

# **Hydrothermal carbonization of dried olive pomace: energy potential and process performances**

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## **Abstract**

Hydrothermal carbonization (HTC) of dried olive pomace (DOP) was performed in subcritical water under HTC conditions (180-250 °C) to assess the potential of the generated hydrochar to produce energy. The effects of process parameters (holding time, temperature and DOP/water weight ratio) on the yield and the quality of the hydrochar were examined. The mass yield of hydrochar was between 56% and 71% and its HHV increased by more than 23% compared to the HHV of DOP giving a hydrochar similar to a lignite type coal. The results reveal that a 30 min treatment at 215 °C with DOP/water weight ratio of 1/6 maximizes the energy yield (83%) of the HTC process. Both the DOP and the hydrochar were characterized by ultimate, proximate and thermogravimetric analyses. The ultimate and thermogravimetric analyses showed that the hydrochar is more carbonaceous and more thermally stable than untreated DOP. The HTC conversion of raw DOP was carried out by dehydration reactions. The proximate

analysis showed that hydrochars contained lower ash and volatile matter compared to the raw DOP.

**Keywords:** Hydrothermal carbonization; Dried olive pomace; Solid fuel; Thermochemical properties.

## **Nomenclature**

HTC	hydrothermal carbonization
DOP	dried olive pomace
HHV	higher heating value (MJ/kg)
MC	moisture content (%)
VM	volatile matter (%)
FC	fixed carbon (%)
FTIR	Fourier transform infrared spectroscopy
TG	thermogravimetry
DTG	derivative thermo-gravimetry
MY	hydrochar mass yield (%)
ED	energy densification ratio
EY	energy yield (%)

## **1. Introduction**

Biomass energy or bioenergy is considered as the fourth largest energy source (behind oil, coal and natural gas), accounting for about 14% of global primary energy production [1]. In 2012, 70% of global renewable energy used to generate heat came from biomass [2]. In addition, compared to coal, lower sulfur and nitrogen content in biomass fuels reduce gaseous pollutant emissions during combustion and thereby reduce the emission of greenhouse gases [3,4,5]. Finally, in terms of CO<sub>2</sub>, biomass fuels are considered as carbon neutral.

Biomass energy conversion is carried out by biochemical or thermo-chemical transformations. Biochemical conversion of biomass includes fermentation and anaerobic digestion to produce ethanol and biogas, respectively. Thermo-chemical processes can be classified into two categories: (i) dry processes (combustion, gasification and pyrolysis), and (ii) hydrothermal processes [5-8]. The combustion of biomass produces thermal energy, while gasification, pyrolysis and hydrothermal treatment degrade the biomass into gas, liquid and solid fuels [6]. The optimal conversion method depends on the biomass nature, the desired type of energy vector, the environmental constraints and economic factors. Biomass with high moisture content is suitable for hydrothermal conversion, while biomass with lower moisture content (< 50%) is more suitable for dry thermo-chemical processes. Indeed, high moisture reduces the calorific value of biomass and increases the cost of storage and transportation of the raw material [7]. In addition, a biomass drying process is required.

To overcome this constraint, which is a source of energy consumption, hydrothermal treatment of the original wet biomass fuel can be implemented as an elegant solution. Some studies indicate that it is possible to obtain energy savings of over 50% by using HTC rather than other pre-treatment technologies like dry torrefaction [9–11].

HTC occurs in subcritical water between 180 °C and 250 °C and may last a period of time ranging from few minutes to several hours [11–17]. The pressure is autogenous with the saturated vapor pressure of the subcritical water and the gas produced during HTC process [11,14].

The main product of the HTC process of biomasses is a stable, carbonaceous (55-74% carbon) solid, a lignite-like material called "hydrochar" [16], which is characterized by a high calorific value (21.1 to 30.6 MJ/kg) [4,13,18–21]. The nature of the biomass and the operating conditions (holding time i.e. the HTC process time, temperature and the biomass/water weight ratio) affect the composition of the final products [9,10,22,23]. The condensable phase consisting of sugars (glucose, xylose, fructose, sucrose), furfural derivatives (furfural, HMF), organic acids (formic, acetic, lactic) and phenolic compounds (phenol, catechol, cresol), and the un-condensable fractions including CO<sub>2</sub> and CO, are the by-products of the HTC process [11,13,24]. During HTC, raw biomass is surrounded by hot water in the liquid state in the subcritical phase and undergoes changes in its structure by a series of chemical reactions, such as hydrolysis, dehydration, decarboxylation, aromatization, condensation, depolymerization and Fischer-Tropsch type synthesis [10,16,25–27]. Certain polymers constituting the biomass (hemicellulose, cellulose, lignin) become less stable under hydrothermal conditions [22,27–29]. Libra *et al.* [16] and Kambo and Dutta [27] reported that decomposition of biomass by HTC is dominated by similar chemical reactions to those of pyrolysis. However, these authors indicated that HTC decomposition of biomass is initiated by hydrolysis which leads to lower biomass decomposition temperatures compared to pyrolysis. In addition, and according to Pala *et al.* [10] and Kambo and Dutta [27], HTC reduces the ash content of hydrochar due to biomass demineralization, while pyrolysis generally increases the ash content of the char. Non-lignocellulosic materials may also be investigated by the HTC process such as municipal solid waste [30], sewage sludge [31], wastewater [19], digested maize silage [32] and algae [33].

The olive oil industry sector is very important in the Mediterranean Europe and North Africa, with, for example, around 420 000 t/year of olive pomace generated in Morocco, and 130 000 t/year in the Meknes-Tafilalet region alone. Olive pomace is a by-product of the olive oil industry containing water, oil, olive skin, olive pulp, and olive stones [34]. In fact, three kinds of pomace can be considered depending on the extraction technique. In the traditional system after mechanical pressing two phases are obtained: (i) water and oil; and (ii) pomace. The second technique is called 3-phase decanter process. After a crushing/grinding operation of olive, water is added and centrifugation is applied which creates three phases: (i) vegetation water and process water, (ii) oil, and (iii) pomace. The third olive oil extraction technique is the 2-phase decanter process where no water is added; therefore only two phases are obtained after centrifugation generating (i) oil and (ii) olive pomace.

The 3-phases extraction system presents several advantages (complete automation, better quality oil, smaller area needed) compared to traditional pressing but with some disadvantages also like high energy and water consumption, huge wastewater generation and important installation cost. To reduce water consumption, 2-phases extraction system was developed and widely used. However, great difficulties exist for a second oil extraction process from 2-phase olive pomace [35]. These wastes need to be treated to prevent potential negative effects on the environment, especially on water sources. Energy recovery from this waste could provide both a solution for its disposal and for generating additional energy for different needs, such as heat or steam for olive trituration units and for domestic heating in the olive producing regions.

To improve the oil extraction yield, some oil extraction units are equipped with a system able to separate the olive pulp from the olive stones [35]. Álvarez-Murillo *et al.* [17] studied the influence of operating parameters (holding time, temperature and biomass/water ratio) on the HTC conversion of olive stone. Only limited studies have been performed on the HTC treatment of olive pomace [11]. Volpe and Fiori [36] worked on the waste material issued from a 2-phase olive oil extraction process. They studied the effect of temperature between 120 °C and 250 °C and that of biomass/water ratio from 7% to 25% at 250 °C considering that holding time has no influence on the HTC process results.

On the basis of this background, the main objective of the present work is to assess the energy potential of hydrochar obtained from HTC processing of olive pomace produced from 3-phases olive oil extraction process. The influence of the process parameters (holding time, temperature and biomass/water weight ratio) on the quality and the yield of hydrochar is investigated. The biomass/water weight ratio is studied up to 50%. The increase of this parameter increases obviously the hydrochar generated per operation and therefore reduce the energy consumption per operation to heat the water. Together with the fact that we are working with solar-dried pomace samples, our intention is to provide data for the HTC processing of olive pomace under relevant conditions for large scale applications by minimizing the energy needs of the process and therefore maximizing the global process energy efficiency.

## **2. Materials and methods**

### **2.1 Feedstock material**

Depending on the olive oil extraction technology, the moisture content of the olive pomace may reach values up to about 70%: approximately 25-35% for traditional processes, 45-55% for 3-phase centrifugal and 60-70% for 2-phase centrifugal systems [37]. Dried olive pomace (DOP) used in this work was obtained from 3-phase centrifugal extraction systems [37] in Meknes-Tafilalet region (Morocco). After open-air drying of the olive pomace, the raw DOP had a residual moisture content of 7% and a residual oil content of 10% (determined by Soxhlet hexane extraction). The feedstock was preserved in plastic bags in a refrigerator at  $\sim 5^{\circ}\text{C}$ .

