Production and characterization of biochar from three-phase olive mill waste through slow pyrolysis

Amine Hmid a,b,*, Donato Mondelli c, Saverio Fiore d, Francesco Paolo Fanizzi e, Ziad Al Chamib, Stefano Dumonteta

a Dipartimento di Scienze e Tecnologie, Università degli Studi di Napoli “Parthenope”, Via Ammiraglio Ferdinando Acton, 38, 80133 Napoli, Italy
b CIHEAM Istituto Agronomico Mediterraneo di Bari, Via Ceglie, 9, 70010 Valenzano, Bari, Italy
c Dipartimento di Scienze del Suolo, della Pianta e degli Alimenti, Università degli Studi di Bari “Aldo Moro”, Piazza Umberto I, 1, 70121 Bari, Italy
d Institute of Methodologies for Environmental Analysis–CNR, C.da S. Loja – Zona Industriale, 85050 Tito Scalo, Potenza, Italy
e Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, Università del Salento, Campus Ecotekne, Via provinciale Lecce-Monteroni, 73100 Lecce, Italy

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A B S T R A C T

The influence of temperature and heating rate on the yield and properties of biochar derived from pyrolysis of solid olive mill waste (pomace) was investigated. Three pyrolysis temperatures (430 ± 10 °C, 480 ± 10 °C and 530 ± 10 °C) and 3 heating rates (25 °C min⁻¹, 35 °C min⁻¹ and 45 °C min⁻¹) were studied. The biochar production was carried out using a vertical downdraft gasifier. Increasing the pyrolysis temperature, and/or the heating rate, the biochar yield lowered, the C content and biochar aromaticity increased and the surface functional groups were reduced. The highest biochar yield was obtained by low pyrolysis temperature (430 ± 10 °C) and low heating rate (25 °C min⁻¹). This biochar is characterized by a high heating value (31 MJ/kg) that makes it a possible fuel candidate and, in the meantime, due to its high concentration in C (70.2%–84.1%), low electrical conductivity (0.28 dS m⁻¹–0.47 dS m⁻¹) and the lack of phytotoxicity it is suitable for amendment in agricultural soils and for long term carbon sequestration.

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1. Introduction

The production of olive and olive oil is key industrial, economic and social factor of the Mediterranean agricultural sector [1,2]. In the last decades, the establishment of intensive olive orchards, the large degree of mechanization and the improvement of production technology led to a considerable rise in olive oil and table olive production. The International Olive Council (2013) reported for the 2012/2013 production season, a making of 2.7 million tons of olive oil worldwide, 94% of which in the Mediterranean region.

* Corresponding author. Dipartimento di Scienze e Tecnologie, Università degli Studi di Napoli “Parthenope”, Via Ammiraglio Ferdinando Acton, 38, 80133 Napoli, Italy. Tel.: +39 388 8247722.
E-mail addresses: amine.hmid@uniparthenope.it, hmidamine@gmail.com (A. Hmid).
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This considerable production of olive oil is coupled with a significant quantity of waste generated from the making process [3,4]. Barbera et al. [5] reported that the olive oil industry produces 30 million of tons of waste per year. Thanks to recent technological improvements the amount of process wastewater is greatly reduced, even though the production of solid waste (pomace) has increased [6,7]. The olive oil making processes most commonly used nowadays are the three- and two-phase centrifugal systems based on continuous extraction systems by horizontal centrifuges (decanters). The two-phase systems generate oil and a highly wet olive pomace, while the processes of three-phase systems are oil olive, olive pomace and olive mill wastewater (OMWW) [8]. The olive pomace is composed of small pieces of skin, pulp, seed and stone [9]. The chemical composition of olive pomace largely depends on the olive variety and the extraction process. On a dry basis, olive pomace obtained from a three-phase extraction system is composed from 10% to 56% by lignin, from 12% to 24% by cellulose and from 7% to 22% by hemicellulose [10–12]. In addition its metals and polyphenols content may contain the pomace phytoxic and resistant to biological degradation [9] representing a threat to the fauna, flora, soil and water integrity [6,7,13,14].

Pyrolysis, a ‘carbon negative process’ [15,16], is a technology particularly useful to deal with the solid waste issued from olive oil production [17].

