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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, and depending on the residues' characteristics, their direct combustion in boilers presents some challenges which could be overcome with a carbonization pre-treatment. 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.

**Keywords:** olive stone, agricultural waste, biochar, energy conversion, combustion

## **Highlights:**

- Carbonization of olive stone stones leads to improved fuel properties
- There is a three-fold increase in heating value after carbonization at 800 °C
- Higher pretreatment temperatures penalizes combustion performance
- Olive stone biochar capacity as alternative fuel for industrial use is shown

## **1 Introduction**

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The use of renewable biomass and agricultural residue sources for thermal energy and power generation are of high interest for a sustainable development owing to their CO<sub>2</sub> neutral emissions, worldwide abundance, self-sufficiency and relatively low cost [1, 2]. Biomass precursors are 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 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 the 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 in 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 have 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. [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 decreased 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 its properties in direct combustion [31], its pyrolysis characteristics [32], 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 parameter dependence developed in these processes is achieved, they could be modeled and designed for achieving an optimum efficiency when modeled 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

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### 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 pyrolysis, 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 a flow rate of nitrogen to a heating rate of  $1\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  up to  $500^{\circ}\text{C}$  and  $5^{\circ}\text{C}\cdot\text{min}^{-1}$  up to the peak temperature followed by a holding time of 30 minutes. This temperature program was chosen to avoid cracks formation due to rapid release of volatile matter content upon heating.

Peak carbonization temperatures ranged from  $400\text{ }^{\circ}\text{C}$  to  $1400\text{ }^{\circ}\text{C}$  in intervals of  $200^{\circ}\text{C}$ . Therefore, six types of biochar samples were obtained with peak temperatures of  $400$ ,  $600$ ,  $800$ ,  $1000$ ,  $1200$  and  $1400^{\circ}\text{C}$ . These temperatures were chosen to study the influence of this parameter on microstructural and thermal behavior.

Throughout the text, biochar samples will be referred 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<sup>-1</sup> 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 obtained 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 up from room temperature to 1000°C at constant heating rates of 10°C·min<sup>-1</sup>. 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 ( $\eta_{\text{biochar}}$ ) of the biochars was calculated on the basis of the heating value of the raw material and biochars as well as the biochar yield [ $\eta_{\text{biochar}} (\%) = (\text{HV}_{\text{biochar}} \cdot \text{biochar yield} (\%)) / (\text{HV}_{\text{raw material}})$ ] [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 (average value of three measurements) [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 by TGA measurements (Solid yield (%) = biochar weight/raw material weight x 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 fell within the detection limits of the instrument.

### 2.2.3 Peak carbonization temperature dependence

Evolution of real and apparent density in carbon samples was determined by helium pycnometry (*Pentapycnometer 5200, Quantachrome Instruments*) and geometrical measurements, respectively. Scanning electron microscopies (*Jeol 6460-LV* and *Hitachi S-5200*) were used for microstructural characterization. Energy dispersive X-ray analysis (*EDX- Inca 7573, Oxford Instruments*) was used to identify chemical composition. Trace components presented were determined by an X-Ray fluorescence spectrometer (*Axios, PANalytical*) equipped with a Rhodium X-ray tube. Measurements were carried out on disks, which were pressed in a hand press (*Retsch*) over a mold of boric acid, using a semi-quantitative method (*Omnian-10*). The specific surface area was determined by nitrogen adsorption at 77K according to the BET method (*ASAP 2420, Micromeritics*). Samples were previously outgassed at 400°C during 10 hours and then were placed in a Dewar vessel to analyze the adsorbed and desorbed nitrogen amount while the relative pressure ( $P/P_0$ ) was being ranged from 0 to 1. All these properties were studied as a function of the peak carbonization temperature.

## 3 Results and Discussion

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### 3.1 Raw olive stones

#### 3.1.1 Thermal analysis

The thermochemical properties of the carbonization and combustion processes of the raw material were analyzed using TGA measurements in controlled atmospheres of nitrogen and air, respectively. In [Fig. 1](#) are

illustrated the weight loss percentage and the weight loss rate as a function of the temperature in both carbonization (Fig.1-A) and combustion (Fig.1-B).