### **2.2 HTC experimental procedure**

HTC experiments were conducted in a 50 mL batch reactor (purchased from Top Industrie, France) made of a nickel base alloy (Inconel 718). The HTC autoclave was placed in a furnace connected to a control panel which allowed adjusting and displaying the temperature during the experiment. DOP and distilled water were introduced into the batch reactor at room temperature. For each experiment,  $30 \pm 0.001$  g of distilled water was used, except for experiments with a biomass/water ratio equal to 1/2 where  $18 \pm 0.001$  g was introduced. The mass of raw DOP was weighed to obtain the

biomass/water ratio target. So the mass of raw DOP varied from  $3\pm0.001$  g to  $9\pm0.001$  g. The mixture was manually stirred to ensure thorough wetting of the feedstock. To eliminate the residual air, vacuum was applied to the reactor ~~Air was purged~~ with a ~~vacuum~~ pump. After ~~purging~~ reaching a pressure less than  $60.10^{-3}$  bar, the heating program was started to reach the pre-set temperature. Once the temperature reached the set value, the experiment was carried out for a fixed duration of time. At the end of this time, the reactor was cooled to room temperature using air circulation. Pressure ( $P_{\text{exp}}$ ) and temperature ( $T_{\text{exp}}$ ) were measured permitting to calculate the gas volume produced at room temperature. For this purpose the total volume, including the reactor, pipes and valves volumes has been measured giving a total volume of 66 mL. Gaseous products were purged. The solid and liquid products were separated *via* Büchner filtration. The liquid phase was weighed, stored and protected from light in a refrigerator ( $\sim 5$  °C). The pH of the liquid phase was measured, and the collected hydrochar was weighed and dried at 105 °C for 24 h [11,38]. The analytical techniques used to characterize the raw DOP and the hydrochar are described in the next section.

The holding time, temperature and DOP/water ratio were chosen to study the effect of operating parameters on the performance of HTC conversion. In a first series of experiments, the conditions 215 °C and 1/6 DOP/water weight ratio (equivalent to 86% of moisture content) were fixed while the holding time was varied between 0 and 120 min. The holding time is the duration for which the process temperature is maintained fixed. In fact, the holding time was increased until observing a decrease of the energy yield (Eq. 3). A flash test (holding time = 0 min) was also carried out to study the influence of the heating and cooling steps of the reactor on the HTC process (Fig. 1). In additional experiments, the temperature was varied between 180 °C and 250 °C at the optimized holding time and the DOP/water weight ratio of 1/6. Finally, the DOP/water weight ratio was varied between 1/10 and 1/2 (equivalent to: 91% to 67% of moisture content, respectively) at both optimal holding time and temperature.

## 2.3 Biomass and hydrochar characterization

Analyses of extractives, i.e. hemicellulose, cellulose and acid insoluble lignin fractions of raw DOP were performed according to the literature protocols [39,40]. The analyses were repeated in duplicate giving a maximum standard deviation of 3.3%.

- **Ultimate and proximate analysis**

Elemental composition was determined using a FLASH 2000 CHNS/O analyzer (Thermo Scientific). The moisture content (MC) of the samples was measured by a gravimetric method in accordance with European standards (EN 14774-3: 2009: E). Thermo-gravimetric analysis (TGA) was carried out using a STA 449 F3 thermogravimetric analyzer (NETZSCH) to determine the volatiles, fixed carbon and ash contents. The TGA was carried out using a heating rate of 10 °C/min. The ash content was obtained by the combustion of the sample in air at 550 °C for biomass and 815 °C for hydrochar over a period of 2 h (EN 14775: 2009: E). For the volatile matter (VM), the analysis was performed at 900 °C for 7 minutes in N<sub>2</sub> ambience (EN 15148: 2009 E). The fixed carbon (FC) percentage was obtained from the following relationship:  $FC (\%) = 100 - [MC (\%) + \text{ash} (\%) + VM (\%)]$ . The standard deviation of triplicate runs is: 0.3% for VM, 0.2% for ash, 0.1% for MC and 0.4% for FC.

The high heating value (HHV) was determined using a bomb calorimeter (Parr 1261) and HHV values are given in MJ/kg on a dry basis. The measurements were repeated in duplicate giving a maximum standard deviation of 0.5 MJ/kg.

- **Fourier transform infrared spectroscopy**

The functional groups of raw DOP and hydrochars were analyzed by Fourier transform infrared spectroscopy (FTIR) on a NICOLET 6700 FT-IR spectrometer (Thermo Scientific). Each spectrum was recorded over 64 scans, in a wavenumber range from 4000 cm<sup>-1</sup> to 800 cm<sup>-1</sup> with a resolution of 16 cm<sup>-1</sup>.

- **Criteria to determine HTC performances**

The mass yield of the HTC experiments was obtained from the amount of dry biomass introduced in the reactor. Gas fraction was obtained by considering that the gas was



CO<sub>2</sub> [36]. The ideal gas law was then applied using  $P_{exp}$  and  $T_{exp}$ . The volume occupied by the gas ( $V_{exp}$  at  $T_{exp}$ ) was calculated by difference:  $V_{exp} = \text{total volume} - \text{residual liquid} - \text{hydrochar volume}$ . Hydrochar density was measured and found equal to 0.37; while the density equal to 1 was used for the liquid. The liquid fraction was calculated by difference as: Liquid yield (wt.%) = 100 – Hydrochar yield (wt.%) – Gas yield (wt.%). The experiments with a holding time of 120 min were carried out in triplicate giving a maximum standard deviation of 2.5% for the hydrochar yield.

The HTC performance to produce hydrochar was based on three criteria:

$$\text{Mass yield (\%)} = \frac{\text{Mass}_{\text{dried hydrochar}}}{\text{Mass}_{\text{dried DOP}}} \quad (1)$$

$$\text{Densification energy ratio} = \frac{\text{HHV}_{\text{dried hydrochar}}}{\text{HHV}_{\text{dried DOP}}} \quad (2)$$

$$\text{Energy yield (\%)} = \text{Mass yield (\%)} \times \text{Densification energy ratio} \quad (3)$$

For simplicity, the abbreviation (HC-DOP-X) is used hereafter to denote the hydrochar (HC) in accordance with the studied operating parameters, where X represents the holding time or the HTC treatment temperature or the DOP/water weight ratio. DOP was olive pomace as received from the olive oil factory after the open air drying process and is HTC processed without any grinding or other preparation. Dried DOP was the DOP without 7% of moisture.

### 3. Results and discussion

Systematic HTC experiments were performed in order to examine the influence of different parameters on the DOP conversion process. Holding times were in the range of 0 to 120 min, chosen temperatures were 180 °C, 200 °C, 230 °C and 250 °C and DOP/water weight ratio was between 1/10 and 1/2 (equivalent to: 91% to 67% of moisture content, respectively).

### 3.1 Raw material characterization

The results of proximate and ultimate analyses of the raw ~~row~~ DOP are given in Table 1. The MC of DOP (7.4%) is of the same order of magnitude as those encountered in the literature (5.8%) [41,42]. Both VM (74.2%) and FC (16.1%) fractions of DOP in this work are close to the values found by Di Blasi *et al.* [42]. The DOP has low ash content (2.3%), which is an advantage for energy recovery. Ultimate analysis revealed that raw DOP has higher carbon (53.5% vs. 47.5%) and lower oxygen (38.6% vs. 45.8%) contents than a conventional woody biomass, such as red oak bark [43].

The extractives, hemicellulose, cellulose and acid insoluble lignin contents of raw DOP are also given in Table 1. The results show that the raw DOP contains 39% of hemicellulose and 13% of cellulose with a fraction of acid insoluble lignin and extractives of 29% and 19%, respectively.

The DOP shows a HHV of 22.5 MJ/kg (comparable to the value of 22.3 MJ/kg reported by Chiou *et al.* [41]). For example, this HHV is higher than traditional woody biomass, such as red oak bark (18.9 MJ/kg), fir (21.0 MJ/kg), beech wood (19.3 MJ/kg) and pine wood (19.9 MJ/kg) [5,43,44].

