Ignition and explosion characteristics of olive-derived biomasses

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HIGHLIGHTS

- Dust samples of olive stone and exhausted olive cake were fully characterised.
- Both materials could form explosive atmospheres or lead to a dust layer fire.
- Olive stone is a higher quality fuel but requires severe safety measures.
- Self-heating risk is medium for olive stone but low for exhausted olive cake.

GRAPHICAL ABSTRACT
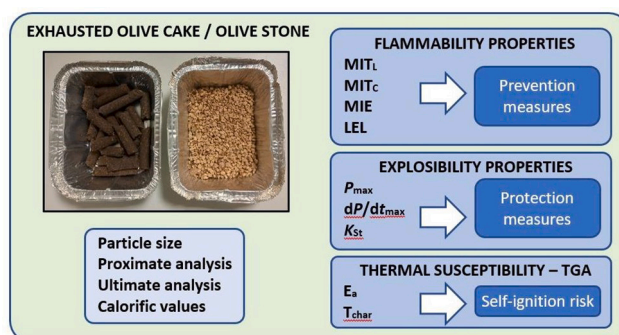
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ABSTRACT

The flammability and explosibili3ty properties of olive stone and exhausted olive cake dusts were determined in this study. The results indicated that both materials could form explosive atmospheres or lead to a dust layer fire. However, it was found that the former requires more severe safety measures, since it is more prone both to spark ignition and to hot-surface ignition than the latter. Furthermore, a dust explosion would also be stronger and faster for olive stone than for olive cake. TGA tests were also carried out to study the thermal behaviour of these materials and to estimate their self-ignition risk. Olive stone presented a greater tendency to oxidation and a medium self-ignition risk, whereas olive cake showed a low risk. The experimental data presented in this study fill gaps in literature and have implications for the design and management of industrial facilities.

1. Introduction

Energy and climate change targets adopted by governments are

promoting the use of renewable sources of energy. For example, the EU Directive 2018/2001 has established an ambitious binding target of a share of at least 32% of energy from renewable sources in the Union's
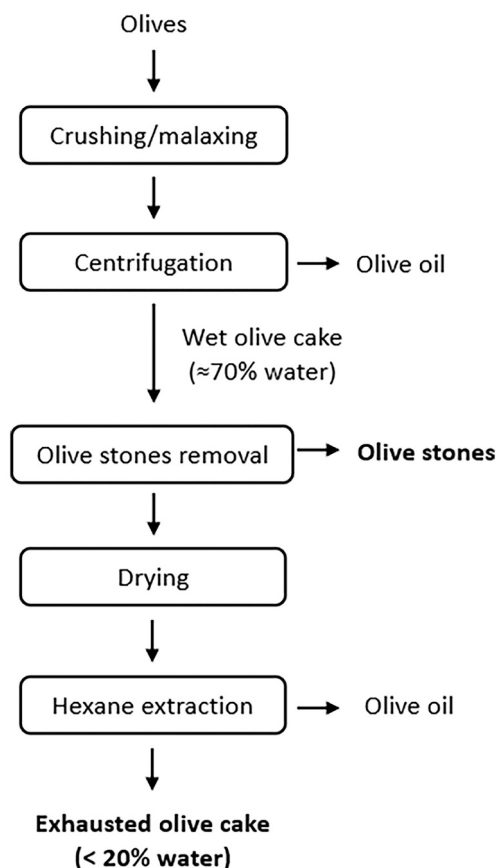

Fig. 1. Simplified processing scheme for olive oil production and by-products (two-phase continuous extraction system). Biomasses considered in this study are indicated in bold.

gross final consumption of energy by 2030 [1]. Biomass resources can play an important role to achieve these targets and to contribute to the reduction of crude oil and gas dependency.

There exists a great variety of biomasses. Some are used for producing biogas or liquid biofuels in industrial facilities [2,3], while others are burned as solid biofuels for heat and/or electricity production. Standard ISO 17225-1 [4] compiles a list of vegetal solid biofuels according to their origin and sources.

The olive oil processing industry produces several different biomass residues, including the crude and exhausted olive cakes (olive pomace) and the olive stones (also named olive pits) [5]. Fig. 1 illustrates the main steps of the most usual process for olive oil extraction in Spain (the so-called two-phases continuous system), although some variations are possible, and other systems, which are labour intensive or have lower water and energy efficiencies, are still applied in other countries (pressing systems and three-phases continuous systems) [6].

Olive pits and the crude wet olive cake are by-products of the first industrial olive oil extraction process and have no chemical treatment. On the contrary, the exhausted olive cake is a by-product of the second industrial olive oil extraction process, which removes oil from the above crude olive cake by means of a chemical treatment. The crude olive cake is a sludge that consists of a mixture of skin, pulp and pieces of stone (the wood shell plus the inner seed or kernel). In some cases, there is no removal of stones, so the final exhausted olive cake also contains olive

pits. However, stone removal has become more and more frequent in both olive mills and olive cake processing plants, since it is a valued energy source [7] and has other potential industrial applications [8]. For example, it was estimated in 2015 that 79% of the olive mills in Andalusia –the main producing region in Spain– separated the olive stone fraction [9]. In addition, the whole stone is always removed in the olive table industry.

Although the biomass residues derived from the olive oil processing are already commonly used to obtain energy in some areas, for example in Southern Spanish production regions, they remain untapped in other areas and countries [10]. Thus, the use of these biomasses still has a large potential to grow. It is important to remark that the world production of olive oil was 3,097,803 t in 2019 [11] and that 1 t of olives generates 0.28 t of olive oil, 0.083 t of stones and 0.197 t of exhausted olive cake [10]. Moreover, the world area of olives trees shows an increasing tendency, from 8.35 million ha in 2000 up to 12.76 million ha in 2020 [11]. The top ten producers of olive oil are located in the Mediterranean area (see Table 1).

Olive stone is considered as a high-quality biomass that can be used in a broad range of facilities, from domestic to industrial boilers, particularly if drying and fines elimination were applied to reduce ashes and humidity content [10,12]. On the contrary, olive cake is only used in industrial facilities due to its high ash, N, S and Cl contents [10,13], although its blends with another biomass of higher quality seems a promising option [14,15]. Olive pomace is often pelletised to facilitate manipulation and reduce the quantity of fine particles.

These biomasses represent an opportunity for the olive producer areas to obtain energy by using local renewable sources [16], while at the same time preserving the environment; storage of great amounts of olive cake in the process industries represent an environmental, economic and technical problem [17]. Therefore, these different reasons suggest that an increase on the use of these residues is expected in the near future. Moreover, exporting these biomasses to northern Europe as biomass fuel, mainly olive cake, has been usual since the first years of this century [18,19].

However, storage, transport and handling of large amounts of biomass is associated with safety hazards. These problems are most pronounced with the presence of fine particles, which are generated by the abrasion and crushing of the larger particles during the bulk material handling processes [20]. Biomasses are able of absorbing oxygen to produce exothermic oxidation reactions, leading to self-heating processes that under certain circumstances can initiate a self-ignition process and a smouldering combustion [21,22]. This phenomenon is a main concern in bulk storage facilities [23] and can be initiated by several different causes, such as biological activity and moisture condensation [21]. In addition, open flame fires and dust explosions are other mayor risks associated to biomass materials [24]. Ignition of dust layers and deposits is a common cause of fires and explosions in industrial facilities [25]. However, these hazards are not always adequately identified and controlled; data about major accidents in the bioenergy sector are quite worrying [26–28] and indicate the necessity for improving in risk awareness and safety culture in the biomass and bioenergy sector.

Although research on biomass safety has increased in recent years, the heterogeneous composition of these materials makes essential to study the different types of biomasses to know their behaviour for a safe storage and handling [29]. Moreover, the ignition sensitivity (or flammability) of biomasses, their tendency to self-ignition and their explosion severity can differ from those corresponding to coal or to other types of biomasses; unawareness of the specificity of the biomass materials can lead to an inadequate risk assessment if a company uses

Table 1
Olive oil production (t) by country in 2019 [11].

