

Low-energy thermo-chemical conversion processes of municipal wet waste

Marco Milanese, Gianpiero Colangelo^{*}, Andrea Mellone, Arturo de Risi

University of Salento, Department of Engineering for Innovation, 73100 Lecce, Italy

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ABSTRACT

Hydrothermal carbonization (HTC) is a low-energy thermochemical process that converts wet biomass into a carbon-rich solid, commonly called hydrochar, for use in a variety of areas, such as soil amendment, biofuels or to produce carbon-based materials. The purpose of this paper is to increase knowledge for the economic valorization of municipal wet waste, considered as a raw material to obtain high value-added products through an HTC process and an additional chemical activation procedure. In the first part of the work, a 4.5-liter batch reactor was designed, built, and used in the HTC experimental campaign by varying the main process parameters, namely reaction time, amount and type of organic waste (e.g. vegetables, fruits, bread, pasta), water concentration, temperature and pressure. In addition, some experiments were conducted by applying the steam explosion technique at the end of the HTC process. The HTC results showed that in biomass with high water content, increasing residence time decreases the hydrochar yield. Considering a dry heterogeneous waste with high carbon content, the yields at the end of the process are much higher. In the second part of this work, the hydrochar samples were treated with a high-temperature activation process based on the use of KOH, obtaining activated carbon. Particularly, the best results were achieved by using high KOH: hydrochar ratios, resulting in high-quality activated carbons with good porosity and a high surface area of 2890 m²/g. Finally, an energy analysis was carried out to evaluate how to make the whole process cost-effective.

1. Introduction

Nowadays, one of the greatest challenges of the scientific world is to develop and improve as much as possible the production of energy from renewable sources, trying to supplement and replace fossil resources with technologies with less environmental impact [1–3]. Several systems have been developed in this scenario, including passive techniques to enhance energy efficiency in buildings [4], based on phase change materials [5–7] or bio-sourced hemp material [8,9] and biomass plants that exploit the transformation and subsequent combustion of organic material, both natural and anthropogenic, to obtain energy, minimizing emissions [10–12].

Popular technologies use organic waste from civil households, as biomass. Specifically, waste is treated through biochemical (waste composting, anaerobic digestion, fermentation, etc.) or thermochemical processes (combustion, gasification, pyrolysis, hydrothermal carbonization). Waste composting is an increasingly less used technique because of the foul odor released during the process and the difficulty of using the resulting product (compost) on a large scale. Anaerobic digestion, by producing biogas, allows energy recovery and currently

seems to be the preferred choice among the various methodologies. However, anaerobic digestion also has significant disadvantages, including the management of the digestate, which is obtained at the end of the process.

Conventional thermochemical processes (combustion, air gasification, pyrolysis) have the disadvantage of pretreating, with a drying process, the wet biomass, making the whole process unsustainable from energy and economic points of view. The use of hydrothermal carbonization (HTC) can provide a solution to the problems just described [13]. HTC is a thermochemical process that produces a carbonized material of coal-like composition. In general, moist raw materials and carbohydrates are used, because water acts as a catalyst in the reaction, which takes place at a relatively low temperature (180 °C–300 °C) for several hours [14]. This conversion process produces a solid charcoal-like compound with high porosity and good heating value. Other products are also generated during the process, including non-condensable gases (mainly CO₂ in small amounts) and aqueous phase products (sugars and organic acids) [15,16]. As described by P. Saetea and N. Tippayawong [17], all biological wastes (food and plant material, animal manure, sewage sludge, etc.) can be treated by the HTC process, converting them into biochar or biocharcoal.

^{*} Corresponding author.

E-mail address: gianpiero.colangelo@unisalento.it (G. Colangelo).

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Nomenclature		Subscripts	
C_p	Specific heat [J/kg K]	<i>Act</i>	Activation process
D	Diameter [m]	<i>Amb</i>	Ambient
L	Specific latent heat [J/kg]	<i>ch</i>	Charcoal
m	mass (kg)	D	Drying
Q	Thermal energy [J]	h	Hydrochar
R	Percentage of recovered heat in HTC process (-)	<i>KOH</i>	Potassium hydroxide
S	Specific surface area [m ² /g]	<i>TOT</i>	Total
T	Temperature [K]	<i>ws</i>	Municipal wet waste
V	Specific volume [m ³ /g]	w	Water
X	content of water (-)	Abbreviations	
Y	hydrochar yield (-)	BET	Brunauer-Emmett-Teller analysis
		HTC	Hydrothermal carbonization
		SEM	Scanning electron microscope

Biochar has multiple uses: as an agricultural soil conditioner in arid or depleted soils [18]; through activation processes, it can work as an adsorbent material for water purification or CO₂ absorption [19] and, as a permeable reactive barrier for water contaminated with Uranium, Copper and Cadmium [20,21]; it can be used as a nanostructured carbonaceous material for use in catalytic processes [19,22,23]. Hydrothermal carbonization of biomass has several advantages over common biological treatment. It typically takes only a few hours, instead of the days or months required for biological processes, and has the advantage that process temperatures are high enough to destroy pathogens and potentially harmful contaminants, such as active pharmaceutical compounds [24]. Because heat is released during the HTC process [25], energy management of the plant can be cost-effective, by maximizing heat recovery from the treated material to the material to be treated. According to this hypothesis, heat and energy recovery is a key element for the industrial success of the project [26].

According to Titirici et al. [27], Fig. 1 compares different biomass conversion processes, in terms of obtained product and efficiency: the HTC process, unlike other techniques, converts all incoming raw material into product.

In scientific literature, the HTC process has been studied for many years and research has been focused on the effects of various operating parameters on the different raw materials. Mendecka et al. [28] did analyses on the environmental impacts of the HTC process performed on olive pomace for energy recovery. Nizamuddin et al. [29] studied the influence of reaction time (from 10 to 60 min) and reaction temperature (from 200 °C to 240 °C) on oil palm shells. Liang et al. [30] studied the effect of different types of binders on pellets obtained through hydrothermal carbonization of tobacco stems. Zbair et al. [31] in 2020 evaluated the use of Hydrochar, obtained from Argan nut shells, as an adsorbent for the removal of bisphenol A and diuron. A test campaign was carried out by Elaigwu and Greenway [32] on coconuts by varying the reaction temperature from 150 °C to 200 °C and the residence time from 5 to 30 min.

