



Hydrothermal carbonization of the filter bed remained after filtration of olive mill wastewater on olive stones for biofuel application

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Abstract

In the present study, the olive stones (OS) filter bed used for the filtration of olive mill wastewater (OMWW), named OMWW/OS-FR, was converted via hydrothermal carbonization (HTC) into solid biofuel. HTC was operated at three different temperatures (180, 240, and 300 °C) and the chemical and combustible characteristics of the produced hydrochars were investigated. The hydrochars prepared at 240 and 300 °C HTC temperatures exhibited high carbon recovery (80.1–84.2%) and fixed carbon content (45.8–46.8%), reduced volatile matter concentration (49.9–52.2%), low hydrogen to carbon (H/C) and oxygen to carbon (O/C) ratios (0.91–0.98 and 0.18–0.22, respectively) and high heating value (29.7–31 MJ/kg). The characteristics of the HTC-hydrochars were compared to those of biochar prepared by low temperature pyrolysis (LTP) at 400 °C. The results highlighted the improved fuel properties of HTC-hydrochars as compared to those of LTP-biochar in term of energy yield and energy content; this indicates the adaptability of HTC for OMWW/OS-FR upgrading. The temperature of 240 °C was selected as the optimal HTC temperature for the production of hydrochar with enhanced biofuel properties and with lower energy consumption for the thermal treatment of the water contained in the OMWW/OS-FR. Consequently, the use of HTC at 240 °C instead of dry LTP allowed for an energy saving over 49%. Accordingly, it can be concluded that HTC, in term of energy consumption, is more appropriate than LTP to manage the moisture in the OMWW/OS-FR.

Keywords Olive mill wastes · Filtration residue · Hydrothermal carbonization · Biofuel · Energy efficiency

1 Introduction

A worldwide increase in the population has resulted in an increased energy demand by more than 1.5% per year [1]. Such an increase is accompanied by a rapid depletion of conventional fossil fuels and an increase in environmental pollution and climate change impacts, which prompted the use of renewable energies to replace fossil energy sources [2, 3]. The use of lignocellulosic biomass, an abundant and renewable organic material, as a feedstock for the production of fuel is

a growing area of research [4, 5]. In 2017, 12.4% of the total final energy consumption was insured by bioenergy [6], while in 2019, the energy supply from biomass of the world annual energy demand was increased to 14% and thus become the fourth largest energy source after the conventional energy sources [7]. In the period 2018–2023, bioenergy will still be the energy source with the largest growth rate in renewable energy usage [8].

As the demand increases, the interest into the effects of biomass use also increases. The direct application of biomass in energy generation could be limited by their inherent properties. The high moisture content lowers combustion temperature and leads to an increase in CO emission [9, 10]. In addition, the presence of impurities in biomass, particularly alkali metals such as potassium and sodium can cause operational problems of agglomeration, fouling and corrosion [11, 12]. Furthermore, the large variability of physical properties, size and energy density among different feedstock make difficult its transportation, storage and sizing which may also limit its use for fuel production [13]. To overcome these

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problems, a homogenization of different kind of biomass into a form similar to coal to upgrade its fuel properties before combustion is necessary. Among the thermochemical conversion methods, low temperature pyrolysis (LTP) was largely proposed to improve the physicochemical properties of biomass [14–16]. During LTP, biomass feedstock is heated between 300 to 500 °C under oxygen-free atmosphere and with low heating rate to improve their combustion properties [17, 18]. In comparison to other dry technologies such as torrefaction, LTP generates biochar with higher carbon content and fuel ratio, in addition to its improved hydrophobicity and HHV [14, 17]. However, the high inorganic metallic content in ash within the pyrolytic biochar still remains a significant challenge of LTP in addition to its inefficiency to treat feedstock with high moisture content [15, 19]. A relatively new approach of hydrothermal carbonization (HTC) is recently gaining more attention as an attractive technology for high energy density materials production. This method is well adapted to wet feedstock without need of energy intensive drying step; it allows high conversion efficiency of biomass to a carbonaceous material with relatively high yield at low temperature and time [10]. The pretreatment of biomass by HTC follows different mechanistic pathways, resulting in three phases: solid, liquid and gases; its distribution is depending on the experimental conditions as well as on the nature of the feedstock [20, 21]. Depending upon the process conditions used, the major part of carbon contained in the starting feedstock is remained within the final hydrochar, while a considerable amount of inorganics is removed from the hydrochar and dissolved in the liquid phase [22, 23].

The Mediterranean countries have a great biomass potential especially from olive oil extraction processes, since they contribute by over 98% of the worldwide olive oil production [24]. Large quantities of olive wastes, olive mill wastewater (OMWW), and olive solid wastes (OMSW), are produced annually and considered as very high polluting by-products due to their high content in organic matter and some phytoxic compounds [25]. The common strategies adopted by most of olive oil mills, were to evaporate OMWW in evaporation ponds, while the major part of OMSW is generally used for animal feed (fresh) and as feedstock for direct combustion or for pellet manufacturing. These practices, however, may generate in certain cases additional environmental issues and are not economically efficient. HTC as a wet thermal treatment start to be widely used for the treatment/valorization of olive wastes. HTC of olive stones [26], two-phase olive mill waste [27], and olive pomace [28–30] were found to produce high energy density hydrochars. In an earlier study performed by Poerschmann et al. [31], it was concluded that OMWW alone is not an ideal substrate for HTC-process based on the low yield of the produced hydrochar. More recently, Atallah et al. [32] treated the sludge from dried OMWW by HTC at different water-sludge ratios. Operating the process at the

lowest water-sludge ratio leads to hydrochars with high energy content; however, the adoption of this solution could be limited by the high cost of evaporation step.

