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## Ageing effect on ignition sensitivity of lignocellulosic dust

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### ABSTRACT

As the use of biomass as a carbon-neutral energy source increases, so does the need for storage facilities, especially for those that are highly seasonal. Consequently, the stored materials may be subject to a natural ageing process before they are used. Such ageing can modify the deflagration parameters of the materials since it can reduce hygroscopicity, increase stiffness and brittleness and change chemical composition in terms of cellulose, hemicellulose and lignin contents. Hydrothermal treatment is a process that accelerates the ageing of wood and lignocellulosic materials. In this work, several lignocellulosic powders from industrial processes were subjected to accelerated ageing to investigate their influence on flammability properties. Grape marc, cork flour, olive pomace, wood dust and lignocellulosic residues from processing waste were selected based on their morphology, chemical characterization and lignin/cellulose content. Based on literature data, ageing conditions in terms of temperature and humidity were chosen to reproduce naturally aged materials. In this study, the effects of ageing on the minimum ignition energy (MIE) and combustion/pyrolysis behaviour were investigated by chemico-physical screening and thermogravimetric analysis and differential scanning calorimetry (TGA and DSC) in an inert and oxidative atmosphere. Results showed how ageing can change the risk of ignition. For example, the MIE of grape marc decreases, while wood-based samples do not ignite after ageing. The decrease in the case of grape pomace is consistent with the decrease in lignin content and moisture. At the same time, passivation of the particle surface could explain the behaviour of the wood samples.

## 1. Introduction

### 1.1. Biomass utilization overview and explosion hazards

The use of biomass as an energy source has been steadily increasing for many years now. According to IEA data in 2021, 56.1 EJ of energy from biomass were obtained in the world, a significant increase compared to 45 EJ obtained in 2010 (IEA, 2022a). The share attributable to solid biomass amounts to 26.2 EJ, compared to 16.7 EJ obtained in 2010. According to IEA Bioenergy (2013 b), the consumption of solid biomass for heat, power generation, and conversion into liquid and gaseous biofuels in 2021 was around 35 EJ (IEA, 2022b). This figure is expected to significantly increase by 2030, rising by 30% in the Stated Policies Scenario (STEPS), by 50% in the Announced Pledges Scenario (APS) scenario, and by just over 60% in the Net Zero Emission (NZE) Scenario.

One of the main positive aspects of biomass is its wide availability in many regions: forest and agricultural waste and/or municipal waste could potentially be collected in any rural or urban environment. The contribution of biomass to the share of renewable energy used for heating in Europe reaches 87%. This result is likely a consequence of EU policies shifting to zero-carbon energy sources (recently reinforced by the 2030 climate and energy framework (European Environment Agency, 2019; Joint Research Centre European Commission, 2019)) and the widespread use of district heating networks for residential buildings. It is worth noting that burning either fossil fuels or biomass releases carbon dioxide (CO<sub>2</sub>). However, the plants that are the source of biomass for energy capture almost the same amount of CO<sub>2</sub> through photosynthesis while growing as is released when biomass is burned, which can make biomass a carbon-neutral energy source. Moreover, the renewable energy carriers differentiation, also thanks to hydrogen, will play a key role in replacing traditional fossil fuels.

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Europe is also leading biogas production and municipal waste to energy transformation due to the intensive adoption of technologies, such as gasification, pyrolysis and direct combustion to convert biofuels into energy materials (or to generate energy directly).

The supply of biomass for energy can take place from three primary sources.

- From agriculture;
- From waste;
- From the management of forests.

The pellet sector has recently experienced strong growth, becoming the most produced and used biomass. More than half of the consumption of wood pellets occurs in European countries. Among these, Italy has recently ranked first for using wood pellets for heating (World Bioenergy Association, 2019). Wood and lignocellulosic material are the best candidates for generating pellets, but other promising raw materials can be used. EN ISO 17225 defines the different materials according to their origin and origin, classifying them as woody, herbaceous, fruity, aquatic biomass and mixture/mixture (BS EN ISO 17225-1:2021, 2021). The search for alternatives instead of forest fuels will reduce the impact on the forest sector and mitigate differences in the use rate of natural biomass between different world areas. Several industrial and academic figures focus on this direction, although integrating the alternative biomass market for the production of pellets, as a significant example, has some constraints. EN ISO 17225, while introducing the possibility of using waste for pellet production, appears to be demanding regarding product specifications and combustion characteristics (Miranda et al., 2015). Nevertheless, this process is undoubtedly a stimulus to the increase in the use of biomass and, consequently, a significant increase in the processing and storage of biomass even aged.