Concerning the utilization of food waste, in the HTC process, several researchers have carried out experiments investigating various aspects of the process and possible uses. Kassim et al. [33] and Somorin et al. [34] in their work demonstrated the usefulness of food waste conversion for the production of valuable bioenergy resources. Tests were carried out by Metyouy et al. [35] in order to compare the HTC process with anaerobic digestion using fruits and vegetables as feedstock. These studies showed that the anaerobic process is more suitable than the HTC process for biofuel production as it has a positive energy balance. Periyavaram et al. [36], on the other hand, focused a study on end-of-process water, evaluating the potential of its possible use for methane production with a subsequent anaerobic digestion treatment. Motavaf et al. [37] described how the HTC process on food waste yields hydrochar from which large amounts of fatty acids can be recovered.

The product that is obtained from an HTC process does not have a high economic value, having very limited potential uses. In order to valorize hydrochar, many researchers have experimented with alternative methods to increase its surface area, turning it into activated carbon. Among the methods that have provided the best results are chemical activation processes. Chen et al. [38], in their study on tobacco stems, conducted a test campaign using different activating agents, including KOH, ZnCl₂ and K₂CO₃, to evaluate which one gave better results in terms of increasing surface area. El Hadrami et al. [39], in 2022, conducted tests on argan nut shells and, after subjecting them to an HTC process, performed activation tests with sulfuric acid. Khoshbouy et al. [40] compared activation with CO₂ with that with KOH, showing that activation with potassium hydroxide provides much higher surface area values on the final product. Zhang et al. [41], by inserting additives (NH₄Cl) during the HTC process, obtained a hydrochar with a much lower surface area than the classical values, but the resulting product, once chemically activated, had significantly higher surface area values than the common values.

The purpose of this work is to increase the level of knowledge related to the economic valorization of municipal wet waste, considered as a

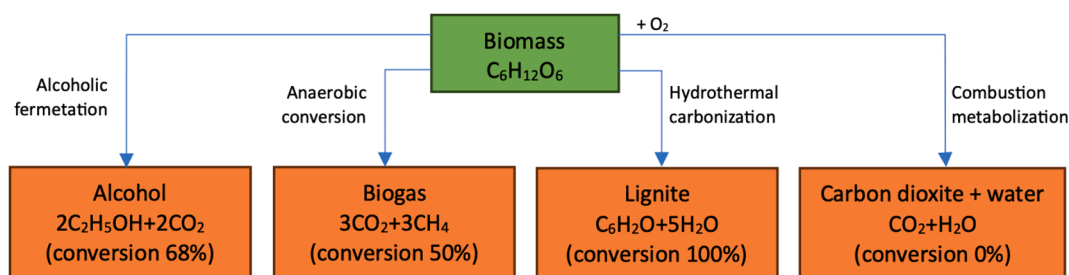


Fig. 1. Comparison of efficiencies among different biomass conversion processes.

raw material to obtain high value-added products through an HTC process and an additional chemical activation procedure: these processes together have never been tested on municipal wet waste. Initially, an HTC testing campaign on the types of raw materials most commonly found in municipal waste (e.g. vegetables, fruits, bread, pasta) has been carried out. During the single test, the effects of operating parameters and the nature of waste on the final hydrochar were evaluated. Additional tests were conducted using the steam explosion technique at the end of the classical HTC process. Steam Explosion is an operation that involves the saturation of biomass with steam, the subsequent increase in temperature and pressure inside a closed vessel, and the subsequent abrupt expansion of the steam that produces an explosion-like effect; this leads to an increase in structural disorder and the consequent increase in porosity of the material. Finally, the hydrochar obtained from the various tests was subjected to a thermochemical activation process, evaluating the quality, in terms of increased surface area, of the activated carbon obtained.

This article can be a valuable guide to converting municipal organic waste into high value-added products, by improving the level of knowledge in the waste management sector.

2. Materials and methods

2.1. HTC experimental setup

The reactor used for the HTC process consists of a cylindrical DN100 stainless steel vessel, having a thickness of 8 mm. The cylinder has a tubular shape with a funnel structure at the bottom to convey the solution during the discharge process; because the HTC reaction occurs at high pressure and high temperature, the system is designed to withstand pressure values above 110 bar. As for filling, the cylinder has a maximum capacity of 4.5 L. Heating bands having a total heat power of about 10 kW (2 central elements of 3.4 kW and 2 elements mounted at the top and bottom of the tube, respectively, of 1.7 kW) are placed on the outer surface of the vessel. Two flanges are screwed on the top and bottom of the vessel, and the whole is surrounded by a layer of rock wool to thermally insulate it and preserve the absorbed heat. The outermost layer, which acts as an enclosure for the entire structure, is made of thin sheet metal. A forced cooling circuit, consisting of an AISI 304 helical coil having an outer diameter of 60 mm, is used inside the reactor.

Two stainless steel tanks with a capacity of 50 L have been used in the circuit. The first one (TANK1) has the function of containing the

discharged product at the end of HTC tests; the second one (TANK2), is a tank for emergency discharge if the maximum allowable pressure is exceeded resulting in the opening of the pressure relief valve (110 bar). Temperature measurement is made by a K-type thermocouple having three sensing points located at 300 mm, 400 mm, and 500 mm from the upper flange. Pressure values are measured both analogically and digitally. Fig. 2 shows the system just described. The temperature and pressure data are processed by a software developed in LabView, which enables continuous control and monitoring.

For tests using the steam explosion technique (at 280 °C and 65 bar), modifications had to be made to the reactor so that it could operate safely. Specifically, the reactor configuration was modified by adding an automatic remote steam valve and a 75 kg ballast to compensate for the boost generated during the steam explosion.

2.2. HTC experimental campaign and procedure

In this study, wet waste obtained from household separate collection was used. The first tests were conducted using only vegetable waste, and then heterogeneous household wet waste was employed. In all cases, the waste was first shredded to reduce its size, facilitating both the loading of the reactor and the HTC process, and then mixed with the set amount of water.