All studies cited above were interested in treating OMSW and OMWW separately. Enaime et al. [33] proposed a novel and integrated process for the treatment/valorization of both liquid and solid olive wastes. It consists on the use of olive stones (OS), a low-cost and available material in the same industry, for the filtration of OMWW. The use of OS as a support media for the filtration of OMWW has proved its efficiency to reduce suspended solids and fatty matter as well as acceptable fractions of organic substances and phenolic compounds contained in the raw OMWW. However, this system generates another residue, consisting of OS and retained solids and organic compounds from the raw OMWW, which has to be also managed. This residue has an important moisture content allowing it to be well adapted to be upgraded by HTC for biofuel production. The proposed integrated process, which consists on the filtration of OMWW on OS followed by the HTC of the OS filter and its conversion to solid biofuel could be a promising and a scalable technology that can be easily built up in olive mills to manage both liquid and solid wastes without high investment costs and/or high costs associated to residue transportation to the process facilities.

Given this context, the present study aims to the valorization of the OS filter bed resulted from the filtration of OMWW on OS by HTC for biofuel production. The physico-chemical properties of hydrochars produced at three HTC temperatures (180, 240, and 300 °C) were investigated to evaluate their combustion behavior and the feasibility of their use as a solid biofuel. The calculation of the energy invested on the hydrothermal treatment of the moisture contained in the OS filter at the three temperatures was investigated. For comparison, the properties of the produced hydrochars were compared to those of biochar produced from the OS filter by LTP and the potential energy saving of HTC versus LTP for the thermal treatment of the water involved in both processes was also evaluated.

2 Experimental

2.1 Hydrothermal carbonization

In the present study, the filter bed remained after filtration of OMWW on OS, named OMWW/OS-FR, was thermally valorized via HTC. The filtration of OMWW on OS filters was reported in detail in our previous study [33]. About 30 g of the OMWW/OS-FR, having a particle size between 3.15 and 4 mm and a liquid to solids ratio of about 57%, was loaded into a reactor inserted in an autoclave that was heated up to the target temperature set (180, 240, and 300 °C) at a heating rate

of 5 °C/min and kept constant for a holding time of 4.5 h. Note that no solvent apart from the moisture content of the OMWW/OS-FR was added for the HTC reaction. The experiment ended once ambient temperature was reached inside the autoclave, then the resulting solid product was separated from the liquid phase by filtration and both fractions were weighed. Hydrochars were then dried in an oven at 105 °C for 24 h. Solid, liquid and gas yields for each experiment were determined using the following equations (Eqs. 1, 2, 3, 4):

$$\text{Hydrochar mass yield [\%]} = \frac{m_{\text{hydrochar}}}{m_{\text{OMWW/OS-FR}}} \times 100 \quad (1)$$

$$\text{Moisture yield [\%]} = \frac{m_{\text{moisture}}}{m_{\text{OMWW/OS-FR}}} \times 100 \quad (2)$$

$$\text{Liquid phase yield [\%]} = \frac{m_{\text{liquid}}}{m_{\text{OMWW/OS-FR}}} \times 100 \quad (3)$$

$$\text{Gas yield [\%]} = 100 - \text{Hydrochar mass yield} - \text{Moisture yield} - \text{Liquid phase yield} \quad (4)$$

Where $m_{\text{hydrochar}}$ is the mass of the hydrochar after being dried, m_{moisture} is the mass of water that still remains within the hydrochar after being separated from the liquid phase, and m_{liquid} is the mass of the liquid phase.

Carbon recovery in hydrochars ($\text{Hydrochar}_{C,\text{rec}}$) and in liquid phase ($\text{Liquid}_{C,\text{rec}}$) was calculated using Eqs. 5 and 6 [34]:

$$\begin{aligned} \text{Hydrochar}_{C,\text{rec}} [\%] &= \frac{C_{\text{hydrochar}} [\%] \times \text{char mass}}{C_{\text{OMWW/OS-FR}} [\%] \times \text{mass}_{\text{dry OMWW/OS-FR}}} \quad (5) \end{aligned}$$

$$\text{Liquid}_{C,\text{rec}} [\%] = \frac{\text{Total organic carbon} \times \text{Volume of liquid phase}}{C_{\text{OMWW/OS-FR}} \times \text{mass}_{\text{dry OMWW/OS-FR}}} \times 100 \quad (6)$$

The physico-chemical properties of the produced hydrochars were compared to those of biochar prepared by LTP. During the LTP experiment, the dried OMWW/OS-FR was heated up to 400 °C and maintained at this final temperature under N₂ atmosphere during 1 h.