Spain	Italy	Greece	Tunisia	Turkey	Morocco	Portugal	Syria	Algeria	Egypt
1,129,233	336,581	290,476	239,500	217,800	204,200	154,063	153,829	92,200	41,300

Table 2
Data retrieved from previous studies.

Sample	LEL (g/m^3)	MIE (mJ)	MIT$_L$ (°C)	MIT$_C$ (°C)	P_{max} (bar g)	dP/dt_{max} (bar/s)	K_{St} (bar·m/s)
Olive stone (D_{50} = 68.2 µm) [32]	–	–	300	–	–	–	–
Olive stone (D_{50} = 1300 µm) [32]	–	–	>400	–	–	–	–
Olive stone (< 63 µm) [33]	30	–	–	–	9.0	–	112
Olive cake (< 63 µm) [33]	125	>1000	–	470	10.0	–	74
Olive cake and stone (sample IV, < 75 µm) [31]	–	–	–	590	–	–	–
Olive cake and stone (sample III, <250 µm) [31]	200	–	–	490	6.8	182.1	49
Olive cake and stone (sample V, < 250 µm abrasion) [31]	–	–	–	–	–	–	29
Olive cake and stone (sample II, 500–250 µm) [31]	>1250	–	–	660	5.9	78.8	21
Olive cake and stone (sample I, 1000–500 µm) [31]	–	–	–	740	–	–	–
Olive cake and stone (sample D, dried, < 45 µm) [31]	90	>1000	–	550	7.6	255	69
Olive cake and stone (sample C, dried, 75–45 µm) [31]	100	>1000	–	540	7.8	258	70
Olive cake and stone (sample B, dried, 212–75 µm) [31]	110	>1000	–	480	8.4	166	45
Olive cake and stone (sample A, dried, 425–212 µm) [31]	140	>1000	–	500	7.3	84	23

previous facilities and operating conditions that were designed for a different material [30]. In this sense, Table 2 presents the only data previously published on olive-derived biomasses (the flammability and explosibility parameters are defined in Section 2). Pietraccini et al. [31] presented a comprehensive study of the effects of particle size, moisture and milling technique on the explosion behaviour of a type of olive-derived residue. Fernandez-Anez and Garcia-Torrent [32] determined the ignition temperature of olive stone dust layers. The GESTIS-DUST-EX Database [33] reports the explosion severity and minimum explosive concentration of olive stone dust and most of the explosion properties of an olive cake sample, but it does not provide information about what type of olive cake was or its chemical composition.

As can be seen in Table 2, many aspects of these biomasses remain unexplored.

and several gaps exist in the literature. First, there are no available data on some of the properties of olive stone (MIE and MIT$_C$); the three samples were only partially characterised. Second, information about the ignition temperature of olive cake layers (MIT$_L$) does not exist. And third and even more important, there are no data about the thermal susceptibility of these two materials in relation to their self-heating tendency. In addition, it should be noted that the material studied by Pietraccini et al. [31] was described as a mixture of olive stone and olive cake (skin, pulp, pit and kernel), i.e. the material was an olive pomace with no prior stone removal. Furthermore, the sample in database [33] is not described, so it is not possible to know if it corresponds to a des-toned or to a non-destoned olive cake. The properties of olive cake residues could differ depending on the presence or not of stones. In this sense, Pietraccini et al. [31] pointed out the interest of analysing pulp-and pit-rich fractions of olive pomace in order to give precise indications on the explosion risk level in the different industrial operations; these materials are precisely the object of the present study. Therefore, it is quite clear that neither olive stone nor olive cake has been fully characterised yet. The current trend towards stone recovery to make use of its superior characteristics justifies the importance of studying both the destoned olive cake and the olive stone.

For all the above reasons, accurate knowledge of flammability and explosibility properties of the dusts of biomasses derived from olive fruits is essential to manage plans that process, store or combust these materials. The aim of this study was to fully characterise this type of dusts in order to design safe technologies and facilities.

2. Materials and methods

2.1. Preparation and characterization of samples

The samples –olive stone and exhausted destoned olive cake from *Olea europaea*– were residues from the Spanish olive oil processing industry. Olive stone was supplied by an olive mill (S.C.A. Agraria San José, Jaén) and consisted on a granular material made up of a great

Fig. 2. Samples as received: on the left, exhausted olive cake pellets; on the right, olive stone.

variety of different coarse and fine particles. On the contrary, the olive cake was obtained from a solid biofuels supplier (Pellets del Sur, Sevilla) in the form of pellets of approx. 35–45 mm in length and 10 mm in wide; from here on, this sample will be referred to as olive cake. Fig. 2 shows the visual aspect of the biomasses as received.

Both materials were prepared by milling and sieving in order to obtain a fraction <500 µm, which corresponds to the definition of dust by NFPA 652 [34]. This size criterion is also considered for potentially hazardous dust particles by standard ISO-IEC 80079–20-2, which establishes that materials that have no particles <500 µm and do not contain fibres (combustible flyings) are not combustible dusts; the presence of any particles <500 µm imposes the necessity of determining whether the material is a combustible dust [35].

The granulometry of the prepared samples was determined using a Malvern Mastersizer laser diffraction apparatus (Malvern, UK). In addition, proximate and ultimate analyses of the two materials were performed applying conventional techniques for coal characterization. For the elemental analysis, the American Society for Testing and Materials standard ASTM 5373 was followed for the determination of the carbon, hydrogen and nitrogen contents [36], the ASTM 4239 for sulphur content [37] and the ASTM 2361 for chlorine [38]; the oxygen content was calculated by difference. Regarding proximate analysis, Spanish standards UNE 32019 for volatile matter content and UNE 32004 for ash were applied [39,40], along with ASTM 3302 for moisture [41]; fixed carbon content was later estimated by difference. Finally, higher (HHV) and lower (LHV) heating values were obtained according

to the UNE 32006 procedure [42]. A Memmert oven (Schwabach, Germany) and a Selecta 367 PE muffle furnace (Barcelona, Spain) were used for the proximate analyses, a CHNS Micro TruSpec LECO analyser (St. Joseph, Michigan, USA) for the ultimate tests and a 6300 Parr calorimeter (Moline, Illinois, USA) for the heating value determination.

2.2. Ignition sensitivity

Ignition tests were conducted to evaluate the flammability easiness of samples (fraction <500 μm). The ignition sensitivity or flammability of a combustible dust is defined through several parameters that are

Table 3
Standards and apparatuses used in this study to determine the flammability and explosibility parameters and some of their industrial applications.

Parameter	Nomenclature	Standard	Test device	Industrial applications
Lower explosion limit	LEL	EN 14034–3	20-L litres sphere	Control of suspended dust whenever feasible
Minimum ignition energy	MIE	EN ISO/IEC 80079–20-2	MIKE 3	Removal of ignition sources. Grounding and bonding
Minimum ignition temperature of a dust layer	MIT_L	EN ISO/IEC 80079–20-2	Heated plate	Control of process and surface temperatures
Minimum ignition temperature of a dust cloud	MIT_C	EN ISO/IEC 80079–20-2	G-G furnace	Control of process and surface temperatures
Maximum explosion pressure	P_{max}	EN 14034–1	20-L sphere	Containment. Isolation. Venting, suppression or partial inerting to reduce pressure and violence
Maximum rate of explosion pressure rise	dP/dt_{max}	EN 14034–2	20-L sphere	Containment. Isolation. Venting, suppression or partial inerting to reduce pressure and violence
Explosion index of the dust	K_{St}	EN 14034–2	20-L sphere	Containment. Isolation. Venting, suppression or partial inerting to reduce pressure and violence

Fig. 3. Laboratory devices for flammability and explosibility tests: 20-L sphere (A), MIKE 3 (B), hot plate (C) and Godbert-Greenwald furnace (D).

determined in laboratory tests following standardised methods defined in standard ISO/IEC 80079–20-2:2016 [35]. These parameters are useful to identify the hazards pose by a specific material and the potential ignition sources in relation to the operating conditions and the equipment in biomass facilities. Therefore, these parameters are used to choose and design prevention measurements (see Table 3) [43].