### 3.2 Mass yield

Fig. 2 shows the mass yield for the studied experimental conditions. In the first series of experiments, representing the influence of holding time (Fig. 2A), hydrothermal degradation reactions allow the production of 61% to 70% of hydrochar, at 120 min and 5 min, respectively. The mass yield evolution as a function of holding time reveals a maximum value at 5 min and a decrease until 61% at 120 min. Besides, the treatment with a holding time equal to 0 min (flash experiment) shows the influence of the equipment. In our case, the heating and cooling rates are equal to 6 °C/min and 4 °C/min, respectively (Fig 1). These conditions allow a hydrochar production of 66%. The liquid yield is similar between 5 and 60 min and reaches its maximum values in the 0 and 120 min experiments. During the flash experiment, the reactor temperature is higher than 160 °C, i.e. the start temperature of hemicelluloses hydrolysis, during 33 min which might explain the high yield of the liquid fraction. For 120 min, high liquid

fraction is produced from solid phase decomposition. The gas yield remains low and increases with holding time.

Fig. 2B shows that when temperature increases, the hydrochar yield decreases, while the liquid and gas yields increase. Liquid fraction is produced in largest quantity at a temperature of 250 °C where the lowest hydrochar yield is observed.

For the last series of experiments (Fig. 2C), when the DOP/water weight ratio is between 1/6 and 3/10, there is no effect on the hydrochar yield. For the 1/10 DOP/water weight ratio, lower percentages of solids but higher percentages of liquid fraction are observed in comparison to the previous cases. This may be explained by a higher solvent proportion promoting the solubilization of biomass.

For the conditions of 0 min and 1/10 DOP/water weight ratio, a significant amount of liquid phase is produced. In fact, the solubilization of hemicellulose and extractives into liquid phase is favored at weak HTC conditions [11,24]. When holding time or the temperature increase, the gas and liquid yields increase, while the yield of hydrochar decreases due to the intensification of HTC reactions [11,14,45]. The release of the VM also decreases the yield of hydrochar [13]. At the strongest HTC conditions of temperature (250 °C) and holding time (120 min), the highest quantity of liquid phase is obtained by the degradation of the solid phase during the HTC process.

At a fixed 30 min holding time and a DOP/water weight ratio of 1/6, the temperature effect is more dominant in comparison to the effects of holding time and of DOP/water weight ratio at the set temperature of 215 °C. In fact, the temperature indirectly affects the HTC by changing the properties of pure water. Lower temperatures favor ionic reactions which structure the solid residue, whilst higher temperatures favor biomass decomposition into liquid and gas fractions [26,46]. The dielectric constant of the water decreases from 40 F.m<sup>-1</sup> (180 °C and 10 bars) to 28 F.m<sup>-1</sup> (250 °C and 40 bars) which increases the solubility of organic compounds in subcritical water [25,27]. In addition, the ionic product ( $K_w$ ) varies from 10<sup>-11.6</sup> (180 °C) to 10<sup>-11</sup> (250 °C) favoring acid and base-catalyzed reaction [25,27].

The pH level of the aqueous phase is between 4 and 5 for all experiments. This can be explained by the formation of organic acids such as acetic acid, with smaller amounts of formic and lactic acids [8,13,24,26,47].

### 3.3 Hydrochar characterization

Proximate analysis establishes the propensity of the solid fuel for combustion, pyrolysis or gasification. Table 2 highlights the influence of different parameters on the proximate analysis of DOP after HTC conversion. Hydrochar is less humid than raw DOP (1.8-3.7% vs. 7.4%). The same observation was reported by Yan *et al.* [12] and Sermyagina *et al.* [23]. In fact, HTC eliminates hydroxyl and carboxyl groups during hemicellulose and cellulose hydrolysis reactions, giving rise to a more hydrophobic residue than the initial raw material [12,26]. Hence, lower moisture reduces the transport cost of solid waste and avoids biological deterioration (fermentation) during storage.

VM and FC contents determine the ease with which solid fuel can be gasified or converted by combustion [5]. Generally, a high VM fraction reduces the combustion efficiency and raises pollution emission levels [10,20]. Experimental results in Table 2 show that the VM/(VM+FC) ratio of the carbonaceous matrix in DOP decreases after HTC reactions, as also reported in the literature by Sermyagina *et al.* [23]. In the case of peat, this ratio is equal to 0.7 and as it can be seen from Table 2, four present experimental conditions allow to produce hydrochars with VM/(VM+FC) ratio inferior to this value [4]. So the hydrochar produced by HTC of DOP could become a promising alternative to solid fossil fuels.

The presence of inorganic compounds in the fuel causes the fouling and slagging of the equipment during combustion, pyrolysis or gasification [48]. HTC of DOP allows the restructuring of hydrochar to show lower ash content than raw DOP (<0.1-1.8% vs. 2.3%) which reduces the problems related to slagging and fouling. Inorganic compounds of biomass are transferred into the liquid phase by acid solvation *via* the acetic acid generated during the HTC reactions [10,27].

Table 3 shows the results of the ultimate analysis of raw DOP and produced hydrochar. For all hydrochars, the content of carbon is higher than that of raw DOP, while the

fraction of oxygen is lower and the content of hydrogen remains constant. The nitrogen content is found unchanged. ~~and~~ Sulfur is not-detectable detected meaning that its percent weight is less than the detection limit.

The Van-Krevelen diagram provides general information on the quality and nature of the solid fuel: lower atomic O/C and H/C ratios reduce the energy loss by fumes and steam released during combustion [20,27]. The characteristic zones for biomass, peat, lignite, coal, and anthracite are also shown (Fig. 3). The evolution of the atomic O/C and H/C ratios permit the estimation of the degree of deoxygenation of the biomass by decarboxylation or by dehydration.

Fig. 3 shows that the hydrochars produced in this work are well in the domains of peat and lignite [20]. The evolution of atomic H/C and O/C ratios shows that the HTC conversion of raw DOP was carried out essentially by dehydration reactions as reported by Reza *et al.* [49]. This result was confirmed by ultimate analysis (Table 3). Indeed, the oxygen content decreases and hydrogen does not change with respect to raw DOP. In the case of no losses of hydrogen, its weight fraction should increase.

As can be seen in Fig. 3, the HC-DOP-180 °C run shows that a temperature of 180 °C with a holding time of 30 min and a DOP/water weight ratio of 1/6 are insufficient to complete the conversion of raw by HTC. However, the produced hydrochar evolved from the biomass region to peat and lignite by increasing the HTC temperature. Indeed, increasing the temperature reduces the atomic O/C and H/C ratios and produces a hydrochar similar to lignite, as evidenced for the HC-DOP-250 °C run. The same evolution was observed in the works of Liu *et al.* [20] and Reza *et al.* [49]. Besides, the hydrochars produced at 215 °C remain in the peat region despite increasing the holding time and the DOP/water weight ratio.

### **3.4 Thermal behaviour (TG/DTG) of raw DOP and hydrochar**

Fig. 4 presents the thermo-gravimetric (TG) and the derivative thermo-gravimetric (DTG) results of raw DOP and produced hydrochars as a function of the studied parameters (holding time, temperature and DOP/water weight ratio). The experiments

were carried out in a nitrogen environment with a heating rate of 10 °C/min in a thermogravimetric analyzer.

The degradation of the raw DOP in an inert atmosphere begins at ~175 °C. The TG curves show that the hydrochar is generally more thermally stable than the untreated DOP. In fact, no degradation of hydrochar is observed below 192 °C, while raw DOP loses about 7% of its initial mass at this temperature, suggesting the formation of a more carbonaceous material. Figures 4A and 4C show that the holding time and DOP/water weight ratio have no effect on the thermal behavior of the hydrochar except for HC-DOP-60 min, which is characterized by a weaker loss of mass beyond 380 °C. In Fig. 4B, increasing the temperature increases the thermal stability of the hydrochar. The residual mass is around 25% for the HC-DOP-180 °C but it is between 29-31% at the temperature range of 200-230 °C. A higher residual mass of 38% is observed for the HC-DOP-250 °C.

The DTG curves show that the raw DOP reaches its fastest mass loss at 267 °C and 333 °C which can be attributed to hemicellulose and cellulose decomposition, respectively [50]. A comparable profile has been observed by Guizani *et al.* [51]. Beyond 333 °C, the mass loss of raw DOP may be attributed to the pyrolysis of lignin that breaks down gradually over the broad temperature range of 275-500 °C [52,53].

Fig. 4A presents the DTG curves of hydrochars for various holding times. DTG curves peaks are shifted respectively from 267 °C and 333 °C to about 282 °C and 348 °C. The same phenomenon is observed when temperatures (Fig. 4B) and DOP/water weight ratio (Fig. 4C) were varied. This shift can be explained by the formation of carbonaceous materials by polymerization from furfural-like compounds [14,54]. For all hydrochars, degradation takes place over a wider temperature range, with mostly one sharp peak located between 280 °C and 350 °C. This peak indicates that the largest mass loss is related to cellulose and lignin. The disappearance of the first DTG peak observed for raw DOP can be attributed to hemicellulose destruction during the HTC process.