The energy consumption during the thermal treatment of the moisture contained in the OMWW/OS-FR by HTC (E_{HTC}) was calculated. In the present study, the energies considered are the energy required to heat the reactor until the desired temperature (180, 240, and 300 °C) and the energy required to dry the hydrochar after each HTC run. The heat necessary to heat up the hydrothermal material was reduced to the theoretical amount necessary to heat up the water up to the desired temperature. While, neither the energy invested in the solid during HTC experiments nor the energy required to heat the solid during the drying step were considered, assuming that both energies are negligible compared to the energies required to heat and evaporate water [30, 35]. For comparison,

the total energy required during the HTC performed at the optimal temperature is compared to that required for drying the moisture contained in the OMWW/OS-FR before LTP.

The energy required to heat the water until the desired HTC temperature (Energy 1), assuming that the steady state during the HTC reaction was closed to the vapor-liquid equilibrium, was defined following the Eq. 7:

$$\text{Energy 1} \left[\text{kJ/kg}_{\text{OMWW/OS-FR}} \right] = m_1 \left[\int_{T_1}^{T_2} C_p(T) dT \right] \quad (7)$$

Where m_1 is the mass of water in the OMWW/OS-FR, equal to its liquid/solid ratio; T_1 is the ambient temperature, T_2 is the desired HTC temperature (180, 240, and 300 °C) and $C_p(T)$ is the specific heat capacity of water as a function of temperature.

The energy required to evaporate the residual moisture contained in the hydrochar after HTC experiment (Energy 2) and the energy required for the complete evaporation of the moisture contained in the OMWW/OS-FR before dry LTP (Energy 3) are calculated by using the following equation (Eq. 8):

$$\text{Energy}_{2,3} \left[\text{kJ/kg}_{\text{OMWW/OS-FR}} \right] = m_i \left[\int_{20^\circ\text{C}}^{105^\circ\text{C}} C_p(T) dT + \Delta H_{\text{vap}} \right] \quad (8)$$

Where m_i is the mass of water in samples: m_2 is the mass of water in the hydrochar after being separated from the liquid phase and m_3 is the mass of water in the OMWW/OS-FR (equal to its liquid/solid ratio). $C_p(T)$ is the specific heat capacity of water as a function of temperature and ΔH_{vap} is the enthalpy of vaporization of water at 105 °C and 1.01325 bar.

The total energy required in each process is calculated by the following equations (Eq. 9, 10):

$$E_{\text{HTC}} = \text{Energy 1} + \text{Energy 2} \quad (9)$$

$$E_{\text{LTP}} = \text{Energy 3} \quad (10)$$

The energy that can be potentially saved by using HTC instead of dry LTP is calculated using the Eq. 11:

$$\text{Energy saving (\%)} = \frac{E_{\text{LTP}} - E_{\text{HTC}}}{E_{\text{LTP}}} \times 100 \quad (11)$$

The energy efficiency of both HTC and LTP conversion processes was calculated following the Eq. 12:

$$\begin{aligned} \eta_{\text{process}} [\%] &= \frac{\text{HHV}_{\text{char}}}{\text{HHV}_{\text{OMWW/OS-FR}} + E_{\text{heating}} + E_{\text{drying}}} \\ &\times \text{Yield} \quad (12) \end{aligned}$$

2.2 Characterization of hydrochars

Proximate analysis used to determine the weight percentage of volatile matter (VM), ash and fixed carbon (FC) was conducted according to the XP CEN/TS 15148, AFNOR NF EN

1860-2 and AFNOR XP CEN/TS 14774–3 methods. For ash content measurement, 1 g of sample was spread uniformly over a capsule and placed in a muffle furnace. The sample was combusted for 30 min at 250 °C, then the temperature was increased from 250 to 500 °C during 30 min, from 500 to 710 °C for an additional 60 min and maintained at 710 °C until a constant mass (almost 2 h). The capsule was then removed from the furnace and placed in the desiccator until it reached room temperature before being re-weighed. The ash content was calculated as mass loss suffered by the sample having been heated in air at 710 °C. For the VM measurement, the sample was heated without contact with air at 900 °C for 7 min, and the VM was defined as the weight loss ratio in the initial sample subtracted by its moisture content measured by drying the sample at 105° until constant weight. The FC content of samples was determined by subtracting the ash and VM contents from 100%. Carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) percentages in solid samples were measured using an elemental analyzer (Thermo Fisher Flash EA-1112). Oxygen (O) content was calculated by difference and the higher heating value (HHV) was subsequently calculated by using the following equation (Eq. 13):

$$\begin{aligned} \text{High heating value (HHV)} = & 0.3491 C + 1.1783 H \\ & + 0.1005 S - 0.1034 O - 0.0151 N - 0.021 \text{ Ash} \end{aligned} \quad (13)$$

