

Quality assessment of olive stones and nut shells for residential combustion applications

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ABSTRACT

The main objective of this work is to study the quality of typical Mediterranean biofuels (almond shells, pine nut shells and olive stones) that could be used in a sustainable way from a CO₂ saving perspective in the same combustion facilities as wood pellets, i.e. residential, small commercial and public building applications. With this purpose, olive stones were collected during four sampling campaigns (2011, 2015, 2019 and 2023) and nut shells in two campaigns (2011 and 2015) and their fuel quality properties were determined. Wood pellets were used as the solid biofuel of reference.

Significant sustainability and global CO₂ savings (>13 Mt CO₂/yr) could be achieved by using solid biofuels in domestic thermochemical biomass systems near production sites. Olive stones and wood pellets present similar chemical compositions and, in general, better fuel quality than nut shells, in terms of ash content (≤ 0.8 wt% for olive stones and ≤ 1.6 wt% for nut shells), nitrogen (≤ 0.4 wt%), sulphur (≤ 0.04 wt%) and calorific values (18.0–19.3 MJ/kg, d.b.). An overestimation of the ash content, determined according to ISO 18122:2022 [1], was obtained for compounds with high lignin content, standing at around 20 wt% in the case of pine nut shells. However, the notable tendency of olive stones and almond and pine nut shells to form sinters should be taken into account when designing and operating domestic combustion applications for this type of fuels.

Introduction

Regional and international trade of nut shells and olive stones is increasing worldwide, and it is important to specify not only the quantity but also the quality of the different classes of nut shells and olive stones. According to the new Renewable Energy Directive, which sets a new target of 32% from renewable energy in final consumption for the EU by 2030 [2], an increase in the use of solid biofuels is expected in different sectors. Furthermore, within the framework of the circular bioeconomy, it is necessary to valorise these residues, and combustion is one of the main processes.

Replacing fossil fuels with solid biofuels from olive and dry nut shells can also help to significantly reduce CO₂ emissions. Use needs to be at the local level to ensure sustainability not only from an environmental point of view but also from a social and economic point of view. However, local use implies the application of these solid biofuels in stoves and boilers in the domestic sector, which means that they must be of an acceptable quality to be utilised in small, non-industrial domestic systems.

Although the scientific literature is very scarce, some authors have found that the quality of some nut shells, such as almond shells and olive stones, makes them an optimum biomass to replace wood pellets, charcoal and briquettes in grate boilers [3,4]. In this sense, almond shells and olive stones could be burnt in the same domestic systems as those fired with wood pellets [4,5].

Nevertheless, it should also be taken into account that the alkaline compounds contained in olive stones and nut shells may form sinter and slag in stoves and furnaces faster or at lower temperatures than wood pellets [6], which could cause undesirable shutdowns, of special concern for the domestic sector. Corrosion and explosions—the later mainly derived from the fine particles of this type of solid biofuels, which are partially milled—could also pose a risk. The proportion of ash, nitrogen, sulphur, chlorine and trace elements contained in olive stones and nut shells also needs to be measured, due to the scarcity of information available on the variability of their chemical characteristics as a function of time, and in order to predict the emissions of hazardous compounds [7].

Therefore, an assessment of the combustion quality of these biofuels

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is of particular interest, as their application in residential, small commercial and public buildings may require a readjustment of the equipment settings or even the development of new designs to achieve optimum efficiency, avoid malfunctions, and minimise the emission of harmful compounds.

This study aims to provide additional data and offer valuable information on global and European production and CO₂ savings, as well as the on main properties of olive stones and nut shells marketed in a Mediterranean region during different sampling campaigns. The research explores ash, nitrogen, sulphur and chlorine content, bulk density, particle size distribution, calorific values, major and minor elements, ash melting and corrosion behaviours, thermal properties and others that could affect the combustion behaviour of these fuels such as fine particle content, oil content, etc. The quality of these biofuels collected from a variety of producers is compared mainly with the quality of wood pellets, which are much more widely used in domestic thermal applications than olive stones and nut shells.

Materials and methods

Solid biofuels and samplings

Three typical Mediterranean solid biofuels were considered: olive stones, almond shells and pine nut shells. The selected olive stones were derived from a two-phase process used extensively in Spain to obtain olive oil [8]. There are several types of nut shells, among the most produced are almond shells, walnuts, cashews, pistachios and hazelnuts. In this work, two types have been collected and physically and chemically analysed (almond shells and pine nut shells) from all the nut shell types.

Additionally, wood pellets were also chosen as the biofuel of reference for residential, small commercial and public buildings applications due to their good quality and performance.

All the samples collected were being commercialised in the Spanish market by different producers at the time of sampling and were intended for use in the domestic sector. For each sample type (pellets, olive stones, and nut shells), a bag weighing more than 10 kg was collected. These bags (belonging to different batches) were obtained from supermarkets (pellets and olive stones) or directly from factories (olive stones and almond and pine nut shells), all of them ready for sale. Randomly selected bags were collected from the main producers by AVEBIOM (Valladolid), OCU (Madrid) and CIEMAT (Soria) in order to obtain representative samples of the solid biofuel market in Spain. Table 1 shows the number of samples collected per solid biofuel and year and codes used. Four samplings of olive stones and wood pellets were performed in 2011, 2015, 2019 and 2023. Two samplings of almond shells and pine nut shells were carried out in 2011 and 2015. The first two letters of the sampling codes indicate the type of fuel, whereas the last part of the code shows the number of the sampling campaign (S1 for 2011, S2 for 2015, S3 for 2018 and S4 for 2023). Table 1 details the percentage of the producers selected with regard to the overall

producers in the Spanish market as well as the percentage of the amount manufactured per biofuel and year related to the total amount produced in the country.

Estimation of production and CO₂ savings

A brief sequence for calculating CO₂ savings is as follows: first, the worldwide production of olive stones and nutshells is estimated, and then the energy saved is calculated. Natural gas is selected as a fossil fuel to be substituted. Using the natural gas emission factor (0.202 t CO₂ per MWh of energy used), the CO₂ savings are calculated.

The olive stone production was estimated with the help of the UNdata website [9] and taking into account the fact that each ton of olives contains approximately 8.3 wt% olive stones [10].

The almond and pine nut shell production was estimated consulting the statistical yearbook of the International Nut & Dried Fruit Council [11] and taking into account the fact that almond shells make up approximately 70 wt% of the whole almond fruit weight [10].

In order to calculate CO₂ savings, natural gas was selected as the fossil fuel of reference. According to the IPCC emission factors database and, specifically, in the emission factor worksheet dedicated to stationary combustion [12], natural gas exhibits a net calorific value (NCV) of 48 TJ/Gg and emits 2692.80 kg CO₂/t, which results in 0.202 t CO₂ per MWh of energy used, taking into account the following equation:

$$\text{Emission factor (t CO}_2\text{/MWh)} = 0.2693 \text{ (t CO}_2\text{/Mg)} / 48 \cdot 10^3 \text{ (MJ/Mg)} \cdot 1/3600 \text{ (MWh/MJ)} = 0.202.$$

For each solid biofuel, the CO₂ savings were estimated by calculating the energy produced. The energy produced was derived by multiplying the production of each solid biofuel by their mean net calorific value (w. b.), which is shown in Table 5. The equation used is presented below and the CO₂ savings are shown in Table 4 (Section 3.1):

$$\text{CO}_2 \text{ savings (Mt/yr)} = \text{Production (kg/yr)} \cdot \text{NCV (MJ/kg)} \cdot 1/3600 \text{ (MWh/MJ)} \cdot 0.202 \text{ (t CO}_2\text{/MWh)} \cdot 10^{-6} \text{ (Mt/t)}.$$

Similarly and in the case of other types of nuts with the highest global production [11]: walnuts, cashews, pistachios and hazelnuts, their shell production was estimated, also considering that 70% of the weight is due to the shells. The CO₂ savings were achieved in the same way as with almond shells, but using the average net calorific value of the almond shells.

Analytical methods

The analytical samples were prepared according to ISO 14780:2017 ‘Solid Biofuels — Sample preparation’, which consists of homogenisation, division, milling and drying processes. The international standards used, together with the analytical methods for each parameter, are shown in Table 2. The tests were performed in the Laboratory of Biomass Characterisation of CEDER-CIEMAT. Each sample bag was divided up to analyse the moisture, bulk density, particle size distribution and fine particle content.

The remaining analyses—ash, C, H, N, Cl and S, calorific value,

Table 1
Sampling details and codes.