### 3.5 FTIR of raw DOP and hydrochar

The decomposition of DOP by HTC process is also supported by the FTIR spectra obtained from DOP and produced hydrochar (Fig. 5). As described in the paper of Rizzi et al [55], we observe on Fig 5 bands in specific wavenumber regions of biological materials which are between 3600 - 2800  $\text{cm}^{-1}$  and 800-1800  $\text{cm}^{-1}$ . These absorption bands are more visible in the case of raw DOP spectra. The signal centered at 3313  $\text{cm}^{-1}$  corresponds to an overlap of hydroxyl and amino groups. The presence of hydroxyl group suggests the presence of cellulose hemicellulose [55] and also lignin [56]. Peaks at 2920 and 2840  $\text{cm}^{-1}$  indicate the presence of the C—H stretching in methyl, methylene and methine groups present in lignin [55,56], and aliphatic compounds [55]. The presence of aliphatic compounds can be attributed also to the residual oil. Peaks at 1730  $\text{cm}^{-1}$  and 1630  $\text{cm}^{-1}$  are attributed to C=O stretching vibration of carbonyl groups unconjugated and conjugated with aromatic rings [17]. Peak at 1032  $\text{cm}^{-1}$  reveals the presence of saccharidic-like structures, i.e. hemicellulose and cellulose [55,56].

Fig. 5 shows that the HTC treatment decreases the peaks ranges of hydrochars in comparison with raw DOP. This can be explained by the transformation of the raw DOP structure by chemical reactions such as hydrolysis, dehydration, decarboxylation, aromatization and polymerization [10,16,25–27]. As expected, the decrease of the signal at 3313  $\text{cm}^{-1}$  corresponding to hydroxyl group after HTC treatment can reveal that dehydration occurred during HTC process [17,57]. This finding is in agreement with the elemental analysis and the Van-Krevelen diagram. Weaker range of peaks at 2920  $\text{cm}^{-1}$  and 2840  $\text{cm}^{-1}$  of produced hydrochar suggest that it contains less residual oil than untreated DOP. Finally, HTC treatment decreases the amplitude of the peak at 1032  $\text{cm}^{-1}$  which indicate the degradation of hemicellulose and cellulose of feedstock during the HTC process.

### 3.6 HTC performance

Table 4 shows the influence of the studied parameters on HTC energy performances. The evolution of the HHV of the DOP and the produced hydrochar is also given in

Table 4. As reported in the literature [11,12,17,20,36], the HHV of the hydrochar increased with the carbon content while the percentage of oxygen decreased. Heating and cooling steps (holding time = 0 min) are sufficient to increase the HHV of the hydrochar by 11% compared to raw DOP. A maximum increase of 23% is reached for the HC-DOP-250 °C giving a HHV of 27.6 MJ/kg which is higher than lignite (25.7 MJ/kg) [20]. These are promising values for solid fuel applications of DOP processed by HTC. The produced hydrochar has a HHV between 24.9 and 27.6 MJ/kg, giving an energy densification ratio (ED) of 1.2 compared with DOP used for the HTC experiments (Eq. 2).

The energy yield (EY) is a consequence of trade-off effects between the hydrochar mass yield and its energetic quality ( $EY = MY \times ED$ ). The experimental data (Table 4) show that its values range between 67% and 83%. Its minimal value is obtained with the lowest MY but with the highest HHV. So MY has a strong influence on EY values. Furthermore, the results show that a 30 min treatment at 215 °C with a DOP/water weight ratio equal to 1/6 maximizes the energy yield ( $EY = 83\%$ ) for hydrochar elaboration. Similar results have been obtained by Hoekman *et al.* [13] on a mix of Jeffrey Pine and White Fir.

#### 4. Conclusions

This work was focused on investigating the HTC treatment of DOP at several process conditions, i.e. holding time, temperature and DOP/water weight ratio. Hydrochars were produced and characterized. The resulting hydrochar was more carbonaceous and more thermally stable than the raw DOP. The results show that the HTC conversion of raw DOP was mainly carried out by dehydration reactions. Proximate analysis showed that hydrochars contained lower ash and volatile matter than DOP. Heating and cooling steps only were sufficient to increase the HHV of the hydrochar by 11% compared to DOP. A maximum increase of 23% was reached at 250 °C giving an HHV for the hydrochar similar to lignite. Results reveal that a 30 min treatment at 215 °C with DOP/water weight ratio equal to 1/6 maximizes the energy yield (83%) of the HTC process of DOP.

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## References

- [1] C. Baskar, S. Baskar, and R. S. Dhillon, *Biomass Conversion The interface of Biotechnology, Chemistry and Materials Science*, Springer. Verlag Heidelberg: Springer, 2012.
- [2] IEA, “Tracking Clean Energy Progress 2015 - Energy Technology Perspectives 2015 Excerpt IEA Input to the Clean Energy Ministerial,” International Energy Agency, 2015.
- [3] M. Balat, M. Balat, E. Kırtay, and H. Balat, Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 1: Pyrolysis systems, *Energy Convers. Manag.*, vol. 50, no. 12, pp. 3147–3157, Dec. 2009.
- [4] S. V. Vassilev, D. Baxter, L. K. Andersen, and C. G. Vassileva, “An overview of the chemical composition of biomass,” *Fuel*, vol. 89, no. 5, pp. 913–933, May 2010.
- [5] P. McKendry, “Energy production from biomass (part 1): overview of biomass,” *Bioresour. Technol.*, vol. 83, pp. 37–46, 2002.
- [6] P. McKendry, “Energy production from biomass (part 2): conversion technologies,” *Bioresour. Technol.*, vol. 83, no. 1, pp. 47–54, 2002.
- [7] J. Cheng, *Biomass to renewable energy processes*. USA: CRC Press, 2010.
- [8] J. A. Ruiz, M. C. Juárez, M. P. Morales, P. Muñoz, and M. A. Mendiál, “Biomass gasification for electricity generation: Review of current technology barriers,” *Renew. Sustain. Energy Rev.*, vol. 18, pp. 174–183, Feb. 2013.

- [9] Q.-V. Bach, K.-Q. Tran, R. A. Khalil, Ø. Skreiberg, and G. Seisenbaeva, "Comparative Assessment of Wet Torrefaction," *Energy Fuels*, vol. 27, no. 11, pp. 6743–6753, Nov. 2013.
- [10] M. Pala, I. C. Kantarli, H. B. Buyukisik, and J. Yanik, "Hydrothermal carbonization and torrefaction of grape pomace: A comparative evaluation," *Bioresour. Technol.*, vol. 161, pp. 255–262, Jun. 2014.
- [11] V. Benavente, E. Calabuig, and A. Fullana, "Upgrading of moist agro-industrial wastes by hydrothermal carbonization," *J. Anal. Appl. Pyrolysis*, vol. 113, pp. 89–98, May 2015.
- [12] W. Yan, T. C. Acharjee, C. J. Coronella, and V. R. Vásquez, "Thermal pretreatment of lignocellulosic biomass," *Environ. Prog. Sustain. Energy*, vol. 28, no. 3, pp. 435–440, Oct. 2009.
- [13] S. K. Hoekman, A. Broch, and C. Robbins, "Hydrothermal Carbonization (HTC) of Lignocellulosic Biomass," *Energy Fuels*, vol. 25, no. 4, pp. 1802–1810, Apr. 2011.
- [14] D. Basso et al., "Agro-industrial waste to solid biofuel through hydrothermal carbonization," *Waste Manag.*, May 2015.
- [15] N. U. Saqib, M. Oh, W. Jo, S.-K. Park, and J.-Y. Lee, "Conversion of dry leaves into hydrochar through hydrothermal carbonization (HTC)," *J. Mater. Cycles Waste Manag.*, Apr. 2015.
- [16] J. A. Libra et al., "Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis," *Biofuels*, vol. 2, no. 1, pp. 71–106, Jan. 2011.
- [17] A. Álvarez-Murillo, S. Román, B. Ledesma, and E. Sabio, "Study of variables in energy densification of olive stone by hydrothermal carbonization," *J. Anal. Appl. Pyrolysis*, vol. 113, pp. 307–314, May 2015.
- [18] L.-P. Xiao, Z.-J. Shi, F. Xu, and R.-C. Sun, "Hydrothermal carbonization of lignocellulosic biomass," *Bioresour. Technol.*, vol. 118, pp. 619–623, Aug. 2012.
- [19] J. Poerschmann, I. Baskyr, B. Weiner, R. Koehler, H. Wedwitschka, and F.-D. Kopinke, "Hydrothermal carbonization of olive mill wastewater," *Bioresour. Technol.*, vol. 133, pp. 581–588, Apr. 2013.