The flammability parameters determined in this study were the following (a comprehensive description of the experimental methods and apparatuses can be found in [35,44,45]):

- Lower explosion limit (LEL): It is the lowest concentration of dust dispersed in air that could lead to ignition (also named minimum explosive concentration, MEC). This parameter was obtained using a 20-L sphere manufactured by Adolf Kuhner AG (Birsfelden, Switzerland). Fig. 3 shows this apparatus (see image A). The dust sample was pressurised with air up to 20 bar and injected into the vessel through a fast-acting valve, a pipe and a dispersion nozzle (known as the rebound nozzle). Partial vacuum down to 0.4 bar absolute was created prior to injection, so the vessel was back to standard atmospheric pressure after the dust dispersion. The sphere had a water jacket to dissipate the heat from the explosions and control the initial temperature of the tests. A set of two chemical igniters (2 kJ in total) triggered the explosion with a delay of 60 ms between the dispersion onset and the activation of the ignition source. The pressure was recorded by two piezoelectric pressure sensors and a control unit, and it was considered that an ignition had taken place if the overpressure (relative to the initial pressure and including the influence of the chemical igniters) was ≥0.5 bar. Different concentrations were tested in order to find the minimum dust concentration for which ignition occurred.
- Minimum ignition energy (MIE): It is the lowest energy that ignites the most sensitive mixture of dust/air. The tests were carried out using a MIKE 3 apparatus (Adolf Kuhner AG, Birsfelden, Switzerland), which is based on the Hartmann tube [46] (see Fig. 3, part B). The device consists of a cylindrical glass tube with two opposing ignition electrodes connected to a high-voltage capacitor. The sample was placed in a cup at the bottom of the tube so that it could be dispersed by an air blast from a pressurised air reservoir. The energy E (in joules) applied was calculated as $E = \frac{1}{2} \cdot C \cdot U^2$, where C is the total capacitance of the discharge circuit (in farads) and U the voltage (in volts). An iterative procedure according to [35] was applied to determine the optimum dust concentration and turbulence level. The MIE value lies between the highest energy (E_1) at which ignition fails to occur in 10 successive tests and the lowest energy (E_2) at which ignition occurred in at least one of the 10 tests; MIE was estimated using Eq. (1), where I_{E2} is the number of concentrations with ignition at energy E_2 and $(NI + I)_{E2}$ is the total number of concentrations tested at energy E_2 [47].
- Minimum ignition temperature of a dust layer (MIT$_L$): It is the lowest temperature of a hot surface at which ignition occurs in a dust layer. This parameter was measured using a hot plate device that was heated electrically and its temperature could be controlled and measured (see Fig. 3, part C). This device was designed and assembled ad hoc (LOM laboratory, Madrid, Spain) following the standardised characteristics [35]. The sample was prepared by filling a metallic ring of 100 mm in diameter and 5 mm in height. A thermocouple measured the temperature within the dust layer. The test was repeated with fresh layers of dust at different plate temperatures, which were allowed to become steady before testing the dust during 30 min. The MIT$_L$ was the lowest temperature of the plate, rounded down to the nearest multiple of 10 °C, at which the temperature within the layer exceeded the plate temperature or at which either glowing or flaming was observed.
- Minimum ignition temperature of a dust cloud (MIT$_C$): It is the lowest temperature of a hot surface at which ignition occurs in the most ignitable mixture of dust/air. The MIT$_C$ was determined by

using the classical Godbert-Greenwald furnace [48], which consists of a vertical cylinder that was electrically heated to a fixed temperature. The furnace (Yuyang Industrial Co., Dongguan City, Guang-Dong, China) is shown in Fig. 3, part D. The dust was dispersed in the furnace by an air blast. Temperature, air pressure and dust quantity were varied in order to find the lowest temperature of the furnace at which ignition could be detected by visual inspection; this temperature minus 20 °C for furnace temperatures above 300 °C or minus 10 °C for ≤300 °C was the MIT$_C$.

$$MIE = 10^{logE_2 - \frac{I_{E2} \bullet (logE_2 - logE_1)}{(NI+I)_{E2} + 1}} \tag{1}$$

2.3. Explosibility

Explosion severity tests were carried following the corresponding European standards [49,50]. These tests are useful for evaluating the potential explosion consequences, and consequently to select and design protection measurements (see Table 3) [43]. The explosibility parameters are the following:

- Maximum explosion pressure (P_{max}): maximum overpressure in a closed vessel during the explosion of a dust cloud.
- Maximum rate of explosion pressure rise (dP/dt_{max}): maximum slope of the pressure/time curve registered during a dust explosion in a closed vessel.
- Explosion index or characteristic index of the dust (K_{St}): it is calculated by using the so-called "cubic law" equation ($K_{St} = (dP/dt_{max}) \cdot V^{1/3}$), so it can be defined as the volume-normalised maximum rate of explosion pressure rise; numerically it is equal to the (dP/dt_{max}) value determined in a vessel of 1 m^3, though the units are not the same (bar•s^{-1} for dP/dt_{max}, bar•m•s^{-1} for K_{St}).

The apparatus used was the 20-L sphere described above. In these tests the ignition source consisted of two pyrotechnical igniters with 10 kJ in total. P_{max}, dP/dt_{max} and K_{St} values were determined for concentrations ranging from 125 to 1500 g/m^3 in order to find the maximum values. Gauge pressure in bars (1 bar = 100 kPa) is used throughout this paper for P_{max}, as stated by the relevant standards [49,50]. Table 3 summarises the apparatuses and standards applied to the determination of the above parameters.

2.4. Thermal susceptibility

Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA-DSC T50 apparatus. The tests were carried out with 20 ± 1 mg of dust sample, which was placed inside a 70 μL alumina crucible under an air atmosphere and heated from 30 °C up to 800 °C using three different heating rates ($\beta = 5$, 10 and 20 K/min). From these tests, the induction temperature (IT), which is the temperature at which the reaction accelerates, and the maximum weight loss temperature (MWLT), which is the temperature at which the degradation rate is maximum, were obtained following the same methodology than in previous works [51,52].

In addition, a kinetic study was carried out and the apparent activation energy (E_a) was obtained using four different methods: Cumming's equation [53], Kissinger-Akahira-Sunose (KAS) [54], Friedman [55] and Flynn-Wall-Ozawa (FWO) [56]. The first method (Cumming's equation) was used to carry out a self-ignition risk characterization according to the methodology proposed by García-Torrent et al. [57]. However, this method applies first order kinetics, which can induce errors when assessing kinetic parameters. Because of that, the three other methods mentioned above –isoconversional methods– were also applied, as they provide more accurate results than model-fitting methods [58].

Finally, another TGA test was carried out using an oxygen

atmosphere and a 5 K/min heating rate, since from this type of test it is possible to obtain the characteristic temperature (T_{char}) required for the self-ignition risk characterization [57]. When applying an oxygen atmosphere, combustion takes place faster and the mass drop is represented almost as a vertical line. In this case, the MWLT value corresponds to the characteristic temperature (T_{char}).

3. Results and discussion

Flammability and explosibility parameters are not physical constants but depend on the techniques used for their measurement and on the characteristics of the samples. For this reason, standardised measurement methods were applied and also the samples studied here were fully characterised in order to provide information that could allow for comparison with other data sets.

Table 4 shows the results for the particle size analysis including polydispersity (σ_D) and skewness (Sk_G) values, which were calculated according to [59,60], respectively. Fig. 4 illustrates the complete density distributions. As can be seen, the sample of olive stone presented a lower D_{10} value and a higher specific surface area (SSA) than the olive pomace sample. Thus, the olive stone was finer that the olive cake in spite of having a slightly higher D_{50} value (251 μm vs. 224 μm).