Biofuel	Year	Code	Samples	Producers	Overall producers	Producers selected	Amount produced
Olive stones	2011	OS_S1	8	7	15	46.7%	35%
Olive stones	2015	OS_S2	8	6	23	26.1%	24%
Olive stones	2019	OS_S3	8	8	25	32.0%	30%
Olive stones	2023	OS_S4	8	7	30	23.3%	25%
Almond shells	2011	AS_S1	6	5	21	23.8%	14%
Almond shells	2015	AS_S2	6	5	19	26.3%	23%
Pine nut shells	2011	PS_S1	6	6	13	46.2%	45%
Pine nut shells	2015	PS_S2	6	6	13	46.2%	46%
Wood pellets	2011	WP_S1	14	14	32	43.8%	54%
Wood pellets	2015	WP_S2	14	13	79	16.5%	34%
Wood pellets	2019	WP_S1	14	14	70	20.0%	24%
Wood pellets	2023	WP_S2	14	14	65	21.5%	26%

Table 2
Analytical methods and standards for the determined fuel properties.

Property	Analytical method (equipment)	Standard
Bulk density	Mass of a known volume	ISO 17828:2015
Particle size distribution	Separation into defined size fractions by sieving	ISO 17827-1 and -2:2016
Mechanical durability of pellets	The pellets are rotated in a drum for 5 min	ISO 17831-1:2015
Fines content of pellets	Sieving with a 3.15 mm round hole sieve	ISO 18846:2016
Oil in olive stones and nut shells	Soxhlet extraction with n-hexane	ISO 659:2009
Proximate analysis	Moisture	Drying at 105 °C
	Ash	Ashing at 550 °C
Ultimate analysis	C, H, N	Elemental analysis (Leco, TruSpec)
	S, Cl	Ion chromatography (Metrohm, 883 Basic IC Plus) after sample combustion in an automatic calorimeter
Calorific value	Automatic calorimetry (Ika, C5000)	ISO 18125:2017
Major elements in ash	Microwave digestion of the ashes obtained at 550 °C followed by ICP-AES (Thermo Fisher Scientific, Jarrell Ash Iris/AP)	ISO 16967:2015
Minor elements (As, Cd, Cr, Cu, Ni, Pb and Zn)	Microwave digestion followed by ICP-MS (Thermo Fisher Scientific, iCAP Q)	ISO 16968:2015
Mercury	Gold amalgamation followed by AAS (Milestone, DMA-80)	ISO 16968:2015
Ash melting behaviour	Heating an ash pellet to 1450 °C by optical heating microscope (Leitz)	ISO 21404:2020
Thermal behaviour	TGA-DSC (Setaram, SETSYS Evolution TGA 16/18)	Not available
Inorganic compounds	X-ray diffraction (Panalytical XPERT-PRO)	Not available
Corrosion tests	Biomass ash on steel coupon for 200 h in a tubular furnace at 700 °C and SEM/EDX (Zeiss, Evo LS-10) study	Not available

ICP: Inductively coupled plasma; AES: Atomic emission spectroscopy; MS: Mass spectrometry; AAS: Atomic absorption spectroscopy; TGA: Thermogravimetric analysis; DSC: Differential scanning calorimetry; SEM: Scanning electron microscopy; EDX: Energy dispersive X-Ray spectrometry.

major, minor and trace elements—were carried out on another analytical sample, which had been milled to less than 0.5 mm in particle size (Table 2).

As there is no standard process for specifically determining the content of oil in solid biofuels, this property was determined according to ISO 659:2009, which was developed by the international technical committee ISO/TC 34/SC 2 for oilseeds.

The ash melting behaviour of the studied fuels was derived from the characteristic ash temperatures, including deformation temperature (DT) and fluid temperature (FT), by applying ISO 21404:2020. The test ash was produced in the laboratory at 550 °C according to ISO 18122:2022.

Thermal analyses were performed with the purpose of studying the volatilization of the major components (hemicellulose, cellulose and lignin) of the studied biofuels as a function of the temperature. A mass portion of 10–20 mg was heated from room temperature to 1000 °C at a rate of 10 °C/min in air atmosphere. For validation, mass losses were compared with a copper sulfate standard. The balance had a very high resolution of 0.03 µg for a measurement range of ± 200 mg. The uncertainty of mass variation expressed as relative standard deviation was lower than 1 wt% between 400 °C and 1000 °C, 3 wt% between 300 °C and 400 °C, and 6 wt% between 200 °C and 300 °C.

X-ray diffraction analyses were performed using a PANalytical Xpert-PRO diffractometer operating at 45 kV and 45 mA. The mineral phases

of the biomass ashes (obtained at 550 °C following ISO 18122) were identified by means of the Inorganic Cristal Structure Database (ICSD, Fiz Karlsruhe, Germany). Semi-quantification was performed using internal standard and/or Rietveld analysis and results were normalised.

Corrosion tests were performed by placing the ash samples—previously prepared at 550 °C from each biomass sample—on steel coupons, which were then placed in a tubular furnace at a temperature of 700 °C for 200 h, with an air flow of 150 mL/min. A diagram of the experiment design is shown in Fig. 1.

The selected steel was Fe-2.25Cr-1Mo. The steel coupons were rectangular in shape with dimensions of about 20 × 10 mm and 2 mm thick. The coupons were polished with sandpaper grades 220, 500 and 1200 and cleaned with acetone. A 50-mg ash sample was placed on each steel coupon and all the coupons were placed in a ceramic sample holder. The holder was placed in the tubular furnace at 700 °C. After 200 h, the steel coupons were removed from the furnace and put in resin. The steel coupons were cut with a Struers Secotom-10 cutter using an Al₂O₃ disc and polished with mineral oil (using sandpaper grade 1200), and washed with hexane in an ultrasound bath. Finally, the coupons were studied using SEM/EDS (Zeiss).

Statistical analysis and reference data

Box and whisker plots and confidence interval plots were used to show the distribution of the dataset by applying the Centurion Statgraphics software. Box and whisker plots show the median (line within the box), mean (cross), upper and lower quartiles (top and bottom of the box), and the maximum and minimum values (whiskers). Outliers, values that lie further than 1.5 by the interquartile range were marked by a little square. Confidence intervals plots show the mean and confidence limit at 95% by considering the standard deviation of each sampling.

The results obtained in the box and whisker plots are compared with the reference values established in ISO 17225-2:2021 for wood pellets to be used in commercial and residential applications [13]. Similarly to the above-mentioned standard, the Spanish national committee of solid biofuels (UNE/CTN 164) developed two standards establishing the specifications and quality classes for olive stones [14] and fruit shells [15]. Class A1 specifications for some of the properties of these solid biofuels are shown in Table 3. As can be seen, the limits are very similar among the different biofuels, with the exception of the ash content allowed for nut shells (1.2 wt%, d.b.), which is higher than that established for olive stones and wood pellets (0.7 wt%, d.b.).

Results and discussion

Production and sustainability of olive stones and nut shells for use as solid biofuels

The production of olive stones and almond shells over the years (2011–2021) is shown in Figs. 2 and 3, respectively. The following data were taken from the most recent available literature (see Section 2.2).

The production of olive stones is mostly located in the Mediterranean area, specifically in Spain, Greece, Italy, Turkey and Tunisia, where there are large concentrations of olive groves exploited by the olive oil extraction industry. Spain is the biggest producer, followed by Italy and

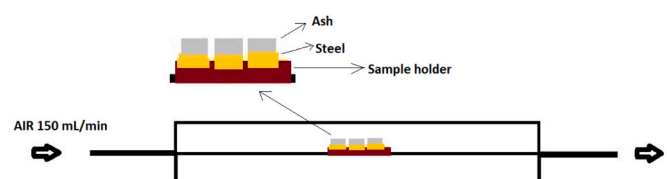


Fig. 1. Diagram of the corrosion test in a tubular furnace.

Table 3

Class A1 specifications for certain properties of almond and pine nut shells (AS/PS), olive stones (OS) and wood pellets (WP) for commercial and residential applications.

	AS/PS	OS	WP
Ash (wt.% d.b.)	1.2	0.7	0.7
N (wt.% d.b.)	0.4	0.3	0.3
S (wt.% d.b.)	0.03	0.03	0.04
Cl (wt.% d.b.)	0.02	0.03	0.02
Net calorific value (MJ/kg w.b.)	15.0/16.0	15.7	16.5
Oil (wt.% d.b.)	0.6	0.6	NA

NA: not applicable.