- [20] Z. Liu, A. Quek, S. Kent Hoekman, and R. Balasubramanian, "Production of solid biochar fuel from waste biomass by hydrothermal carbonization," *Fuel*, vol. 103, pp. 943–949, Jan. 2013.
- [21] M. Hitzl, A. Corma, F. Pomares, and M. Renz, "The hydrothermal carbonization (HTC) plant as a decentral biorefinery for wet biomass," *Catal. Today*, vol. 257, pp. 154–159, Nov. 2015.
- [22] E. Dinjus, A. Kruse, and N. Tröger, "Hydrothermal Carbonization - 1. Influence of Lignin in Lignocelluloses," *Chem. Eng. Technol.*, vol. 34, no. 12, pp. 2037–2043, Dec. 2011.
- [23] E. Sermyagina, J. Saari, J. Kaikko, and E. Vakkilainen, "Hydrothermal carbonization of coniferous biomass: Effect of process parameters on mass and energy yields," *J. Anal. Appl. Pyrolysis*, vol. 113, pp. 551–556, May 2015.
- [24] M. T. Reza, E. Rottler, L. Herklotz, and B. Wirth, "Hydrothermal carbonization (HTC) of wheat straw: Influence of feedwater pH prepared by acetic acid and potassium hydroxide," *Bioresour. Technol.*, vol. 182, pp. 336–344, Apr. 2015.
- [25] I. Pavlovič, Ž. Knez, and M. Škerget, "Hydrothermal Reactions of Agricultural and Food Processing Wastes in Sub- and Supercritical Water: A Review of Fundamentals, Mechanisms, and State of Research," *J. Agric. Food Chem.*, vol. 61, no. 34, pp. 8003–8025, Aug. 2013.
- [26] A. Funke and F. Ziegler, "Hydrothermal carbonization of biomass: a summary and discussion of chemical mechanisms for process engineering," *Biofuels Bioprod. Biorefining*, no. 4, pp. 160–177, 2010.
- [27] H. S. Kambo and A. Dutta, "A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications," *Renew. Sustain. Energy Rev.*, vol. 45, pp. 359–378, May 2015.
- [28] Ortw. Bobleter, "Hydrothermal degradation of polymer's derived from plants," *Prog Polym Sci*, vol. 19, no. 94, pp. 797–841, 1994.
- [29] S. Kang, X. Li, J. Fan, and J. Chang, "Characterization of Hydrochars Produced by Hydrothermal Carbonization of Lignin, Cellulose, D-Xylose, and Wood Meal," *Ind. Eng. Chem. Res.*, vol. 51, no. 26, pp. 9023–9031, Jul. 2012.

- [30] I.-H. Hwang, H. Aoyama, T. Matsuto, T. Nakagishi, and T. Matsuo, "Recovery of solid fuel from municipal solid waste by hydrothermal treatment using subcritical water," *Waste Manag.*, vol. 32, no. 3, pp. 410–416, Mar. 2012.
- [31] G. K. Parshetti, Z. Liu, A. Jain, M. P. Srinivasan, and R. Balasubramanian, "Hydrothermal carbonization of sewage sludge for energy production with coal," *Fuel*, vol. 111, pp. 201–210, Sep. 2013.
- [32] J. Mumme, L. Eckervogt, J. Pielert, M. Diakité, F. Rupp, and J. Kern, "Hydrothermal carbonization of anaerobically digested maize silage," *Bioresour. Technol.*, vol. 102, no. 19, pp. 9255–9260, Oct. 2011.
- [33] A. Broch, U. Jena, S. Hoekman, and J. Langford, "Analysis of Solid and Aqueous Phase Products from Hydrothermal Carbonization of Whole and Lipid-Extracted Algae," *Energies*, vol. 7, no. 1, pp. 62–79, 2013.
- [34] D. K. Yanik, "Alternative to traditional olive pomace oil extraction systems: Microwave-assisted solvent extraction of oil from wet olive pomace," *LWT - Food Sci. Technol.*, vol. 77, pp. 45–51, Apr. 2017.
- [35] A. Roig, M. L. Cayuela, and M. A. Sánchez-Monedero, "An overview on olive mill wastes and their valorisation methods," *Waste Manag.*, vol. 26, no. 9, pp. 960–969, Jan. 2006.
- [36] M. Volpe and L. Fiori, « From olive waste to solid biofuel through hydrothermal carbonisation: The role of temperature and solid load on secondary char formation and hydrochar energy properties », *J. Anal. Appl. Pyrolysis*, vol. 124, pp. 63–72, mar 2017
- [37] International Olive Council, "Quality management guide for the olive-pomace oil extraction industry." 2006.
- [38] Z. Liu and R. Balasubramanian, "Upgrading of waste biomass by hydrothermal carbonization (HTC) and low temperature pyrolysis (LTP): A comparative evaluation," *Appl. Energy*, vol. 114, pp. 857–864, Feb. 2014.
- [39] F.-X. Collard, "Nouvelles stratégies catalytiques pour la gazéification de la biomasse : influence des métaux imprégnés sur le mécanisme de pyrolyse," Thèse de doctorat, Université de Technologie de Compiègne (UTC), France, 2012.

- [40] S. Li, S. Xu, S. Liu, C. Yang, and Q. Lu, ‘Fast pyrolysis of biomass in free-fall reactor for hydrogen-rich gas’, *Fuel Processing Technology*, vol. 85, no. 8–10, pp. 1201–1211, Jul. 2004.
- [41] B.-S. Chiou et al., “Torrefaction of pomaces and nut shells,” *Bioresour. Technol.*, vol. 177, pp. 58–65, Feb. 2015.
- [42] C. Di Blasi, C. Branca, F. E. Sarnataro, and A. Gallo, “Thermal Runaway in the Pyrolysis of Some Lignocellulosic Biomasses,” *Energy Fuels*, vol. 28, no. 4, pp. 2684–2696, Apr. 2014.
- [43] W. Jin, K. Singh, and J. Zondlo, “Pyrolysis Kinetics of Physical Components of Wood and Wood-Polymers Using Isoconversion Method,” *Agriculture*, vol. 3, no. 1, pp. 12–32, Jan. 2013.
- [44] D. Neves, H. Thunman, A. Matos, L. Tarelho, and A. Gómez-Barea, “Characterization and prediction of biomass pyrolysis products,” *Prog. Energy Combust. Sci.*, vol. 37, no. 5, pp. 611–630, Sep. 2011.
- [45] W. Yan, J. T. Hastings, T. C. Acharjee, C. J. Coronella, and V. R. Vásquez, “Mass and Energy Balances of Wet Torrefaction of Lignocellulosic Biomass <sup>†</sup>,” *Energy Fuels*, vol. 24, no. 9, pp. 4738–4742, Sep. 2010.
- [46] A. Jain, R. Balasubramanian, and M. P. Srinivasan, “Hydrothermal conversion of biomass waste to activated carbon with high porosity: A review,” *Chem. Eng. J.*, vol. 283, pp. 789–805, Jan. 2016.
- [47] J. G. Lynam, M. Toufiq Reza, V. R. Vasquez, and C. J. Coronella, “Effect of salt addition on hydrothermal carbonization of lignocellulosic biomass,” *Fuel*, vol. 99, pp. 271–273, Sep. 2012.
- [48] A. M. Smith, S. Singh, and A. B. Ross, “Fate of inorganic material during hydrothermal carbonisation of biomass: Influence of feedstock on combustion behaviour of hydrochar,” *Fuel*, vol. 169, pp. 135–145, Apr. 2016.
- [49] M. T. Reza, B. Wirth, U. Lüder, and M. Werner, “Behavior of selected hydrolyzed and dehydrated products during hydrothermal carbonization of biomass,” *Bioresour. Technol.*, vol. 169, pp. 352–361, Oct. 2014.
- [50] Y. Lee et al., “Comparison of biochar properties from biomass residues produced by slow pyrolysis at 500°C,” *Bioresour. Technol.*, vol. 148, pp. 196–201, Nov. 2013.