3 Results and discussion

3.1 HTC by-products distribution, carbon distribution, and solid hydrochar characterization

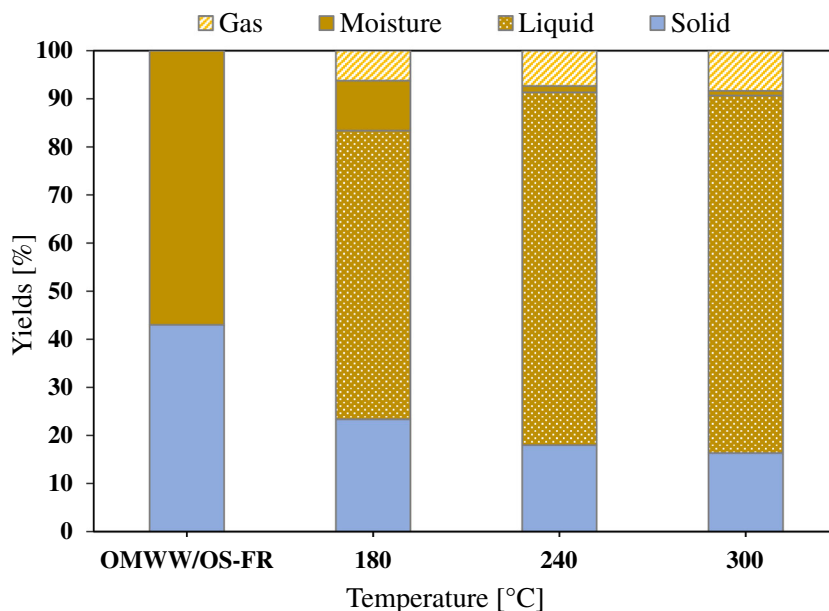
Figure 1 shows the reaction products yields during the HTC experiments. At 180 °C, the HTC solid product consists of a brown lignocellulosic solid with a mass yield of around 23.4%. As the conditions become more severe, the solid yield decreases giving favor to the formation of liquid and gas phases as shown in Fig. 1. The lower mass yields of HTC-240 °C and HTC-300 °C are attributed to the high primary decomposition of the feedstock and the fragmentation of their constituents to gaseous and liquid products as a result of the intensification of the involved reactions of hydrolysis and dehydration [36, 37]. Besides, water above its saturation pressure, remains in its liquid state at high temperatures, allowing the acceleration of the carbonization process; since water behaves as a solvent and also as a catalyst that enhances hydrolysis of hemicellulose and cellulose and leads probably to the dilution of aqueous extractives present in the solid [38–40], this leads to a significant decrease in the hydrochar mass yield giving favor to the formation of liquid and gas phases.

After hydrolysis and following the HTC temperature increase, the hydrolysis products undergo further reactions, which induces an increase in the carbon concentration in hydrochars as compared to the feedstock, while hydrogen and oxygen contents decrease (Table 1). Peterson et al. [41] and Biller and Ross [42] reported that dehydration and decarboxylation reactions are the mainly reactions responsible for the decrease of hydrogen and oxygen contents, respectively, while the carbon enrichment in the hydrochar is attributed to the reactions of condensation and aromatization. The decrease in oxygen and hydrogen concentrations and the increase in carbon content are more pronounced when increasing the temperature from 180 to 240 °C following the intensifications of dehydration and decarboxylation reactions, while only small difference was observed when the temperature is raised from 240 to 300 °C indicating a probable stabilization of the degradation rate. The carbon contents of hydrochars prepared at 240 and 300 °C ranging between 71.7 and 75.2%, are higher than those of lignite (61.6%) and slightly similar to the biochar prepared by LTP at 400 °C (72%), whereas the oxygen percentages were lower. As for hydrogen and oxygen, nitrogen showed a decreasing tendency at 180 °C HTC temperature. However, an increase of nitrogen was observed as the temperature increased from 180 to 240 °C. This can be due to the further hydrolysis of amino acids at higher temperatures, which increases the concentration of nitrogen in the liquid phase, and eventually leads, probably, to the incorporation of nitrogen into the hydrochar following Maillard reaction [12, 43]. The further increase in the HTC temperature to 300 °C induced a decrease in the nitrogen content following deamination reactions, which causes the transfer of amino group from the solid phase as ammonia to the liquid phase [44].

The percentage recovery of carbon in the hydrochars based on that of the carbon content in the OMWW/OS-FR showed a decreasing tendency following the HTC temperature increase. A smaller fraction of carbon initially present in the OMWW/OS-FR was solubilized in the liquid phase at lower HTC temperature (180 °C). As the temperature increases to 240 °C and then to 300 °C, the carbon in the produced hydrochars become more soluble and its concentration in the liquid phase increased accordingly. Despite, a significant fraction of carbon was retained within the hydrochars even at high temperatures (Table 1). The amount of carbon recovered in the HTC-240 °C and HTC-300 °C samples (80.1–84.2%) was higher than that of the LTP-400 °C (58.3%) even samples presented relatively the same carbon percentage. This can be due to the higher mass of char recovered during HTC as compared to LTP. The same tendency was observed by Fuertes et al. [45].

Hydrochar with high carbon recovery can not only increase the energetic efficiency during its combustion but also can provide a means for carbon sequestration. However, the long-term stability of carbon within the hydrochar is not well understood so far. In a study performed by Spokas [46],

Fig. 1 Reaction products yields from the HTC of OMWW/OS-FR at 180, 240, and 300 °C



authors showed that a more reliable predictor of overall stability of hydrochar in soil might be the O/C molar ratio. Hydrochar with an O/C molar ratio of less than 0.2 are typically the most stable, possessing an estimated half-life of more than 1000 years. In the present study and although the carbon recovery was higher at low HTC temperature (180 °C), the hydrochars prepared at 240 and 300 °C showed the lowest O/C and H/C atomic ratios, which leads to suggest that they would be the most stable hydrochars. The changes in H/C and O/C ratios could be clearly analyzed with the aid of Van Krevelen diagram (Fig. 2).

