen at relatively low temperatures (180–250 °C) under autogenous pressure, i.e. self-generated by water vapor due to the heating of a sealed vessel (HTC reactor). According to the typical process temperatures, the autogenous pressure changes approximatively between 10 to 40 bars. The HTC process usually takes place in 1-6 hours, but in some specific cases it can last until 24 hours. The HTC process is convenient because wet biomass with a water content of 70 - 90% by weight can be converted without prior drying (Mastellone et al., 2019). SubCW Processes favour corrosion process, which could be a huge problem regarding design consideration and safety (Kritzer, 2004), because of some typical favorable characteristics (acidic and oxidizing conditions,

extreme pH values, sharp pressure changes, etc.). The HTC process generates solid, liquid and gases. The characteristics and the yield of these products strongly depend on the process conditions (i.e. reaction temperature, reactor pressure, water/biomass ratio) and feedstock composition, which also affect their next utilization (Guo et al., 2016).

The solid product, is of great interest because it can be used to produce high added-value products such as solid fuels, activated carbon, carbon-based catalysts and other useful carbonaceous materials. The authors (Lucian and Fiori, 2017) proved that HC production can be economically feasible on the industrial scale.

The aqueous fraction (bio-oil for short) is rich in organic acids, among others acetic, formic, levulinic, and glycolic acid, 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 an economical and environmental point of view.

In this paper, the role of residence time and reaction temperature on the composition and yield of hydrochar produced by using digestate from the anaerobic digestion of OFMSW was evaluated. In addition, the economic and environmental interesting perspective of using leachate instead of water as reaction medium was explored.

Experimental Section

1.1 Hydrothermal carbonization experimental apparatus

The experimental work was carried out by using a bench-scale HTC apparatus composed of three main sections, a reactor, a heat exchanger and a condenser, as shown in Figure 1. The HTC reactor is a stirred-batch reactor made of AISI 316L with a reaction volume of 3 litres. It is heated-up by two electric heating elements of 1.2 kW each. The temperature at the reactor bottom is guaranteed by a control loop that includes a thermocouple (TT_1) connected to the reactor bottom, a comparator that receives the temperature set-point and the voltage controller for tuning the current into the resistance. To minimize the reactor heat dissipation a 3 cm thick insulating layer of glass wool was used. The reactor top ends with a flange where different connectors are located: three are for the thermocouples (TT_1, TT_2 at bottom and TT_3 at top), one is dedicated to the shaft of the mechanical agitator, one for the reaction mixture input and one for the gas exit. The reactor can be operated at a maximum reaction temperature of 300°C and a pressure up to about 100 bar.
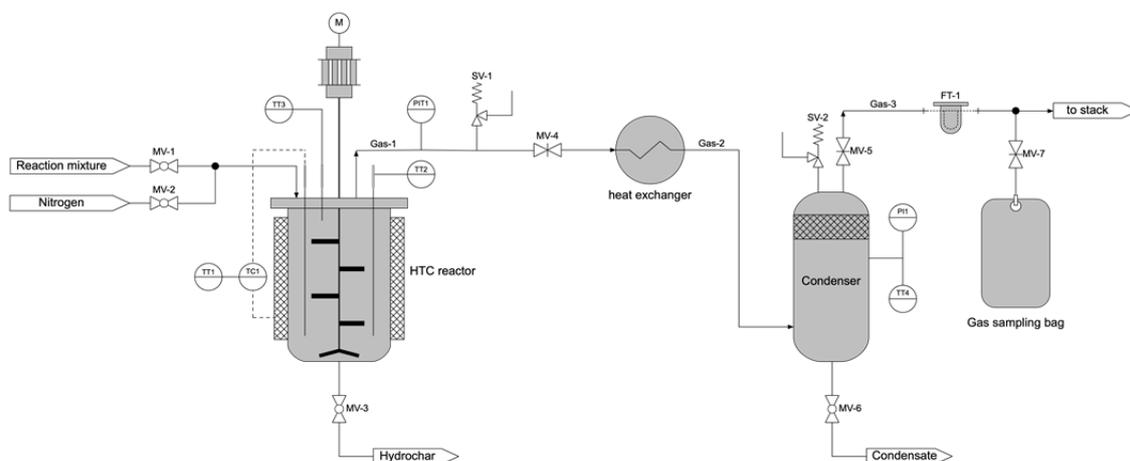

Figure 1: Schematic illustration of the bench-scale HTC apparatus

1.2 Testing procedure

The experimental procedure for producing hydrochar can be schematically divided into reaction mixture preparation, conversion and products recovery.

