

# Upgrading of Olive Tree Trimmings Residue as Biofuel by Hydrothermal Carbonization and Torrefaction: a Comparative Study

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A comparative study of hydrothermal carbonization (HTC) in a 50 ml batch reactor and low temperature pyrolysis (LTP) in a fixed bed reactor was carried out on olive tree trimming residue with the goal of obtaining solid biofuels with higher energetic properties. Olive tree trimmings (OT) milled and sieved to 425-850 mm particle size range, was pyrolysed at peak temperatures between 200 and 325 °C and hydrothermally carbonized at peak temperatures between 120 and 250 °C and biomass to water ratio 0.25. Residence time at peak temperature of 30 minutes and an inert atmosphere of N<sub>2</sub> was used for both the thermal processes. The results of comparison, on the basis of fuel qualities of biochars obtained, showed that the hydrothermally prepared biochar had higher energy Densification while the torrefied biochar had higher energy yield due to higher mass yield. The hydrochar obtained at 200 °C showed similar Mass Yield (MY), Energy Densification Ratio (EDR) and High Heating Value (HHV) of the torrefied char at 250 °C; (HTC char 200 °C: MY = 73.0 %, EDR = 1.17, HHV = 23,180 kJ/kg; LTP char 250 °C: MY = 76.3 %, EDR = 1.18, HHV = 23,326 kJ/kg). Hydrocarbonization processes lead to an increase on the high heating value of the biochars, up to 27,257 kJ/kg, (250 °C peak temperature) with a corresponding Energy Densification Ratio (EDR) of 1.37 when compared with the starting material. More severe conditions (300 °C peak temperature) were needed for torrefaction to obtain a biochar with the same EDR and a high heating value of 27,206 kJ/kg.

## 1. Introduction

The growth in energy demand boosted by the fast industrialization of the emerging countries has dramatically increased the consumption of energy resources causing the depletion of fossil fuels like oil and coal. In this scenario there is a growing interest in the development of exploiting alternative resources like biomass for clean renewable energy production. The use of residual biomass as a carbon neutral energy source involve some inherent difficulties associated with its lower physicochemical properties if compared to coal. Raw biomass has lower energy density, poor grindability, higher hydrophilicity and short storage life. Among different technologies, to overcome the difficulties of the direct use of raw biomass as a fuel, torrefaction, also denoted as low temperature pyrolysis (LTP) and hydrothermal carbonization (HTC), also known as wet torrefaction, are two thermal approaches to upgrade biomass feedstocks improving their energy density, stability, lowering their moisture content and increasing grindability. Thus LTP and HTC chars can be used in coal co-firing plant or either energetically valorized by direct gasification (Castello et al., 2014). The increased grindability lead to a lower energy consumption for biomass grinding while the elevated energy density reduces the operating cost for the handing logistics (Messineo et al., 2014). Torrefaction is a thermochemical conversion reaction where raw biomass is heated up, in inert atmosphere, in a temperature range between 200 and 300 °C typically for 0.5 to 1 hours (Prins et al., 2006). Hydrothermal carbonization is a thermochemical batch process where wet organic materials, in an oxygen free environment, are directly converted into an enriched carbon solid residue (hydrochar) in a temperature range of 180 – 250 °C, self-sustained vapor pressure of water up to 4.0 MPa and residence time between few minutes to several hours (Sabio et al., 2016). On one hand, the studies of fuel thermal up grading of agro-industrial residue by LTP are

numerous, as for example citrus wastes (Volpe M. et al., 2015), olive industry wastes (Messineo, et al., 2012; Volpe R. et al.. 2015), and HTC of olive stones (Álvarez et al., 2015) and wine industry wastes (Basso et al., 2016). On the other hand, very few studies have been carried out on the comparison between LTP and HTC technologies (Liu et al., 2014; Kambo et al., 2015). In this work we present a comparative study of biochars energy properties of olive tree trimming produced via LTP and HTC processes.