According to the results, as depicted in Fig.1-A, when the olive stone is submitted to a controlled heating rate under inert atmosphere, the sample is subjected to a thermal degradation [44]. On the DTG curve, three well-defined main stages can be distinguished [45]. The first one small peak, which takes place at temperatures up to 200°C, corresponds to the release of water molecules absorbed into the structure of the raw material. This step is followed by two abrupt peaks (with maximum weight loss rates at 275°C and 350°C in the DTG curve). A prolonged heating at temperatures above 200°C in non-oxidizing atmosphere causes the decomposition and break down of the main polysaccharide constituents present in lignocellulosic materials: hemicellulose, cellulose and lignin [46]. The polymer decomposition of hemicellulose happens at a temperature range of approximately 220-315°C, whereas the breakdown of cellulose takes place from 320°C to 400°C. Meanwhile, the decomposition range of the lignin is not as narrow as that of hemicellulose and cellulose. Its decomposition rate increases slowly over a broad range, with most of the decomposition occurring from 220°C to almost 700°C [47-49]. From 700°C onwards, the carbonization process is almost complete as the bulk of volatile matter has been released, leaving a solid carbonaceous residue with around 25% of the initial mass. Nevertheless, when olive stone is heated under air, four main stages are observed due to the heterogeneous combustion of the fixed carbon content also taking concurrently with thermal degradation [50]. This behavior is depicted in Fig.1-B, where the first three stages are coincident with the results reported in inert atmosphere, while the last peak corresponds to the burning of the resulting char in air after the release of volatile matter content.

As has been suggested in previous works, the temperature ranges and weight loss percentages of these processes in both inert and oxidative conditions can be substantially affected by parameters such as the sample mass, the particle geometry, chemical differences in the precursor and heating rate [51]. Since differential scanning calorimetry analysis is an essential technique for better understanding the suitability of a material as fuel for subsequent applications in combustion processes [52], Fig. 2 shows the DSC curves and the amount of heat absorbed or released while the temperature is increasing up to 1000°C under inert and oxidizing flowing gases. The carbonization process is mainly endothermic, as energy is required to break the polysaccharide chains, whereas the combustion process of the olive stone is overall highly exothermic. A pronounced peak of released heat at temperatures between 300 and 600°C is associated with char oxidation. The fixed carbon content of the sample burns out leaving ashes that consist primarily of metal oxides. At 600° C the combustion is almost completed, with a remaining ash content below 1 wt. %.



### 3.1.2 Proximate analysis

Proximate analysis of the raw biomass is listed in [Table 1](#). As shown there, the olive stone shows a moisture content lower than 10 wt. %, which is considered the optimum percentage for biomass combustion [53]. Higher moisture content might adversely affect the heating value causing ignition problems, releasing large amounts of flue gases and worsening the quality of combustion. In addition the remaining ash yield is generally below 1.0 wt. %, a lower percentage than other biomass products which generally show values ranging from 5% to 20% [54]. By comparing volatile matter and ash content of olive stones with those reported in previous works [8, 54], the volatile matter had values close to 70% and an ash content close to 1 wt. % although these values are usually rather dependent on growing conditions and harvesting [29].

### 3.1.3 Chemical properties of the ashes

The ash content and composition are relevant parameters to assess the potentially use of a biomass product as a fuel due to the problems that it might cause: severe slag-ash agglomeration, deposits on the surface of a heat exchanger or in a boiler tube, corrosion problems in the metal and ash emissions in the aerosol state (fly-ash) [55]. Furthermore, a high ash percentage reduces the heating value of a fuel and requires the use of dust removal systems [53]. Major elements in biomass ashes include Ca, K, Al, Si, Fe, Mg, Na, Cl, P, and S, although the amount of each element can be influenced by different factors such as the geographical location, the type of soil or the age [55]. The composition could either be inherent to the precursor or could be modified as a result of processing steps. For instance, salts are frequently bonded chemically to the organic fraction or can be incorporated during growth. During the combustion, the inorganic fraction of the biomass and the ashes undergo transformations such as segregation, precipitation and nucleation, depending on the combustion temperature, residence time and boiler design. Taking into account the combustion problems, one of the most important features of the ash is its melting point. The alkali oxides and salts that form during the combustion of the biomass have low melting points, and higher amounts of potassium and sodium can enhance problems with eventual slagging and fouling in the furnaces [56]. Another major concern related to ashes is the presence of both chlorine and alkali metals in some biomass products. For instance, potassium chloride presents high thermal stability and causes corrosion problems in heater tubes.