The pyrolysis process conditions (temperature and heating rate) determine the quantity and quality of the biochar produced, which can be tuned according to its final use [18]. Biochar characterized by high adsorption and cation exchange capacities and low levels of tars, resins, mobile matter (the organic C that may migrate from the biochar into the soil and can be used by soil microflora as C source) and other short-lived organic compounds [19] is the more suitable for being applied to soil. Such a biochar improves physicochemical and biological soil functions by increasing the net soil surface area [20], enhancing the cation exchange capacity (CEC) and pH, improving the soil water and nutrient retention [21,22]. Biochar could also provide nutrients to crops in their available forms [23]. Biochar with high calorific values are used to produce energy, while biochar with high porosity and highly aromatic can be useful in decontaminating soil and water from organic and inorganic pollutants [25–27].

This study is aimed at investigating the effects of pyrolysis temperatures and heating rates on the yield, morphology and physicochemical properties of biochar produced from three-phase solid olive mill waste.

2. Materials and methods

2.1. Feedstock material

A three-phase olive mill waste was used as a feedstock. The waste, collected from olive mills located in the Apulia region (South Italy), showed a pH of 6.7, EC of 0.9 dS m⁻¹ and the following composition 52.2% C, 6.7% H, 0.1% N, 0.1% S and ash content of 5.7%. The waste was left to dry at ambient air temperature for 30 days and then oven-dried for 24 h. After drying, the aggregates were softly crashed and the particles were sieved to pass through a 1 cm sieve to ensure homogeneous particles size.

2.2. Slow pyrolysis

The slow pyrolysis experiments were carried out in a vertical stainless steel reactor (All Power Labs', Berkeley, California) (Fig. 1) where the bottom part of the reactor is filled with charcoal and the upper compartment is loaded with the feedstock. The reactor is tightly sealed in order to avoid the entrance of air into the feedstock compartment. The process is started with a propane torch that lights the charcoal. A thermocouple is used to measure the temperature and the heating rate of the feedstock. The gases produced by the heated biomass flow downwards and go through a cyclone and a Venturi ejector to swirl burner.

The optimal charcoal and feedstock upload per experiment run were 150 and 800 g, respectively. The feedstock residence time was fixed on 30 min. Three pyrolysis temperatures (PT) (430 ± 10 °C, 480 ± 10 °C and 530 ± 10 °C) and 3 heating rates (HR) (25 °C min⁻¹, 35 °C min⁻¹ and 45 °C min⁻¹) were investigated to assess their effect on the biochar yield and characteristics. Each combination of treatments (PT+HR) was replicated 5 times.

2.3. Biochar characterization

2.3.1. Biochar yield, pH, electrical conductivity and ash content

The biochar yield was expressed as a dry weight percentage of the starting material. The pH was determined by soaking biochar in ultra-pure water (3:50 biochar/water) for 2 h under frequent agitation and measured using pH meter (Basic 20; Crison, Barcelona, Spain) provided with a Crison 52-00 glass electrode. Electrical conductivity (1:10 biochar/water ratio) was measured using a conductimeter (XS cond 510; Eutech Instruments, Singapore). Ash content was measured using a modified ASTM standard [28], based on weight loss determination. Briefly, about 5 g of oven-dried biochar (24 h at 105 °C) was weighed and then combusted at 750 °C for 6 h [29]. The samples were cooled down to room temperature in desiccators and weighed. Ash content was calculated as follows:

\[
\text{Ash content(\%)} = \frac{[g \text{ of ash}]}{[g \text{ dry mass of biochar}]} \times 100
\]

2.3.2. Elemental analyses and heating values

The elemental analyses were performed on micronized samples. The elemental C, N, H and S were determined by a dry oxidation using an elemental analyzer (Flash 2000 series CHNS/O Analyzer; Thermo Scientific, UK) operating according to the dynamic flash combustion method (modified Dumas method) [30]. Oxygen was determined by difference.

The higher heating value (HHV) was determined using the unified correlation proposed by Channiwala and Parikh [31]:

\[
\text{HHV} = 0.3491C + 1.1783H + 0.1005S - 0.01034O - 0.0151N - 0.0211A \text{MJ/kg}
\]

where C, H, O, N, S and A represent carbon, hydrogen, oxygen, nitrogen, sulfur and ash contents, expressed in mass percentages on dry basis.
On the other hand the lower heating value (LHV) was determined using the conversion of the HHV according to IPCC:[32]

$$LHV = \frac{HHV}{C_{0.212H}} - C_{0.008O};$$

where H is percent Hydrogen, O is percent Oxygen.