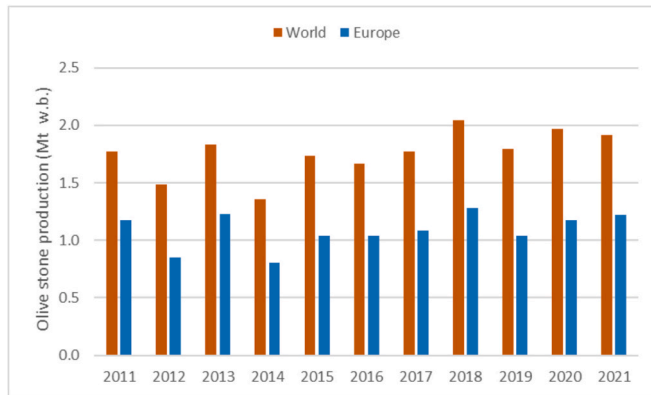


Fig. 2. World and European olive stone production from 2011 to 2021.

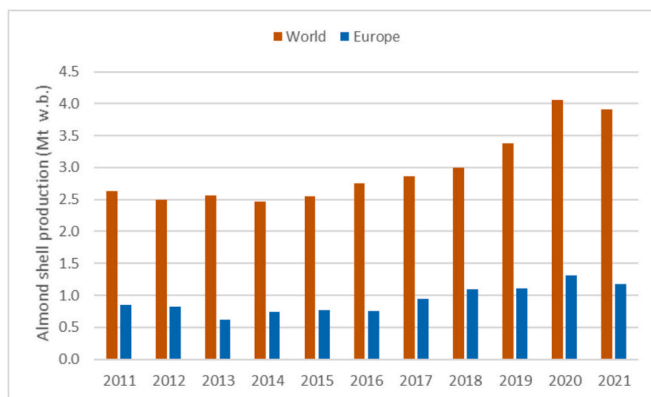


Fig. 3. World and European almond shell production from 2011 to 2021.

Greece. The annual global production of olive stones is about 1.8 Mt/yr (Fig. 2), although this figure can fluctuate significantly due to the cyclical variations in olive yield. On average, Spain produces around 0.6 Mt/yr of olive stones for energy purposes, which is a significant quantity if we consider that to date the national production capacity of pellets is about 0.77 Mt/yr [16].

The Mediterranean is also a traditional almond-growing region, although the USA is the main producer with three quarters of global potential annual production, which is estimated at about 4.0 Mt/yr (Fig. 3).

The production of pine nuts is more widely spread due to the diverse species of the *Pinus* genus that produces nuts used for food. China (30%), Russia (18%) and North Korea (11%) are the main pine nut producers (from *Pinus chinensis*) with a global pine nut production of about 0.041 Mt/yr in the 2022/2023 season [11]. It is very difficult to determine the quantities that are used locally, and thus this type of fuel could have a much higher potential, although currently production is much lower

than that of almond shells.

Considering that the nut makes up 30 wt% and the shells 70 wt% of the whole fruit, the weight of almond shells produced is around 4.0 Mt/yr (Fig. 3). If these shells were recovered for combustion as biofuel and taking into account the net calorific value of almond shells and natural gas, along with the CO₂ emissions factor of natural gas, valued at 0.202 tons of CO₂ per MWh (see Section 2.1) the emissions savings would reach around 3.62 Mt of CO₂/yr. In terms of olive stones, for which production is valued at about 2.0 Mt/year (Fig. 2), the potential emissions savings by using them as biofuel would be a further 1.88 Mt of CO₂/yr. These results are shown in Table 4.

Other nut shells, especially from walnuts (1.2 Mt/yr), cashews (1.1 Mt/yr), pistachios (0.75 Mt/yr) and hazelnuts (0.58 Mt/yr) can be combined to double the almond production (1.5 Mt/yr) [11]. Considering that the nut represents 30 wt% and the shells 70 wt% of the whole fruit, the weight of shells produced is around 8.5 Mt/yr, which if used as biofuel would represent additional CO₂ savings of about 7.66 Mt of CO₂/yr (Table 4). This amount of 7.66 Mt CO₂/yr added to the 3.62 Mt CO₂/yr of almond shells plus 1.88 Mt CO₂/yr of olive stones would generate a total CO₂ savings of 13.2 Mt/yr.

When nut shells and olive stones are used locally, the emissions generated by their transport is almost negligible. In this sense and as an example, according to Annex VI of RED II [17], savings of around 90% in greenhouse gas emissions are achieved when the transportation distance of biomass fuels is less than 500 km. Savings are reduced to 60% when the distance is between 2,500 km and 10,000 km. Furthermore, nut shells and olive stones are more economically sustainable because they are agro-industrial residues that, when recovered for energy purposes, become cost-effective byproducts with a price lower than that of wood pellets. The current market prices for these solid biofuels in Spain (2024) are 293 €/t for bulk olive stones [18], 169 €/t for bulk almond shells [19], and 345 €/t for wood pellets [20], which represent cost reductions around 10% and 50% for olive stones and almond shells, respectively, when compared to wood pellets. Therefore, if these solid biofuels are consumed mainly in their own production areas, i.e., within a radius of less than 500 km, environmental and economic sustainability is guaranteed.

Ash content and thermal behaviour

The averaged results for the main properties for each biofuel and sampling campaign are summarised in Table 5.

Low ash content is probably the most important quality requirement when it comes to solid biofuels for the domestic sector [21]. As mentioned, the stoves and boilers used for residential and commercial applications require high-quality fuels because, among other factors, they are not fitted with particle cleaning systems. As can be seen in Table 5 and Fig. 4, the ash content of clean olive stones is similar to that of the analysed wood pellets. Around half of the analysed olive stone samples showed ash content below 0.7 wt%, and would therefore meet the ash quality requirements set in ISO 17225-2:2021 [13] for the highest quality class of wood pellets (A1). This result is consistent with

Table 4

Biomass production and CO₂ savings from olive stones and nut shells.

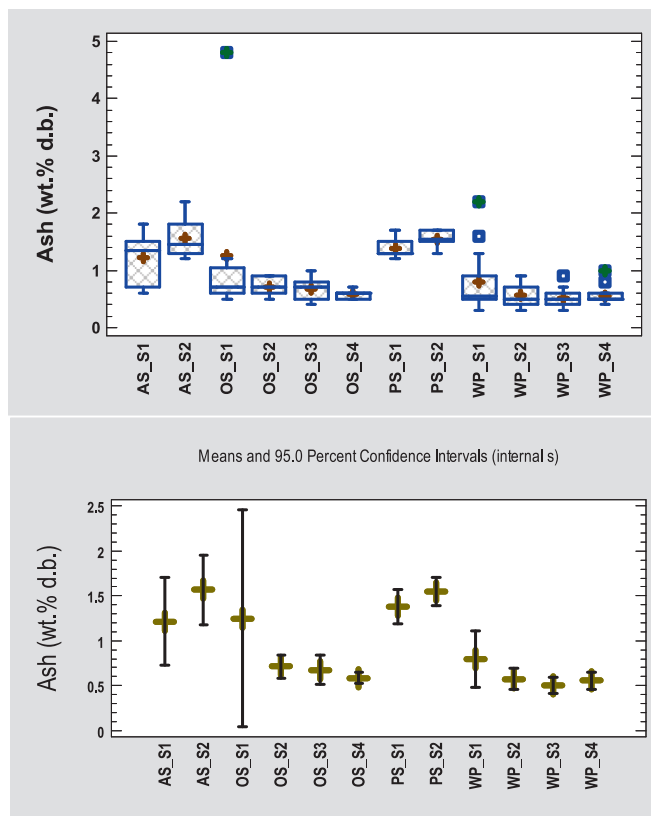
	Production	NCV	Energy	CO ₂ savings
	Mt/yr	(MJ/kg w.b.)	TWh/yr	Mt/yr
Olive stone	2.0	16.71	9.3	1.88
Almond shell	4.0	16.11	17.9	3.62
Partial 1	6.0		27.2	5.50
Walnut shell	2.8	16.11	12.5	2.53
Cashew shell	2.6	16.11	11.5	2.32
Pistachio shell	1.8	16.11	7.8	1.58
Hazelnut shell	1.4	16.11	6.1	1.22
Partial 2	8.5		37.9	7.66
Global Total	14.5		65.1	13.2

Table 5

Main properties of the solid biofuels studied in the sampling campaigns (mean values per sampling campaign).