The testing campaign aimed to obtain information on both the final yield (kg hydrochar/kg waste) and the quality and appearance of the post-treatment product. The experimental trials were conducted by testing four types of waste (vegetables, fruits and vegetables, mixed wet, and coffee pods). For each type of waste, the final result was evaluated by varying the main process parameters.

In the following, the steps involved in performing a HTC test are described:

- 1) The waste is initially shredded and mixed with a fixed amount of water.
- 2) The resulting mixture is put inside the reactor and heated until the set point temperature is reached. Heating of the reactor is achieved through the four heating bands placed outside the reactor, in a time varying between 30 and 60 min depending on the temperature value to be reached.
- 3) Once the set temperature is reached, the HTC time count begins.
- 4) At the end of the process, the reactor is cooled by running water inside the coil.

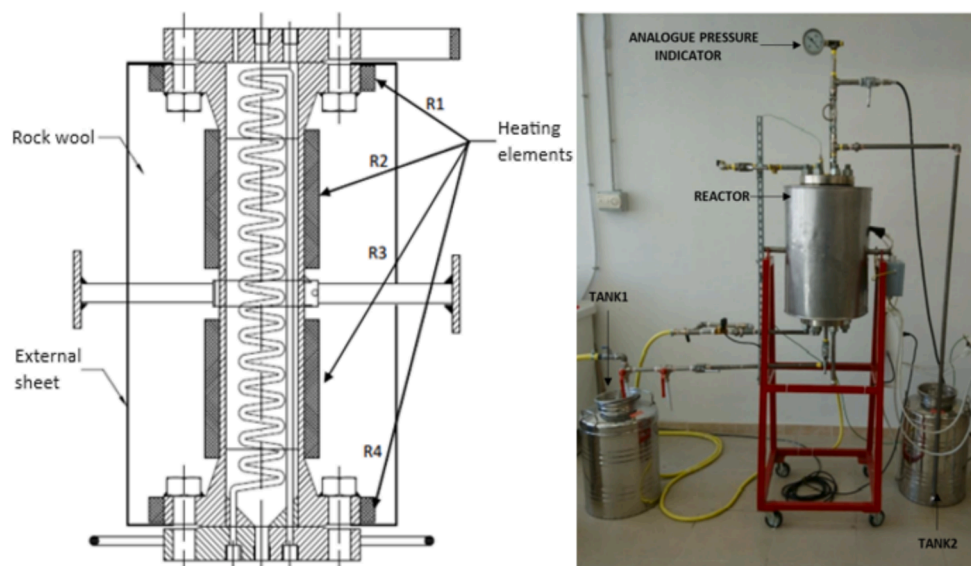


Fig. 2. Setup of HTC reactor.

- 5) When the reactor is cold, the wet final product is collected.
- 6) In the case of steam explosion tests, the reactor is not cooled, but once the HTC process is completed, the exhaust valve is opened, causing the high-pressure product discharge.
- 7) The hydrochar obtained from both types of tests is dried, at a temperature of 160 °C, for one day.
- 8) The dried sample of the final product is ready for subsequent analysis.

The test campaign consists of 16 tests divided into:

- 4 Tests (P1-P4) with only vegetable waste.
- 4 Tests (P5-P8) with fruit and vegetables.
- 4 Tests (P9-P12) heterogeneous wet waste.
- 1 Test (P13) with coffee pods.
- 3 Tests (P14-P16) with Steam Explosion on heterogeneous wet waste.

Table 1 summarizes the HTC tests carried out in the experimental campaign. The parameters (amount of waste and water, temperature, and process time) were chosen considering experiments described in literature. Particularly, in the first 4 tests carried out on vegetables, it was decided to keep constant the parameters of introduced biomass, water and temperature in order to evaluate yield trends as a function of residence time alone.

In the testes with fruits and vegetables, it was decided to keep unchanged the residence time, the amount of material and the temperature and to evaluate the change in yield only as a function of the amount of water added. Besides, it was decided to do two tests for each water ratio in order to check whether the results were similar even on different batches of starting material.

The first two tests with heterogeneous waste were carried out with larger amounts of water and shorter residence times in order to evaluate the influence of water content on the amount of hydrochar produced. In the next two trials, paper towels were added to evaluate the time required to completely carbonize cellulosic material.

The coffee pods were very dry, compared to the materials used previously, so it was decided to add more water and to work with an intermediate residence time compared to the P11 and P12 tests, considering the presence of cellulose enveloping the pods.

Finally, in the first 2 tests with steam explosion, the effect of time reduction (from 8 to 5 h) was evaluated, and in the last test the process temperature was increased so that a higher internal pressure value could be exploited at the end of the process.

Table 1

Main parameters of HTC tests carried out in the experimental campaign (*Presence of cellulosic material, napkins.).

Sample	Starting Material [g]	Mass of water [g]	Temperature [°C]	Time [h]
P1	1000	1000	250	0.5
P2	1000	1000	250	1
P3	1000	1000	250	2
P4	1000	1000	250	3
P5	1500	500	280	3
P6	1500	500	280	3
P7	1500	1000	280	3
P8	1500	1000	280	3
P9	1500	1500	250	1
P10	1500	1500	250	1
P11*	1500	1500	250	3
P12*	1500	1500	250	8
P13	1000	2000	250	6
P14	1500	1500	250	8
P15	1500	1500	250	5
P16	1500	1500	280	5

2.3. Activated carbon: Sample preparation and activation procedure

The hydrochar samples, obtained from the HTC process, were used for the next thermochemical activation step. This process was carried out according to the procedure suggested by Khoshbouy et al. [40], mixing potassium hydroxide (KOH) with hydrochar in a porcelain vessel in different ratios of 1:1, 2:1 and 3:1 (w/w); the resulting mixture was then placed in a closed steel tube and placed in a muffle furnace at 700 °C–800 °C for 60–90 min. The entire process, including the heating, activation and cooling steps, was carried out in an N₂ atmosphere. Once the activation step was finished, the obtained sample was immersed in a beaker containing a solution of hydrochloric acid (HCl 5 M) at a ratio of 1:2 w/v (weight of hydrochar and KOH in grams / volume of HCl in ml), and stirred for 2 h. The obtained product was subjected to a series of washes, to remove chemical residues, initially with hot and then cold distilled water until a pH of 6–7 was obtained, and then placed back in the muffle furnace at 140 °C for 3 h to dry. Table 2 summarizes the main parameters of the thermochemical activation tests.