Table 5 gives the results for the proximate and ultimate analyses and the calorific values of the samples. The values obtained clearly indicate the different quality level of these two biomasses. The olive cake sample presented a relatively high Cl content that prevents its use in small domestic boilers, since they could develop corrosion problems [10]. Also, its fixed carbon and volatiles values were inferior and its ash content was higher, what indicates a lower heating value in comparison to the olive stone sample. On the contrary, both samples had a rather low S value, which indicates low SO_2 emissions.

The results for the flammability and explosibility tests carried out in this study are presented in Table 6. As can be seen, the MIT_L results indicated that both materials could be ignited by a hot surface: at ≥310 °C, a layer of 5 mm would ignite in both cases. If the layer were thicker, the ignition temperature would decrease [32]. However, when in the form of dust clouds, the behaviour of these two materials was significantly different: both MIT_C and MIE values for olive stone were lower than those for olive cake. In the case of the lower explosion limit (LEL), both biomasses obtained the same value, i.e. the minimum quantity of dust dispersed in air to form a potentially explosive
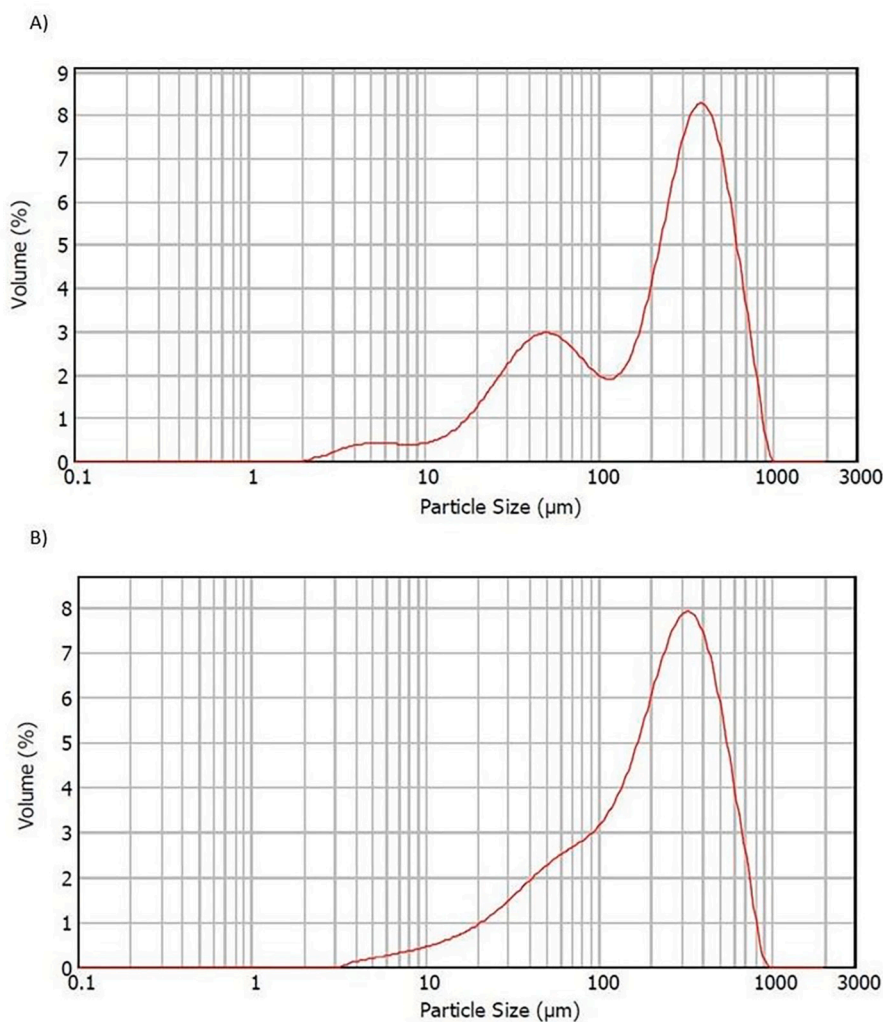
Table 4
Particle size of samples.

Sample	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)	$D_{3,2}$ (μm)	SSA (m²/g)	σ_D	Sk_G
Olive stone	28.2	251.1	569.6	60.1	0.0999	2.156	−0.064
Olive cake	37.0	223.5	519.9	81.7	0.0734	2.161	−0.243

Fig. 4. Particle size distribution (fraction <500 μm) of olive stone (A) and olive cake (B).

Table 5

Moisture content (wt%, wet basis), proximate (wt%, dry basis) and ultimate (wt%, dry ash-free basis) parameters, and higher and lower heating values (MJ/kg, dry basis) of samples.

Sample	Moisture	Volatiles	Ash	Fixed carbon	C	H	N	O	S	Cl	HHV	LHV
Olive stone	11.2	78.7	1.2	20.1	51.04	6.03	0.34	42.54	0.03	0.025	20.2	19.0
Olive cake	10.4	74.3	7.2	18.5	51.29	6.24	1.49	40.72	0.10	0.162	18.9	17.7

Table 6

Flammability and explosibility properties of olive stone and olive cake.

Sample	LEL (g/m^3)	MIE (mJ)	MIT$_L$ (°C)	MIT$_C$ (°C)	P_{max} (bar)	dP/dt_{max} (bar/s)	K_{St} (bar·m/s)
Olive stone	125	67	310	460	7.9	350	95
Olive cake	125	>1000	310	570	7.0	280	76

Table 7

Wood and coal dust samples retrieved from [61] for comparison purposes.

Sample	LEL (g/m^3)	MIE (mJ)	MIT$_L$ (°C)	MIT$_C$ (°C)	P_{max} (bar g)	dP/dt_{max} (bar/s)	K_{St} (bar·m/s)
Wood dust (90% birch +10% spruce, D_{50} = 240 μm)	30	60	340	420	7.8	–	87
Coal (lignite, Spain, D_{50} = 60 μm)	90	420	240	400	7.8	–	107

atmosphere would be the same in both cases but the energy required to ignite the dust cloud (MIE) should be much higher for the olive pomace; this could be partially explained by the fact that standard EN 14034–3 [45] considers specific dust concentrations to be tested (60, 125, 250, 500, 750, etc., in g/m^3), so intermediate values of minimum explosive concentration are not detected. In case of explosion, it would be stronger and faster for olive stone (higher values of P_{max} and dP/dt_{max}). As a conclusion, both biomasses (particles <500 μm) behaved as a combustible dust that formed explosive atmospheres, and a layer or deposit of these materials could also lead to a fire event.

The flammability and explosibility results of the olive stone obtained in the present study (Table 6) are entirely coherent in comparison with previous data shown in Table 2: the finer granulometry of the sample tested, the lower the LEL and MIT$_L$, and the higher the P_{max} and K_{St}. In the case of olive cake, the comparison with the fine sample reported by [33] showed the same trends explained before, excepting for LEL, MIE and K_{St}, which did not show any significant variation with particle size.

It is remarkable that the behaviour of the olive cake tested in this work –exhausted destoned olive cake– showed a quite different behaviour in comparison to the samples by Pietraccini et al. [31] in Table 2. However, the material analysed in this study and the samples reported by Pietraccini et al. were not the same type of residue, as explained above; this could explain the differences detected. In addition, the results by Pietraccini et al. [31] involve narrow fractions of the particle size distribution. Moreover, samples A, B, C and D were dried during 24 h at 110 °C, reducing the moisture content from 6.1% in weight down to a value between 1.1 and 0.6%. Both moisture and particle size are well known to greatly influence the flammability and explosibility properties of dusts [43,52]. Therefore, all these differences hinder a straightforward comparison between data.

The present sample needed a lower concentration in air to be ignited (LEL) and exhibited a higher explosion severity (P_{max} and K_{St}) than the non-dried samples in [31], even if it had a coarser granulometry and a higher moisture content, what could be explained by its higher volatiles content and its much lower ash content: 80.1% vs. 72.8% (dry-ash-free basis), and 7.2% vs. 15.5% (dry basis), respectively. The contents reported in [31] correspond to the original pellets as received, but some small differences are expected in the sample fractions prepared by milling and sieving. Regarding the dried samples in [31] (see Table 2), they showed lower MIT$_C$ and LEL values than the olive cake analysed here, with the exception of coarse sample A, what is logical in view of their much lower moisture contents. However, it is remarkable that these dried samples by Pietraccini et al. also gave lower K_{St} values, even the finest samples; again, this discrepancy may originate from the

differences in origin and composition, and the resulting variations in volatiles and ash contents.