Some technical problems have been found in producing energy material from biomass other than wood, mainly due to unsuitable properties of the raw material (resistance to grinding or strong abrasiveness), difficulty in pelletizing, and the lack of experience and know-how of operators in the sector. At present, fire safety issues relating to the management and storage of biomass do not seem to be considered in sufficient depth, except for the wood industry (Huéscar Medina et al., 2015). In general, the procedures and operations for storing biomass, both in the energy and food sectors, are derived from those consolidated for grain or flour silos and therefore deserve further study (Krause, 2009). The use of biomass-derived fuels or feedstocks implies facing several hazards. Silos storage, handling, conveying, gasification, and pyrolysis in reactors, undesirable deposits in milling, and/or grinding systems may affect fire and explosion hazards. It is known that using biomass as fuel or feedstocks entails a risk of dust explosion that can also be generated during the handling of biomass (Huéscar Medina et al., 2015). It is reasonable to expect that dust derived from biomass shows peculiar aspects in the course of explosivity tests. Some research groups have recently studied the risk of explosion of biomass dust. This is likely due to some severe episodes that occurred in the last years, as reported by Ennis (2016), Krause U. (2009), Hedlund (2018), IEA Bioenergy (2013) (Ennis, 2016; Hedlund, 2018; IEA Bioenergy, 2013; Krause, 2009). Furthermore, if statistical data collected by Cloney C. (2021) is reviewed, the category “wood & wood products” and “agriculture & food products” account for 68.5% of the total combustible dust fire and explosions in 2021 (Cloney, 2021). Therefore, biomass materials could be considered under these categories: whether in the form of wood pellets/fine powder adopted as fuel in combustors directly or as a mixture in co-firing plants with coal (Fernandez-Anez et al., 2015; Kukfisz, 2018). Besides this, biomass cumulation as waste from agricultural production could constitute environmental and safety issues (Danzi et al., 2021; Pietraccini et al., 2021; Portarapillo et al., 2021a).

## 1.2. Factors influencing flammability

Biomass dust is typically identified as “nontraditional” dust since its shape and morphology differ from the spherical-like particles considered in the “classic” dust explosion study, cellulosic and lignocellulosic pulverulent material are mainly composed of flakes and irregular particles. For this reason, all the issues associated with nontraditional dust, as reported by Amyotte et al. (2012), Worsfold et al. (2012), Marmo et al. (2019) and Di Sarli et al. (2019), must be considered if an explosion risk assessment in this sector is considered (Amyotte et al., 2012; Di Sarli et al., 2019; Marmo et al., 2019; Worsfold et al., 2012). In the most recent years, the interest in these systems has increased and, in addition to CFD simulations in standard apparatus for classical powders (Portarapillo et al., 2020b, 2022), studies on dispersibility and explosivity have been carried out for this type of powder (Islas et al., 2022, 2023).