Thermochemical activation tests were carried out to optimize the process parameters to obtain the maximum value of surface area. The campaign was divided into two parts. In the first one (3 tests), by using the hydrochar obtained from the heterogeneous wet waste, the best KOH-hydrochar ratio was studied. In the second part, once the best ratio was defined, the hydrochar obtained from fruits and vegetables was used to perform six additional tests: the first three with the same parameters as in the previous tests, while in the subsequent tests, the best KOH-hydrochar ratio was again studied. Given the large amount of KOH, it was decided to increase the temperature to 800 °C and the processing time to 90 min, to allow maximizing the completion of the activation reaction.

All samples were characterized in terms of surface area through Brunauer-Emmett-Teller (BET) analyses.

3. Discussion of results

3.1. HTC test results

As a first step, HTC tests were evaluated in terms of the weight percentage of biomass converted into hydrochar (Fig. 3). Particularly, the hydrochar yield was defined as the mass ratio of hydrochar obtained after the drying process to the initial raw material, as in equation (1).

$$Y = \frac{m_h}{m_{ws}} \quad (1)$$

In Fig. 3, the P8 test was taken as a reference since fruits and vegetables represent the species most found in domestic waste and the others were evaluated against it, while Fig. 4 shows some images of final HTC product related to the P8, P11 and P12 tests.

The first 4 tests were carried out on vegetables, and the yield in hydrochar was evaluated by varying the residence time (from 0.5 h to 3 h) while keeping constant the other parameters. The first two tests were used to define the minimum time for complete carbonization of the

Table 2

Thermochemical activation tests.

Test	Sample	Temperature [°C]	Time [min]	Ratio [w/w]
H-AC-1	P10	700	60	1:1
H-AC-2	P10	700	60	2:1
H-AC-3	P10	700	60	3:1
F-AC-4	P5	700	60	2:1
F-AC-5	P6	700	60	2:1
F-AC-6	P7	700	60	2:1
F-AC-7	P8	800	90	3:1
F-AC-8	P8	800	90	4:1
F-AC-9	P8	800	90	5:1

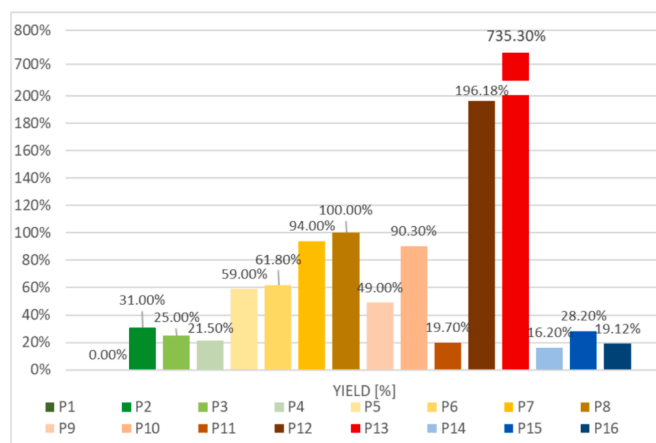


Fig. 3. Weight percentage of biomass converted into hydrochar.

material. Particularly, in the first test (P1), with a duration of 30 min, the output material was not yet carbonized but had vegetable residues. The next test (P2), with a duration of 1 h, allowed for complete carbonization. The second test then defined the minimum time required for the HTC process to take place for waste of vegetable origin only. In the next tests, the treatment time was increased to 2 h and 3 h and the amount of final hydrochar decreased by 20 % and 30 % compared to the test P2. This result is due to the high-water content and low carbon content in the initial biomass, which produce more liquid phase than solid hydrochar at the end of the HTC process.

In the tests with fruits and vegetables (P5-P8), the effect of the amount of water on the final hydrochar yield was evaluated. The P5 and P7 tests were performed with the same raw material, as were the P6 and P8 tests. Besides, the increase in the amount of water resulted in a yield increase of about 60 %. Besides, comparing the P5 and P6 tests performed with the same parameters, the yield is comparable even though the raw material was from different batches. The same result can be seen when comparing P7 and P8.

Heterogeneous wastes (pasta, bread, dried fruit peels) with lower water content than vegetables were considered in the subsequent tests. In the P9 and P10 tests, raw materials from different batches were used. Unlike fruits and vegetables, Fig. 3 shows that the yield values are very different. This is due to the great heterogeneity of the raw material. A wet waste with a reduced amount of internal water has a higher percentage by weight of carbon capable of reacting than a substance with a higher internal water content. A comparison of yields from the P10 test with those from vegetable-only tests shows that the use of a drier raw material increases the amount of product achievable after the HTC process.

In the next two tests, P11 and P12, cellulosic materials such as napkins (waste material that is often present in wet waste) were also treated. The P11 test was carried out with a duration of 3 h; it was noted

that this time did not allow complete carbonization of napkins, as Fig. 4b shows, so the final hydrochar yield was very low. In the P12 test, to solve this problem, the residence time was increased up to 8 h, and with this duration, it reached the complete carbonization even of paper napkins.

According to the result of the P12 test, it was decided to carry out a single test, P13, treating an extremely dry material, compostable coffee pods. As expected, the yield was much higher than in the previous cases (about four times compared to the P12 test), because the material had a much higher carbon content and, therefore, more hydrochar was formed during the process.

Concerning the tests carried out with the steam explosion technique, the yield values turn out to be much lower than in the previous tests on heterogeneous waste. This result is due to the process itself, as the instantaneous release of pressure goes to break up the smallest hydrocarbons making them more difficult to separate from the liquid phase. The goal of steam explosion tests is to evaluate whether the morphology of hydrochar can change, and, thus, whether an increase in surface area can be achieved. To evaluate this effect, porosimetric analyses were carried out on the P12 test (without steam explosion) and the P14 test, since the raw material belonged to the same batch and the HTC process was done for both tests with the same parameters.