Biofuel	Sampling	Moisture (% w.b.)	Ash (% d.b.)	N (% d.b.)	S (% d.b.)	Cl (% d.b.)	NCV (MJ/kg w.b.)	(MJ/kg d.b.)
Olive stones	OS_S1	11.1	0.75	0.21	0.013	0.024	16.61	18.99
Olive stones	OS_S2	9.90	0.71	0.17	0.021	0.021	16.85	18.97
Olive stones	OS_S3	10.1	0.68	0.10	0.013	0.014	16.76	18.92
Olive stones	OS_S4	10.9	0.59	0.17	0.007	0.014	16.63	18.96
Almond shells	AS_S1	10.7	1.2	0.34	0.016	0.008	15.89	18.09
Almond shells	AS_S2	9.67	1.6	0.25	0.020	0.020	16.32	18.33
Pine nut shells	PS_S1	10.8	1.4	0.37	0.020	0.030	16.76	19.09
Pine nut shells	PS_S2	10.9	1.6	0.30	0.037	0.042	16.94	19.31
Wood pellets	WP_S1	5.26	0.82	0.23	0.021	0.028	17.48	18.59
Wood pellets	WP_S2	6.34	0.62	0.23	0.018	0.009	17.39	18.73
Wood pellets	WP_S3	5.94	0.51	0.22	0.010	0.011	17.66	18.93
Wood pellets	WP_S4	6.16	0.56	0.16	0.012	0.010	17.63	18.95

NCV: net calorific value at constant pressure; w.b.: wet basis; d.b.: dry basis.

**Fig. 4.** Ash content of the biofuels studied in the sampling campaigns. Box and whisker plot (top) and confidence interval plot (bottom). The codes for solid biofuels and samplings are given in Table 1.

those reported by Mata-Sánchez [5], who analysed 176 olive stones samples. However, much higher values have been found in other studies, such as that by Demirbas, which reported values of around 4 wt% [22].

Almond and pine nut shells averaged higher ash contents and showed mean values around 1.4 wt%, meeting the ash criterion established in ISO 17225-2:2021 for Class B wood pellets. According to the Spanish limits shown in Table 3, some results for almond and pine nut shells do not meet the ash content limit set for Class A1. Similarly, the scientific literature shows considerable variability in the ash content of almond shells, with some studies reporting lower values (0.74 wt%) [23] and others reporting higher values, around 4 wt% [22,24]. In the latter case, Aktas et al. [24] attribute the high ash content to sand contamination of the almond shells.

A decreasing variability was observed over time for olive stones and

wood pellets, with higher mean values in 2011 as compared to the samplings performed in 2015, 2019 and 2023 (Fig. 4). The improvement in the homogeneity and qualities of olive stones and wood pellets could be due to the establishment of control and certification bodies, which has led to better practices by biofuel producers and distribution companies.

For almond and pine nut shells, data dispersion was also reduced in 2015 (the last sampling campaign for both fuels). However, mean and median ash content increased slightly: almond and pine nut shells averaged ash content of 1.2 and 1.4 wt% d.b., respectively, in 2011, and 1.6 wt% d.b. in 2015. A certain variability between years is expected to occur naturally, given that ash content—as well as the levels of certain elements such as N, Cl and S—can depend on a wide array of factors, some of which are beyond the control of producers, such as the meteorological conditions (e.g. amount and time of year of rainfall). Rainfall fell by up to 75% in the year of the second sampling campaign [25]. According to the main Spanish producers, the outer skin tends to be more firmly attached to the shells in dry years, rendering industrial separation processes less efficient. In addition, the fruits tend to be smaller, with a higher concentration of minerals and increased ash, N, Cl and S content in the fuel.

The results of the thermal analysis in air atmosphere of the solid biofuels are shown in Fig. 5. The top of this figure shows the thermogravimetric analysis (TGA), where the mass loss was completed between 500 °C and 600 °C in most of the biofuels, with the exception of pine nut shells that lost their full mass at about 700 °C, indicating the presence of unburnt organic material at 550 °C. Consequently, the ash content as determined at 550 °C in the ISO 18122:2022 standard is overestimated (17%) in pine nut shells. This different behaviour could be due to a higher lignin content in this type of biofuel and/or the presence lignin compounds that are more difficult to burn, as can be seen in the bottom of Fig. 5 when applying differential scanning calorimetry (DSC). The two exothermic decomposition peaks of cellulose and lignin in the wood pellet sample were determined to be about 360 °C and 460 °C, respectively. Both peaks are more closely overlapped for the other biofuels, especially pine nut shells, as a consequence of their higher content of lignin in comparison with wood pellets. Therefore, longer combustion times or higher combustion temperatures may be needed in the heating systems to burn all the organic matter present in this type of fuel, particularly in the case of pine nut shells.

The averaged net calorific values at dry basis (Table 5) throughout the period studied were slightly higher for pine nut shells (19.2 MJ/kg) and olive stones (18.9 MJ/kg) than for wood pellets (18.7 MJ/kg) and almond shells (18.1 MK/kg). As the calorific value of lignin is higher than that of cellulose, lignin-rich fuels exhibit relatively high net calorific values.

It is important to mention that transportation in Europe of olive stones with an oil content over 3 wt% is subject to additional taxes [26].

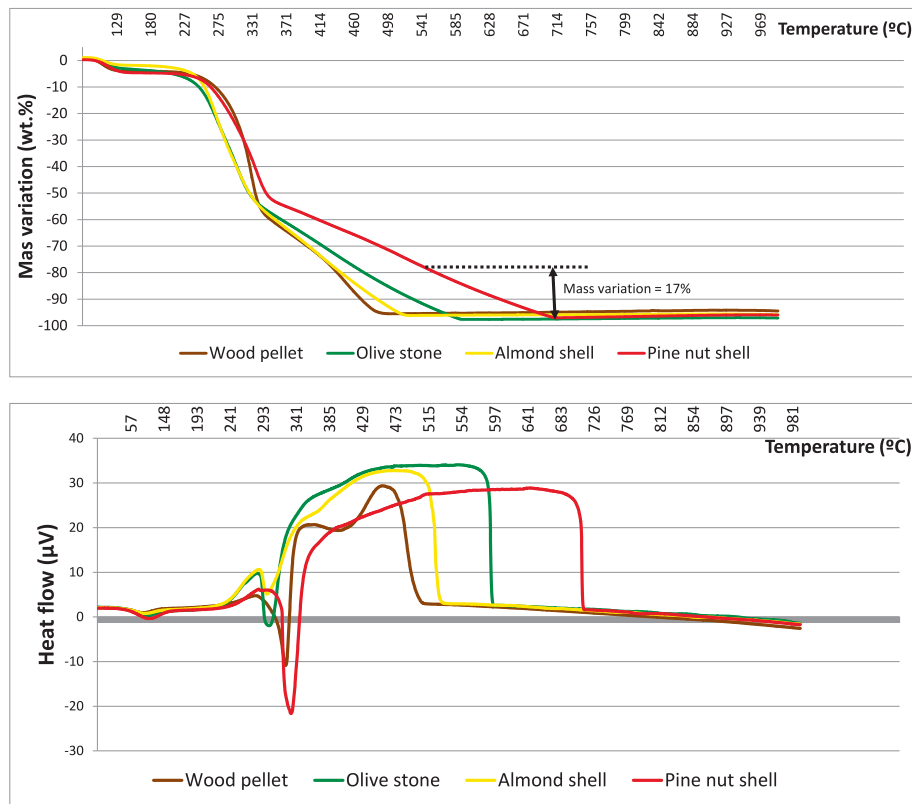


Fig. 5. Thermogravimetric analysis (top) and differential scanning calorimetry (bottom) curves for each type of solid biofuel.

Some countries like Greece limit the oil content of residues from the olive oil processing industry to a maximum value of 2 wt% to deter the direct combustion of olive cake and to ensure that residues are further processed by pomace mills. As can be seen in Fig. 6, all the analysed almond shells and pine nut shells showed oil contents below 1.5 wt%, but exceeded, in an important number of samples, the limit value of 0.6 wt% set in the Spanish standard (Table 3). Olive stones showed lower oil contents (≤ 0.6 wt%) than the nut shells considered. As for nut shells, the Spanish standard [15] limits the oil content to ensure proper pulp separation from shells.

Oil-rich fuels are beneficial in terms of increased calorific values. However, a previous study [27] showed that oil content above 1 wt% resulted in an increase in CO, TOC (total organic carbon), and fine particle (TSP, PM1 and PM0.1) emissions when combusting olive stones in domestic devices. In addition, an increase in oil content was found to

increase NOx emissions, due to the elevated N content in the fuel. Moreover, excessively sticky fuels could hinder the flow of movement on conveyor belts or in feeding systems. Based on the previous study [27], it is recommend not to exceed an oil content of 1 wt%. However, according to Table 3, the oil content for class A1 is already limited to 0.6 wt%.