[Table 2](#) shows the main composition of ashes remaining after the combustion of olive stones. As can be seen, the ash composition is mostly dominated by metal oxides of Ca and K. Small traces of Mg, Fe and P are also

found. Compared with other solid wastes from agroindustry or mineral coals, the olive stones in this study appear to have lower content than those reported in the literature [54].

## 3.2. Carbonization pre-treatment

### 3.1.4 Characterization

Fig. 3 shows representative SEM micrographs of the resulting char samples obtained by carbonization of olive stones up to 1000°C. They consist of carbon scaffolds with high porosity, consisting of pores with different geometry (elongated and cylindrical) and sizes that retain the precursor's microstructure and morphology. The proximate analysis as a function of the temperature is included in Table 1. The evolution of volatile matter, fixed carbon content and biochar yield is illustrated in Fig. 4. From the proximate analysis, it can be seen that the volatile matter fraction and biochar yields tend to decrease with the carbonization temperature due to the previous release and thermal decomposition of main constituents during carbonization pre-step, but maintain almost invariable at temperatures above 1000°C (small variances can be attributed to the progressive thermal decomposition of lignin which takes place at higher temperatures than cellulose and hemicellulose). By contrast, the fixed carbon content increases from 24 to 95 %, a variation of 71% from the lowest to the highest temperature considered [5]. The ash percentage also increases with carbonization temperature, as observed by other authors [29]. Traces of other elements found in the carbonaceous samples were studied by X-ray fluorescence (XRF), and results are listed in Table 3. The major elements present as traces are Ca and K. In smaller proportions, Fe, Mg, P and Na are also found. Traces of Si, S and Sr are observed but with very small proportions (less than 0.5 wt. %).

In Fig. 5-A real and apparent densities as a function of peak carbonization temperature are shown. Apparent density decreases due to the reduction in volume associated with the thermal degradation, whereas real density depends heavily on the maximum temperature, showing a point of inflection that is consistent with similar observations by other authors [57, 58]. At 400°C, solid samples reach the minimum value while at 800°C they undergo thermal decomposition atomic rearrangement of carbon atoms. The increase in density of the sample pyrolyzed at 800°C is attributed to the conversion of disordered low-density carbon into a more compact turbostratic carbon structure with a higher density due to volumetric shrinkage. Above 800°C, the lateral growth of graphitic layers continues and the atomic arrangement reduces the interlaminar spacing between them. Closed micropores in the samples appear, producing a decrease in the density values of up to

1000°C since these closed micropores are not accessible to helium. This same trend is also found in relation to the surface area and the volume of micropores as obtained by the BET method, as shown in [Fig. 5-B](#).

### 3.1.5 Fuel properties

The heating value of a material reflects the amount of energy produced when burned in air. We have studied the effect of a previous carbonization on the heat released upon combustion and the difference in both efficiency and combustion characteristics between using raw olive stones and biochars derived from them. [Fig. 6](#) shows the weight loss and the heat flow released when all the types of samples are heated under oxidizing atmosphere.

The temperature at which combustion is completed increases with peak carbonization temperature ([Fig. 6-A](#)). The curve corresponding to raw olive stone shows several weight loss stages due to the release of volatile matter and moisture prior to fixed carbon combustion. This multi-stage combustion is also observed in solid char samples produced at lower temperatures (mainly CO-400°C), because that carbonization temperature was not enough to complete the thermal degradation. Therefore, carbonization takes place and is completed as a first-step prior to combustion. Nevertheless, for chars produced at higher temperatures, the weight loss is mainly related to the combustion of the char itself.

[Fig. 6-B](#) shows the heat flow released during oxidation in non-isothermal analysis. Clearly, this plot reveals that this process is highly exothermic with only one characteristic peak arising from the combustion, and suggests that the previous carbonization treatment is a key parameter for the efficiency and thermal characteristics as fuel since a noticeable difference in the area of the heat release curve is reflected. The heating value of combustion was therefore estimated under these experimental conditions by integrating the heat flow curve with respect to time, taking into account the devolatilized mass.