Before using the hydrochar for the next process of producing activated carbon, S.E.M. analyses were carried out on the various samples to assess the morphology of the hydrochar, as this parameter is critical to the quality of the final product, and in addition, analyses were conducted on the end-of-process HTC water. Fig. 5 shows the S.E.M. images of the hydrochar obtained for each type of wet waste treated.

After the HTC process, the physical structure and surface morphology of the hydrochar change, and as the temperature increases, they become gradually rougher.

The hydrochar produced from vegetables, Fig. 5.a, has an agglomerated structure that is still smooth with irregularities. This result is due to the hydrolysis process [42] and the short treatment time (1 h). Indeed, Fig. 5.c and 5.d, related to the tests with heterogeneous waste and coffee pods, show that a longer process time, 6–8 h, produced a more homogeneous structure with more developed pores. The test with fruit and vegetable waste, Fig. 5.b, was carried out at higher temperatures (280 °C). This caused the layers at the base of the biomass to be more exposed, thus promoting decomposition into Hydrochar. Besides, the higher temperature facilitates the destruction of walls between adjacent pores, resulting in pore enlargement [43].

Finally, the addition of steam explosion to the HTC process (Fig. 5.e) resulted in a further morphological change that led to an increase in microsphere-shaped structures and, consequently, an expansion of the surface area.

Further analysis was carried out on the residual water from the HTC process to assess whether it could be used and, thus, valued. The results of the analysis (Table 3) show that the water has a good level of nitrogen and phosphates, essential elements for agriculture [44]. The water obtained at the end of the HTC process can then be used by integrating it within the plant growing process as a liquid fertilizer.



Fig. 4. Final product of a) P8 test, b) P11 test with napkin residues, c) P12 test.

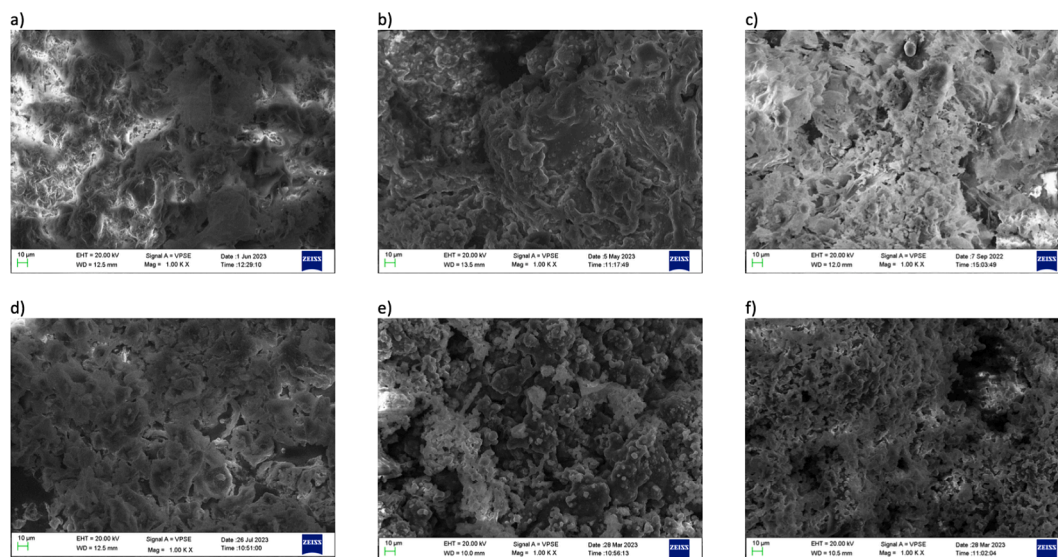


Fig. 5. a) S.E.M. test on vegetables P2, b) S.E.M. test on fruits and vegetables P7, c) S.E.M. test on heterogeneous waste P12, d) S.E.M. test on coffee pods P13, e) S.E. M. test with Steam Explosion P16, f) S.E.M. test on heterogeneous waste with steam explosion P14. The analyses were conducted with SEM ZEISS EVO40.

Table 3
Post-process water analysis.

Parameter Method	U.M.	Results	Uncertainty
pH APAT CNR IRSA 2060 Man 2003	pH unit	5.1	
Nitric Nitrogen UNI EN ISO 10304-1:2009	mg/l	4.490	±1.360
Nitrous Nitrogen UNI EN ISO 10304-1:2009	mg/l	38.330	±9.490
Phosphate UNI EN ISO 10304-1:2009	mg/l	93.0	±2.0
BOD5 (Biochemical Oxygen Demand) APAT CNR IRSA 5120 Man 29 2003	mg/l O ₂	9200.0	
COD (Chemical Oxygen Demand) ISO 15705:2002	mg/l O ₂	22,500	±1564

Looking at Fig. 6, the P12 test obtained a surface area of 6.375 m²/g, while the analysis carried out on the steam explosion test, P14, gave a value of 45.505 m²/g. By observing the distribution, in the P14 test, the percentage with a radius less than 1 μm increased due to the creation, during the steam explosion, of new pores. An increase in the number of pores with a radius of about 10 μm was also observed (Fig. 6.b), due to the collapse of walls between adjacent pores during the passage of steam. The use of the steam explosion technique, as expected, resulted in a good improvement of the hydrochar surface area, which increased by about nine times. By analyzing the two samples at S.E.M., Fig. 5, there was a post-steam explosion morphological change: the sample structure begins to have the typical features, albeit in smaller amounts, of activated carbons.

3.2. Activation test results

The thermochemical activation process with KOH was applied to the hydrochar samples, obtained in the previous HTC tests.