### 2.3.3. Biochar morphology

Microscopic observations of the produced biochar were performed using a Field Emission Scanning Electron Microscope (FESEM, Zeiss Supra 40) equipped with an Energy Dispersive X-ray Spectrometer (EDS, Oxford Inca Energy 350). Few milligrams of sample were dispersed on polycarbonate filter using distilled water, dried at room temperature and carbon coated. Accelerating voltage was between 5 and 15 kV. The samples produced under different heating rates and under the same pyrolysis temperature were mixed to have a representative sample. Therefore, we investigated solely the effect of pyrolysis temperatures on the morphology of the produced biochars without considering the heating rate.

### 2.3.4. Nuclear magnetic resonance (NMR)

The three types of biochar, produced at different temperature (430 ± 10 °C, 480 ± 10 °C and 530 ± 10 °C) were analyzed through $^1$H and $^{13}$C NMR spectroscopy by recording mono (1D) and multidimensional (2D) spectra. The biochar samples were pulverized in a porcelain mortar. For each sample, 2 amounts of 1 g each were mixed, the first with 100 mL of CHCl$_3$[33] and the second with 100 mL of H$_2$O/MeOH (1:1) solution[34,35]. The mixtures were agitated for 1 h, filtered on Whatman grade 42 filter papers and then with sterile 0.45 μm cellulose acetate membrane. The samples were then dried using a rotating evaporator. The solid residues of the extracts in CHCl$_3$ were solubilized in 700 μL of CDCl$_3$ and the solid residues of the extracts in H$_2$O/MeOH were solubilized in 1 mL of D$_2$O using TPS as an internal standard. The acquisition and processing of spectra were performed using the software Topspin 2.1 (Bruker Biospin). The FIDs were multiplied by an exponential weighting function corresponding to a line broadening of 0.3 Hz before Fourier transformation, phasing, and baseline correction. The chemical shift of spectra in CDCl$_3$ was referenced to TMS by the residual protic solvent peaks as internal references (δ$_H$ = 7.24 ppm; δ$_C$ = 77.0 ppm). All spectra acquired in D$_2$O were referenced to the TSP signal (δ = 0.00 ppm), used as an internal reference.

All measurements were performed on a Bruker Avance III NMR spectrometer (Bruker, Karlsruhe, Germany) operating at 400.13 MHz for $^1$H observation and 298 K, equipped with a z axis gradient coil and automatic tuning-matching (ATM). For samples in CDCl$_3$, $^1$H spectra were acquired with 32K data points, spectral width of 6009.615 Hz, 64 scans with a 2 s repetition delay. 2D $^1$H J resolved spectra were recorded with a spectral width 6009.615 Hz on F2 and 200.056 Hz on F1, 4K data points, 16 dummy scans, 32 scans for 128 experiments, and 1.5 s repetition delay. 2D $^1$H COSY spectra were acquired with
4K data points, spectral width of 6009.615 Hz, 16 dummy scans, 32 scans for 256 experiments, 2 s repetition delay. 2D $^1$H–$^{13}$C HSQC and $^1$H–$^{13}$C HMBC NMR spectra were acquired with 4K data points, spectral width of 6009.615 Hz on $^1$H and 25,154.953 Hz on $^{13}$C, 16 dummy scans, 64 scans for 512 experiments, 2 s repetition delay.

For samples in D$_2$O, $^1$H spectra water gate experiment, with water suppression using 3–9–19 pulse sequence with gradients, were acquired using 256 free induction decays (FIDs), 32K data points, a spectral width of 4795.396 Hz on F2 and 60.020 Hz on F1, 4K data points, 16 FIDs for 128 experiments, and 2 s repetition delay. 2D $^1$H COSY spectra with presaturation during relaxation delay were recorded with a spectral width 4795.396 Hz on F2 and 60.020 Hz on F1, 4K data points, 16 FIDs for 128 experiments, and 2 s repetition delay. 2D $^1$H J resolved spectra with pre-saturation during relaxation delay were acquired with 4K data points, spectral width of 4795.396 Hz, 16 dummy scans, 32 FIDs for 256 experiments, 2 s repetition delay. 2D $^1$H–$^{13}$C HSQC and $^1$H–$^{13}$C HMBC NMR spectra were acquired with 4K data points, spectral width of 4795.396 Hz on $^1$H and 25,154.211 Hz on $^{13}$C, 16 dummy scans, 32 FIDs scans for 256 experiments, 2 s repetition delay.