This comparison with data shown in Table 2 highlights the idea that previous information on databases can only be considered as an approximation; the material actually handled in the industry being assessed should be tested to obtain accurate data. Although the moisture, volatiles and ash contents seem to partly explain these discrepancies, it is not fully known the influence of both the methodology followed to prepare the samples [31] and the techniques used to measure the particle size distribution, most of which assume that the particles are spherical, introducing some degree of error when applied to fibrous particles [29]. Clearly, all these are critical issues that deserve further research.

Table 7 includes two examples of other common fuels: wood and coal [61]. It is evident that the differences in particle size, moisture, volatiles, ashes, etc., prevent from comparing results between studies. However, these two fuels are included to illustrate that it is essential to manage the risk of changes in industrial facilities [30]. If a company handling the coal (or wood pellets) shown in Table 7 planned to use these alternative olive biomasses, it would be useful to compare the parameters for the new materials with the properties of the materials which the facility was designed for. In this sense, it is remarkable the strong differences in MIE: results for olive stone indicate that this is a sensitive material, with significantly lower MIE than the coal sample in Table 7, whereas olive cake would require much more energy than the other materials. In relation to the minimum ignition temperatures, MIT$_C$ for olive stone was higher than that for wood or coal samples, and MIT$_C$ for olive cake was significantly higher than the other values, whereas MIT$_L$ for both olive stone and olive cake were lower than for wood dust but considerably higher than for coal. About the explosion severity, both olive biomasses presented values that are comparable to the coal and wood samples in [61]; it is remarkable that the explosion severity of olive stone is stronger than that of wood dust in Table 7. Thus, this comparison highlights the importance of assessing risks when materials handled by industry are replaced by others; new biomass materials may be more flammable and explosive than traditional fuels, or may be less, or may be the same. It is important to note that different values from those shown in Table 7 for wood and coal can be found in literature, for example in [33,62,63], so risk assessments always need to be tailored to each specific case, and no general conclusions should be drawn from this simplified comparison presented here.

The results obtained from the TGA test are plotted in Fig. 5, together with the first derivative curve (DTG). Several stages can be differentiated. First of all, up to 110 °C, there was a mass loss due to moisture
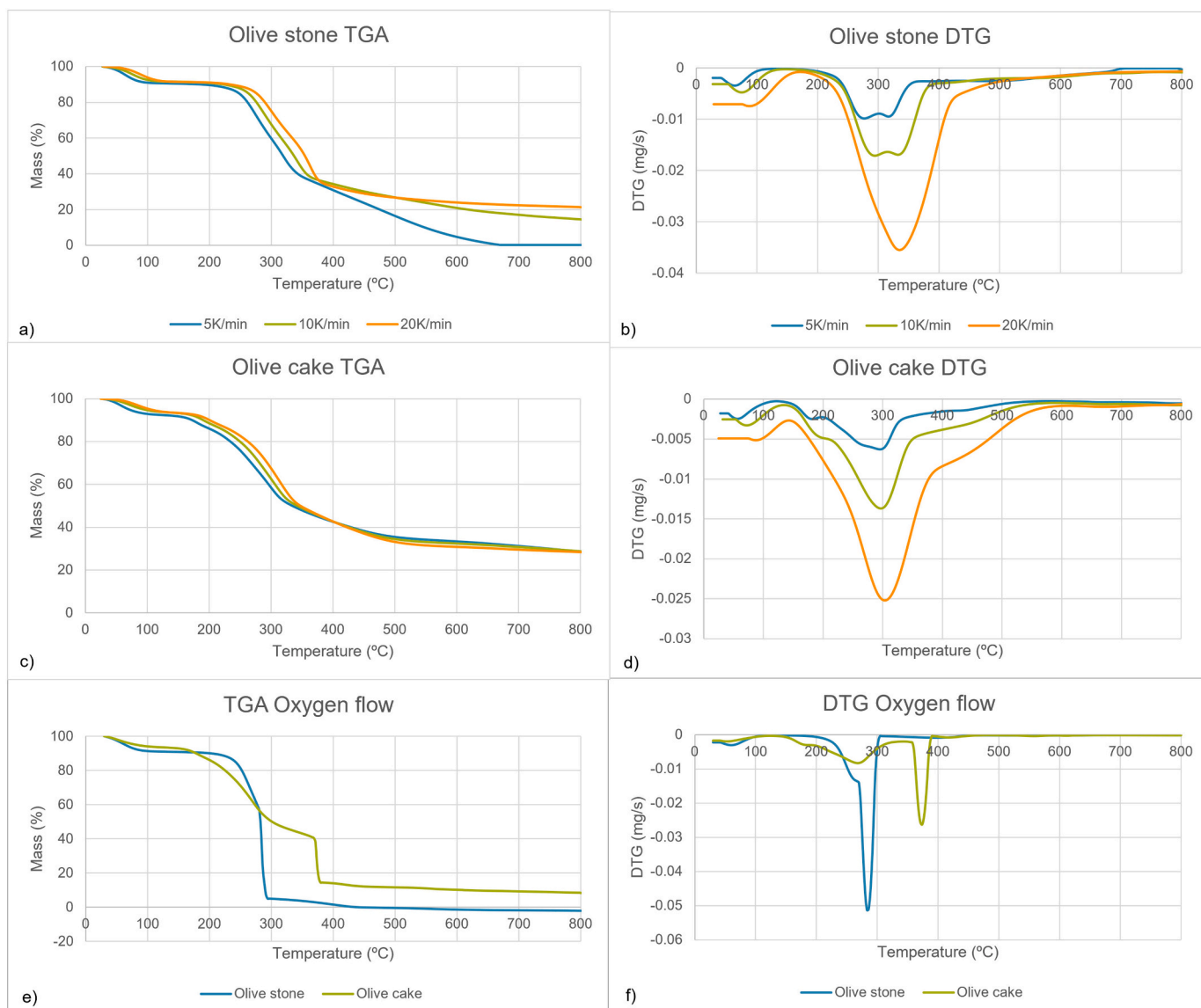
Fig. 5. Thermogravimetric analysis plots.

release. After that, a devolatilization process took place, in which mainly cellulose and hemicellulose decomposed up to 320 °C [64]. Plots a) and c) in Fig. 5 show that the TGA curve presented a change of slope around 330 °C, when the cellulose and hemicellulose degradation was almost completed. After that point and up to 700 °C, mass loss was produced due to lignin decomposition, which constituted the second devolatilization stage, at a slower rate due to the lignin's stable polyaromatic structure. The remaining mass represents ashes and char, which were greater for olive cake than for olive stone (see values in Table 5). As previously noticed by other authors, olive cake presented a smaller content of volatile matter and a higher ash content than olive stone [65,66]. When performing the tests at higher heating rates, the TGA curves slightly shifted to the right and the reaction acceleration point and maximum weight rate took place at higher temperatures [67]. The results for the three heating rates are summarised in Table 8.

Small differences between the two samples were detected in the TGA analyses. Considering the average values, olive stone required higher temperatures than olive cake for both the reaction acceleration (IT) and the point of maximum weight loss rate (MWLT). This behaviour could be explained by its composition, as olive cake usually presents a slightly higher content of holocellulose (the sum of hemicellulose and cellulose)

Table 8
Parameters obtained from the TGA and DTG curves.

Parameter	Heating rate	Olive stone	Olive cake
IT (°C)	5 K/min	240.8	208.6
	10 K/min	255.2	230.1
	20 K/min	257.7	242.7
MWLT (°C)	5 K/min	276.7	295.6
	10 K/min	294.4	296.9
	20 K/min	355.1	303.5
$IT_{average}$ (°C)	–	251.2	227.1
$MWLT_{average}$ (°C)	–	308.7	298.7
T_{char} (°C)	5 K/min (O_2)	302.4	398.1

[65,66], which requires a lower devolatilization temperature than lignin.