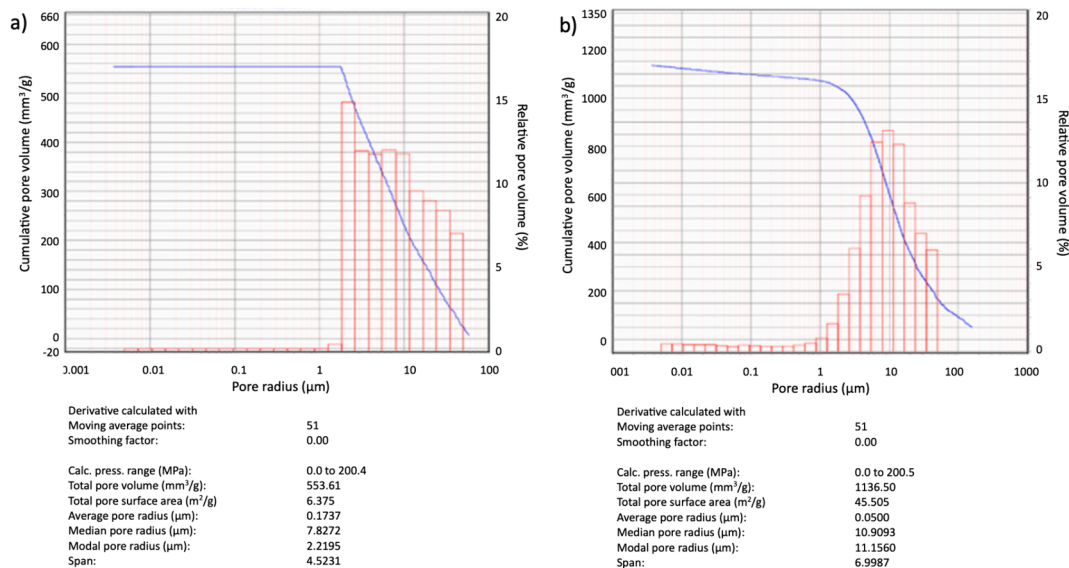


Fig. 6. a) Porosimeter analysis of P12 sample, b) Porosimeter analysis of P14 sample. The measurements were conducted with Mercury Porosimeter Pascal 240 series + Pascal 140 series.

The activation process can be divided into several steps: initially, KOH reacts with the carbon in the hydrochar, generating potassium carbonate (K_2CO_3) and potassium metal (K). At the same time, hydrogen (H_2) and a small amount of carbon dioxide (CO_2) obtained from the gasification of some compounds in the hydrochar are released. Besides, metallic K penetrates the carbon layers and reacts with them [45,46]. In the last phase, the samples are washed with HCl and, therefore, the potassium trapped in the layers is removed, thus generating the pores.

Table 4 resumes the results of several Brunauer-Emmett-Teller (BET) analyses, carried out on the hydrochar samples, before and after the activation process. The surface area of activated hydrochar varies from 171 to 2890 m^2/g ; these results demonstrate how the activation process has an important effect on the morphology of hydrochar, as it results in a significant increase in surface area.

Considering that, generally, the surface area of commercial activated carbon is between 400 and 1500 m^2/g [40], the hydrochar obtained in this work has a very high added value.

In the first part of the activation campaign, it was investigated the best KOH:hydrochar ratio to obtain high values of surface area. The first three tests showed that the change from 1:1 to 2:1 ratio significantly increased the S_{BET} , while the 3:1 ratio gave a lower value than the previous one. Therefore, it was defined that for a process at 700 °C with a duration of 60 min, the 2:1 ratio is the most suitable. Based on this result, three more tests were performed on hydrochar obtained from fruits and vegetables, obtaining slightly better results.

In the last part of the activation campaign, the operating conditions were changed by switching to 800 °C with a duration of 90 min and a larger amount of KOH (up to 5:1). In these experiments, the improvement in terms of S_{BET} , as expected, was very high, obtaining a value of 2890.851 m^2/g . Therefore, as hypothesized, the increased temperature and duration of the tests allowed for greater inclusion of potassium atoms within the coal, thus, generating more pores at the end of the process.

Fig. 7 shows four images of a hydrochar sample before and after the activation process. In this case, the volume occupied by hydrochar has greatly increased, filling almost the entire tube. Fig. 7.c shows that the surface of the activated carbon has extremely porous areas. Fig. 7.d shows a SEM image of the hydrochar sample after activation: on the surface there is a very high distribution of pores, resulting in a high S_{BET} value.

Fig. 8.a shows the adsorption isotherms related to the activation tests performed; desorption isotherms were omitted from the graph since they were found to be coincident with adsorption isotherms. According to the results of [47], activated carbons exhibit type 1 isotherms, that is trends

typical of highly porous materials. The ratio of KOH:hydrochar affects the pore size of the samples. At low KOH:hydrochar ratios during activation there is the formation of new pores and the opening of previously inaccessible pores generating an activated carbon with many micropores. Increasing the ratio results in an additional step involving the collapse of the walls of the created pores, resulting in the formation of larger pores [48]. Observing Fig. 8.a, for relative pressures up to 0.3 the adsorption volume rises sharply as many mesopores are present, while above the relative pressure of 0.3 the volume continues to increase as larger mesopores and macropores are filled.

Fig. 8.b shows the pore size distribution of the hydrochar samples subjected to activation. In agreement with the adsorption curves above, the samples have a very high concentration of mesopores. The pores were found to be concentrated in the diameter range of 3.0 to 4.0 nm. Increasing the amount of KOH led to an enlargement of the pores, in the F-AC-9 test, unlike the previous ones there was a very high peak on the 3.037 nm diameter.

3.3. Energy analysis

To assess the economic impact of the process of producing activated carbon from municipal wet waste, an energy analysis was carried out, considering both the energy required for HTC treatment and the energy used for thermo-chemical activation. The curves in Fig. 9 represent the total energy required to produce 1 kg of activated carbon; in particular, calculations were carried out according to the following mathematical model:

$$Q_{HTC} = (m_{ws} \cdot C_{p,ws} + m_w \cdot C_{p,w}) \cdot (T_{HTC} - T_{amb}) \cdot R \quad (2)$$

$$Q_D = m_{ws} \cdot Y \cdot X \cdot L \quad (3)$$

$$Q_{Act} = m_{ws} \cdot Y \cdot (1 - X) \cdot (C_{p,ch} + 5C_{p,KOH}) \cdot (T_{Act} - T_{amb}) \quad (4)$$

$$Q_{TOT} = Q_{HTC} + Q_D + Q_{Act} \quad (5)$$

In addition, the following assumptions were made:

- Adiabatic reactors.
- HTC process with temperature between 220 and 280 °C.
- Thermo-chemical activation according to the parameters of the F-AC-9 test.
- Heat recovery in the range 0–70 % both in the HTC and in the thermo-chemical activation processes.
- Product yield in the range 20 %-60 % with respect to the initial biomass.