2.3.5. Phytotoxicity germination test

The Lepidium sativum test was used to assess the biochar phytotoxicity according to Zucconi et al. [36]. Both non-washed and water-washed biochar samples were tested. Biochar samples were spread over filter papers in perforated containers and were carefully washed with deionized water (10:1 v/w) adding one volume of water, waiting till it percolates totally then repeating again. After washing, the samples were dried in oven at 60 °C.

The washed and non-washed biochar samples were brought to 60% humidity and both centrifuged for 10 min at 5000 RPM, then they were filtered through a 0.22 μm filter. Two solutions with different concentration of extracts (10% and 30%) were used as a germination medium. The test was carried out in Petri dishes with a filter paper (80 mm Whatman grade 1) on the bottom. Each dish contained 1.5 mL of diluted solutions and 10 seeds and was wrapped by parafilm. The Petri dishes were placed in germination chamber at 25 °C for 48 h. The seed germination in distilled water was used as a control. All treatments were performed in 5 replicates. The number of germinated seeds and the root elongation were measured to calculate the germination index as follows:

\[
GI(\%) = \frac{Gt \times Lt}{Gc \times Lc} \times 100
\]

where Gc is the average number of germinated seeds in the control

$Gt$ is the average number of germinated seeds in the treatment and

$Lt$ is the average root elongation in the treatment

2.4. Statistical analysis

The data were analyzed using two-way ANOVA to determine whether there is interaction between the two factors; pyrolysis temperature and heating rate. The data was subjected then to one way ANOVA and means were compared using a post-hoc Tukey test.

For the phytotoxicity germination data, a one way ANOVA was used and means were compared using a post-hoc Tukey test.

3. Results and discussion

3.1. Effect of pyrolysis temperatures (PT) and heating rates (HR) on biochar yield

Biochar yield was significantly affected by both PT and HR, but their interaction was not significant (Table 1). At an HR of 25 °C min$^{-1}$, the rise of PT from 430 ± 10 °C to 530 ± 10 °C reduced significantly the biochar yield from 41.5% to 29.3%. A similar decreasing trend was observed rising the HR while keeping the same PT (Table 2). These data are in agreement with Şensoz et al. [37] who studied the yield of biochar issued from olive bagasse pyrolysis. At an HR of 50 °C min$^{-1}$, the authors recorded a drop of char production from 35.3% to 30.6% when PT increased from 350 °C to 550 °C. Similar results were obtained using olive husk [38], cellullosic and lignocellulosic biomass such as rice straw and safflower seed press cake [29,39,40]. Parihar et al. [41] explained such a biochar yield decline as the result of primary decomposition of the biomass and a possible secondary decomposition of the produced biochar during the pyrolysis process.

Similarly to PT, increasing the HR induced a drop in biochar yield. Rising the HR from 25 °C min$^{-1}$ to 45 °C min$^{-1}$ at a PT of 430 ± 10 °C resulted in a biochar yield decline from 41.5% to 35.4%. Şensoz et al. [37] reported that, at a PT of 350 °C, the pyrolysis of olive bagasse dropped from 38% to 35% while increasing the HR from 10 °C min$^{-1}$ to 50 °C min$^{-1}$. Higher yields of biochar under low HR could be due to the conversion of cellulose into the more stable form of anhydro-cellulose [37,42]. On the contrary, heating the biomass rapidly, causes a delay in dehydration of cellulose into anhydro-cellulose and consequently favoring the gas production [43,44].

3.2. pH, electrical conductivity (EC) and ash content

The statistical analysis showed that PT and HR affected significantly the biochar pH, EC and ash content. The interaction of the two factors had a significant effect on biochar pH, EC but not on the ash content (Table 1). All the biochar had a pH in the alkaline range (8.9–9.7) (Table 2). The statistical analysis showed a significant difference between the means but no clear trend was highlighted [39].

Contrarily to pH, the EC showed increasing trends. At an HR of 25 °C min$^{-1}$, the rise of PT from 430 ± 10 °C to 530 ± 10 °C was coupled with an increase of EC from 0.29 dS m$^{-1}$ to 0.40 dS m$^{-1}$. The same parameter augmented from 0.31 dS m$^{-1}$ to 0.47 dS m$^{-1}$ increasing the HR from 25 °C min$^{-1}$ to 45 °C min$^{-1}$ while keeping the same PT of 530 ± 10 °C. Cantrell et al. [45] measured, on manure derived biochar, an EC value of 2.2 dS m$^{-1}$, which is 4.6 times higher than the highest value recorded here. The low EC of our biochar would prevent from
causing any unfavorable salts effects in case of high quantities of biochar being incorporated into the soil [17].