Acid rain-related elements and trace elements

Inefficient industrial stone cleaning or pulp separation processes result in products with not only higher oil content but also greater quantities of N, S, and Cl. The distribution of N, S, and Cl—elements closely related to the formation of air pollutants in combustion processes such as particulate matter (in the form, for example, KCl or K_2SO_4) and gases including SO_2 , NOx and HCl, which generate acid rain—is shown in Figs. 7, 8 and 9, respectively. Cl and S are also involved in corrosion and sintering within combustion plants.

In contrast to ash content, the majority of the olive stone, almond shell, and pine nut shell samples were within the N limits set in the UNE standards for Class A1 (Table 3). Moreover, most of the wood pellets and olive stones analysed met the N requirements set for Class A1 in ISO 17225-2:2021 for wood pellets (0.3 wt% d.b.). Nut shells generally exhibited higher N content than wood pellets or olive stones. The upper outlier (about 0.8 wt% in PS_S1) found for pine nut shells may be related to a higher fraction of nut than initially expected. The wood pellets showing a higher N content (about 1.8 wt% in WP_S1) than expected may have been produced from biomass containing used wood or demolition wood: highly nitrogenised compounds, such as urea and melamine resins, are introduced as adhesives during the manufacturing process of particleboard and plywood, thus significantly increasing the levels of N in this type of biomass.

As for S content, wood pellets, olive stones and almond and pine nut shells (Fig. 8) were all within the S limit established in ISO 17225-2:2021 for commercial and residential applications (0.04 wt%). In general, most of the sulphur values, including the 75th percentile, are

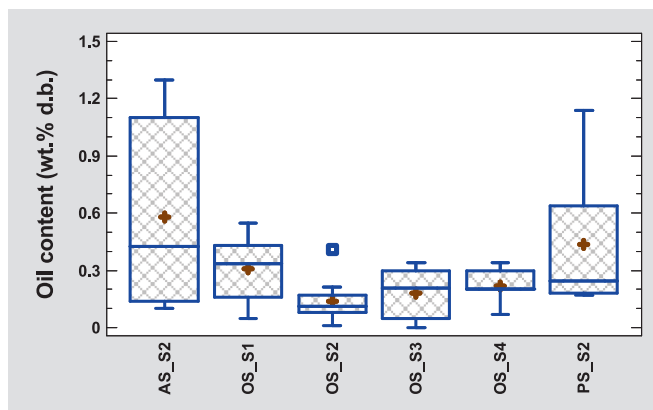


Fig. 6. Oil content of olive stones, almond shells and pine nut shells. The codes for solid biofuels and samplings are given in Table 1.

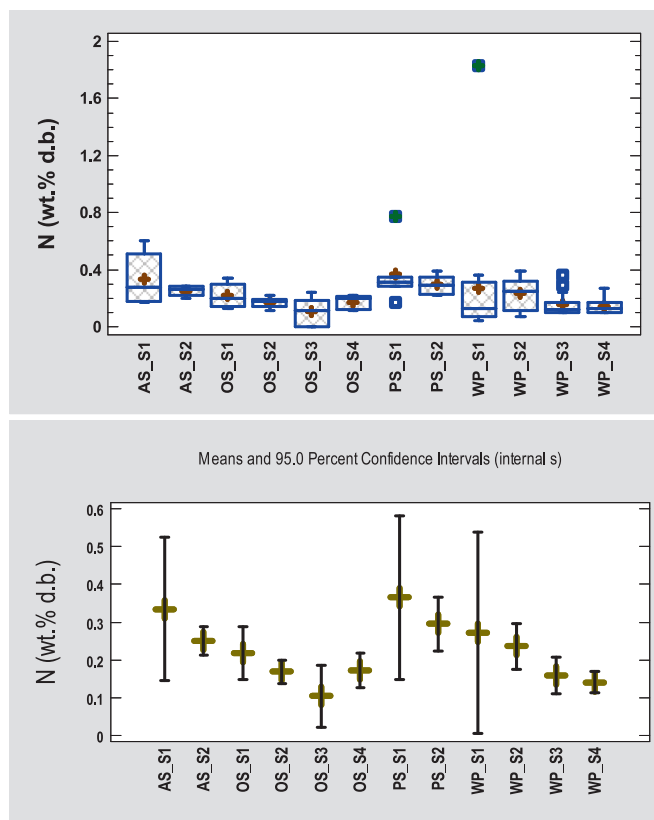


Fig. 7. N content of the solid biofuels studied in the sampling campaigns. Box and whisker plot (top) and confidence interval plot (bottom). The codes for solid biofuels and samplings are given in Table 1.

below 0.04 wt%, with median and mean values around 0.02 wt%. It should be noted that UNE standards for olive stones and nut shells set a S limit of 0.03 wt%.

The average Cl content (Fig. 9) for olive stones and almond shells was about 0.02 wt%, the limit set by ISO 17225-2:2021 for the highest quality class of wood pellets (A1) for domestic and residential applications (Table 3). In turn, pine nut shells averaged higher Cl content, with a range of 0.01–0.07 wt%, given by the confidence interval. The exceptionally high Cl content observed in the first sampling of wood pellets, reaching 0.2 and 0.1 wt%, could be a consequence, e.g., of blending wood biomass with herbaceous biomass, which is known to be high in chlorine.

The levels of toxic elements and heavy metals in the analysed samples (Table 6) were very low and frequently below the quantification limits of the analytical methods currently available. All of these elements were only found at trace levels and the limits established in the standards of reference for these solid biofuels were not exceeded in any case.

In general, Cr and Ni levels were lower in the samples collected during the 2nd, 3rd and 4th campaigns. Other elements, such as Cu or Pb, were also higher in the first sampling, which could indicate the presence of paint and plastic contaminants in some of the samples. As and Cd content was always below <0.1 mg/kg, and Hg below 0.005 mg/kg.

Physical and mechanical characteristics

Bulk density is an important parameter in the calculation of transportation and storage capacities and costs. It is also a factor influencing the feeding systems in heating installations, as it can influence combustion performance, efficiency, and pollutant emissions. Therefore,

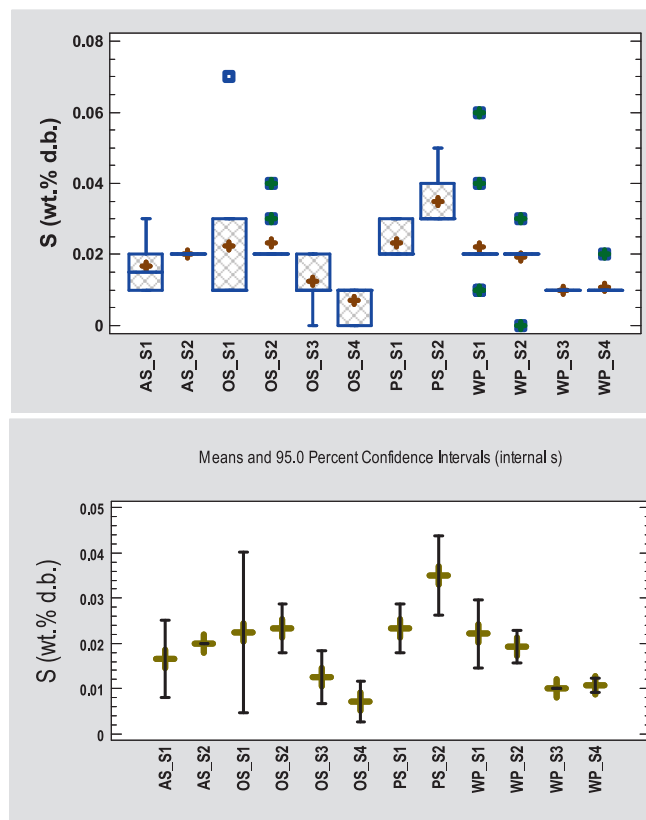


Fig. 8. S content of the solid biofuels studied in the sampling campaigns. Box and whisker plot (top) and confidence interval plot (bottom). The codes for solid biofuels and samplings are given in Table 1.

bulk density is one of the properties that has been included in the standards that set the specifications and classes of solid biofuels. As shown in Fig. 10, olive stones showed higher mean bulk densities (760 kg/m³ w.b.) than wood pellets (660 kg/m³ w.b.), which needs to be taken into account when designing or adjusting boilers and stoves for domestic applications. Considering the relatively high calorific value and bulk density of olive stones, this fuel can be considered very cost-effective in terms of transportation and storage.