Both graphs show that temperature changes have little impact on energy demand. Fig. 9.a shows the trends in total energy as a function of the percentage of heat recovered in the process. Specifically, the curves were obtained considering a hydrochar yield in HTC treatment of 50 %. Heat recovery greatly affects the energy demand and, thus, the efficiency of the process. A process with no heat recovery requires between 7.4 and 8.1 kWh of energy; by applying 70 % heat recovery instead, the energy consumption drops to 4.17–4.37 kWh with an energy saving of about 43–46 %.

Fig. 9.b shows the trend in energy demand as the amount of yield of the HTC process changes, maintaining a fixed value of heat recovery of 60 %. In this case, the increase in yield allows the total energy demand of the process to be reduced: less initial raw material is required to produce 1 kg of activated carbon and reducing the initial raw material decreases the energy demand of the HTC process, which, among the various stages, has the greatest impact on the final energy. This result demonstrates the need to select wet waste before the HTC process, as this reduces the energy consumption of the whole process. Finally, a comparison of the two graphs shows that the improvement from heat recovery is more

Table 4

Brunauer-Emmett-Teller (BET) analysis results. The analyses were conducted with BET NOVA 2200e.

TEST	INITIAL S_{BET} [m^2/g]	POST-ACTIVATION S_{BET} [m^2/g]	V_{PORE} [cm^3/g]	D_{PORE} [nm]
H-AC-1	3.665	171.513	0.206	3.773
H-AC-2	3.665	722.390	0.362	3.755
H-AC-3	3.665	640.863	0.438	3.378
F-AC-4	5.415	1175.527	0.080	3.769
F-AC-5	3.754	1362.552	0.180	3.757
F-AC-6	1.876	1603.060	0.096	3.799
F-AC-7	2.233	2078.218	0.299	3.335
F-AC-8	2.233	2499.078	0.279	3.366
F-AC-9	2.233	2890.851	0.545	3.037

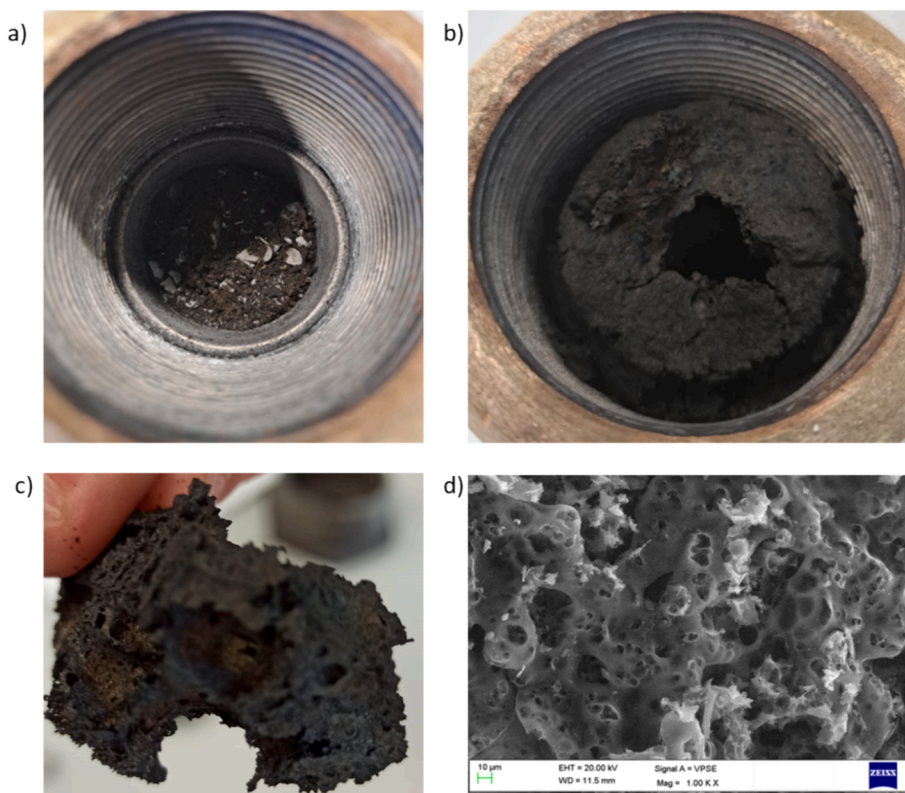


Fig. 7. a) Image of a hydrochar sample before the activation process, b) Image of a hydrochar sample after the activation process, c) Image of the internal side of the hydrochar sample after activation, d) SEM image of hydrochar sample after activation.

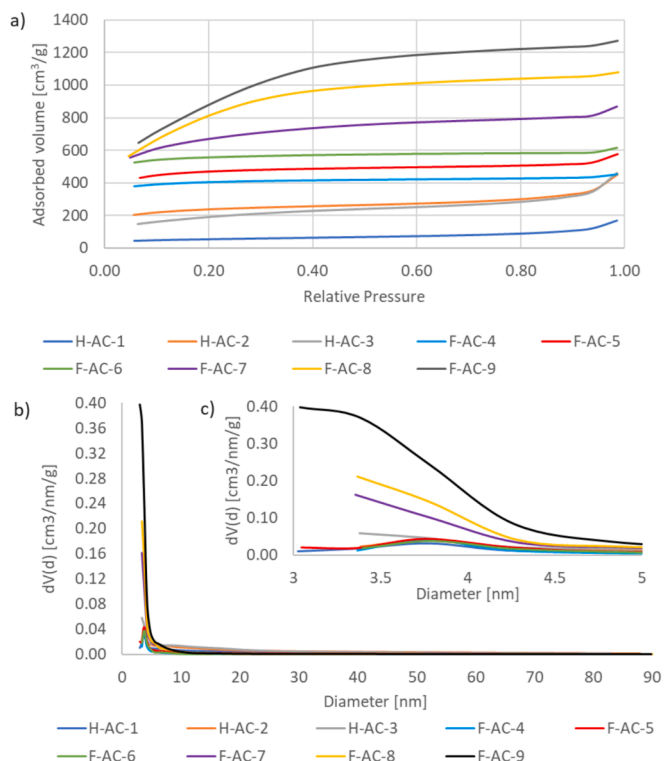


Fig. 8. a) Adsorption isotherm, b) pore distribution, c) region of pore distribution that includes pores with diameters between 3–5 nm. The analyses were conducted with BET NOVA 2200e.

significant than that from increasing the yield percentage.