Reaction mixture preparation. The digestate from the AD process usually contains coarse organic matter (fruits, vegetables, branches, etc.) and inorganic foreign materials (glass, stones, plastics, etc.). To obtain a high-quality feedstock, the digestate is pulped, for recovering the organic matter, and sieved, to remove the inorganic foreign materials. Then, the pre-treated digestate is mixed with a defined amount of water (DW) or leachate (DL), generated by the same AD process. The two different reaction mixtures were prepared in order to obtain a desired water/dry matter ratio (R). After that, the reaction mixture is weighed and placed into the reactor. The empty head space of the reactor was about 10% of the total volume.

The R value is determined by applying the following Eq(1):

$$R = \frac{M_{digestate} + M_{leachate} + W_{H_2O,add}}{W_{reaction\ mixture\ dried}} \tag{1}$$

being $M_{digestate}$ the moisture of the digestate, $M_{leachate}$ the moisture of the leachate, $W_{H2O,add}$ the mass of the added water and $W_{reaction\ mixture\ dried}$ the mass of the reaction mixture dried.

Conversion. The reactor is heated immediately after its filling with the reaction mixture. The heating process lasts the time necessary to attain the set-up temperature, usually around 1 h. During the heating phase, the pressure inside the reactor increases until steady state is attained, indicated by constant values of temperature and pressure. Once the reaction temperature is reached, HTC reactions occur breaking and reorganizing the chemical bonds of the feedstock. The advancement of the process leads to the formation of the HTC products (hydrochar, bio-oil and gas).

Products recovery. Reaction time is an important parameter in hydrochar formation because it determines the degree of decomposition of the raw material at a given temperature. Generally, high reaction times generate a low hydrochar yield and vice versa. When the desired reaction time is reached, the process is stopped by switching off the electric power to the heater and by opening the valve of gas vent. The connection to the shell and tubes heat exchanger and to the condenser promotes the flashing of the water contained in the reactor under pressure; when the valve is opened, the gas phase is cooled and transferred to the condenser where the separation of permanent gases from the condensed liquid occurs. The gas is sampled in a tedlar bag from the condenser by using a suction pump. Then, it is analyzed by means of a micro gas-chromatograph. The liquid remaining in the reactor is drained from a bottom nozzle. Both liquids drained from the reactor and the condenser are mixed and analysed. The hydrochar produced after the reaction is taken out by removing the flange from the top of the reactor and then dried and analysed.

2. Experimental Results

The HTC experimental tests were carried out using two different reaction mixtures and varying the reactor temperature and the residence time. The first reaction mixture, reported as DW, was obtained by blending digestate and water, while the second one, indicated with DL, was obtained by blending digestate and leachate. Both reaction mixtures were prepared in order to obtain an R value equal to 8. This R value was chosen according to the results obtained in preliminary tests which demonstrated a good digestate to hydrochar conversion degree. In addition, this ratio could guarantee the utilization of about the total amount of leachate produced by a dry AD process of organic waste, providing significant economic and environmental advantages. Table 1 reports the proximate and ultimate analyses on dry basis (db) of the reaction mixtures utilized for the HTC tests.

Table 1. Proximate and ultimate analyses of the tested reaction mixtures

Test ID	VM	FC	Ash	C	H	N	O
-	wt.%db			wt.%db			
DW	60.81	1.11	38.08	35.48	4.45	2.40	19.59
DL	62.41	2.50	35.09	38.71	4.74	2.51	18.96

The proximate analysis shows that both reaction mixtures have a volatile matter (VM) content of about 60% and a high ash fraction which ranges from 35 to 38%. The carbon contents of the feedstocks are quite low (between 35 and 39%) while the oxygen amount is about 19% for both mixtures.

Table 2. Operating parameters of the HTC experimental runs

Test ID	Reaction mixture	T	τ	P
-	-	°C	h	bar
DW-180-6	Digestate/Water	180	6	10
DW-250-2	Digestate/Water	250	2	40
DW-250-6	Digestate/Water	250	6	42
DL-180-6	Digestate/Leachate	180	6	11
DL-250-2	Digestate/Leachate	250	2	44
DL-250-6	Digestate/Leachate	250	6	45

The experimental runs were performed either at the lower (180°C) or at higher (250°C) limits of the HTC process temperatures, the residence time was 2 or 6 hours (h) while the pressure was autogenous. Table 2 reports the operating conditions of the HTC tests.