In contrast to the excellent bulk densities of olive stones, this solid biofuel contains a significant proportion of fine particles (Table 7), which could not only aggravate the risk of dust explosions but also reduce the combustion efficiency and emission quality parameters, the latter due to the very small biofuel particles passing through from feed to fumes without burning completely, thus increasing the emissions of ash particles. Olive stones have a considerably smaller particle size than almond and pine nut shells as a result of the production process, in which the olives are ground to extract the oil. It is worth noting that, in the second sampling, the fraction of fine particles in the olive stone samples exceeds the Class A1 limit (15 wt%) set by the Spanish standard [14]; therefore, improved control during the industrial fuel manufacturing process is required. Screening is the most effective method for reducing fines content, and producers should apply this step before shipping the final product to end users.

With regard to fire prevention, companies must comply with ATEX guidelines to avoid the formation of dust clouds during the transport of olive stones and nut shells. In the absence of a specific standard for the handling and storing of olive stones and nut shells, the standard for wood pellets (ISO 20023:2018 – Safe handling and storage of wood pellets in residential and other small-scale applications) may be applied. This standard covers storage volumes below 100 tons. For storage volumes exceeding 100 tons (commercial and industrial applications), ISO

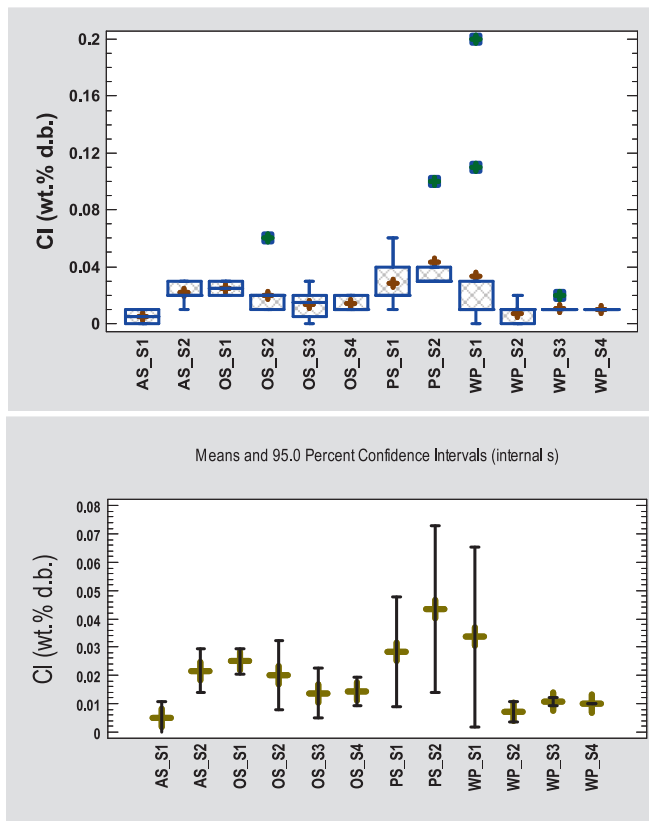


Fig. 9. Cl content of the solid biofuels studied in the sampling campaigns. Box and whisker plot (top) and confidence interval plot (bottom). The codes for solid biofuels and samplings are given in Table 1.

20024:2021 applies.

In any case, the impact of fine particles of different sizes (<3.15 , <2 , and <1 mm) present in olive stones and nut shells on particle emissions is not well documented in the scientific literature and further research should be conducted in the future to establish accurate and efficient specifications in this regard.

Ash melting and corrosion behaviour

The mean deformation temperatures for the ash of wood pellets were around 1300°C (Table 8). Therefore, wood pellets might not cause any significant sintering problems at the usual operational combustion temperatures ($\sim 1000^{\circ}\text{C}$). In contrast, sintering problems should be expected when using olive stones, almond shells and pine nut shells due

to their low DTs, which were found to be even below 800°C in some cases. These low DTs should be taken into account when designing and operating domestic boilers and stoves for this type of biofuels, i.e., by decreasing the combustion temperature or by applying other strategies such as the installation of a slag breaker.

Different fuel indexes have been developed in literature to predict biofuels sintering [6,24]. The relation between alkaline earth oxides and alkaline oxides is used to predict the ash melting behaviour [6]. The higher the alkaline earth to alkaline oxides ratio, the higher the sintering temperature. In general, it could be said that biomasses with $(\text{CaO} + \text{MgO})/(\text{K}_2\text{O} + \text{Na}_2\text{O})$ values higher than 2 should not present a risk of sintering. As can be seen in Table 9, the alkaline earth oxide ($\text{CaO} + \text{MgO}$) content relative to alkaline oxides ($\text{K}_2\text{O} + \text{Na}_2\text{O}$) is higher in wood pellets than in almond and pine nut shells and olive stones. Values lower

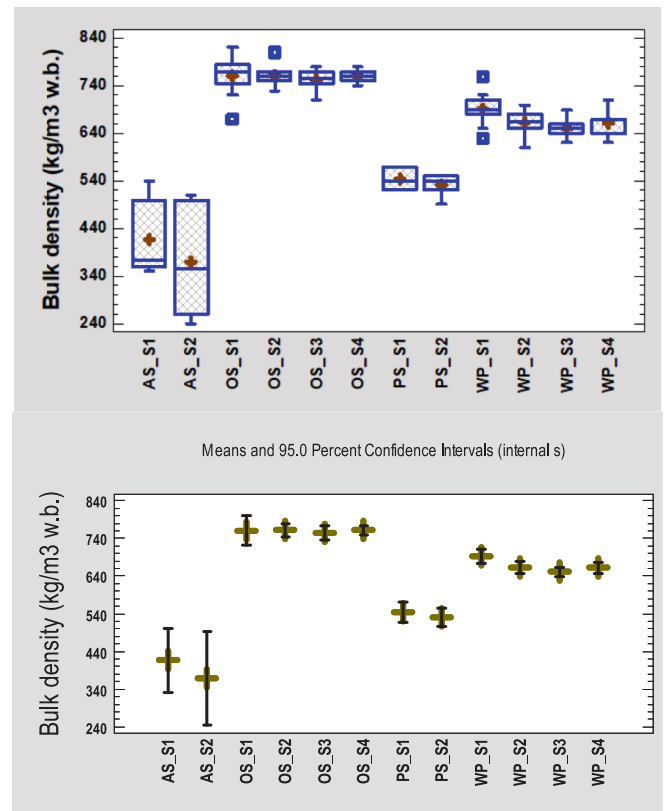


Fig. 10. Bulk density of the solid biofuels studied in the sampling campaigns. Box and whisker plot (top) and confidence interval plot (bottom). The codes for solid biofuels and samplings are given in Table 1.

Table 6

Minor and trace elements in the solid biofuels studied in the sampling campaigns (mean values per sampling campaign).

Biofuel	Sampling	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
		(mg/kg d.b.)							
Olive stones	OS_S1	< 0.1	< 0.1	2.3	5.3	1.0	0.001	2.9	6.6
Olive stones	OS_S2	< 0.1	< 0.1	< 1.0	5.4	1.6	< 0.001	< 1.0	3.2
Olive stones	OS_S3	< 0.1	< 0.1	1.6	2.7	< 0.2	0.001	< 1.0	5.1
Olive stones	OS_S4	< 0.1	< 0.1	1.1	2.2	< 0.2	< 0.001	< 1.0	3.7
Almond shells	AS_S1	< 0.1	< 0.1	2.6	6.1	0.9	0.001	3.0	4.7
Almond shells	AS_S2	< 0.1	< 0.1	< 1.0	3.1	< 0.2	< 0.001	< 0.1	4.1
Pine nut shells	PS_S1	< 0.1	< 0.1	1.5	5.8	1.9	0.003	4.3	6.3
Pine nut shells	PS_S2	< 0.1	< 0.1	< 1.0	3.2	< 0.2	0.004	1.0	4.9
Wood pellets	WP_S1	< 0.1	< 0.1	4.7	4.9	4.4	0.005	4.0	16
Wood pellets	WP_S2	< 0.1	< 0.1	< 1.0	< 2.0	< 0.2	0.003	< 1.0	7.8
Wood pellets	WP_S3	< 0.1	< 0.1	< 1.0	< 2.0	< 0.2	0.003	< 1.0	7.2
Wood pellets	WP_S4	< 0.1	< 0.1	< 1.0	< 2.0	< 0.2	0.002	< 1.0	7.9
Class A1, ISO 17225-2		≤ 1	≤ 0.5	≤ 10	≤ 10	≤ 10	≤ 0.1	≤ 10	≤ 100

Table 7

Particle size distribution (wt.% partial) of the solid biofuels studied in the sampling campaigns. The codes for solid biofuels and samplings are given in Table 1.