4. Conclusions

At the state of art, there are two main methods for the processing of organic waste: composting and anaerobic digestion through the action of microorganisms, the waste is converted into compost (material rich in nutrients that is used as an organic fertilizer) or biogas (mixture of methane, CO₂, and other gases, that can be used to generate heat and electricity).

An alternative and viable way to treat organic waste is described in this paper, which is aimed to increase the level of knowledge related to the economic valorization of municipal wet waste, considered as a raw material to obtain high value-added products through an HTC process and an additional thermochemical activation procedure.

An HTC testing campaign on four types of wet municipal waste (vegetables, fruits, bread, pasta) has been carried out, to evaluate the changes in hydrochar yield as the main operational parameters of the carbonization process change. The HTC results showed that in biomass with high water content, increasing residence time decreases the hydrochar yield. Considering a heterogeneous waste or coffee pods, a dry material with high carbon content, the yields at the end of the process are much higher.

One way to economically enhance the hydrochar obtained from HTC is to increase its surface area (at least up to 1000 m²/g) so that it can be considered activated carbon. Therefore, further tests were conducted to evaluate the effect of the steam explosion technique, applied at the end of the classical HTC process, on the quality of hydrochar. The results demonstrated an increase in the hydrochar surface area from 6.375 m²/g to 45.505 m²/g, but this value is not sufficient to consider the hydrochar as activated carbon.

Finally, the hydrochar obtained from the various tests was subjected to a high-temperature activation process with KOH, obtaining a

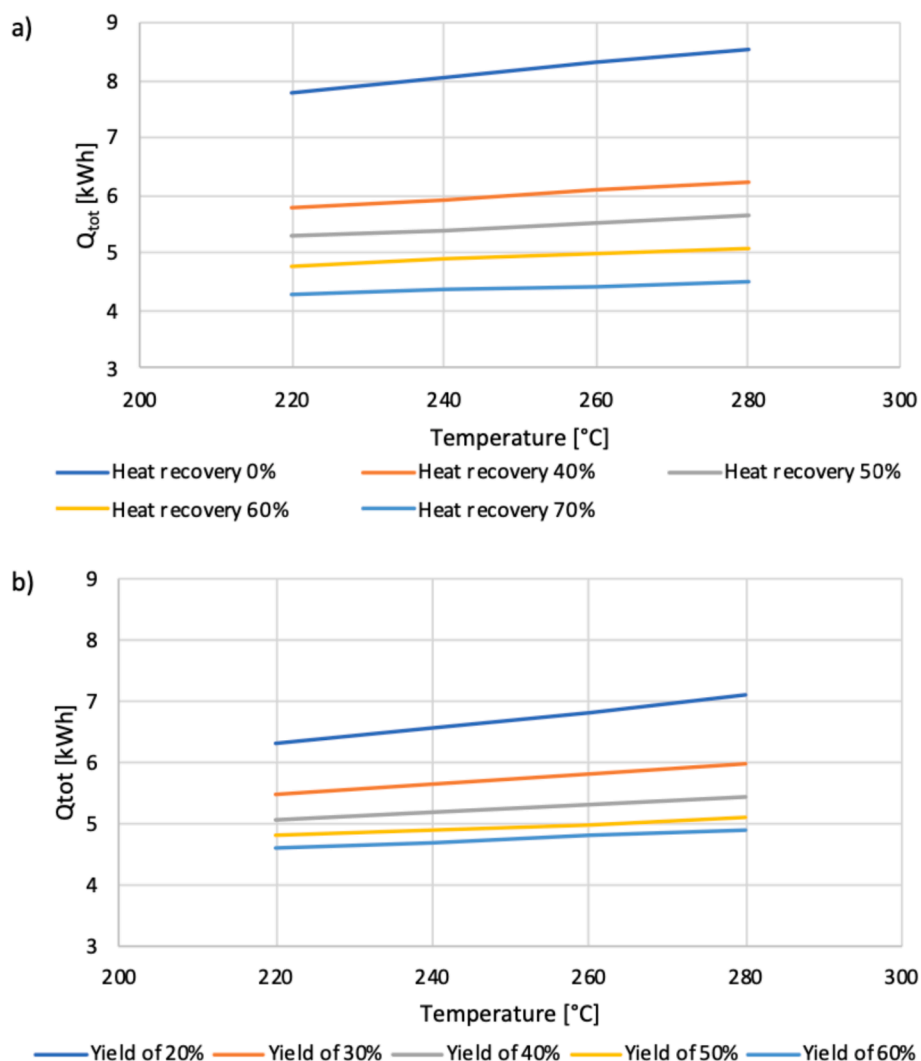


Fig. 9. a) Process heat trend with 50% product yield, b) process heat trend with 60% heat recovery.

maximum S_{BET} value of 2890.851 m^2/g . Particularly, the best results were obtained by using high KOH:hydrochar ratios, resulting in high-quality activated carbons with good porosity.

Finally, an energy analysis was conducted on the entire conversion process from municipal wet waste to activated carbon. This analysis made it possible to quantify the impact of heat recovery on the energy requirements of the entire treatment.

Although further study appears necessary in order to fully understand the issues involved in the use of organic waste for the production of activated carbon (e.g., different types of waste, presence of any hazardous substances in the waste, etc.), the use of the HTC process coupled with thermochemical activation may be a viable way to valorize municipal wet waste.

CRedit authorship contribution statement

Marco Milanese: Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Gianpiero Colangelo:** Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Formal analysis. **Andrea Mellone:** Writing – original draft, Investigation, Formal analysis, Data curation. **Arturo de Risi:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Gianpiero Colangelo reports financial support was provided by DITNE. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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