## 2. Materials and methods

### 2.1 Raw material and sample preparation

Olive trimmings (OT) including leaves were collected from three 30 years old randomly selected trees of the 'Moresca' variety, in Enna province, Sicily. All samples were oven dried at 40 °C for 48 h in order to release excess moisture. The samples were then ground using a rotatory knife mill to particle sizes of < 20 mm and milled to particle size < 2 mm. The milled material was then sieved and the fraction between 425 and 850 µm particle size was selected for the thermochemical reactions and analytical determinations. All the samples were stored in sealed containers at room temperature and oven dried for at least two hours just before each experiment.

### 2.2 Analytical determinations

Proximate analyses were carried out using a LECO Thermogravimetric Analyser TGA 701. Approximately 300 mg of solid samples were used to evaluate composition in terms of moisture content (M), volatile fraction (VF), fixed carbon (FC) and ashes (Ash). M was evaluated with a thermal ramp of 20 °C/min to 105 °C in air; and holding the temperature until weight constancy (< ±0.05 %); the VF was evaluated with a ramp rate in an inert atmosphere (N<sub>2</sub>) of 50 °C/min from 105 °C to 900 °C, holding time 7 min and finally ash content was determined with an isothermal at 800 °C in air until weight constancy (< ±0.05 %).

Higher heating values (HHV) of raw and solid residues were evaluated according to the CEN/TS 14918 standard by means of a LECO AC500 calorimeter.

### 2.3 Torrefaction and hydrothermal carbonization procedures

Torrefaction experiments were carried out by a lab scale quartz horizontal fixed bed reactor (FBR). The reactor and the system set-up features have been already fully described (Volpe M. et al., 2014). The reactor was loaded with approximately 10.00 (± 0.01) g of dry OT sample and left at room temperature while N<sub>2</sub> was left flowing at 1.5 L/min for approximately 10 min to ensure an inert atmosphere in the system. After evacuation of air in the system the reactor was heated up, with a thermal ramp rate of 50 °C/min, to the reaction peak temperature (200, 250, 300 and 325 °C), holding time at peak temperature of 30 min. Furnace and sample temperatures were recorded by RS-1384 four channel temperature data-logger. At the end of reaction the system was left to cool down to room temperature and solid and liquid residues were recovered and their mass yields evaluated. Hydrothermal carbonization reactions were carried out in a stainless steel (AISI 316) 50 ml internal volume batch reactor. The HTC system lay-out (Fiori et al., 2014) and modelling (Baratieri et al., 2015) have been already reported. For each experiment the HTC reactor was loaded with approximately 5.00 (± 0.01) g of dry raw biomass and about 20.00 (± 0.01) g of distilled water (biomass to water ratio 0.25 wt/wt). Once closed, the system was carefully purged with N<sub>2</sub> in order to eliminate any air, and the reactor heated up to desired peak temperature by means of a band heater. Time of heating at the peak temperatures (120, 150, 180, 200, 220, 235 and 250 °C) was kept constant at 30 minutes. Typically, the times to reach the set point temperatures varied between 15 to 25 minutes. Longer times of reaction were not investigated in this work as this variable is proved to be less influent than peak temperature, (Álvarez et al., 2015; Basso et al., 2015).

At the end of reaction the system was cooled down to 30 °C and gas, solid and liquid residues mass yields evaluated. Table 1 show the set of conditions used during HTC and LTP experiments.

*Table 1: Olive Trimmings - LTP and HTC reaction conditions*

Residence time [min]	Temperature [°C]	Thermal Process
30	120	HTC
	150	HTC
	180	HTC
	200	HTC, LTP
	220	HTC
	235	HTC
	250	HTC, LTP
	300	LTP
	325	LTP

Mass yields of the residues were evaluated by the following equation Eq(1):

$$\text{Mass Yield (MY)} = \left( \frac{M_{cdb}}{M_{rdb}} \right) \times 100 \quad (1)$$

where  $M_{rdb}$  represents the sample raw mass on dry basis before thermal treatment and the  $M_{cdb}$  denotes the mass after thermal treatment on a dry basis.