The interaction between PT and HR did not reveal a significant effect on the biochar ash content, while the single factor effect was significant. At an HR of 25 °C min⁻¹, the increase of the PT from 430 ± 10 °C to 530 ± 10 °C caused a significant augmentation of the biochar ash content from 7.9% to 9.7% (Table 2). Similar results were also reported by several authors for number of different biomass, such as oak wood, corn stover and poultry litter [46]. On the contrary, a slight decrease of the biochar ash content was observed when the HR was increased maintaining the same PT. Indeed, rising the HR from 25 °C min⁻¹ to 45 °C min⁻¹ induced a decrease in ash content from 8.8% to 8.5% at a PT of 480 ± 10 °C.

### 3.3. Elemental analysis and heating values

The elemental composition, H/C ratio and heating values of the biochars are presented in Table 3. PT had significant effect on all the measured parameters while the HR showed a significant effect only on C, H and H/C ratio. The interaction between the 2 factors revealed a significant effect on all the measured parameters (Table 1). The values of S% were below the instrument detection limit.

The C content of biochar increased significantly from 70.2% to 94.1% by rising PT from 430 ± 10 °C to 530 ± 10 °C at a fixed HR of 25 °C min⁻¹. At a PT of 430 °C min⁻¹, the rising of HR from 25 °C min⁻¹ to 45 °C min⁻¹ resulted in an increase from 70.2% to 76.9%. It is important to highlight that at a PT of 530 °C the C content of biochar showed a decreasing trend while the HR rose. The C content reached a maximum at a PT of 530 °C and an HR of 25 °C min⁻¹. Contrarily to the carbon content, the H, N and O contents of biochar decreased with increasing PT keeping the same HR and vice-versa (Table 3).

The H/C molar ratio, an index of biochar aromaticity, followed the same decreasing trend pointing out that the produced biochar became more aromatic and more carbonaceous at higher PT and higher HR (Table 3). This conclusion is consistent with previous studies carried out on various feedstocks [17,38,45,47]. At a PT of 530 °C, rising the HR resulted in an augmentation of the H/C ratio. In addition Lehmann et al. [17] reported that H/C molar ratio is suggestive of bonding arrangements.

An H/C ratio between 0.4 and 0.6 is displayed by compounds in which every second to third C is connected with a proton, whereas an H/C ratio <0.1 indicates a graphite-like
structure. The H/C ratio of cellulose and lignin is nearly 1.5, whereas black carbon have an H/C < 0.2 [48].

The potential use of biochar as fuel is defined by the LHV and HHV values. The higher heating value of any fuel is defined as “the energy released per unit mass or per unit volume of the fuel when the fuel is completely burned” [49]. The HHV accounts for all the released heat during combustion, in addition to the heat that might be carried away with water vaporization. On the contrary, the LHV excludes the latent heat of water formed during combustion. To express the efficiency of a thermal system, European countries use normally LHV, whereas in USA and Canada HHV is used [15,49].

The analysis of variance showed that the HR did not affect significantly the higher heating value (HHV) and the lower heating value (LHV) of the biochar. On the contrary, PT and PT*HR affected significantly these values showing an increasing heating value (LHV) of the biochar. On the contrary, PT and HR affected significantly these values showing an increasing heating value (LHV) of the biochar. On the contrary, PT and HR affected significantly these values showing an increasing heating value (LHV) of the biochar.

### 3.4. Biochar morphology

The micro-structural features of the biochars produced at the 3 pyrolysis temperatures were investigated by means of scanning electron microscopy (SEM). Observations performed on a number of mounts confirmed that there were not significant differences among different SEM preparations. The samples produced at 430 ± 10 °C showed a hardly visible porosity. The presence of crystalline phases with cubic, tubular and elongated shapes on the particles surfaces made the particles rough and grainy. As the pyrolysis temperature increased (480 ± 10 °C and 530 ± 10 °C) the biochar particles showed smooth surfaces and the porosity increased. The pore sizes were not uniform and were in the range of tens of nanometers to several tens of microns (Fig. 2).