- [51] C. Guizani, K. Haddad, M. Jeguirim, B. Colin, and L. Limousy, “Combustion characteristics and kinetics of torrefied olive pomace”, *Energy*, vol. 107, pp. 453–463, Jul. 2016.
- [52] E. Apaydin-Varol, E. Pütün, and A. E. Pütün, “Slow pyrolysis of pistachio shell,” *Fuel*, vol. 86, no. 12–13, pp. 1892–1899, Aug. 2007.
- [53] Y. Lee, P.-R.-B. Eum, C. Ryu, Y.-K. Park, J.-H. Jung, and S. Hyun, “Characteristics of biochar produced from slow pyrolysis of Geodae-Uksae 1,” *Bioresour. Technol.*, vol. 130, pp. 345–350, Feb. 2013.
- [54] M. Sevilla and A. B. Fuertes, “The production of carbon materials by hydrothermal carbonization of cellulose,” *Carbon*, vol. 47, no. 9, pp. 2281–2289, Aug. 2009.
- [55] V. Rizzi, F. D’Agostino, P. Fini, P. Semeraro, and P. Cosma, « An interesting environmental friendly cleanup: The excellent potential of olive pomace for disperse blue adsorption/desorption from wastewater », *Dyes Pigments*, vol. 140: pp. 480–490, May 2017.
- [56] Xu, F., Yu, J., Tesso, T., Dowell, F., Wang, D., “Qualitative and quantitative analysis of lignocellulosic biomass using infrared techniques: A mini-review”. *Appl. Energy*, vol 104, pp.801–809, Jan 2013
- [57] W. Yan, S. Perez, and K. Sheng, “Upgrading fuel quality of moso bamboo via low temperature thermochemical treatments: Dry torrefaction and hydrothermal carbonization “, *Fuel*, vol. 196, pp. 473–480, May 2017.

## Figure captions

**Fig. 1:** Temperature profile during a flash experiment (holding time=0 min, T=215 °C, DOP/water weight ratio=1/6)

**Fig. 2:** Mass yield (%) for various **A)** holding times (T=215 °C, DOP/water weight ratio=1/6), **B)** temperatures (holding time=30 min, DOP/water weight ratio=1/6) and **C)** DOP/water weight ratios (holding time=30 min, T=215 °C).

**Fig. 3:** Van Krevelen diagram of raw DOP and hydrochars obtained at various holding times (T=215 °C, DOP/water weight ratio=1/6), temperatures (holding time=30 min, DOP/water weight ratio=1/6) and DOP/water weight ratios (holding time=30 min, T=215 °C).

**Fig. 4:** TG and DTG curves for raw DOP and hydrochars obtained at various **A)** holding times ( $T=215\text{ }^{\circ}\text{C}$ , DOP/water weight ratio=1/6), **B)** temperatures (holding time=30 min, DOP/water weight ratio=1/6) and **C)** DOP/water weight ratios (holding time=30 min,  $T=215\text{ }^{\circ}\text{C}$ ).

**Fig. 5:** FTIR spectra of raw DOP and hydrochar obtained at various **A)** holding times ( $T=215\text{ }^{\circ}\text{C}$ , DOP/water weight ratio=1/6), **B)** temperatures (holding time=30 min, DOP/water weight ratio=1/6) and **C)** DOP/water weight ratios (holding time=30 min,  $T=215\text{ }^{\circ}\text{C}$ ).

#### **Table caption**

**Table 1:** Proximate, ultimate, structural and heating values characteristic of untreated DOP

**Table 2:** Proximate analysis for hydrochar samples and raw DOP

**Table 3:** Ultimate analysis for hydrochar samples and raw DOP

**Table 4:** HTC performance of experiments

**Table 1:** Proximate, ultimate, structural and heating values characteristic of untreated DOP

<b>Proximate analysis (%)</b>	
MC	7.4
VM	74.2
FC	16.1
Ash	2.3
<b>Ultimate analysis (%)</b>	
C	53.5±0.2
H	6.8±0.1
N	1.1±0.1
O <sup>a</sup>	38.6±0.3
S	n.d
Extractives (%)	18.6±3.3
Hemicellulose (%)	39.4±0.1
Cellulose (%)	12.6±3.2
Acid insoluble lignin (%)	29.3±0.2
<b>HHV (MJ/kg)</b>	<b>22.5</b>

MC: moisture content, VM: volatile matter, FC: fixed carbon, <sup>a</sup>: by difference, n.d: not detectable (< 0.1%).

± Standard deviation of the results



**Table 2:** Proximate analysis for hydrochar samples and raw DOP

Holding time (min)	Temperature (°C)	DOP/water weight ratio	Proximate analysis (%)				VM/ (VM+FC)
			MC	VM	FC	Ash	
0	215	1/6	1.9	72.3	25.2	0.6	0.74
5			2.6	72.9	23.5	1.0	0.76
30			3.2	70.5	25.2	1.1	0.74
60			3.3	70.2	26.0	0.5	0.73
120			1.8	68.1	28.9	1.2	0.70
30	180	1/6	3.7	71.6	23.6	1.1	0.75
	200		1.9	70.5	27.6	<0.1	0.72
	230		2.0	66.4	31.1	0.5	0.68
	250		1.9	61.0	36.2	0.8	0.63
30	215	1/10	2.8	70.7	24.6	1.8	0.74
		7/30	2.0	66.7	30.2	1.1	0.69
		3/10	2.0	69.1	28.8	0.1	0.71
		1/2	2.8	65.8	30.2	1.2	0.69
Raw DOP			7.4	74.2	16.1	2.3	0.82

MC: moisture content, VM: volatile matter, FC: fixed carbon.

**Table 3:** Ultimate analysis for hydrochar samples and raw DOP

Holding time (min)	Temperature (°C)	DOP/water weight ratio	Ultimate analysis (wt.%)				
			C	H	N	O <sup>a</sup>	S
0	215	1/6	62.3±1.0	7.1±0.2	1.4±0.1	29.2±1.3	n.d
5			61.2±2.0	6.8±0.2	1.5±0.1	30.5±2.3	n.d
30			64.0±1.6	7.0±0.1	1.5±0.1	27.6±1.8	n.d
60			63.3±2.7	6.8±0.1	1.3±0.1	28.5±2.7	n.d
120			65.2±1.1	6.5±0.3	1.4±0.2	26.8±1.4	n.d
30	180	1/6	57.8±1.0	6.7±0.1	1.6±0.2	33.9±1.2	n.d
	200		60.7±0.6	6.6±0.1	1.4±0.0	31.2±0.6	n.d
	230		64.8±0.4	6.7±0.1	1.2±0.1	27.2±0.5	n.d
	250		67.8±0.4	6.5±0.0	1.4±0.1	24.3±0.4	n.d
30	215	1/10	62.1±1.3	6.8±0.1	1.3±0.1	29.9±1.4	n.d
		7/30	63.6±0.4	6.9±0.1	1.4±0.1	28.2±0.6	n.d
		3/10	64.6±0.1	6.9±0.1	1.5±0.1	26.9±0.1	n.d
		1/2	62.3±0.4	6.8±0.1	1.2±0.1	29.6±0.4	n.d
Raw DOP			53.5±0.2	6.8±0.1	1.1±0.1	38.6±0.3	n.d

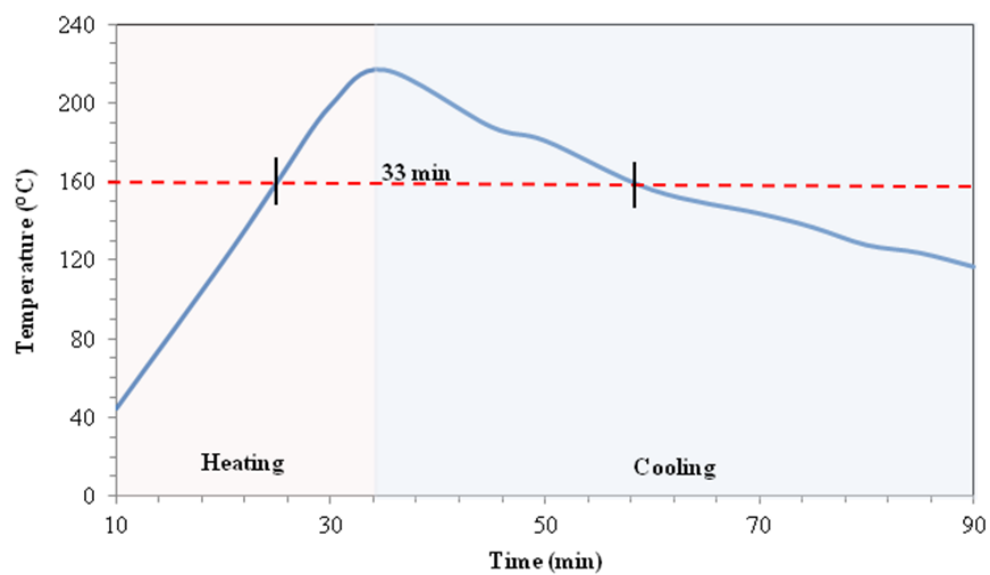
<sup>a</sup>: by difference, n.d: not detectable (< 0.1%).