#### 2.4 Energy properties of biochars

Once determined the solid residues high calorific values the energy yields and the energy densification ratios of the chars were calculated according to the following equations, Eq(2,3):

$$\text{Energy Yield (EY)} = \left( \frac{HHV_c}{HHV_r} \right) \times MY \quad (2)$$

$$\text{Energy Densification Ratio (EDR)} = \left( \frac{HHV_c}{HHV_r} \right) \quad (3)$$

where  $HHV_c$  is the high calorific value of char and  $HHV_r$  is the high calorific value of the raw material.

### 3. Results and discussion

#### 3.1 Proximate analysis of raw material and biochars

The results of proximate analysis for raw material and HTC and LTP chars are reported in Table 2. The values reported in table 2 are the average of at least two analyses (VM and FC showed percentage relative errors ( $E_r\%$ )  $\leq 3\%$  but M and Ash showed  $E_r\%$  up to 20%). Increasing the severity of the treatment in HTC and LTP experiments the moisture content at equilibrium decreases as already found previously. HTC and LTP chars become more brittle and homogeneous with a decreased ability of absorbing moisture. Volatile matter content (VM) is somehow retained until 200 °C treatments both in HTC and LTP treatments but at higher temperatures it decreases sharply to reach a value between 72 and 73 % at 250 °C. On the other hand the fixed carbon content (FC) increases with temperature faster for hydrochar than for LTP chars denoting that hydrothermal carbonization is a more severe process than low temperature pyrolysis, this finding has already been reported in literature (Semyagina et al., 2015). Moreover, the ash content increases in pyrolysis residues with severity while it remains constant or reduces in hydrochars. At 250 °C the LTP and HTC solid residues show an ash content of 4.69 and 3.15 % respectively. Ashes contain inorganic elements that are undesirable in a fuel, as during combustion they can cause fouling and slagging resulting in an increase of co-firing complexity and lowering the efficiency of the boilers. During hydrothermal carbonization low molecular organics (extractives) and a considerable amount of inorganic elements are extracted in liquid solution while those species are retained in pyrolysis chars (Reza et al., 2013).

Table 2: Proximate analysis of raw material and biochars

Thermal treatment	Reaction peak temperature [°C]										
	raw	120	150	180	200	220	235	250	300	325	
HTC	M [%]	4.3	3.5	2.7	1.7	2.6	1.6	1.1	1.2	-	-
	VM [%]	75.0	79.0	77.4	79.0	78.2	77.1	74.9	71.8	-	-
	Ash [%]	3.9	3.4	3.5	2.1	3.2	2.4	3.1	3.2	-	-
	FC [%]	16.8	14.1	16.3	17.3	16.1	18.3	21.0	23.0	-	-
LTP	M [%]	4.3	-	-	-	1.6	-	-	0.8	1.6	1.3
	VM [%]	75.0	-	-	-	77.1	-	-	72.8	64.3	58.3
	Ash [%]	3.9	-	-	-	4.7	-	-	4.7	4.7	7.9
	FC [%]	16.8	-	-	-	16.5	-	-	21.7	29.3	32.6

#### 3.2 Mass and energy yields of biochars

Tables 3 and 4 report the mass yields of solid (MYS), liquid (MYI) and gas (MYg) of HTC and LTP residues obtained at different reaction peak temperatures, together with the calorific values (HHVs), Energy Yields (EYs) and Energy Densification Ratios of the solid residues. The data shown are the average of at least two different experiments and analytical determinations. Mass yields showed  $E_r\%$  not higher than  $\pm 1.7\%$  while

for calorific value determinations the  $E_r\%$  were lower than  $\pm 1.4\%$ , all the values reported are on a dry basis (d.b.).