In literature, calorific values are frequently measured using a bomb calorimeter or estimated from empirical equations taking into account the ultimate and proximate analysis as the values given through DSC measurements, being the area under the curve proportional to the calorific value, are sometimes underestimated and are generally lower than the true heating values [\[59-62\]](#). However, we consider DSC analysis as a viable alternative which enables us to obtain further insight into the thermal behavior of our samples (not only the heat released, but also the ignition point and the combustion extent). Since all our experiments were carried out at the same experimental conditions (heating rate, particle size, air flow, and so

on), DSC analysis serves as a valuable tool to compare the combustion characteristics of biochars obtained at different peak temperatures and estimation of the increase in energy yield of our samples.

The correlation between the integrated heat released via DSC analysis (heating value) and the carbonization temperature is shown in Fig. 7. Clearly, there is an increase in heating value with increasing carbonization temperature. This trend could be caused mainly by the decomposition of polysaccharides, which causes the breakdown of the C-O, C-C and C-H chains and thus a decrease in hydrogen and oxygen content [5]. This effect leads to an increased fixed carbon fraction and, hence, to an increase in its heating value. It is worth noting that by performing a pre-treatment of olive stones at 800°C, the heating value of the combustion is greatly increased compared to the original biomass, reaching values up to 3 times higher than the raw material. Nevertheless, at higher temperatures there is a slightly decrease, although average heating values remain essentially constant when standard deviations are considered. Calculated energy conversion efficiencies of biochars are plotted in Fig. 8 as a function of carbonization temperature. This parameter can provide an estimation of the optimum temperature for pre-treatment in terms of energy yield since we defined it based on both the heating value of biochar and raw material as well as the solid yield after carbonization. Energy conversion efficiencies increases within the range 400-800°C, reaching the highest value at 800°C. Hence, the ideal temperature of the previous carbonization treatment in terms of combustion energy yield is within the range 600- 800°C as higher treatment.

Analysis in oxidizing atmospheres also reveals changes in combustion characteristics and reactivity depending on the previous processing temperature, which are important parameters for the design of boiler equipment. Fig. 9 shows the burned carbon fraction as a function of time and thus the dependence of ignition, peak and burnout temperatures on the carbonization temperature. The ignition temperature reflects the ease of ignition of a fuel [63], while the peak and burnout temperatures are the temperature of the higher weight loss rate and the temperature at which combustion is completed (lower values indicate higher burnout efficiency), respectively. These parameters are directly associated with the reactivity of a fuel and are further influenced by factors such as the carbon content, particle size, surface area, internal heat transfer and oxygen concentration [64].

According to the results shown in Fig.9, the combustion is shifted towards higher temperatures as carbonization temperature increases and thus both the ignition point and the burnout temperature seem to have a strong correlation with this parameter. A gradual increase in the onset of burning is reflected with

temperature, denoting that biochar from lower temperatures are more easily ignited and have a higher reactivity. Since all these experiments were performed under the same conditions, the reactivity variations could be mainly due to differences in carbon and volatile matter content and surface areas, following similar trends as in other studies [65-67]. It is further noted that as shown in Fig. 4, the volatile matter fraction decreases considerably in biochar samples contrary to the fixed carbon content when compared to the original biomass. These two parameters can determine the ease of ignition: the char reactivity generally increases with increasing volatile matter content (as is confirmed in Fig. 10) resulting, as a consequence, in higher ignition temperatures. Hence, a higher carbonization temperature is disadvantageous to the combustion behaviors of the biochars.

## 4 Conclusions

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This paper gives detailed experimental analyses on olive stone combustion and biochar-derived product characteristics as a function of previous carbonization temperature. Such information is of special interest for the design of dedicated combustion equipment for olive stone biomass, where different combustion processes and temperatures can be integrated and to identify their use for direct

Thermochemical transformation of olive stones into biochar samples was conducted via carbonization with peak temperatures from 400 to 1400°C. Thermal behavior in oxidative atmospheres and the effect of peak temperature on energy released has been studied. All the results demonstrate that carbonization was effective at turning biomass wastes into higher fuel products with an enhancement in energy content. With a previous treatment, the heating value of combustion could be significantly increased compared to raw materials, with an ideal temperature of 800°C in terms of both heating value and energy efficiency. Besides, an increase of the temperature during biomass carbonization decreases the char reactivity, with higher ignition and burnout temperatures related to the decrease of volatile matter content.