Biofuel	Sampling	Moisture (% w.b.)	16 mm (% w.b.)	8 mm (% w.b.)	3.15 mm (% w.b.)	2 mm (% w.b.)	1 mm (% w.b.)	< 1 mm (% w.b.)
Olive stones	OS_S1	11.1	0.00	7.20	48.17	34.73	9.15	0.76
Olive stones	OS_S2	9.9	0.00	0.15	50.21	31.25	17.73	0.65
Olive stones	OS_S3	10.1	0.00	0.00	54.60	30.73	14.13	0.54
Olive stones	OS_S4	10.9	0.00	0.00	52.59	38.22	9.05	0.16
Almond shells	AS_S1	10.7	31.50	34.03	30.47	2.64	0.71	0.68
Almond shells	AS_S2	9.67	28.99	32.21	35.01	1.99	0.81	0.99
Pine nut shells	PS_S1	10.8	0.00	53.42	45.56	0.50	0.37	0.16
Pine nut shells	PS_S2	10.9	0.00	52.17	46.82	0.40	0.24	0.38

Table 8

Ash melting behaviour of the solid biofuels studied in the sampling campaigns (mean, minimum and maximum values per sampling campaign).

Biofuel	Sampling	DT			FT		
		Mean	Min.	Max.	Mean	Min	Max.
Olive stones	OS_S1	880	710	1270	1420	1320	> 1450
Olive stones	OS_S2	850	710	> 1450	> 1450	> 1450	> 1450
Olive stones	OS_S3	1000	950	> 1450	> 1450	> 1450	> 1450
Olive stones	OS_S4	970	750	> 1450	> 1450	> 1450	> 1450
Almond shells	AS_S1	910	750	1280	> 1450	> 1450	> 1450
Almond shells	AS_S2	760	740	800	1290	840	> 1450
Pine nut shells	PS_S1	840	800	880	1250	1230	1300
Pine nut shells	PS_S2	930	870	1000	1280	1190	1350
Wood pellets	WP_S1	1360	1260	> 1450	1390	1270	> 1450
Wood pellets	WP_S2	1310	1200	> 1450	1370	1250	> 1450
Wood pellets	WP_S3	1300	1160	> 1450	1340	1200	> 1450
Wood pellets	WP_S4	1360	1220	> 1450	1400	1250	> 1450

DT: deformation temperature; FT: fluid temperature.

than 2 were obtained with olive stones and nut shells, indicating an important risk of sintering.

Molar $(\text{Si} + \text{K} + \text{P})/(\text{Ca} + \text{Mg})$ ratio gives a prediction of the ash-melting temperatures. The index $(\text{K} + \text{Na} + \text{Si})/(\text{Ca} + \text{P} + \text{Mg})$ is applied to describe the probability of the formation of a non-sticky outer coating on a bed material particle. For a ratio smaller than 1, the refractory outer coating is likely to form and prevent the sintering [28].

Table 9

Ash major elements and sintering indices in the solid biofuels studied across sampling campaigns (mean values per sampling campaign). The codes for samplings are given in Table 1.

Sampling	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	Mn ₂ O ₃	Na ₂ O	P ₂ O ₅	SO ₃	SiO ₂	Sum	(CaO + MgO)/(K ₂ O + Na ₂ O)	(Si + K + P)/(Ca + Mg + Al)
	(wt.% d.b.)											(wt.%/wt.%)	mol/mol
OS_S1	0.41	18	0.30	33	2.4	0.09	0.43	1.7	2.5	2.8	62.00	0.6	2.0
OS_S2	1.4	16	0.63	30	5.0	0.14	1.7	2.5	3.8	7.6	68.50	0.7	1.8
OS_S3	1.2	22	0.95	24	3.7	0.07	0.53	2.0	2.3	5.4	61.90	1.1	1.2
OS_S4	1.0	23	0.80	24	3.5	0.07	0.51	2.0	2.4	4.7	61.83	1.1	1.2
AS_S1	1.1	16	0.60	30	3.4	0.06	0.87	2.4	1.8	5.9	62.94	0.6	2.0
AS_S2	0.66	14	0.41	32	3.1	0.04	0.75	2.3	1.5	4.6	59.61	0.5	2.3
PS_S1	0.32	12	0.25	27	3.8	0.14	0.66	2.1	2.4	24	72.83	0.6	3.2
PS_S2	0.86	3.6	0.70	12	4.8	0.12	0.86	4.2	2.3	60	89.34	0.7	6.6
WP_S1	4.8	28	3.2	8.8	5.7	0.82	1.6	2.2	4.2	23	85.20	3.2	0.8
WP_S2	3.0	26	3.3	14	11	3.1	2.2	2.9	6.1	14	85.93	2.3	0.7
WP_S3	4.7	30	2.3	10	7.5	2.1	1.4	4.0	5.0	20	88.37	3.2	0.8
WP_S4	3.8	24	1.7	11	4.9	0.97	1.2	2.5	3.3	21	75.40	2.4	1.0

According to Table 9, only wood pellets fulfil this sintering index. In summary, the ash melting behaviour results (Table 8) are in accordance with both sintering indexes, which corroborated the low DTs obtained for nut shells and olive stones.

Fruits contain relatively high K levels as a result of plant metabolic activity. In order to determine the inorganic compounds contained in the ash of these solid biofuels, crystalline phases were determined by X-ray diffraction (Fig. 11). The main inorganic compounds found in nut shells and olive stones were fairchildite ($\text{K}_2\text{Ca}(\text{CO}_3)_2$) and potassium carbonate (K_2CO_3). In contrast, the main compounds found in wood pellets were calcium carbonate (CaCO_3) and quartz (SiO_2). These crystalline mineral phases explain the lower melting temperatures of nut-shells and olive stones, as fairchildite and potassium carbonate melt at around 800 °C. In contrast, quartz melts at 1713 °C, and CaO, which comes from the decarbonisation of limestone, melts at around 2613 °C.

The main recommendation for reducing slag formation in burners when using olive stones and nut shells is the use of stoves or boilers equipped with movable slag-breaking mechanisms, which are already available on the domestic market. Reducing the combustion temperature is also a strategy currently applied in the domestic sector for olive stones and nut shells. Other strategies include blending these fuels with wood pellets; however, this option is presently more relevant to the industrial sector, although it could be adopted in the domestic sector in the future. The use of additives represents another alternative, mainly considered for industrial applications due to the potential need for flue gas purification to remove the excess additives. Overall, the combined use of fluidised bed combustors with anti-agglomeration bed materials may represent an optimal solution for both industrial and domestic sectors [29].

Regarding corrosion tests (see Section 2.4), the SEM images of the interface between the steel and the ash of the different biofuels studied are shown in Fig. 12. For comparison, a sample of wheat straw was simultaneously analysed due to the high corrosion tendency of this biomass as a consequence of the presence of elevated KCl levels in the ash [30]. As can be observed, the thickness of the layer of iron oxide

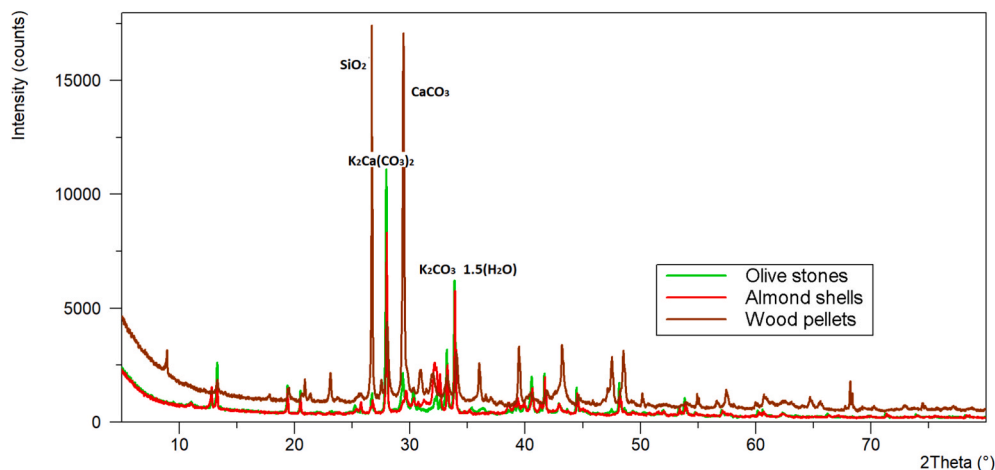


Fig. 11. Crystalline phases of olive stones, almond shells and wood pellets detected by X-ray diffraction.