± Triplicate standard deviation of analyses results.

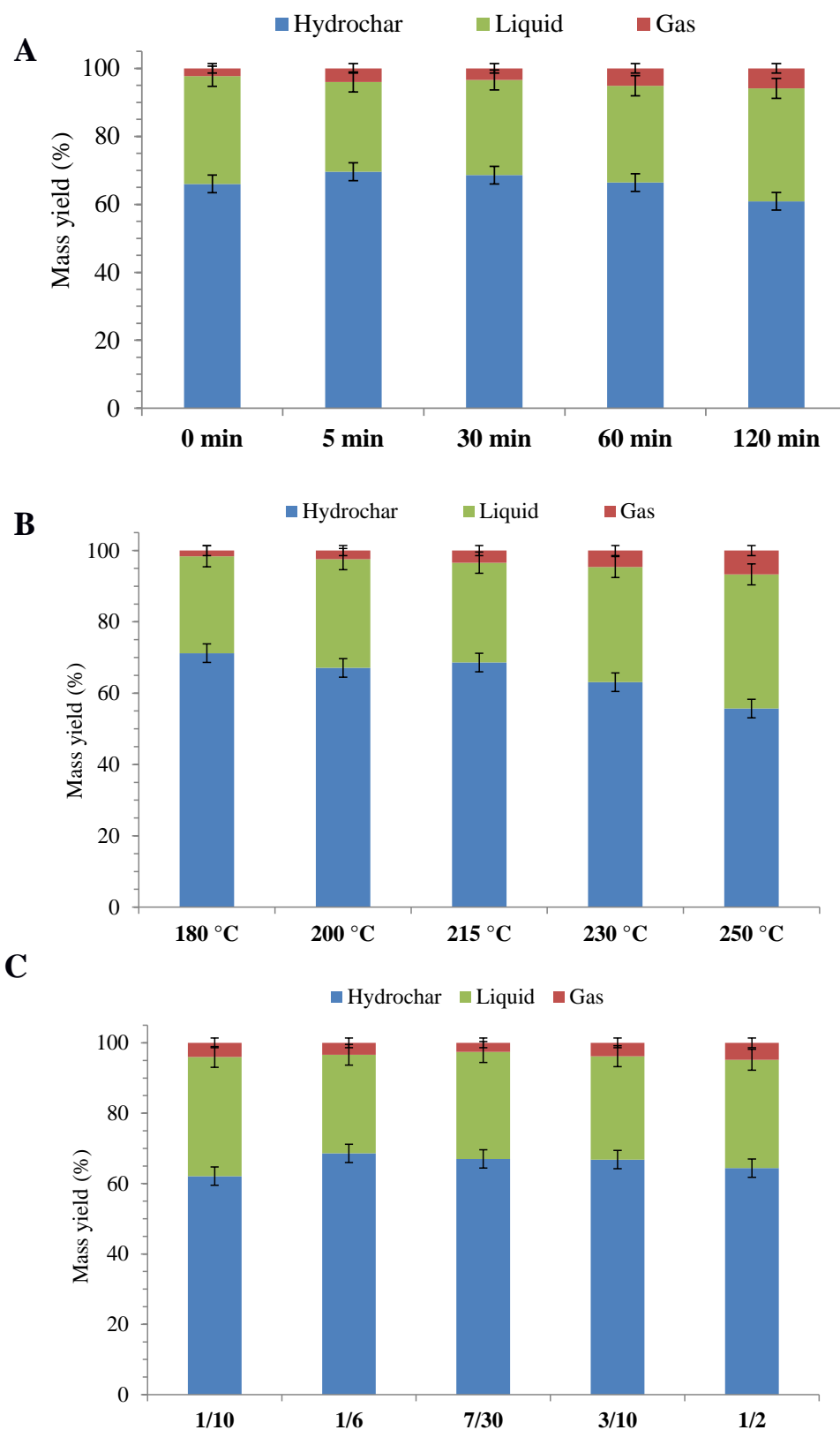
**Table 4:** HTC performance of experiments

<b>Holding time (min)</b>	<b>Temperature (°C)</b>	<b>DOP/water weight ratio</b>	<b>MY (%)</b>	<b>HHV(MJ/kg)</b>	<b>ED (-)</b>	<b>EY (%)</b>
<b>0</b>			66	24.9	1.1	73
<b>5</b>			70	25.6	1.1	77
<b>30</b>	215	1/6	69	26.8	1.2	83
<b>60</b>			66	26.5	1.2	79
<b>120</b>			61	26.2	1.2	73
	<b>180</b>		71	24.1	1.1	78
	<b>200</b>		67	25.0	1.1	74
<b>30</b>	<b>230</b>	1/6	63	26.1	1.2	76
	<b>250</b>		56	27.6	1.2	67
		<b>1/10</b>	62	26.1	1.2	74
		<b>7/30</b>	67	26.3	1.2	80
30	215	<b>3/10</b>	67	26.5	1.2	80
		<b>1/2</b>	64	26.3	1.2	77
<b>Raw DOP</b>	-	-	-	22.5	-	-

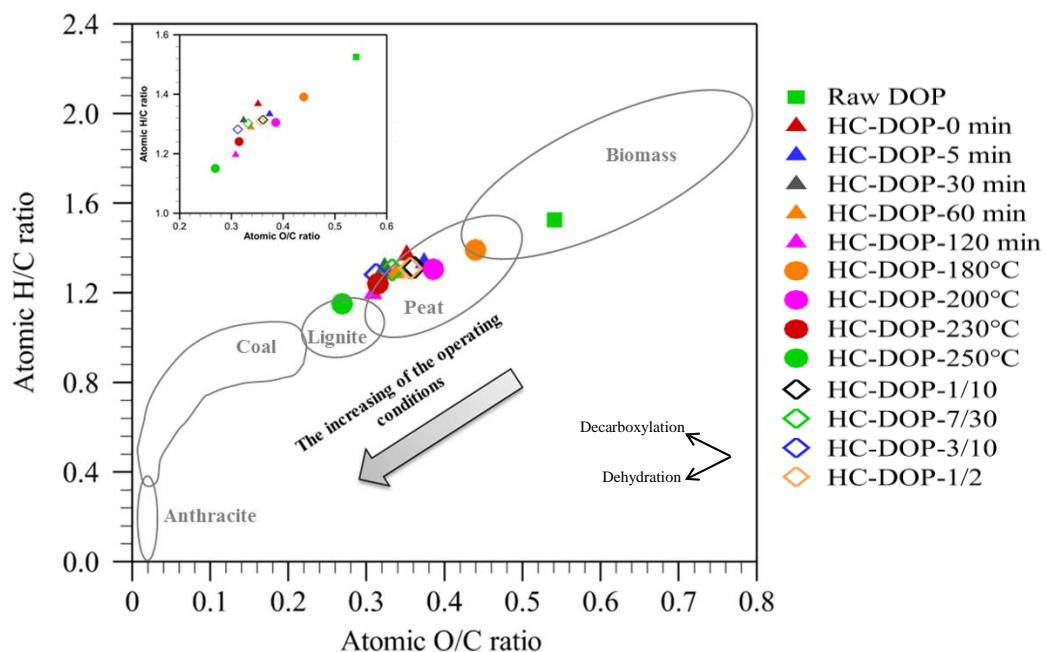
MY: hydrochar mass yield, ED: energy densification ratio, EY: energy yield, HHV: dried sample high heating value.