According to the results presented in this paper, the performance of carbon samples derived from this agroindustrial waste via carbonization demonstrates the potential of this product as an effective biomass alternative fuel, that can be used on existing combustion technologies designed for coal operation.

## Acknowledgements

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## Tables

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Table 1. Proximate analysis of olive stone and related biochar from TGA measurements.

Sample	Volatile matter (%)	Fixed carbon (%)	Ash (%)	Biochar yield (%)
Raw olive stone	75.36	24.02	0.62	100
CO-400°C	19.53	79.97	0.50	35.10
CO-600°C	16.52	82.44	1.04	26.49
CO-800°C	11.28	87.74	0.98	24.59
CO-1000°C	8.74	90.03	1.23	23.88
CO-1200°C	7.64	90.22	2.14	22.91
CO-1400°C	4.05	94.65	1.30	21.67

Table 2. Main traces of inorganic materials presented in the ashes from olive stone combustion (ICP-MS analysis).

Element	Ca	K	Fe	Mg	P
Wt. %	49.69 ± 0.05	36.58 ± 0.03	6.92 ± 0.01	6.46 ± 0.01	0.33 ± 0.01

Table 3. Traces of elements in carbon samples pyrolyzed at 1000° C.

Element	Ca	K	Fe	Mg	P	Na	S	Sr	Si	Cl
Wt. %	0.72	0.42	0.03	0.02	0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01

# Figures

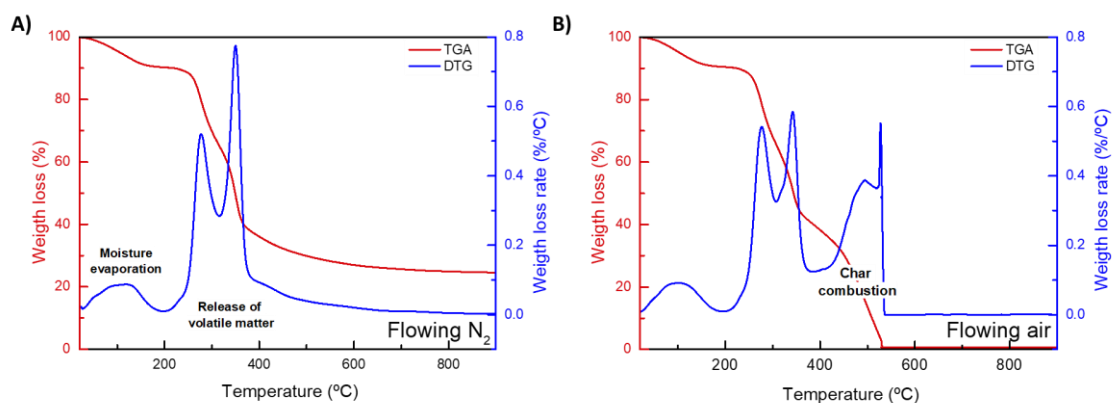


Figure 1. Thermogravimetric (TGA) (left y-axis) and differential thermogravimetric analysis (DTG) (right y-axis) of olive stones during pyrolysis and combustion under A) inert and B) oxidizing atmospheres at gas flow rates of  $100 \text{ ml}\cdot\text{min}^{-1}$  with a heating rate of  $10^\circ\text{C}\cdot\text{min}^{-1}$ .