From the van Krevelen diagram, it could be clearly denoted that the evolution of O/C and H/C atomic ratios from OMWW/OS-FR to hydrochars follows the paths of dehydration and decarboxylation reactions, while the contribution of the demethanation reaction was negligible. This tendency was similar to that reported for some other lignocellulosic biomass [47–49]. As shown in the diagram, dehydration and decarboxylation are more intense as the HTC temperature increases

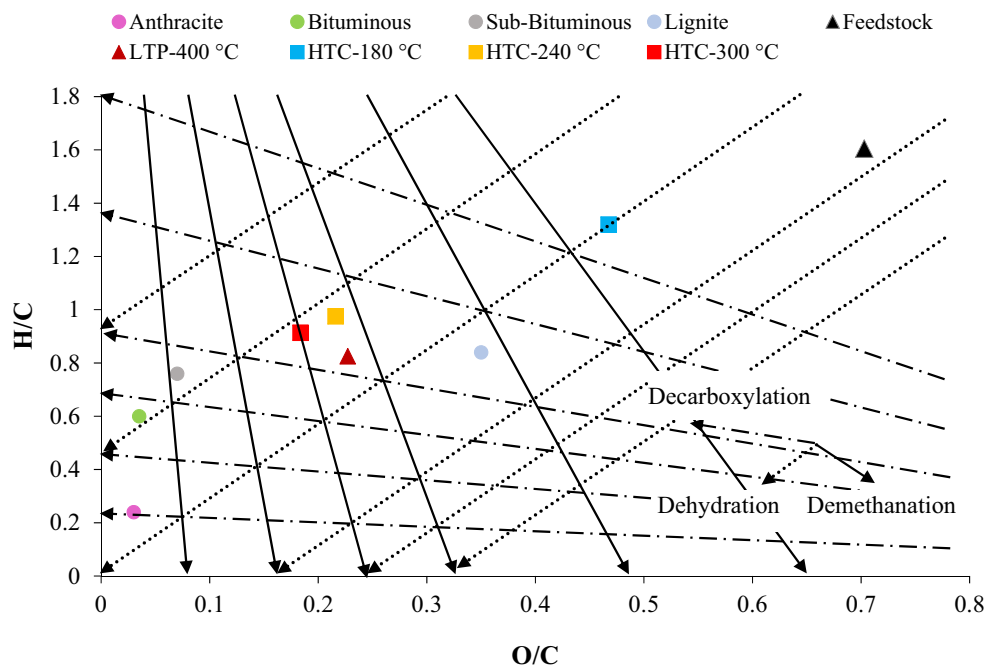
resulting in low O/C and H/C atomic ratios. It can be also observed that HTC-240 °C and HTC-300 °C showed very similar O/C and H/C ratios. This is in line with the results of Cai et al. [36], who reported that dehydration and decarboxylation reactions become stable at temperature around 260 °C and the HTC conversion becomes nearly complete at this range of temperature. Figure 2 shows also the H/C-O/C ratios for the biochar prepared by LTP at 400 °C. A slightly higher percentage of retained oxygen was observed for the LTP-400 °C compared to that of the HTC-240 °C and HTC-300 °C as expressed by the O/C ratio, while the H/C ratio was lower in the LTP-400 °C. This suggests that the ratio of reaction rates of decarboxylation to dehydration is higher in HTC compared to that in the LTP process [23]. The H/C molar ratio can be used as a parameter of carbonization or aromaticity [50, 51]. Hence, the lower value of H/C ratio of the LTP-400 °C indicates that it is less polar and contains more aromatic structures as compared to the HTC-hydrochars. To evaluate the energy utilization value of the produced chars,

Table 1 Elemental and proximate analyses of raw feedstock and biochars compared to those of lignite

	Elemental analysis [%] (d.b.)					Carbon recovery [%] (d.b.)		Proximate analysis [%] (d.b.)		
	C	H	O ^a	N	S	Solid	Liquid	Ash	VM	FC
OMWW/OS-FR	47.9	6.4	44.9	0.8	<0.1	–	–	4.1	72.8	23.2
HTC-180 °C	57.5	6.3	35.8	0.4	0.0	87.6	10.2	4.9	65.5	29.6
HTC-240 °C	71.7	5.8	20.6	1.8	0.0	84.2	13.7	1.9	52.2	45.8
HTC-300 °C	75.2	5.7	18.4	0.7	0.0	80.1	15.1	3.2	49.9	46.8
LTP-400 °C	72.0	5.0	21.8	1.2	0.1	58.3	–	6.6	37.8	55.6
Lignite	61.6	5.7	30.1	1.7	0.8	–	–	10.3	48.8	40.9

^a Calculated by difference

Fig. 2 Van Krevelen diagram for OMWW/OS-FR and produced chars



their H/C and O/C ratios were compared to those of four typical coals reported in a previous research investigated by Parshetti et al. [52]. It could be seen that the atomic ratios of the HTC-hydrochars at 240 and 300 °C and the LTP-400 °C were ranging from those of lignite to those of sub-bituminous coal. Both processes essentially followed dehydration-decarboxylation reactions, with decarboxylation was more intense during HTC than LTP.