Notably, several factors may modify the ignition susceptibility, flammability, and explosibility of dusty samples, apart from particle size and moisture content. More specifically, for nontraditional biomass dust, the lignocellulosic components content can play a crucial role. Biomass energetic content is related to its Net Heating Value (NHV), dependent on pseudo-components share (cellulose, hemicellulose, lignin) and moisture degree. An explosion is the main concern if biomass is present as fine dust. Several factors may influence its dynamics. If pseudo-components are considered, some recent results indicate that hemicellulose and cellulose positively affect maximum pressure rise and maximum rate of pressure rise, respectively, while lignin limits the pressure peak (Liu et al., 2021). Composition influences pyrolysis rate share and could be evaluated through thermogravimetric analysis (TGA) and coupled gas chromatography (Zhao et al., 2017): lignin likely decreases reaction rate, while cellulose and hemicellulose have a positive influence. A synergistic effect is found in biomass-coal mixtures by adding corn starch to coal (Lin et al., 2019), while the addition of functional O<sub>2</sub>-containing groups enhances coal explosibility. Fernandez-Anez et al. (2015) reported how the addition of biomass to a coal/waste mixture increases the rate of pressure rise and flame length while reactivity is slightly reduced, as shown by an increase of the minimum explosive concentration (MEC) (Fernandez-Anez et al., 2015). Different factors also influence ignition sensitivity. For example, Lignin content is considered likely negligible on the MIE values (Castells et al., 2020), while volatile matter content (VM) is dependent on lignin share and other components (Andrews, 2014); generated pyrolysis gases, in turn, influence the flammability, depending on whether flammable (e.g., CH<sub>4</sub>, CO) or inert gases (e.g. CO<sub>2</sub>) are produced. Moreover, Adamski et al. (2021) investigated the effect of the operating parameters of superheated steam drying system for woody biomass and demonstrated that despite the fact that the superheated steam drying system for woody biomass is considered safe, the probability of occurrence of fire or explosion incidents related to the dust and air biomass mixture is high (Adamski et al., 2021). Since biomass samples will experience ageing while stored, the maturity of samples may have a role in their combustion/explosion properties. Lignin content decreases with wood maturity (Berrocal et al., 2004). Consequently, storage lifetime is another variable affecting the chemical-physical properties of biomasses. It may influence their attitude to combustion, and therefore ageing may affect the efficiency of energy production, whether in the form of pellets or raw material (Lee et al., 2015). The ageing of the samples may be obtained through artificial and accelerated treatment, such as hydrothermal treatments (Endo et al., 2016). The hydrothermal treatment causes several modifications in the samples. Thus, an aged sample theoretically will contain a small amount of hemicellulose and lignin and a higher amount of cellulose. Consequently, a chemically altered sample could increase its explosion risk because the transformation enhances its flammability properties and ignition susceptibility (Portarapillo et al., 2021a, 2021b).

In this work, the effect of the abovementioned variables using different biomass samples (woody, agricultural, industrial waste) were

investigated. The procedure described here aims to demonstrate that thermal analysis measurements, in parallel with flammability tests, are useful for identifying variables that most affect ignition sensitivity. The tests were carried out on samples aged by conditioning in the laboratory to simulate the effect of the actual ageing that occurs during biomass storage.

## 2. Material and methods

Samples tested in this work are all lignocellulosic biomass obtained from production processes or waste streams. The different materials were tested as received. The sample I is a residue of olive pomace, analyzed in detail in Pietraccini et al. (2021); sample II is cork flour used as fuel in a facility combustor; sample III is wood sawdust, sample IV is a waste product of a wood recycling plant, sample V is a grape pomace dust, described by (Danzi et al., 2021; Pietraccini, 2019; Portarapillo et al., 2021a).

The microscopic images of the samples are reported in Fig. 1 (left column), and the different morphologies can be easily observed. However, all were characterized in-depth by their size distribution, morphology, thermal behaviour and chemical composition before and after hydrothermal ageing. This approach, including a complete screening of the investigated dust, was successfully used in recent works to get insight into the synergistic behaviour between combustible dust when present in a mixture (Centrella et al., 2020; Portarapillo et al., 2020a). Table 1 reports the experimental tests carried out to study the samples' combustion behaviour (both in air and in an inert atmosphere to simulate oxidation and pyrolysis mechanisms), chemical composition and volatile/ashes content.

TGA analysis was carried out to evaluate the pseudo-component amounts from the deconvolution of the first derivative of TG signal (DTG curve) in an inert atmosphere (Portarapillo et al., 2021a). The procedure was derived from Hu et al. (2016) (Hu et al., 2016). The associated DSC aimed to study the pyrolysis steps through characteristic temperatures, such as Maximum Weight Loss Temperature (MWLT). In addition, temperature thresholds were detected by the test in an oxidant atmosphere (TGA/DSC up to 1000 °C with a heating rate equal to 10 °C/min), such as the Initial Exothermic Temperature (IET) and the Final Exothermic Temperature (FET), which reveal the exothermic reactivity of the samples. Moreover, the thermogravimetric furnace was used to carry out the proximate analysis for the evaluation of moisture (M), volatile matter (VM), ash (A), as well as fixed carbon (FC) contents, according to the standard procedure (ASTM D7582-15, 2009).

Alongside characterization tests, Minimum Ignition Energy (MIE) was measured for all the samples before and after ageing. MIE analysis was carried out with a MIKE III instrument according to the standard procedure (BS EN 13821:2002, 2003). Laser diffraction granulometry (Malvern Instruments Mastersizer, 2000) was used to characterize the granulometric distribution on both the samples before and after the dispersion within the MIKE3.