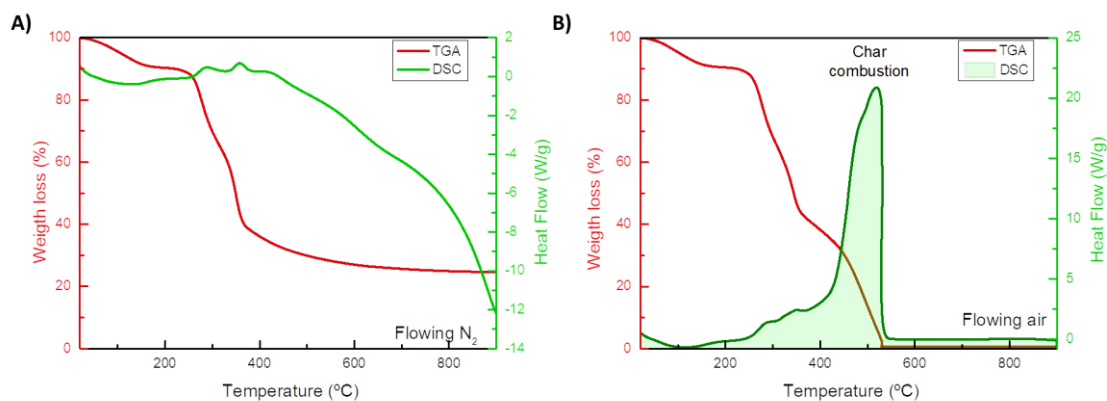


Figure 2. TGA (left y-axis) and DSC (right y-axis) analysis of olive stones heating at  $10^\circ\text{C}\cdot\text{min}^{-1}$  under inert (A) and oxidative atmosphere (B). The heat flow curve shows a pronounced exothermic peak attributed to the char burning.

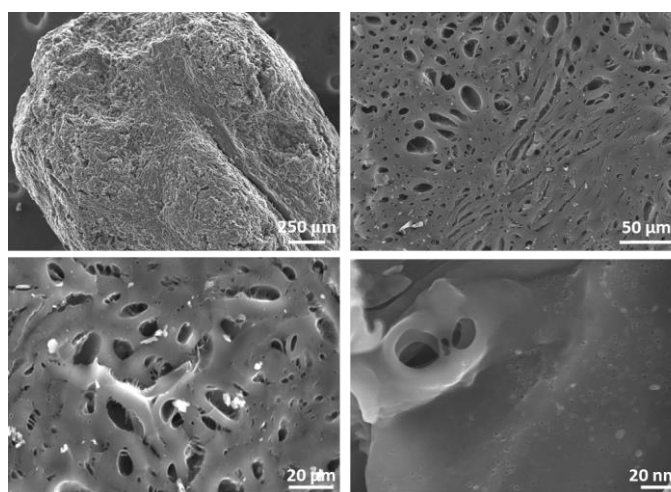


Figure 3. SEM micrographs of biochar samples from olive stones at  $1000^\circ\text{C}$ .

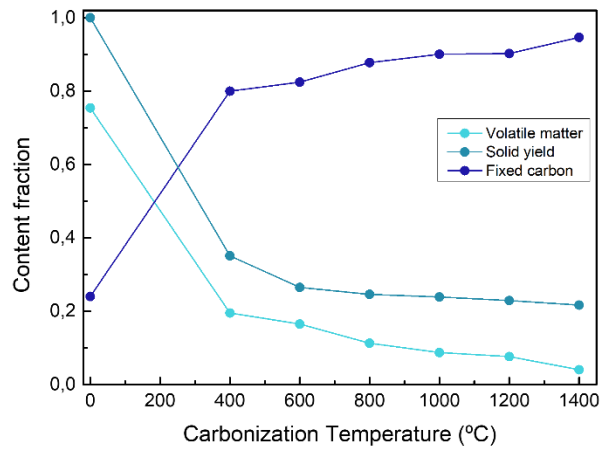


Figure 4. Evolution of volatile matter content, fixed carbon content and biochar yields as a function of peak temperature.