As shown in Table 1, the VM of the feedstock decreased significantly as the HTC temperature increases, this loss was compensated with an increase in the FC content. The FC was enhanced by about 35% when increasing the HTC temperature from 180 to 240 °C and by only 3% when increasing the temperature from 240 to 300 °C, while the VM was decreased by more than 20% and 5% at the same HTC temperature ranges. These tendencies illustrate the high decomposition and carbonization level of the lignocellulosic structure during HTC process, which is enhanced as the temperature increases, and stabilized at the HTC temperature of 240 °C. This temperature is slightly similar to the optimal temperature (250 °C) reported in the literature for most feedstock, allowing the production of hydrochar with greater thermal stability [27, 53, 54]. The ash content showed an increasing tendency at 180 °C, followed by a significant decrease when increasing the HTC temperature to 240 °C. The ash content at this temperature was about 52% lower than that of the feedstock indicating that a considerable amount of minerals was released from the biomass to the liquid phase during HTC. The same tendency was observed by Volpe et al. [55]. An opposite effect was observed when increasing the temperature to 300 °C; at high temperatures, minerals in the ash become

more stable than organic compounds, which induces an increase in the ash content within the hydrochar [56]. This tendency can be also due to the excess loss of VM and to the concretion of minerals on the hydrochar surface, a phenomena that is more pronounced at high temperatures [48]. The same increasing tendency was observed in previous studies performing the HTC at the same range of reaction time [40, 57]. The LTP-400 °C retained a lower VM content as compared to the hydrochars (Table 1), while it was higher in ash content. The lower ash concentration of hydrochars as discussed above could be attributed to the higher amount of inorganics dissolved in the subcritical water during HTC.

3.2 Energy efficiency of HTC for OMWW/OS-FR treatment

The energy parameters variation during the HTC of OMWW/OS-FR as a function of the process temperature is shown in Fig. 3.

As was discussed above, the carbon content of hydrochars increased and the oxygen concentration decreased as a result of the HTC temperature increase. This resulted in an improvement of HHV and energy densification of the hydrochars prepared at 240 and 300 °C, while no significant increase was observed at temperature of 180 °C. As was reported by Kim et al. [58], lignin had a higher HHV (20.4 MJ/kg) compared to hemicellulose (13.9 MJ/kg) and cellulose (16.5 MJ/kg). However, lignin is thermally more stable than other compounds and its decomposition cannot occur if the temperature is not high enough. According to Funke et al. [59], the degradation temperature of lignin under hydrothermal conditions

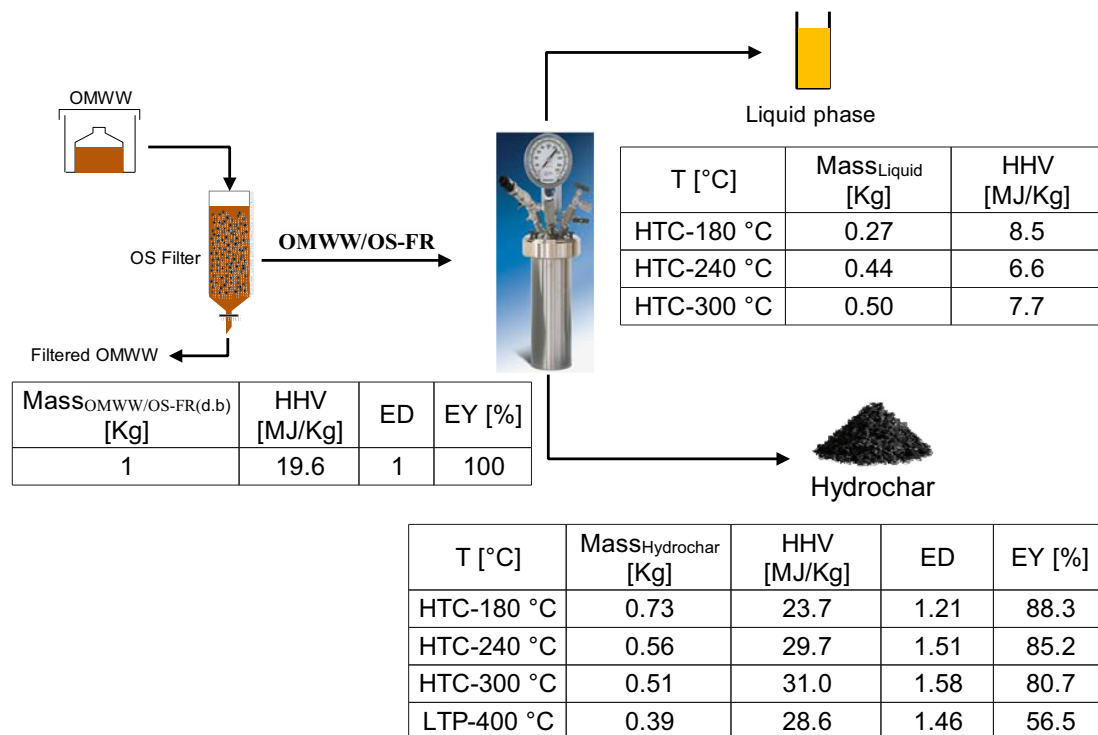
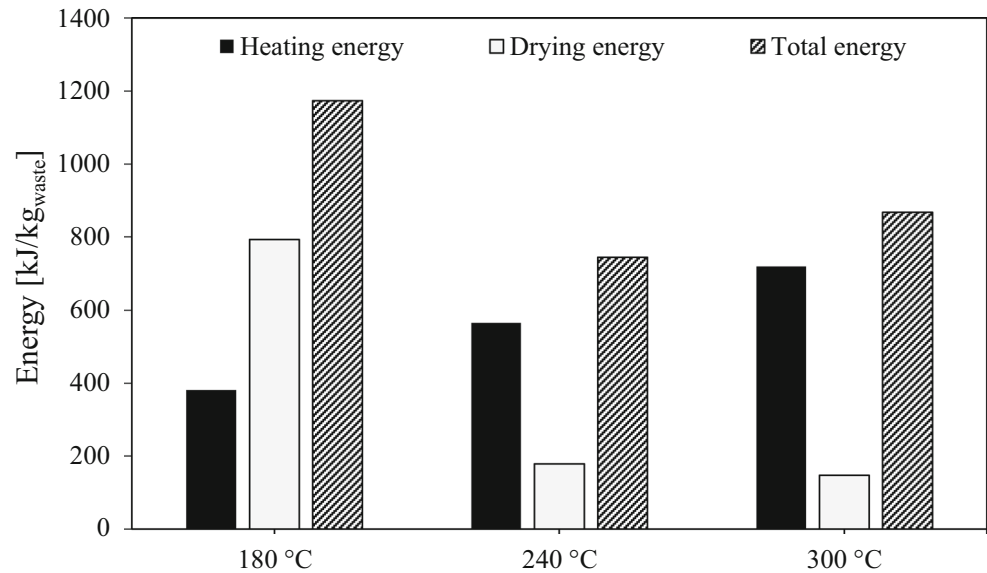