### 2.1. Ageing treatment

Hydrothermal treatment is one method to perform accelerated ageing of wood and lignocellulosic material. In this work, it is used to simulate the storage time effect on the samples. The treatment conditions are derived from the literature (Endo et al., 2016). Samples were thermally treated at 120 °C and relative humidity (RH) 60% for 7 days in an autoclave. The hygroscopicity of non-treated samples may be affected by ageing. Ageing causes the conversion of hemicellulose compounds into less hygroscopic elements. At the same time, the sample's mechanical properties (strength, elasticity) can be modified, i.e. the sample could become more fragile. This is crucial for dust explosion risk assessment: fragile and brittle solids likely generate fines if handled/transported or fall by chute, such as in standard operations in biomass treatment facilities. The ageing treatment could also modify particle

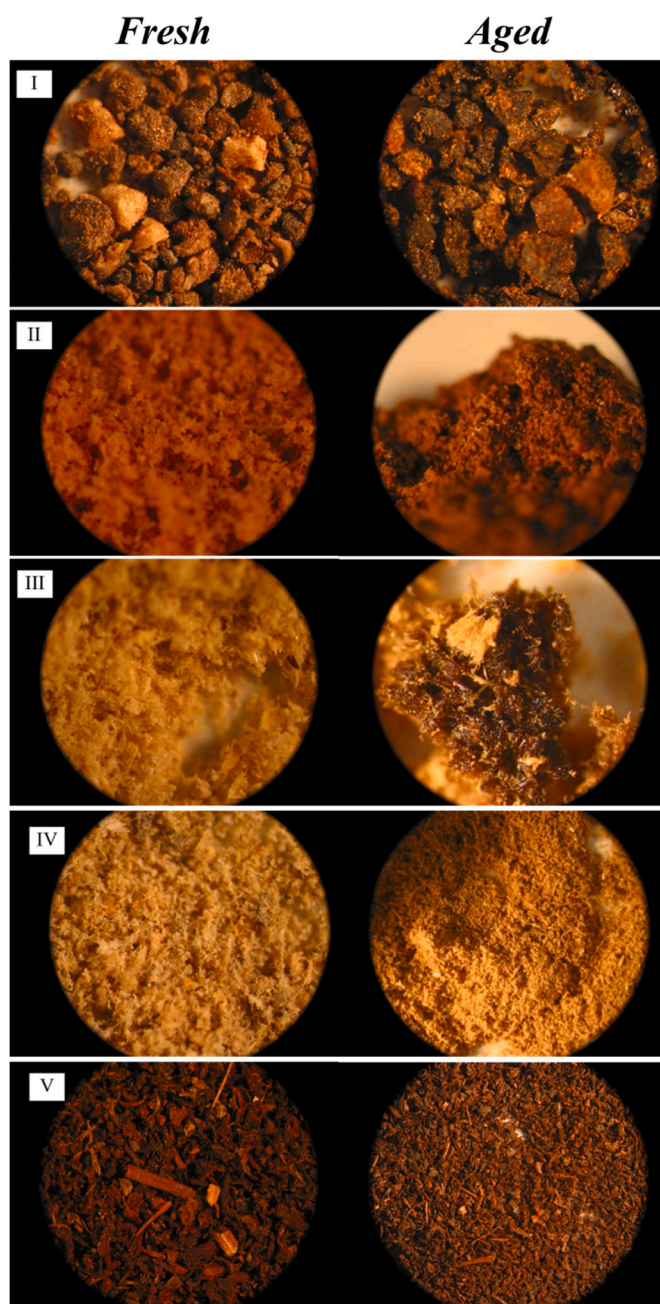


Fig. 1. Optical microscopic images (50x) of samples before (left) and after (right) ageing treatment.

size: this is a direct consequence of altering the water content/hygroscopic behaviour of samples by drying, but also is related to the effect of some physical transformations (decomposition, recrystallization and cross-linking of ligno-cellulosic constituents) which modify the morphology of samples (Sandberg et al., 2013), induce partial passivation of the outer surface, or drive agglomeration of the particles in larger clusters. All the parameters and their effect on the sample's ignition sensitivity are reported in Table 2. These physical effects can be observed qualitatively in the microscopic images of the aged samples reported in Fig. 1 (right column) and Fig. S1 (SEM images). Quantitative results and their effect on the safety parameters will be discussed in the following section.