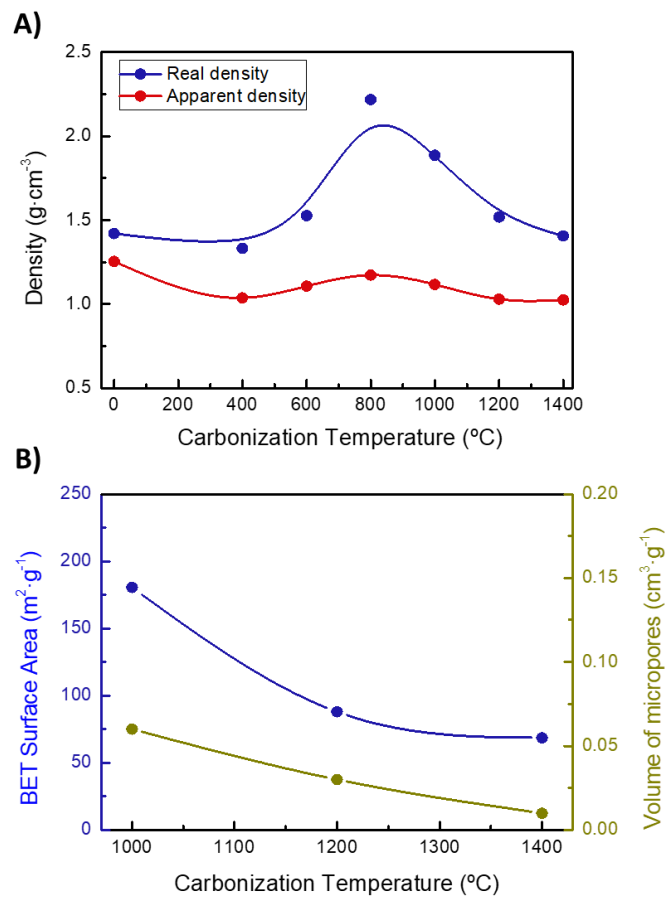


Figure 5. (A) Real density, apparent density, (B) BET surface area and micropore volume evolution as a function of carbonization temperature of olive stones.



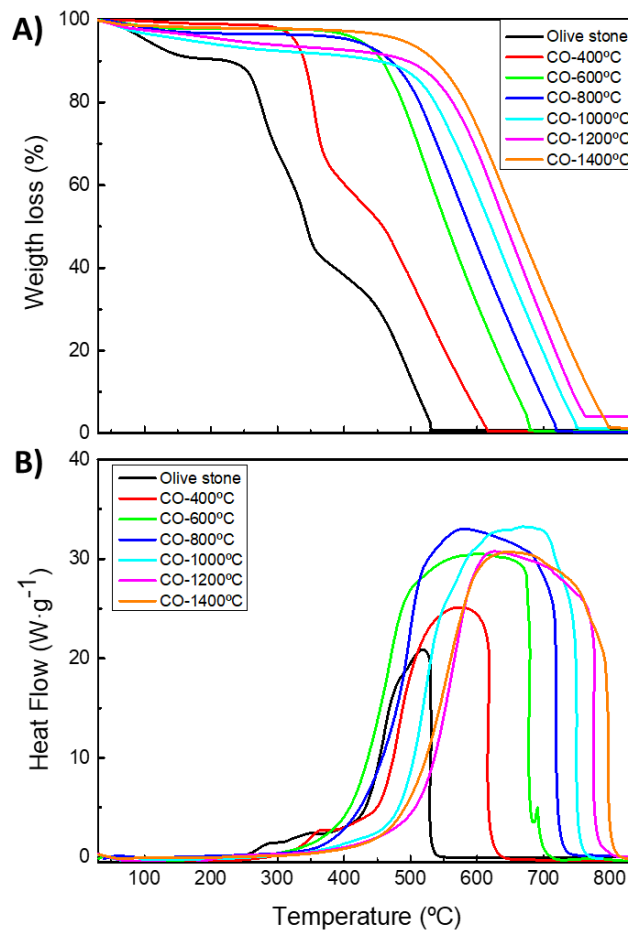


Figure 6. TGA (A) and DSC (B) representative curves under oxidizing conditions. Samples of raw olive stone and biochar derived from its carbonization at different peak temperatures were heat treated up to 800°C with a constant heating rate of 20°C·min<sup>-1</sup> in flowing air.

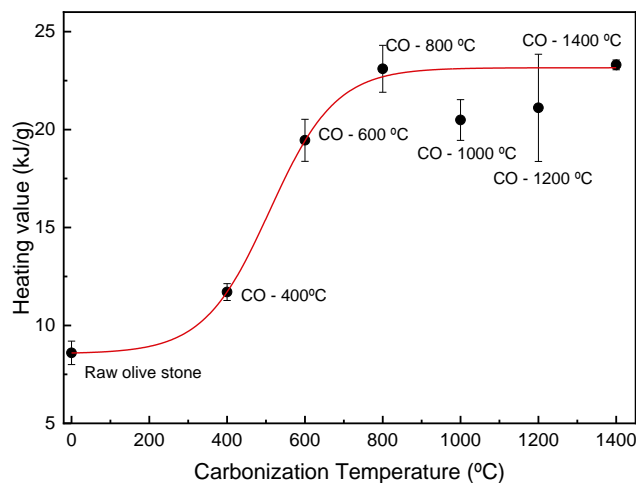


Figure 7. Heating value of combustion via DSC analysis as a function of the peak pre-treatment temperature. The integrated heat released was taken as the average value from three experiments. Errors represent one standard deviation. The solid is included to guide the eye and does not imply a fit to the data.