Fig. 3 Energy properties of OMWW/OS-FR and hydrochars prepared by HTC at different temperatures

could decrease to about 200 °C, while other authors reported that lignin remains relatively intact at lower temperatures due to its highly stable structure and begins to degrade at temperature above 250 °C [58, 60]. The high values of energy densification and HHV of hydrochar prepared at 240 °C HTC temperature, compared to the OMWW/OS-FR and to the HTC-180 °C (Fig. 3), could be due to its higher concentration of lignin following the decomposition of cellulose and hemicellulose. Kim et al. [58] also reported that the decomposition rate of lignin may be very slow at the beginning of 250 °C temperature range, this was consistent with the relatively slight change observed in elemental compositions of hydrochars from 250 to 280 °C [58]. This can explain the very slight improvement in the HHV of the HTC-300 °C as compared to HTC-240 °C. The HHV values of hydrochars prepared at 240 and 300 °C. HTC temperatures are higher than those reported for hydrochar obtained by HTC of two-phase olive pulp [27] and for hydrochar obtained by HTC of wheat straw [61]. The HHV results show that the hydrochars at 240 and 300 °C retained greater HHV as compared to the LTP-biochar at 400 °C. This can be due their relatively higher amount of VM and lower ash content, because the inorganic material in chars is incombustible and would decrease its HHV [62]. The values of the energy yield in Fig. 3 show that most of the energy initially present in the feedstock is conserved in the hydrochars, while only small loss of energy is observed, which is mainly contained in the liquid phase. The values of the energy yield are higher than 80.7%, allowing the hydrochars to be effectively used as biofuel.

The possible advantages of HTC for the energetic valorization of the filtration residue characterized by its high moisture content can only be assessed if the whole process chain including the carbonization and the drying of the produced hydrochars is considered. Fig. 4 shows the variation of heating and drying energies and total energy required for the treatment of the moisture contained in the OMWW/OS-FR by HTC. As observed, even the increase in the water heating energy when increasing the HTC temperature from 180 to 240 °C, the energy required to dry hydrochar after HTC is reduced significantly, which leads to the reduction by 1.6 times the total energy for the HTC process. As previously reported by Benavente et al. [30], the moisture of the hydrochar after its separation from the liquid phase is a key factor in the energy efficiency of the HTC process. The lower the moisture content of the hydrochar, the lower the total energy of the HTC process. The moisture content of the hydrochar after HTC decreases significantly, as the reaction severity increases with the temperature having the most important effect [30]. The decrease in the moisture content following the increase of temperature could be explained as follow: the thermal treatment of lignocellulosic biomass, where the moisture is absorbed into the cell walls and hydrogen-bonded to the hydroxyl groups of the cell wall components, allowed for the breakdown of the hydroxyl groups jointly with the hydrolysis of hemicellulose and cellulose [30]. These reactions become increasingly significant with the increase in temperature [27, 34]. As a consequence, the solid becomes more hydrophobic and showed lower moisture content. The further increase in

Fig. 4 Energy estimation of the HTC process for the thermal treatment of the water contained in the OMWW/OS-FR at different temperatures



the HTC temperature to 300 °C, however, reduces the hydrochar drying energy by only 17%, while increases the heating energy by about 22%. The total energy required for the HTC experiment carried out at 300 °C is closed 1.2 times higher than that of the experiment performed at 240 °C, this make of the HTC operating at 240 °C energetically more advantageous. Regarding the hydrochar

properties, the results discussed above (Table 1 and Fig. 2) indicate the stabilization of the HTC degradation reactions at 240 °C, since no significant improvement in term of biofuel properties was observed above this temperature. In overall, no increase of temperature over 240 °C is significantly needed to achieve better results in term of hydrochar quality and energy efficiency.