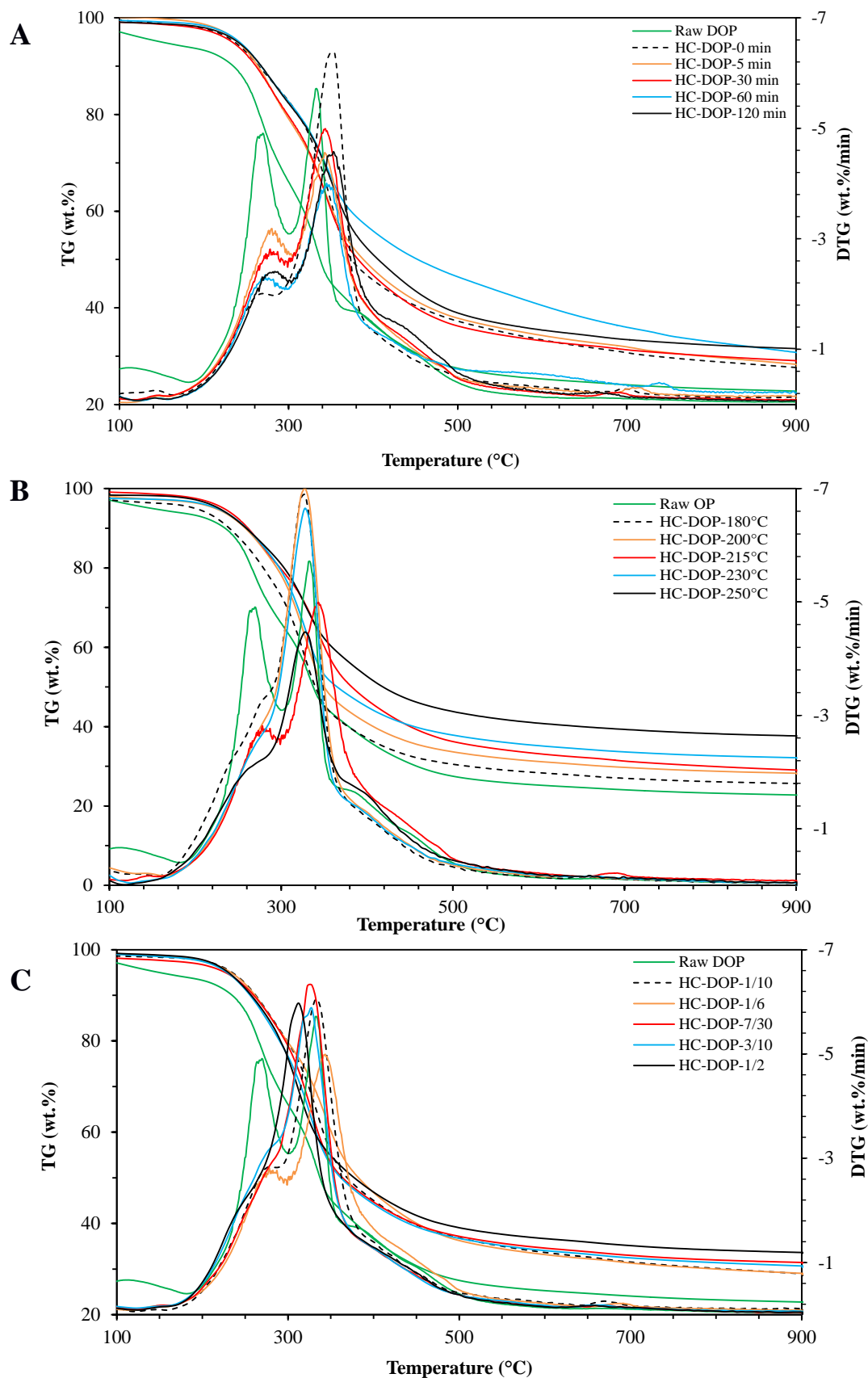
**Fig. 1:** Temperature profile during a flash experiment (holding time=0 min,  $T=215\text{ }^{\circ}\text{C}$ , DOP/water weight ratio=1/6).



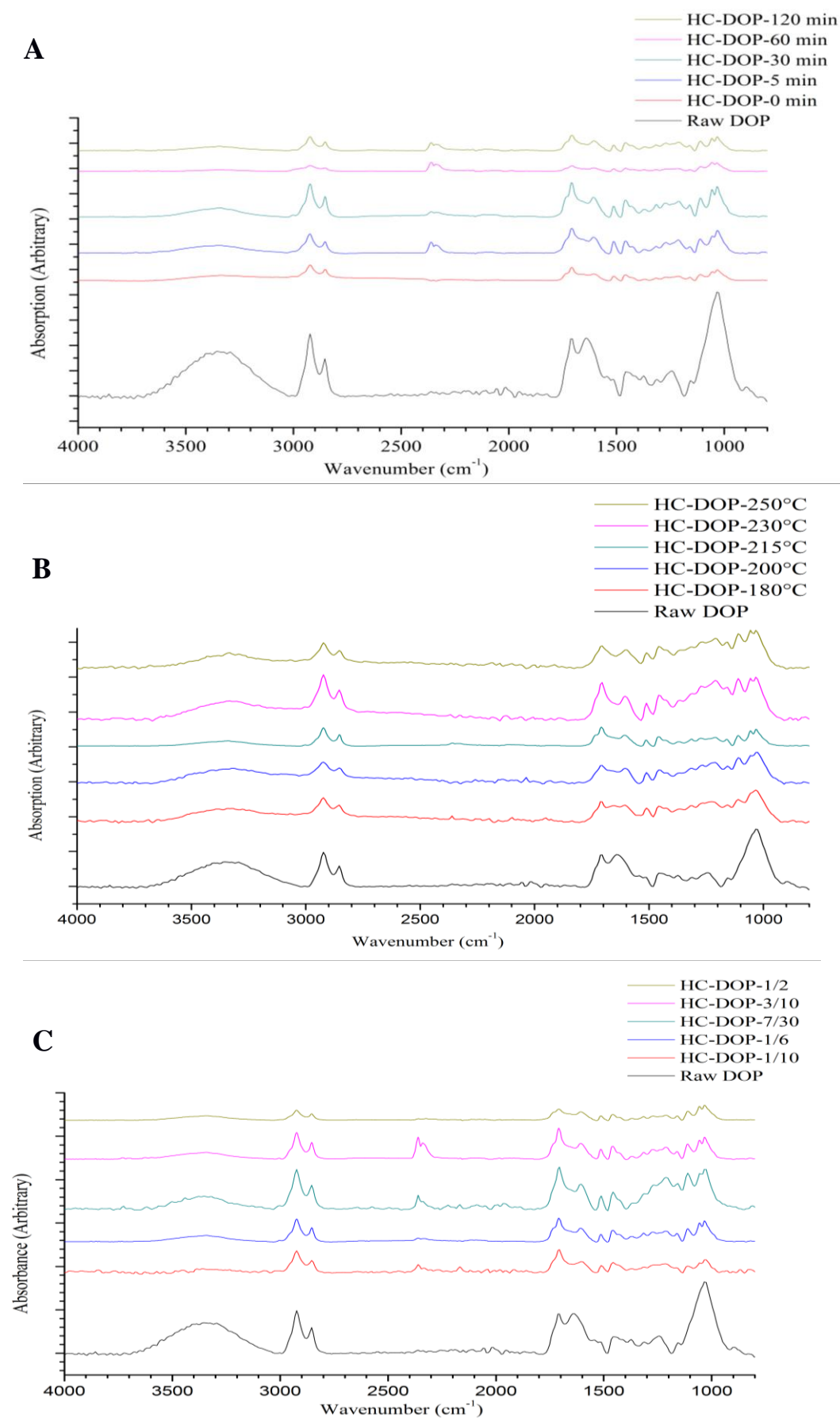
**Fig. 2:** Mass yield (%) for various **A)** holding times ( $T=215\text{ }^{\circ}\text{C}$ , DOP/water weight ratio=1/6), **B)** temperatures (holding time=30 min, DOP/water weight ratio=1/6) and **C)** DOP/water weight ratios (holding times=30 min,  $T=215\text{ }^{\circ}\text{C}$ )



**Fig. 3:** Van Krevelen diagram of raw DOP and hydrochars obtained at various holding times ( $T=215\text{ }^{\circ}\text{C}$ , DOP/water weight ratio=1/6), temperatures (holding time=30 min, DOP/water weight ratio=1/6) and DOP/water weight ratios (holding time=30 min,  $T=215\text{ }^{\circ}\text{C}$ ).



**Fig. 4:** TG and DTG curves for raw DOP and hydrochars obtained at various **A)** holding times ( $T=215\text{ }^{\circ}\text{C}$ , DOP/water weight ratio=1/6), **B)** temperatures (holding time=30 min, DOP/water weight ratio=1/6) and **C)** DOP/water weight ratios (holding time=30 min,  $T=215\text{ }^{\circ}\text{C}$ ).



**Fig. 5:** FTIR spectra of raw DOP and hydrochars obtained at various **A)** holding times ( $T=215\text{ }^{\circ}\text{C}$ , DOP/water weight ratio=1/6), **B)** temperatures (holding time=30 min, DOP/water weight ratio=1/6) and **C)** DOP/water weight ratios (holding time=30 min,  $T=215\text{ }^{\circ}\text{C}$ ).