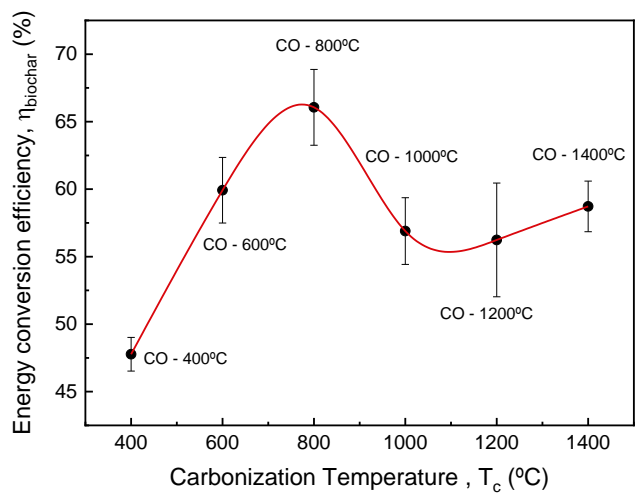


Figure 8. Evolution of energy conversion efficiency as a function of carbonization temperature.

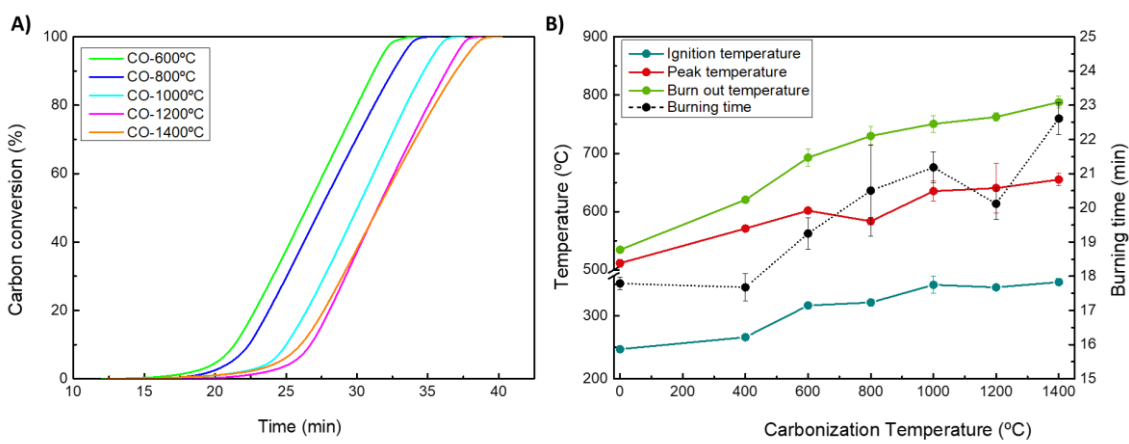


Figure 9. (A) Relation between carbon conversion and time for carbonized olive stones, (B) Dependence of ignition, peak and burnout temperatures on peak pre-treatment temperature along with the burning time.

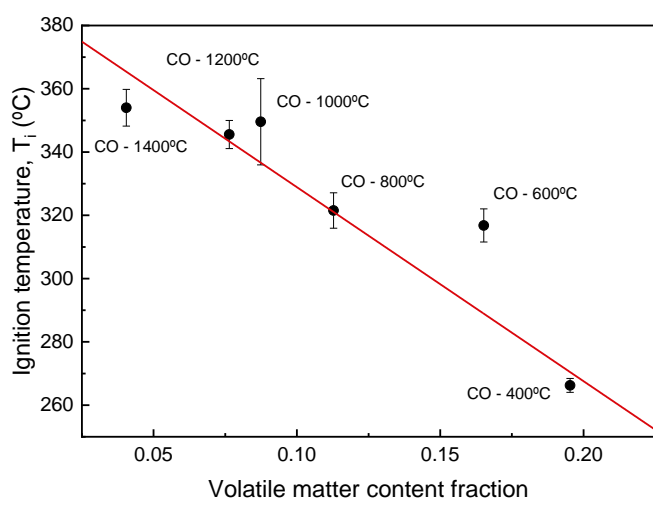


Figure 10. Effects of volatile matter content on the ignition temperature of biochars.

## 5. References

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