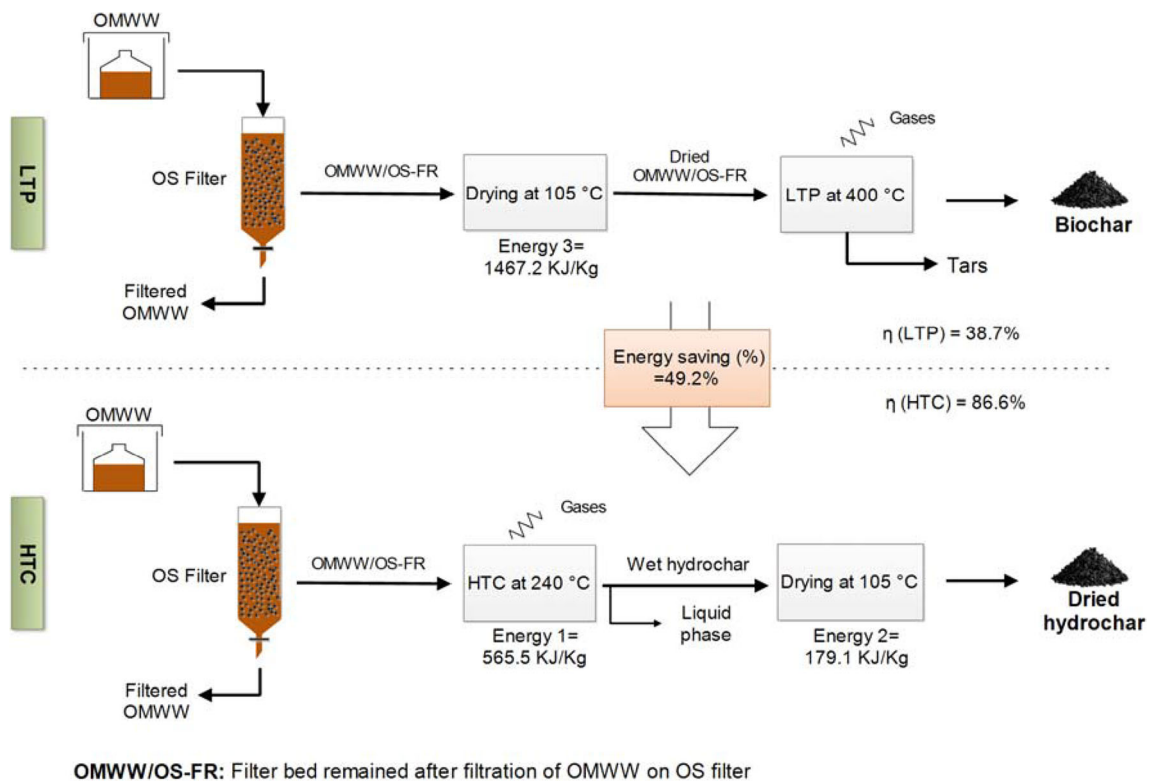


Fig. 5 Comparison between HTC and LTP in term of energy required for the thermal treatment of the water contained in the OMWW/OS-FR

In comparison to LTP and even the slight enhancement of the HTC-240 °C properties as compared to LTP-400 °C, we can say that both chars could be effectively used for biofuel application. The choice of one or other method of conversion may be determined by considering the energy needed for the thermal treatment applied over the water involved in both processes. The results of the energetic comparison between HTC at 240 °C and LTP for the treatment of the moisture contained in the OMWW/OS-FR are summarized in Fig. 5. As shown, the energy required to entirely evaporate the moisture contained in the OMWW/OS-FR before dry LTP is estimated to 1467.2 kJ/kg_{waste}. HTC at a temperature of 240 °C produces hydrochar with more than 90% solid content, by considering both the energy required to heat the water to the reaction temperature (240 °C) and the heat demand to dry the hydrochar to 100% solid content, it is possible to achieve an energy saving of about 49% when using HTC instead of LTP. At this temperature, HTC showed higher thermochemical conversion efficiency (86.6%) as compared to LTP (38.7%).

4 Conclusion

In the present study, the OS filter bed used for the filtration of OMWW was converted to a solid biofuel via HTC. The carbon contents of hydrochars increased to 71.7 and 75.2%, while hydrogen and oxygen contents decreased to about 5.8 and 5.7% and to 20.6 and 18.4% at HTC temperatures of 240 and 300 °C, respectively. At these temperatures, the hydrochars achieved low VM (49.9–52.2%), high FC content (45.8–46.8%) and high HHV (29.7–31 MJ/kg). The hydrochars prepared at 240 and 300 °C showed also enhanced properties as compared to the biochar prepared by LTP at 400 °C in term of energy yield and energy content. Temperature of 240 °C was selected as the optimal HTC temperature for the production of hydrochar with enhanced biofuel properties and with the lowest energy consumption in term of the thermal treatment applied over the water contained in the OMWW/OS-FR. At this temperature, it is possible to achieve an energy saving of about 49% when using HTC instead of dry LTP for the upgrading of the moisture contained in the OMWW/OS-FR.

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