Table 2 indicates that the autogenous pressure established in the HTC reactor is about 10 bars for the tests carried out at 180°C while it ranges from 40 to 45 bars in the tests at 250°C. It is interesting to note how the pressure is higher in the tests with DL mixture (11, 44 and 45 bars) than in those with DW (10, 40 and 42 bars). Probably, this is due to the larger VM content in the mixture DL which generates more gas during the process.

Residence time and reaction temperature affect the composition and the yield of the hydrochar product. In particular, the proximate and ultimate analyses of the hydrochar (Table 3) obtained from the tests conducted at 250 °C show that the ash contents rise from 50.28 to 52.29% for the DW mixture and from 46.83 to 47.34%, for the DL mixture. As far as carbon content, it increases from 35.20 to 37.28% for DW mixture and from 32.50 to 33.66%, using the DL mixture, as the residence time increases from 2 to 6 h. On the other hand, the O/C ratio decreases from 0.23 to 0.10, in the runs with DW, and from 0.47 to 0.39, in the runs with DL.

Table 3: Hydrochar characterization on dry basis

Test ID	VM	FC	Ash	C	H	N	O
-		wt.%$_{db}$			wt.%$_{db}$		
DW-180-6	53.50	1.99	44.51	33.85	4.03	1.86	15.75
DW-250-2	49.31	0.41	50.28	35.20	4.19	2.13	8.20
DW-250-6	44.96	2.75	52.29	37.28	4.74	1.86	3.84
DL-180-6	45.85	16.40	37.75	31.72	3.14	2.06	25.33
DL-250-2	44.40	8.77	46.83	32.50	3.44	1.81	15.42
DL-250-6	43.68	8.98	47.34	33.66	3.75	1.96	13.29

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 is further confirmed considering the yield of hydrochar obtained during the experimental tests. The hydrochar yield is calculated as reported in Eq(2):

$$Y = \frac{W_{hydrochar,dry}}{W_{reaction\ mixture,dry}}$$

(2)

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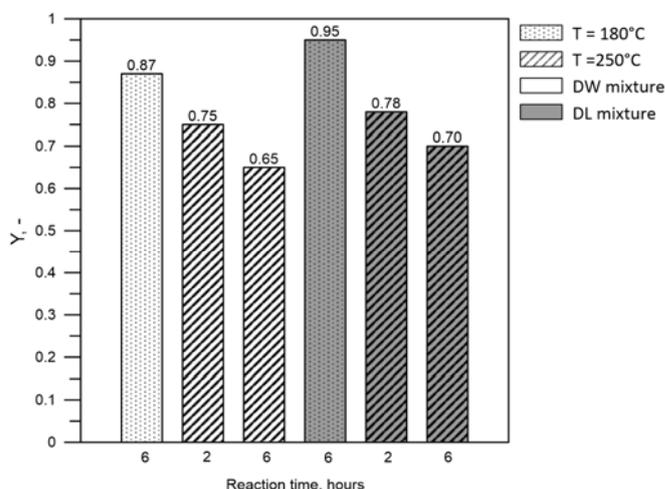

Figure 2: Yield of hydrochar obtained during the HTC experimental runs

Figure 2 shows that the HTC tests carried out at 180 °C generated the highest amounts of hydrochar (0.87 and 0.95 g/g) and that these decrease in the tests at 250 °C (from 0.75 to 0.65 g/g and from 0.78 to 0.70), as the residence time increases from 2 to 6 h for both mixtures. Similar effects of residence time and reaction temperature were observed during the hydrothermal carbonization of digested sewage sludge produced by a wastewater treatment plant (Volpe et al., 2020).

In addition, it should be highlighted that the experimental tests with the DL mixture show a higher yield than that obtained from the tests with the DW mixture. This could be attributed to the organic molecules present in the leachate which may favour the formation of solid carbonaceous structures.