The stages of the thermal analysis can also be noticed in the DTG curves (see plots b) and d) in Fig. 5). In the first devolatilization stage, DTG curves showed two peaks for olive stone and a peak with a shoulder for olive cake that are linked with the hemicellulose decomposition [68]. As pointed out by other authors [67], higher heating rates increase DTG peaks, as individual devolatilization peaks overlap; this also produced the disappearance of both the second peak in olive stone and the

Table 9
Activation energy values (E$_a$) expressed in kJ/mol.

Method	Olive stone	Olive cake
Cumming's	68.30	75.60
Friedman	128.58	294.19
KAS	154.73	251.72
FWO	156.56	248.17

shoulder in olive cake.

Results from the TGA analysis with an oxygen flow showed important differences between samples. Plots e) and f) in Fig. 5 illustrate that olive stone showed an almost complete oxidation reaction in a very short time, while olive cake oxidation was divided into two stages and took a longer time. This means that some conditions may lead to a fast oxidation of olive stone; indeed, this was already noticed when assessing explosion severity, since the explosion rate dP/dt$_{max}$ was greater for olive stone than for olive cake. The effect of the oxygen flow on these TGA tests demonstrated that olive stone presents a greater tendency to oxidation than olive cake. This explains why olive stone showed a lower T$_{char}$ than olive cake, in spite of having greater MLWT and IT average values.

Table 9 presents the activation energy values (E$_a$) calculated following four different methods. As can be seen, activation energy was found to be significantly lower for olive stone than for olive cake. Furthermore, the kinetic results obtained can be related to the ignition sensitivity parameters: the fact that the combustion reaction required less energy in the case of olive stone agreed with the MIE results, and even with the MIT$_C$ values (see Table 6).

The isoconversional methods provided greater values than Cumming's equation, as the latter supposes a first order kinetic while the former ones do not make assumptions regarding the reaction mechanism. Besides that, Friedman results slightly differed from KAS and FWO. This fact has previously been detected by other authors, as Friedman produces numeral instability by applying conversion rate data [69]. Nevertheless, all methods presented the same tendency when comparing both samples: olive stone had a lower E$_a$ than olive cake.

Finally, when assessing the self-ignition risk by simultaneously considering T$_{char}$ and E$_a$, olive stone presented a medium risk –but not far from some types of wood– whereas olive cake had a low risk. As explained above, olive cake showed a greater activation energy value, which again means that it will require more energy to initiate combustion reaction, and a higher characteristics temperature, which indicates that the quick combustion phase will occur at a higher temperature. The self-ignition risk plot is shown in Fig. 6 for both samples, together with literature data [57,70] in order to properly assess the results (sewage sludge can vary greatly depending on the sample, from very high to medium self-ignition risk; sample SEW-3 from [70], which presents a high risk, has been selected here). The low risk of olive cake determined in this study agrees with experimental measurements
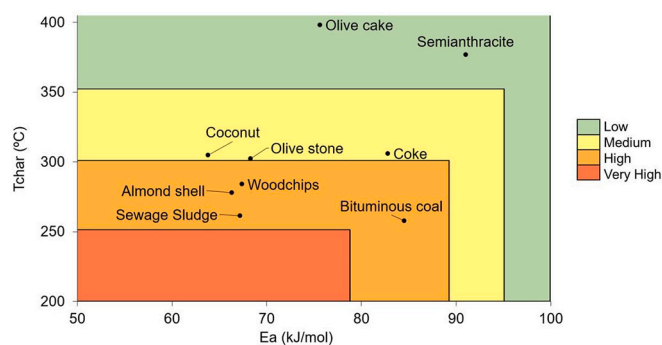
obtained in a large-scale biomass storage [71]. On the other hand, it can be noticed that olive stone located close to coconut and wood chips, which are also strong lignocellulosic structures.

Therefore, it is clear that ignition sensitivity, explosion severity and self-ignition tendency risks were found to be greater for olive stone than for olive cake. Although olive stone can be considered a better fuel due to its higher calorific value and its composition (greater fixed carbon content and much lower ash, N, S and Cl contents), it requires more severe safety measures than olive cake. The results presented here have implications for the design and management of industrial facilities.

4. Conclusions

Olive stone and exhausted olive cake have been analysed to assess their safety behaviour. Dust samples of both materials (< 500 μm) were generated by milling and sieving and were later tested to determine their particle size distribution and chemical composition. Flammability and explosibility properties were measured following standardised methods. In addition, TGA analysis were carried out to study the thermal susceptibility of the samples and estimate their self-ignition risk.

The results indicated that both dust samples could form explosive atmospheres or lead to a dust fire. However, important differences between materials were detected. When dispersed in a dust/air cloud, olive stone was more prone both to spark ignition and to hot-surface ignition than olive cake. In case of explosion, it would be stronger and faster for olive stone than for olive cake. The self-ignition risk assessment based on TGA tests with an oxygen flow concluded that olive stone presented a medium self-ignition risk and, in contrast, olive cake had a low risk.

This study fills gaps in literature and has implications on the specification of safe conditions for handling and storing these olive-derived biomasses in industrial facilities.

CRediT authorship contribution statement

Blanca Castells: Investigation, Visualization, Formal analysis. **Alejandro Varela:** Writing – original draft. **Francisco J. Castillo-Ruiz:** Conceptualization, Resources. **Luis F. Calvo:** Investigation, Formal analysis. **Ljiljana Medic:** Investigation. **Alberto Tascón:** Funding acquisition, Project administration, Writing – review & editing.

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.

Data availability

Data will be made available on request.

Fig. 6. Self-ignition risk assessment of olive stone and olive cake. Other materials are included for comparison purposes (data retrieved from [57,70]).

References

[1] Directive (EU) 2018/2001 of the European Parliament and of the Council of 11 December 2018 on the promotion of the use of energy from renewable sources. Off. J. Eur. Union http://data.europa.eu/eli/dir/2018/2001/2022-06-07.
[2] B. Kumar, N. Bhardwaj, K. Agrawal, V. Chaturvedi, P. Verma, Current perspective on pretreatment technologies using lignocellulosic biomass: an emerging biorefinery concept, Fuel Process. Technol. 199 (2020), 106244, https://doi.org/10.1016/j.fuproc.2019.106244.
[3] J.M. Romero-García, A. Susmozas, C. Padilla-Rascón, P. Manzanares, E. Castro, J.M. Oliva, I. Romero, Ethanol production from olive stones using different process strategies, Renew. Energy 194 (2022) 1174–1183, https://doi.org/10.1016/j.renene.2022.06.022.

[4] ISO 20024:2020, Solid biofuels – Safe handling and storage of solid biofuel pellets in commercial and industrial applications, International Organization for Standardization, Geneva, 2000.

[5] M.D.M. Contreras, I. Romero, M. Moya, E. Castro, Olive-derived biomass as a renewable source of value-added products, Process Biochem. 97 (2020) 43–56, https://doi.org/10.1016/j.procbio.2020.06.013.

[6] P. Sánchez Moral, M.V. Ruiz Méndez, Production of pomace olive oil, Grasas Aceites 57 (2006) 47–55, https://doi.org/10.3989/gya.2006.v57.i1.21.

[7] J. Mata-Sánchez, J.A. Pérez-Jiménez, M.J. Díaz-Villanueva, A. Serrano, N. Núñez-Sánchez, F.J. López-Giménez, Statistical evaluation of quality parameters of olive stone to predict its heating value, Fuel 113 (2013) 750–756, https://doi.org/10.1016/j.fuel.2013.06.019.

[8] M. Antónia Nunes, Filipa B. Pimentel, Anabela S.G. Costa, Rita C. Alves, M. Beatriz, P.P. Oliveira, Olive by-products for functional and food applications: challenging opportunities to face environmental constraints, Innovative Food Sci. Emerg. Technol. 35 (2016) 139–148, https://doi.org/10.1016/j.ifset.2016.04.016.

