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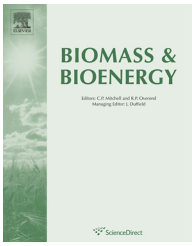

Production and characterization of biochar from three-phase olive mill waste through slow pyrolysis

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ABSTRACT

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.

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.

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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 olive oil and a highly wet olive pomace, while the products of three-phase systems are olive oil, 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 made the pomace phytotoxic 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) ($430 \pm 10\,^{\circ}C$, $480 \pm 10\,^{\circ}C$ and $530 \pm 10\,^{\circ}C$) and 3 heating rates (HR) ($25\,^{\circ}C\ min^{-1}$, $35\,^{\circ}C\ min^{-1}$ and $45\,^{\circ}C\ min^{-1}$) 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:

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

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]:

$$HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A\ (MJ/kg)$$

where C, H, O, N, S and A represent carbon, hydrogen, oxygen, nitrogen, sulfur and ash contents, expressed in mass percentages on dry basis.