*Table 3: Mass yields and energy properties of HTC residues (d.b.)*

T [°C]	MYs [%]	MYI* [%]	MYg [%]	EYs [%]	EDRs [%]	HHVs [kJ/kg]
raw	-	-	-	-	-	19,807
120	97.1	2.7	0.2	98.2	101.2	20,041
150	96.5	2.7	0.8	101.5	105.1	20,826
180	77.9	19.6	2.5	85.6	110.0	21,786
200	73.0	21.1	5.9	85.4	117.0	23,180
220	71.1	23.0	5.8	86.0	120.9	23,944
235	63.0	29.1	7.9	82.8	131.5	26,048
250	57.6	32.2	9.2	79.1	137.4	27,223

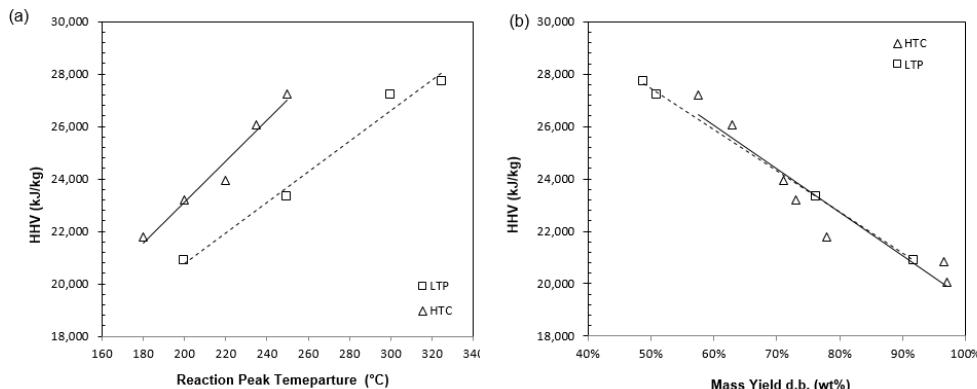
\*calculated by difference

*Table 4: Mass yields and energy properties of LTP residues (d.b.)*

T [°C]	MYs [%]	MYI [%]	MYg* [%]	EYs [%]	EDRs [%]	HHVs [kJ/kg]
raw	-	-	-	-	-	19,807
200	91.8	6.2	2.0	96.8	105.4	20,879
250	76.3	15.6	7.1	89.9	117.8	23,326
300	51.0	35.4	13.4	70.0	137.4	27,206
325	48.9	37.6	13.5	68.4	139.9	27,707

\*calculated by difference

HTC treatments at 120 and 150 °C do not lead to carbonization of the sample but are able to remove part of low molecular organic extractive and inorganic elements thus giving an increase of HHV if compared to the parent material. During HTC (180-250 °C) and LTP (200-325 °C) experiments the solid mass yields decrease sharply with severity of the treatment. Mass yield of hydrochars obtained at 250 °C is 57.6 % while at the highest LTP peak temperature the mass yield of the char is 48.9 %. Comparison of HTC and LTP result clearly show that the hydrochar residues at a fixed temperature have higher energy densification ratio than the corresponding pyrolysed biochar thus confirming that hydrothermal carbonization is a more severe treatment than pyrolysis, due to the active role of water. The hydrochar obtained at 200 °C showed similar MY, EDR and HHV of the torrefied char at 250 °C; (HTC char 200°C: MY = 73.0 % , EDR = 1.17, HHV = 23,180 kJ/kg; LTP char 250°C: MY = 76.3 % , EDR = 1.18, HHV = 23,326 kJ/kg). Hydrocarbonization processes lead to an increase on the high heating value of the biochars, up to 27,257 kJ/kg, (250 °C peak temperature) with a corresponding EDR of 1.37 when compared with the starting material. More severe conditions (300 °C peak temperature) were needed for torrefaction to obtain a biochar with the same EDR and a HHV of 27,206 kJ/kg.