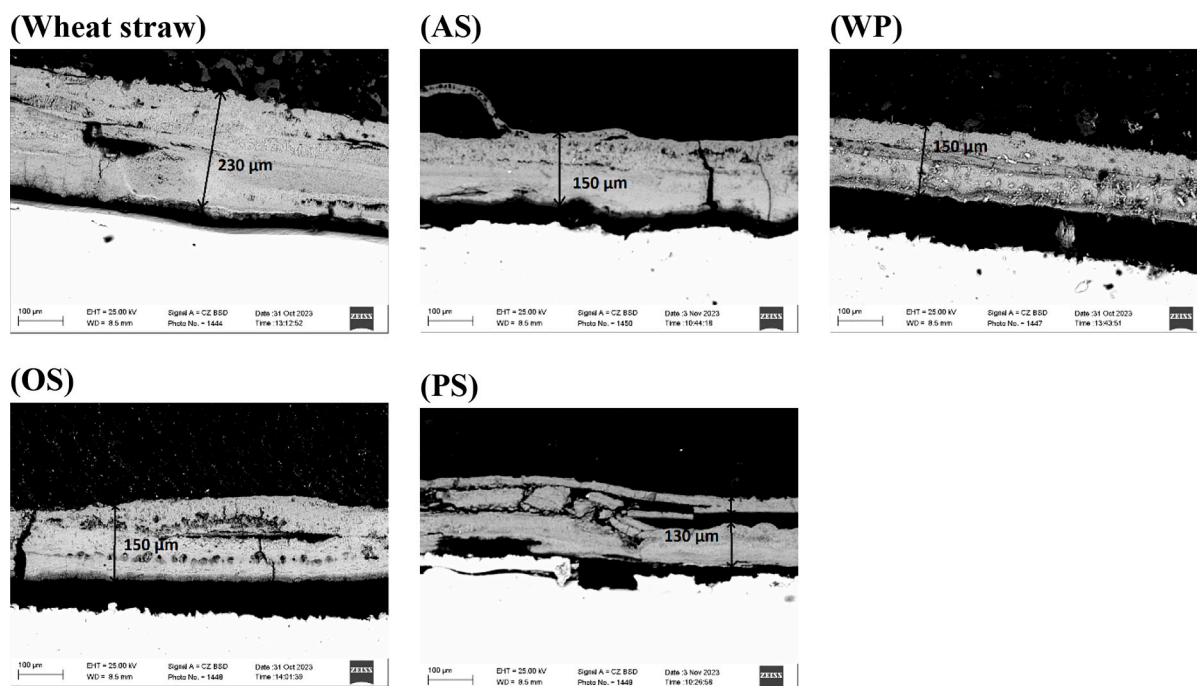


Fig. 12. SEM images of ash/steel interfaces of the solid biofuels studied. The codes for solid biofuels are given in Table 1.

deposited on the coupons after corrosion tests is similar for wood pellets, nut shells and olive stones (about 150 μm) and clearly much lower than that observed for wheat straw (230 μm). In the scientific literature, the thickness of the oxide layer is commonly used to assess the corrosion degree of steel [31]. In this sense, the thicker the iron oxide layer, the greater the corrosion. Therefore, there should be no corrosion problems when burning this type of biofuel in the boilers and stoves used for wood pellets.

The poorer corrosion reduction of straw is attributed to its high content in alkaline compounds. Olive stones and nut shells also exhibit higher content in alkaline compounds than wood pellets, as shown in Table 8 and Fig. 11. Therefore, a worse corrosion behavior for nut shells and olive stones compared with wood pellets would be expected. However, the similar behavior observed for olive stones/nut shells and wood pellets, characterised by an oxide layer of approximately 150 μm , may be explained by the presence of limestone in the wood pellets. According to van Lith et al. [32], the corrosion rate was significantly enhanced when CaO was present in the deposit, instead of SiO_2 , as CaO

particles reacted with HCl in the flue gas, and the resulting CaCl_2 played a key role in the corrosion mechanism. CaO may be partially formed through the decarbonation of CaCO_3 contained in the wood pellets, potentially leading to corrosion mechanisms similar to those described by van Lith et al. Nevertheless, the corrosion mechanisms specific to nut shells and olive stones require further investigation.

The results of the energy, physical and chemical characterisation are applicable to any Mediterranean country, as was demonstrated in the BIOMASUD PLUS project [33], which involved countries such as Portugal, Italy, Greece, Croatia, Slovenia, and Turkey. Differences between samples from a given country depend largely on the process used by companies to recover the pulp and retain only the stones and shells.

Conclusions

Due to their good quality and performance, wood pellets are widely used in the heating systems for residential, small commercial and public buildings. However, residual resources such as olive stones, almond

shells and pine nut shells, typically available in large quantities in the Mediterranean region, could also be used as domestic biofuels with practically no additional associated costs. An estimated 2 Mt of olive stones are produced per year and the volume of almond shells is valued at about 4 Mt/year. If these biomass resources were used to prepare solid biofuels and consumed at a local level in domestic applications, global CO₂ savings would be greater than 5.5 Mt of CO₂ per year. Other nut shells, especially walnuts, cashews, pistachios and hazelnuts, could be added to the almonds to more than double the total nut shells for potential CO₂ savings of 13.2 Mt per year.

Olive stones and wood pellets present similar chemical compositions and, in general, better fuel quality than nut shells. Over the 13 years considered (2011–2023), wood pellets and olive stones showed mean values of ≤ 0.8 wt% ash, ≤ 0.2 wt% N, ≤ 0.02 wt% S, and ≤ 0.03 wt% Cl. During the period in which almond and pine nut shells were sampled (2011–2015), these fuels showed mean ash content ≤ 1.6 wt%, N levels ≤ 0.4 wt%, 0.04 wt%, and S and Cl content ≤ 0.04 wt%. Pine nut shells and olive stones averaged higher net calorific values (19.2 and 18.9 MJ/kg, d.b., respectively) than wood pellets (18.7 MJ/kg) and almond shells (18.1 MJ/kg, d.b.), as lignin-rich fuels exhibit comparatively higher net calorific values. Toxic elements such as As, Cd, Cr, Cu, Hg, Ni, Pb and Zn were present in this type of biofuel only at trace levels and always below the limits set in the quality standards of reference.

Thermal analyses revealed that an ashing temperature of 550 °C, as set by the ISO standard (ISO 18122, 2022 [1]), is too low to remove all the organic compounds, mainly lignin, present in olive stones and nut shells. An overestimation of the ash content of about 20% is obtained for the pine nut shells. As a consequence, longer combustion times or higher combustion temperatures could be needed in the heating systems to burn all the organic matter present in this type of fuel, particularly in the case of pine nut shells.

In addition, taking into account the fact that deformation temperatures as low as 800 °C were found in some cases for olive stones and almond and pine nut shells, this study suggests that precautionary measures (e.g. lower combustion temperatures or the installation of slag breakers) to prevent ash sintering should be taken into account when designing boilers and stoves for this type of fuel. On the other hand, similar corrosion levels were found for olive stones, almond and pine nut shells and wood pellets. Therefore, no other special measure in the combustors is recommended in terms of corrosion.

To obtain high quality fuels for domestic use, the processing of olive stones and nut shells must separate adequately the pulp and nut residues, which are known to increase ash, nitrogen, chlorine or oil contents. It is also important to remove fine particles, mainly in olive stones, which can increase particle emissions, and health and explosion risks.

The homogeneity and qualities of the marketed olive stones and wood pellets clearly improved over the years, probably due to the establishment of control and certification bodies, which has led to better practices by producers and distribution companies. A slight increase in the ash, Cl and S contents of almond and pine nut shells was noticed in the last sampling, which was during a period of low rainfall: in dry years, fruits tend to be smaller, with a higher concentration of minerals, thus causing an increase in ash and some other elements in the fuel.

CRedit authorship contribution statement

M.J. Fernández: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **R. Barro:** Writing – review & editing, Validation, Methodology, Investigation. **P. Pérez:** Visualization, Methodology, Investigation. **R. Fernández-Para:** Validation, Resources, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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