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Performance improvement in olive stone's combustion from a previous carbonization transformation

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ABSTRACT

Under the framework of circular economy, agricultural wastes are an interesting carbon-based feedstock for thermal energy and power generation. Their use could extend the availability of biomass-based fuel and, at the same time, would reduce negative environmental effects. However, depending on the residues' characteristics, their direct combustion in boilers presents some challenges which could be overcome with a carbonization pretreatment. In this paper, the main mechanisms of thermochemical transformation of an abundant agricultural waste, olive stone, into biochar products via slow carbonization are analyzed, with emphasis on the effect of peak carbonization temperature. Thermogravimetric and differential scanning calorimetry analysis are used to evaluate the performance of the resulting biochars compared to raw olive stone in combustion processes and to assess the correlation between the peak carbonization temperature and compositional and fuel properties. Results show that with a prior treatment up to an optimum temperature of 800 °C the energy density is increased up to three times compared to the raw material. These findings suggest that carbonization of olive stones reduces the barriers to their direct use in current biomass boiler technology.

1. Introduction

The use of renewable biomass and agricultural residue sources for thermal energy and power generation is of high interest for a sustainable development owing to their CO_2 neutral emissions, worldwide abundance, self-sufficiency and relatively low cost [1,2]. Biomass precursors are currently the focus of widespread attention as starting material in a wide variety of thermo-chemical energy production processes such as combustion, gasification and pyrolysis [3].

Olive oil extraction and pitted olive production represent two of the most relevant agricultural industries within the Mediterranean countries [4,5]. These industries can in turn be regarded as one of the largest producers of biomass wastes (either in liquid form usually referred to as olive-mill wastewater, or solids residues such as dried pomace, olive stone, olive tree pruning and leaves [6]). Among these wastes, the overall estimated production of olive stones in Spain is approximately 1,050,000–1,400,000 tons per year (campaign of 2017) [7]. Given the abundance and low cost of this byproduct, there is interest in exploring new uses for olive pit biomass [8–10]. Nonetheless, its main use so far has been as direct solid biofuel for domestic applications [11] because, despite the environmental benefits and interesting physical and chemical properties [12], direct combustion has some drawbacks in commercial industrial boilers. Among them are the high moisture content, the low energy density, the limited fixed carbon fraction and problems with storage and handling costs.

There are research lines aimed at upgrading the fuel properties of biomass through a feasible previous thermochemical process including torrefaction, slow pyrolysis or carbonization and hydrothermal carbonization. These processes apply mild energy in the absence of oxygen and thermally decompose the initial biomass material into syngas, bio-oil and a solid biochar as target products, which can serve as an improved direct source for energy conversion and compete, in terms of energy density, with lignite and bituminous coals when environmental impact is taken into account [5,13–17]. The difference between these processes mainly lies in the temperatures considered: torrefaction is usually performed at 200–350 °C, while in the case of slow pyrolysis or carbonization temperatures above 600–700 °C are frequently considered. The effect of parameters such as peak temperature [18–20], heat rate [21], pressure or purge gas [22], starting raw material [23], and residence time [24,25] on biochar's fuel properties has been previously studied in order to select the right operating conditions to the design of combustion equipment. According to the work of Lee et al.

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[24], the energy yield of torrefied mixed softwood showed a stronger dependence on reaction time than on the peak temperature, which was studied below 270 °C. However, in later representative works of Liao et al. [26], Lee et al. [27] and Mundike et al. [21], it was reported for different feedstock precursors that, in slow pyrolysis processes with peak temperatures from 300 to 700 °C, the temperature had the greatest influence in the resulting biochar's characteristics, showing a strong drop in the solid yield but an increase in energy content. In terms of maximum temperature, some works reported a progressive increase in energy content within the range of 300–600 °C [28,29], while others reported a maximum peak at temperatures above 550–600 °C followed by a slightly decrease [21]. Overall, the yield of bio-char decreases with increasing temperature but it is strongly influenced by the cellulose, hemicellulose and lignin contents [23,30].

Prior work on the use of olive-pits as fuel has been devoted to their properties in direct combustion [31], their pyrolysis characteristics [32] and the use of thermal analysis for the determination of combustion and pyrolysis kinetics [7,33]. Only a few recent works have obtained biochars from pre-thermochemical transformation (mostly from slow carbonization or torrefaction) and correlated their treatment temperature with the improved fuel properties in direct combustion [34–39].

Most of the previously published works in this topic investigate pre-treatment temperatures below 900 °C, so the tendency and combustion characteristics of samples treated at higher temperatures is not completely understood. If a greater understanding of chemical reactions and parameters dependence developed in these processes is achieved, they could be modeled and designed for achieving an optimum efficiency at an industrial scale. Within this framework the main aim of this work is to explore the use of an abundant agricultural waste such as olive stone as starting precursor in the preparation of carbon-rich biochar samples through a carbonization pre-treatment in a wide range of temperatures from 400 to 1400 °C, and then optimize and understand the related thermal combustion and physical characteristics.