*Figure 1: Correlation between HHV with reaction peak temperatures (a) and HHV with biochars mass yields (b).*

Figure 1 (a) and (b) show the plot of HHV of the solid versus reaction temperature and mass yield respectively and according to those data in Figure 2 (a) and (b) we report the EDR and the EY trends with reaction peak temperature. HHV values of HTC and LTP biochars increase linearly with temperature Eq(4,5) and decrease linearly with mass yields Eq(6,7) thus using this correlations is possible to predict and design the energetic properties of the bio-fuel by HTC or LTP thermal up-grading.

$$HHV(HTC) = 77.6 \times T + 7,603 \quad - R^2 = 0.965 \quad (4)$$

$$HHV(LTP) = 58.1 \times T + 9,156 \quad - R^2 = 0.980 \quad (5)$$

$$HHV(HTC) = - 16,559 \times MY + 35,976 \quad - R^2 = 0.910 \quad (6)$$

$$HHV(LTP) = - 15,705 \times MY + 35,300 \quad - R^2 = 0.999 \quad (7)$$

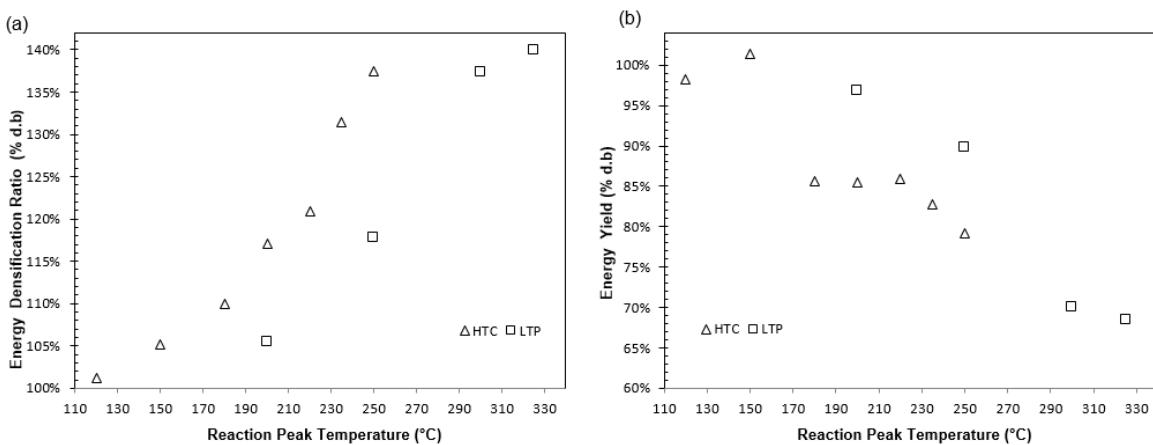


Figure 2: EDR (a) and EY (b) of HTC and LTP of OT, conditions as shown on Tables 3 and 4.

#### 4. Conclusions

HTC and LTP processes of ligno-cellulosic agro-industrial waste material like olive trimming make a solid chars with higher energy density, more brittle and more hydrophobic than the original material. As a results both HTC and LTP represent valuable methods for solid fuel upgrading. However at the same process conditions, temperature, residence time and hence severity of reaction, HTC biochars show higher energy densification ratio than the LTP chars with a lower ash content. Hydrothermal carbonization of olive trimming at 250 °C, 30 minutes of residence time, produces hydrochar with a MY = 57.6 %, EDR = 1.37, HHV = 27,223 kJ/kg and ash content of approximately 3 %, on the other hand 300 °C of reaction peak temperature is necessary during LTP to obtain a char with a MY = 51.0 %, EDR = 1.37, HHV = 27,206 kJ/kg and ash content of about 5 %. HHV values of HTC and LTP biochars increase linearly with temperature and decrease linearly with mass yields thus using this correlations is possible to predict and design the energetic properties of the bio-fuel by HTC or LTP thermal up-grading.

In summary, significantly improved fuels properties of hydrothermally OT prepared biochars indicate that HTC is a more favourable process for fuel upgrading than LTP, but, if it is true that HTC can treat wet biomass directly without drying, the produced hydrochars need to be filtered and dried to remove excess water, thus an accurate energy balance and cost-benefit analysis is needed before deciding which of the two technologies is the most convenient.

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