### 3.5. Nuclear magnetic resonance (NMR)

NMR analysis of biochar extracts has been useful for understanding the chemical structures of leachable material. Several extraction methods using water [34], water/methanol [35], and chloroform [33] have been reported. In the present work extract analysis of both polar (water/methanol extraction) and lipophilic (chloroform) fractions were used to characterize wide varieties of leachable compounds. Such analysis was performed in order to obtain information about the pyrolysis process progression monitoring the residual compounds related to the starting material.

The aqueous and chloroform extracts of biochar produced at 3 different PT (430 ± 10 °C, 480 ± 10 °C and 530 ± 10 °C) were obtained starting from the same amounts of char and solubilizing the residue in the same volume of D$_2$O and CDCl$_3$, respectively. Relevant $^1$H NMR data for both extracts are reported in Table 4. The NMR spectra of the aqueous extract result quite similar to each other, although a gradual broadening of signals were observed raising the pyrolysis temperature. At low frequencies (0.90, 1.06, 1.56, and 2.19 ppm) the

### Table 3 – Mean differences of N, C, H, O, H/C ration, HHV and LHV of biochar.

<table>
<thead>
<tr>
<th>Pyrolysis temperature</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>O (%)</th>
<th>H/Ci</th>
<th>HHV (MJ/kg)</th>
<th>LHV (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>430 ± 10 °C</td>
<td>70.2 ± 2.3 f</td>
<td>4.97 ± 0.08 a</td>
<td>1.02 ± 0.08 a</td>
<td>15.90 ± 2.30 a</td>
<td>0.85 ± 0.03 a</td>
<td>28.55 ± 1.05 c</td>
<td>27.37 ± 1.07 d</td>
</tr>
<tr>
<td>480 ± 10 °C</td>
<td>75.3 ± 0.3 de</td>
<td>3.64 ± 0.05 c</td>
<td>0.94 ± 0.01 ab</td>
<td>11.29 ± 0.24 bc</td>
<td>0.58 ± 0.01 bc</td>
<td>29.21 ± 0.16 bc</td>
<td>28.35 ± 0.15 bcd</td>
</tr>
<tr>
<td>530 ± 10 °C</td>
<td>84.1 ± 1.3 a</td>
<td>1.89 ± 0.03 f</td>
<td>0.73 ± 0.01 c</td>
<td>3.51 ± 1.35 e</td>
<td>0.27 ± 0.00 g</td>
<td>31.03 ± 0.64 a</td>
<td>30.60 ± 0.64 a</td>
</tr>
</tbody>
</table>

Values represent the mean of 3 replicates ± standard deviation of the mean (n = 3). Different letters within the same parameter (C, H, N, O, H/C ratio, HHV and LHV) indicate significant difference (Tukey test at P < 0.05).

b Calculated by difference.

i Atomic ratio.

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signals of free fatty acid chain were observed. Furthermore, low molecular weight metabolites were identified. The doublet at 1.34 ppm was assigned to the methyl group of lactate which in the 2D $^1$H COSY spectrum showed a cross-peak correlation with the multiplet at 4.12 ppm attributed to CH groups of lactate. Other organic compounds were identified, such as acetic acid (singlet at 1.92 ppm), succinic acid (singlet at 2.41 ppm), glutamic acid (multiplet at 2.04 ppm), glutamine (multiplet at 2.51 ppm). The singlets at 2.74 and 2.82 ppm were assigned to the methyl groups of dimethylamine (DMA) and trimethylamine (TMA). At 3.26 and 3.36 ppm the singlets of trimethylamine N-oxide (TMAO) and choline were observed, respectively. The signals at 3.15 and 3.94 ppm were attributed to creatine and the doublets of doublet at 3.56 and 3.64 ppm were assigned to the CH$_2$ groups of free glycerol. The multiplets of CH of threonine and proline were observed at 4.18 and 4.27 ppm, respectively. At higher frequencies the signals at 7.31, 7.36 and 7.47 ppm were assigned to phenylalanine and the singlet at 8.45 ppm to the formic acid. At 9.38 ppm the signal of aldehydic groups was identified which decreased considerably while rising the pyrolysis temperature (480 ± 10°C and 530 ± 10°C).