The structure of the paper is the following. First, a complete experimental characterization of this raw agroindustrial waste is herein performed in order to evaluate its energy potential. Then, the study is focused on a thorough thermal analysis of the olive stone carbonization process, obtaining carbon samples at different maximum temperatures. Afterwards, thermal characteristics of the samples are examined under oxidative atmospheres by means of thermogravimetric and differential scanning calorimetry analysis. Furthermore, the effect of the peak temperature on the combustion efficiency as well as combustion and microstructural characteristics is evaluated.

2. Materials and methods

2.1. Raw material and carbonization process

In this work an agricultural by-product, olive stone [40], was selected as starting material and subsequently carbonized in an inert atmosphere. The selected biomasses sources are solid wastes from the olive-oil extraction process, a procedure where the virgin olive oil is separated from the remaining components. Samples were supplied by *Oleomoron S.L Corporation*, an olive-oil extraction company located in the south of Spain.

Prior to carbonization, a complete material characterization was performed in order to evaluate its suitability as alternative fuel, including studies about thermal behavior and compositional analysis. For this purpose, raw materials as received were first naturally air-dried and were then ground into particles with regular size (4–5 mm in diameter) to avoid heterogeneities. Carbonization was then carried out in a tube furnace under an inert atmosphere. Olive stone samples were submitted under flowing nitrogen to a heating rate of 1 °C·min^{-1} up to 500 °C and 5 °C·min^{-1} up to the peak temperature followed by a holding time of 30 min. This temperature program was chosen to avoid the formation of cracks due to rapid release of volatile matter content upon heating.

Peak carbonization temperatures ranged from 400 °C to 1400 °C in intervals of 200 °C. Therefore, six types of biochar samples were obtained with peak temperatures of 400, 600, 800, 1000, 1200 and 1400 °C. These temperatures were chosen to study the influence of this parameter on microstructural and thermal behavior. Throughout the text, biochar samples will be referred to as CO (Char from Olives) followed by the peak temperature used during the previous carbonization.

2.2. Characterization

2.2.1. Thermal analysis

The thermal behavior of olive stones and biochar-derived samples was characterized by thermogravimetric (TGA) and differential scanning calorimetry (DSC) experiments. Nitrogen and synthetic air at flow rates of 100 ml·min^{-1} were used as inert and oxidizing carrier gases to study carbonization and combustion processes, respectively. Measurements were carried out using a dual system that allowed the simultaneous monitoring of weight loss and the heat flow as a function of the temperature increase (*Thermal Advantage SDT Q-600*). Differential thermogravimetric (DTG) curves were calculated as the result of the derivative of weight loss as a function of temperature. Calibration tests were periodically performed using a standard sapphire sample. For each experiment, samples weighing in the range 15–20 mg were placed in alumina crucibles and were then heated from room temperature to 1000 °C. The initial mass for each of the tests was kept between 15 and 20 mg in order to avoid any additional effect associated to mass and heat transfer as well as to reduce the occurrence of secondary vapor solid interactions [41]. Three experiments at each set of experimental conditions were carried out to ensure the reproducibility of results. Heating value (HV) was estimated by integrating the heat flow curve with respect to time, linking it with the peak temperature of the previous carbonization process. For that, DSC curves were previously corrected with baseline curves obtained from experiments performed with empty crucibles at the same conditions. The ignition temperature (T_i) was defined as the temperature at which the first deviation from the baseline line is observed. The burnout temperature (T_f) was considered as the temperature at which the combustion process is almost completed. The energy conversion efficiency ($\eta_{biochar}$) of the biochars was calculated on the basis of the heating value of the raw material and biochars as well as the biochar yield [$\eta_{biochar}$ (%) = ($HV_{biochar}$ · biochar yield (%))/($HV_{raw\ material}$)] [29].

2.2.2. Proximate analysis

From thermogravimetric experiments, the proximate analysis of raw olive stones and biochars was estimated taking into account the ash, volatile matter and fixed carbon content. The volatile matter (VM) was determined as the mass released during heat treatment up to 900 °C under inert atmosphere including moisture content [42]. Ash content was established as the remaining mass at 600 °C after the complete combustion under air flow. The fixed carbon content (FC) was thus obtained by difference between the ash and volatile matter content [43] [FC (%) = 100 – (Ash + VM)].

The biochar yield at each peak temperature was calculated taking into account the mass remaining at this temperature after carbonization of the raw material (Solid yield (%) = biochar weight/raw material weight × 100). Chemical composition of ashes obtained from combustion of olive stones up to 600 °C was analyzed by inductively coupled plasma mass spectrometry (ICP-MS, *Ultima 2, Horiba Jobin Yvon*). Samples were first digested in nitric acid using a *Milestone ETHOS ONE* microwave and were then diluted to ensure their concentrations were within the detection limits of the instrument.

2.2.3. Peak carbonization temperature dependence

Evolution of real and apparent density in carbon samples was