[9] Consejería de Agricultura, Pesca Ganadería, Desarrollo Sostenible, Evaluación de la producción y usos de los subproductos de las agroindustrias del olivar en Andalucía (Evaluation of the production and uses of the by-products of the olive industry in Andalusia). https://www.juntadeandalucia.es/agriculturaypesca/observatorio/servlet/FrontController?ec=default&action=DownloadS&table=11030&element=1585171&field=DOCUMENTO, 2015 (accessed 21st February 2023).

[10] P. Rodero Mademont, D. García Galindo, A. Mira Uguina, M. Karampinis, A Guide for Agroindustrial Residues to Energy, AgroBioHeat EU project, https://agrobioheat.eu/wp-content/uploads/2022/04/agrobioheat-guide-2022-EN-small.pdf, 2022.

[11] FAOSTAT – Food and Agriculture Data, Food and Agriculture Organization, United Nations. https://www.fao.org/faostat/en/#home.

[12] UNE 164003, Solid Biofuels. Fuel Specifications and Classes. Graded Olive Stones, AENOR, Madrid, 2014.

[13] R. Collado, E. Monedero, V.M. Casero-Alonso, L.J. Rodríguez-Aragón, J. J. Hernández, Almond shells and exhausted olive cake as fuels for biomass domestic boilers: optimization, performance and pollutant emissions, Sustainability 14 (2022) 7271, https://doi.org/10.3390/su14127271.

[14] M. Lajili, L. Limousy, M. Jeguirim, Physico-chemical properties and thermal degradation characteristics of agropellets from olive mill by-products/sawdust blends, Fuel Process. Technol. 126 (2014) 215–221, https://doi.org/10.1016/j.fuproc.2014.05.007.

[15] Y.H. Khraisha, Energetic study on Jordanian olive cake and woody biomass materials, J. Power Energy Eng. 10 (2022) 1–13, https://doi.org/10.4236/jpee.2022.102001.

[16] P. Manzanares, E. Ruiz, M. Ballesteros, M.J. Negro, F.J. Gallego, J.C. López-Linares, E. Castro, Residual biomass potential in olive tree cultivation and olive oil industry in Spain: valorization proposal in a biorefinery context, Span. J. Agric. Res. 15 (2017), e0206, https://doi.org/10.5424/sjar/2017153-10868.

[17] A. Bayram, A. Filibeli, A. Muezzinoglu, F. Sengul, A. Ozer, A review of waste management options in olive oil production, Crit. Rev. Environ. Sci. Technol. 34 (2004) 209–247, https://doi.org/10.1080/10643380490279932.

[18] S. Korhaliller, The UK's Biomass Energy Development Path, International Institute for Environment and Development, London, 2000. https://www.iied.org/sites/default/files/pdfs/migrate/G02921.pdf.

[19] Biomass Magazine, Electric Olives Power Europe. https://biomassmagazine.com/articles/1258/electric-olives-power-europe (accessed 15th December 2022).

[20] E. Oveisi, A. Lau, S. Sokhansanj, C.J. Lim, X. Bi, S.H. Larsson, S. Melin, Breakage behavior of wood pellets due to free fall, Powder Technol. 235 (2013) 493–499, https://doi.org/10.1016/j.powtec.2012.10.022.

[21] J.M. Ashman, J.M. Jones, A. Williams, Some characteristics of the self-heating of the large scale storage of biomass, Fuel Process. Technol. 174 (2018) 1–8, https://doi.org/10.1016/j.fuproc.2018.02.004.

[22] C. Sheng, C. Yao, Review on self-heating of biomass materials: understanding and description, Energy Fuel 36 (2022) 731–761, https://doi.org/10.1021/acs.energyfuels.1c03369.

[23] F.H. Hedlund, Carbon dioxide not suitable for extinguishment of smouldering silo fires: static electricity may cause silo explosion, Biomass Bioenergy 108 (2018) 113–119, https://doi.org/10.1016/j.biombioe.2017.11.009.

[24] F.H. Hedlund, J. Astad, J. Nichols, Inherent hazards, poor reporting and limited learning in the solid biomass energy sector: a case study of a wheel loader igniting wood dust, leading to fatal explosion at wood pellet manufacturer, Biomass Bioenergy 66 (2014) 450–459, https://doi.org/10.1016/j.biombioe.2014.03.039.

[25] R.K. Eckhoff, Understanding dust explosions. The role of powder science and technology, J. Loss Prev. Process Ind. 22 (2009) 105–116, https://doi.org/10.1016/j.jlp.2008.07.006.

[26] R.D. Calvo Olivares, S.S. Rivera, J.E. Núñez Mc Leod, Database for accidents and incidents in the biodiesel industry, J. Loss Prev. Process Ind. 29 (2014) 245–261, https://doi.org/10.1016/j.jlp.2014.03.010.

[27] V. Casson Moreno, V. Cozzani, Major accident hazard in bioenergy production, J. Loss Prev. Process Ind. 35 (2015) 135–144, https://doi.org/10.1016/j.jlp.2015.04.004.

[28] S. Krigstin, S. Wetzel, N. Jayabala, C. Helmeste, S. Madrali, S. Agnew, S. Volpe, Recent health and safety incident trends related to the storage of woody biomass: a need for improved monitoring strategies, Forests 9 (2018) 538, https://doi.org/10.3390/f9090538.

[29] B. Castells, A. Tascón, I. Amez, D. León, N. Fernandez-Anez, J. García Torrent, Reviewing particle size influence in biomass flammability and explosibility, WCPT9: World Congress on Particle Technology, 18–22 September, 2022, Madrid, Spain.

[30] P. Amyotte, An Introduction to Dust Explosions: Understanding the Myths and Realities of Dust Explosions for a Safer Workplace, first ed., Butterworth-Heinemann/Elsevier, 2013.

[31] M. Pietraccini, E. Danzi, L. Marmo, A. Addo, P. Amyotte, Effect of particle size distribution, drying and milling technique on explosibility behavior of olive pomace waste, J. Loss Prev. Process Ind. 71 (2021), 104423, https://doi.org/10.1016/j.jlp.2021.104423.

[32] N. Fernandez-Anez, J. Garcia-Torrent, Influence of particle size and density on the hot surface ignition of solid fuel layers, Fire. Technol 55 (2019) 175–191, https://doi.org/10.1007/s10694-018-0782-3.

[33] IFA, Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung, GESTIS-DUST-EX – Database: Combustion and Explosion Characteristics of Dusts, Germany. https://www.dguv.de/ifa/gestis/gestis-staub-ex/index-2.jsp, 2022 (accessed 17 October 2022).

[34] NFPA 652, Standard on the Fundamentals of Combustible Dust, National Fire Protection Association, Quincy, MA, USA, 2019.

[35] ISO/IEC 80079–20-2:2016, Explosive Atmospheres – Part 20–2: Material Characteristics – Combustible Dusts Test Methods, International Organization for Standardization, Geneva, 2016.

[36] ASTM D5373-21, Standard Test Methods for Determination of Carbon, Hydrogen and Nitrogen in Analysis Samples of Coal and Carbon in Analysis Samples of Coal and Coke, ASTM International, West Conshohocken, PA, USA, 2021.

[37] ASTM D4239-18e1, Standard Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High-Temperature Tube Furnace Combustion, ASTM International, West Conshohocken, PA, USA, 2021.

[38] ASTM D2361-95, Standard Test Method for Chlorine in Coal, ASTM International, West Conshohocken, PA, USA, 2021.

[39] UNE 32019:1984, Hard Coal and Coke. Determination of Volatile Matter Content, AENOR, Madrid, 1984.

[40] UNE 32004:1984, Solid Mineral Fuels. Determination of Ash, AENOR, Madrid, 1984.

[41] ASTM D3302-02, Standard Test Method for Total Moisture in Coal, ASTM International, West Conshohocken, PA, USA, 2002.

[42] UNE 32006:1995, Solid Mineral Fuels. Determination of Gross Calorific Value by Automatic Calorimeter, AENOR, Madrid, 1995.