Variations in the hydrochar composition imply changes in its energy content. Figure 3 reports the feedstock energy efficiency (FEE) calculated as indicated by Eq(3):

$$FEE = \frac{W_{hydrochar,dry} \times HHV_{hydrochar,dry}}{W_{reaction\ mixture,dry} \times HHV_{reaction\ mixture,dry}} \qquad (3)$$

where $W_{hydrochar,dry}$ and $W_{reaction\ mixture,dry}$ are the mass of hydrochar and reaction mixture dried, and $HHV_{hydrochar,dry}$ and $HHV_{reaction\ mixture,dry}$ the higher heating values of the hydrochar and reaction mixture dried. The HHV was evaluated using the following Eq(4), proposed by (Channiwala and Parikh, 2002):

$$HHV = 349.1C + 1178.3H + 100.5S - 103.4O - 15.1N - 21.1Ash \qquad (4)$$

where C, H, S, O, N, and Ash are mass percentages of carbon, hydrogen, sulphur, oxygen, nitrogen and ash determined on a dry basis.

Figure 3 displays a reduction of the FEE of about 10% when the temperature was raised from 180 to 250 °C (comparison of the tests DW-180-6 and DW-250-6; DL-180-6 and DL-250-6) and of about 3% when the residence time was increased from 2 to 6 hours (comparison of the tests DW-250-2 and DW-250-6; DL-250-2 and DL-250-6). These results can be explained considering that the increasing of the operating condition severity favours the migration of molecules from the starting reaction mixture to the liquid and gaseous products generated during the process causing a loss of organic elements such as carbon, hydrogen, nitrogen, sulphur and oxygen (Vallejo et al., 2020b). On the other hand, due to its refractoriness to the reaction environment, the inorganic fraction of hydrochar (ash) increases. Consequently, the chemical energy of the hydrochar reduces.
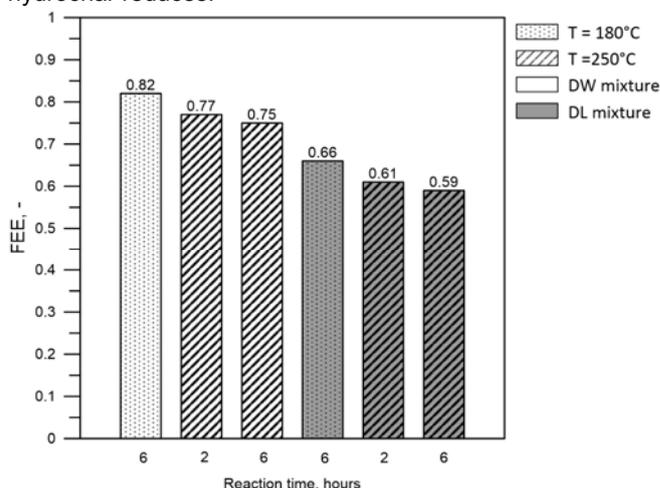

Figure 3: FEE of hydrochar obtained during the HTC experimental runs

The gas produced during the HTC process is composed mainly of CO_2, which ranges from 89 to 98%. The second most abundant gas is CO which can attain concentration up to 10% (Table 4).

Table 4: Composition of the HTC gas.

Test ID	CO_2	CO	H_2	C_mH_n
-		vol.%		
DW-180-6	97.24	0.20	0.07	2.50
DW-250-2	89.45	9.58	0.41	0.56
DW-250-6	89.99	8.22	0.46	1.33
DL-180-6	98.48	0.14	0.21	1.18
DL-250-2	95.21	3.86	0.45	0.48
DL-250-6	97.11	1.13	0.36	1.40

Other gases generated in smaller quantities are H_2 and light hydrocarbons (C_nH_m, sum of CH_4 and traces of C_2–C_4 hydrocarbons such as ethane, ethylene, propane, propylene and butane). The large production of CO_2 could be attributed to decarboxylation reactions. It can be observed that during the experimental tests conducted at 250 °C CO is produced in larger amounts. Probably, this is due to the larger extension, at higher temperatures, of decarbonylation reactions *(Zaccariello et al., 2020)*.

3. Conclusions

The results indicate that the residence time and the reaction temperature affect the composition and yield of the obtained hydrochar. Higher reaction time and temperature determined a considerable increase of ash and carbon contents of hydrochar. On the other hand, oxygen amount reduces. The increasing of the operating condition severity also determined the reduction of the hydrochar chemical energy. This is due to the simultaneous increase of the ash fraction in the hydrochar. The obtained results showed that, in the limited range of the experimental tests conducted, the reaction temperature has a greater impact than the residence time on the conversion of the starting feedstock. Another important result is that leachate can be used in substitution of water in the hydrothermal carbonization process opening interesting economic and environmental perspectives.

Acknowledgments

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