The NMR spectra of the biochar extracts in chloroform show differences between the sample produced at 430 ± 10°C and the samples produced at 480 ± 10°C and 530 ± 10°C. In the $^1$H NMR spectrum of the sample produced at 430 ± 10°C a typical NMR profile of fatty acids of olive oil was observed. Comparison of NMR spectra of chloroform biochar extracts with reported NMR olive oil data, related to olive oil chain production, gives also the opportunity to follow the pyrolysis progression. The spectrum showed a triplet at 0.86 ppm assigned to the methyl groups of fatty acids (saturated and unsaturated except $\omega$3). The multiplets at 1.26, 1.58, 1.99 and 2.30 ppm were attributed to the CH$_2$ of the aliphatic chain, |CH$_2$ to the carbonyl group, |CH$_2$H to the double bond, |CH$_2$H to the carbonyl group, respectively. A multiplet at 5.32 ppm pointed out the presence of vinyl groups of unsaturated fatty acids. Analogously to the olive oil, consisting of about 80% of oleic acids, the unsaturated fatty acids in this sample could be mostly represented by oleic acids. Moreover, no relevant intensity signals around 2.7–2.8 ppm, characteristic chemical shift of the bis-allylic protons of linoleic and linolenic acids, were observed. Interestingly, most of the fatty acids resulted not esterified with glycerol. However, in the 2D $^1$H COSY spectrum the signals at 4.12, 4.27 and 5.20 ppm showed cross-peaks among them and were assigned to the two CH$_2$ groups and to the CH group of the esterified glycerol in the small fraction of the triglycerides present. Moreover, in the 2D $^1$H $^{13}$C HMBC spectrum of the biochar sample produced at 430 ± 10°C (Fig. 3) two C at 173 and 176 ppm showing cross-peak correlation with the |CH$_2$ to the carbonyl groups were observed and assigned to the C of carbonyl groups of esterified fatty acids and the free fatty acids, respectively. By integrating these cross-peaks, the content of free fatty acids was calculated to be...
approximately 70% with respect to the esterified acids (30%). The NMR spectra in CDCl₃ of the samples produced at 480 ± 10 ºC and 530 ± 10 ºC showed a remarkable broadening of signals and did not reveal a clear profile attributable to fatty acids. Interestingly, in the range 6.5–8.0 ppm the presence of aromatic signals was observed. In the 2D ¹H ¹³C HSQC these aromatic signals showed correlations with C in the range of 125–130 ppm. The latter signals detected in extracts of chars produced at 480 ± 10 ºC and 530 ± 10 ºC indicate an enhancement of polyaromatic species with increased final pyrolysis temperature. Indeed, as already reported, polymeric species, such as polycyclic aromatic hydrocarbon, could have been produced due to the higher pyrolysis temperature [53,54].

3.6. Phytotoxicity germination test

No phytotoxic effect of the produced biochar was recorded using the germination and root elongation test with L. sativum (Table 5). Zucconi et al. [36] reported that a germination index above 60% points out a lack phytotoxic effect. The elutrate at 30% of the non-washed biochars produced at 430 ± 10 ºC, 480 ± 10 ºC and 530 ± 10 ºC shown germination indexes of 68.5%, 64.2% and 65.0%, respectively. Water washing increased the germination indexes to 71.2%, 67.9% and 66.7%, respectively. The highest germination indexes were recorded on 10% and 30% elutriates of biochar produced at 430 ± 10 ºC (77.3% and 71.2%, respectively). Increasing PT the germination indexes decreased significantly, confirming the results obtained through NMR analysis which pointed out the formation of polycyclic aromatic hydrocarbons under higher pyrolysis temperature.

4. Conclusions

Solid olive mill waste can be transformed into a useful product through pyrolysis. This process, allowing a biomass reduction up to 73% in terms of mass, is a promising answer to the need of valorizing this waste avoiding, at the same time, a polluting burden on the environment.

The properties of biochar obtained from solid olive mill waste were influenced both by the PT and the HR. An increase of those parameters led to a decrease in biochar yield, N, H content and the surface functional groups, while the C content increased. All the produced biochar showed high heating values and could be used as a valuable alternative fuel. The biochar produced at low temperature, showing low electrical conductivity and high germination index values could be used as a valuable alternative soil organic amendment to improve soil fertility and to sequester C over time.

The modulation of PT and HR allows to customize biochar according to its final use, being the biochar produced under high temperature rich in aromatic C, with lower functional groups and, consequently, with low surface charge and ion exchange. On the contrary, low temperature produced biochar showed significantly higher C=O and C–H functional groups.

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