[43] P.R. Amyotte, R.K. Eckhoff, Dust explosion causation, prevention and mitigation: an overview, J. Chem. Health Saf. 17 (2010) 15–28, https://doi.org/10.1016/j.jchas.2009.05.002.

[44] N. Fernandez-Anez, B. Castells Somoza, I. Amez Arenillas, J. Garcia-Torrent, Explosion Risk of Solid Biofuels, 1st ed., Springer International Publishing, 2020 https://doi.org/10.1007/978-3-030-43933-0.

[45] EN 14034–3, Determination of Explosion Characteristics of Dust Clouds – Part 3: Determination of the Lower Explosion Limit LEL of Dust Clouds, European Committee for Standardization, Brussels, 2011.

[46] A. Janes, J. Chaineaux, D. Carson, P.A. Le Lore, MIKE 3 versus HARTMANN apparatus: comparison of measured minimum ignition energy (MIE), J. Hazard. Mater. 152 (2008) 32–39, https://doi.org/10.1016/j.jhazmat.2007.06.066.

[47] EN 13821:2003, Potentially Explosive Atmospheres – Explosion Prevention and Protection – Determination of Minimum Ignition Energy of Dust/Air Mixtures, European Committee for Standardization, Brussels, 2003.

[48] R.K. Eckhoff, Origin and development of the Godbert-Greenwald furnace for measuring minimum ignition temperatures of dust clouds, Process. Saf. Environ. Prot. 129 (2019) 17–24, https://doi.org/10.1016/j.psep.2019.06.012.

[49] EN 14034–1, Determination of Explosion Characteristics of Dust Clouds – Part 1: Determination of the Maximum Explosion Pressure p_{max} of Dust Clouds, European Committee for Standardization, Brussels, 2011.

[50] EN 14034–2, Determination of Explosion Characteristics of Dust Clouds – Part 2: Determination of the Maximum Rate of Explosion Pressure Rise $(dp/dt)_{max}$ of Dust Clouds, European Committee for Standardization, Brussels, 2011.

[51] Á. Ramírez, J. García-Torrent, A. Tascón, Experimental determination of self-heating and self-ignition risks associated with the dusts of agricultural materials commonly stored in silos, J. Hazard. Mater. 175 (2010) 920–927, https://doi.org/10.1016/j.jhazmat.2009.10.096.

[52] N. Fernandez-Anez, J. Garcia-Torrent, L. Medic-Pejic, Flammability properties of thermally dried sewage sludge, Fuel 134 (2014) 636–643, https://doi.org/10.1016/j.fuel.2014.06.006.

[53] J.W. Cumming, Reactivity assessment of coals via a weighted mean activation energy, Fuel 63 (1984) 1436–1440, https://doi.org/10.1016/0016-2361(84)90353-3.

[54] H.E. Kissinger, Reaction kinetics in differential thermal analysis, Anal. Chem. 29 (1957) 1702–1706, https://doi.org/10.1021/ac60131a045.

[55] H.L. Friedman, Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic, J. Polym. Sci. Part C Polym. Symp. 6 (1964) 183–195, https://doi.org/10.1002/polc.5070060121.

[56] J.H. Flynn, L.A. Wall, A quick, direct method for the determination of activation energy from thermogravimetric data, J. Polym. Sci. Part B Polym. Lett. 4 (1966) 323–328, https://doi.org/10.1002/pol.1966.110040504.

[57] J. Garcia-Torrent, Á. Ramírez, N. Fernandez-Anez, L. Medic, A. Tascón, Influence of the composition of solid biomass in the flammability and susceptibility to spontaneous combustion, Fuel 184 (2016) 503–511, https://doi.org/10.1016/j.fuel.2016.07.045.

[58] S. Vyazovkin, A.K. Burnham, J.M. Criado, L.A. Pérez-Maqueda, C. Popescu, N. Sbirrazzuoli, ICTAC kinetics committee recommendations for performing kinetic computations on thermal analysis data, Thermochim. Acta 520 (2011) 1–19, https://doi.org/10.1016/j.tca.2011.03.034.

[59] D. Castellanos, V.H. Carreto-Vazquez, C.V. Mashuga, R. Trottier, A.F. Mejia, M. S. Mannan, The effect of particle size polydispersity on the explosibility characteristics of aluminum dust, Powder Technol. 254 (2014) 331–337, https://doi.org/10.1016/j.powtec.2013.11.028.

[60] A. Tascón, Influence of particle size distribution skewness on dust explosibility, Powder Technol. 338 (2018) 438–445, https://doi.org/10.1016/j.powtec.2018.07.044.

[61] C. Wilén, A. Moilanen, A. Rautalin, J. Torrent, E. Conde, R. Lödel, D. Carson, P. Timmers, K. Brehm, Safe Handling of Renewable Fuels and Fuel Mixtures, VTT Publications, Technical Research Centre of Finland, Espoo, 1999. https://publications.vtt.fi/pdf/publications/1999/P394.pdf.

[62] C. Huéscar Medina, H.N. Phylaktou, G.E. Andrews, B.M. Gibbs, Explosion characteristics of pulverised torrefied and raw Norway spruce (Picea abies) and Southern pine (Pinus palustris) in comparison to bituminous coal, Biomass Bioenergy 79 (2015) 116–127, https://doi.org/10.1016/j.biombioe.2015.04.001.

[63] A. Liu, J. Chen, X. Huang, J. Lin, X. Zhang, W. Xu, Explosion parameters and combustion kinetics of biomass dust, Bioresour. Technol. 294 (2019), https://doi.org/10.1016/j.biortech.2019.122168.

[64] M.A. Sukiran, F. Abnisa, W.M.A. Wan Daud, N. Abu Bakar, S.K. Loh, A review of torrefaction of oil palm solid wastes for biofuel production, Energy Convers. Manag. 149 (2017) 101–120, https://doi.org/10.1016/j.enconman.2017.07.011.

[65] L. Quesada, A. Pérez, M. Calero, G. Blázquez, M.A. Martín-Lara, Kinetic study of thermal degradation of olive cake based on a scheme of fractionation and its

behavior impregnated of metals, Bioresour. Technol. 261 (2018) 104–116, https://doi.org/10.1016/j.biortech.2018.04.014.

[66] T. Miranda, A. Esteban, S. Rojas, I. Montero, A. Ruiz, Combustion analysis of different olive residues, Int. J. Mol. Sci. 9 (2008) 512–525, https://doi.org/10.3390/ijms9040512.

[67] B. Janković, M.B. Radojević, M. Balac, D.D. Stojiljković, N.G. Manić, Thermogravimetric study on the pyrolysis kinetic mechanism of waste biomass from fruit processing industry, Therm. Sci. 24 (2020) 4221–4239, https://doi.org/10.2298/TSCI200213191J.

[68] M. Broström, A. Nordin, L. Pommer, C. Branca, C. Di Blasi, Influence of torrefaction on the devolatilization and oxidation kinetics of wood, J. Anal. Appl. Pyrolysis 96 (2012) 100–109, https://doi.org/10.1016/j.jaap.2012.03.011.

[69] E. Apaydin-Varol, S. Polat, A.E. Putun, Pyrolysis kinetics and thermal decomposition behavior of polycarbonate - a TGA-FTIR study, Therm. Sci. 18 (2014) 833–842, https://doi.org/10.2298/TSCI1403833A.

[70] L. Medic Pejic, N. Fernandez Anez, J. García Torrent, Á. Ramírez Gómez, Determination of spontaneous combustion of thermally dried sewage sludge, J. Loss Prev. Process Ind. 36 (2015) 352–357, https://doi.org/10.1016/j.jlp.2015.01.013.

[71] P.J. Lara Chaves, J. Terrados Cepeda, F.J. Gallego Álvarez, M.J. Hermoso Orzáez, Large-scale biomass storage for electricity generation: a comprehensive field-test campaign in southern Spain, Biofuels Bioprod. Biorefin. 16 (2022) 766–784, https://doi.org/10.1002/bbb.2337.