**Table 1**

Tests used to characterize the samples, where DTG stands for Differential Thermogravimetry, IET is Initial Exothermic Temperature, FET is Final Exothermic Temperature, MWLT is Maximum Weight Loss Temperature, VM is Volatile matter content, A is Ashes content, M is Moisture content, and FC is Fixed Carbon content.

Analysis	Output parameters	Standard
Laser diffraction granulometry	$d_{10}$ , $d_{50}$ , $d_{90}$ , D(4,3)	ISO 13320:2020
Ultimate analysis	Carbon, Hydrogen, Nitrogen, Oxygen	(ASTM D3176 – 15, 2015)
ATR-FTIR analysis	Spectra	–
Thermogravimetric analysis (TGA) – Inert atmosphere	DTG	–
Thermogravimetric analysis (TGA) – Oxidant atmosphere	IET, FET	–
Differential Scanning Calorimetry (DSC)	MWL Temperature	–
Proximate analysis	VM, A, M, FC	(ASTM D7582-15, 2009)

**Table 2**

Likely effects of parameter variation after ageing application on samples ignition sensitivity.

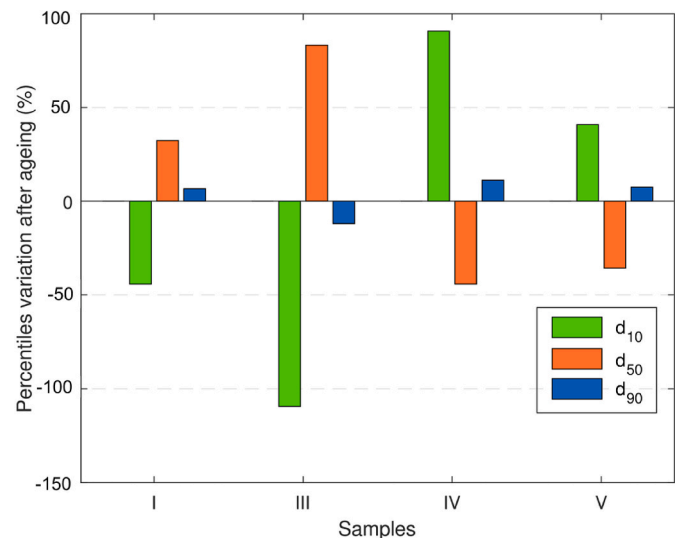
Parameters variation	Ignition sensitivity
Moisture reduction	Enhance
Particle size reduction	Enhance
Chemical composition variation	Enhance/Reduce
Structural characteristics (brittleness, stiffness)	Enhance
Hygroscopic reduction	Enhance/Reduce

### 3. Results and discussion

In the following, the characterization and MIE measurement results on samples subjected to treatment are compared to the original samples.

#### 3.1. Particle size distribution (PSD) and morphology variation

Fig. 2 shows the results of laser diffraction granulometry in terms of percentage variation of the percentile's distribution before and after the ageing. Ageing affects the morphology of samples differently from one to another: while sample I seemed to remain unchanged in the shapes of particles, aged sample V lost its flakes-like shape. Finer samples (II to IV)



**Fig. 2.** Effect of ageing on particle size distribution in terms of percentage variation of the percentile's distribution  $d_{10}$ ,  $d_{50}$  and  $d_{90}$  before and after the ageing.

undergo an agglomeration phenomenon and likely passivation of their outer particle layers (as clearly observed for sample II, where large agglomerates did appear and fines reduced greatly).

A PSD measurement (in terms of volume-weighted mean diameter D(4,3)) was carried out on all samples before and after dispersion in the Hartman tube to detect any PSD change, likely due to the impact of particles on tube walls, collisions, and abrasion (Sanchirico et al., 2015) (Table 3). Some indications could be obtained from the results of this test: samples with finer particles (II, III) likely went through some agglomeration process during the dispersion (D(4,3) slightly higher), while aged coarser samples (I and IV) did behave differently, likely due to the embrittlement of aged particles which are more prone to fracture and size reduction. This likely indicates an enhancement in the ignition sensitivity in the Hartman tube device since smaller particles are generated in the dispersion process and could be ignited more efficiently by the electric arc.

The Sample V size increases after dispersion for both untreated and aged samples. This sample is expected to have a lower ignition sensitivity as larger particles are exposed to the ignition source.

#### 3.2. Physico-chemical composition

Ultimate analysis results provide an overview of the elemental chemical composition of the samples. They are plotted into a Van Krevelen diagram to evaluate Carbon to Oxygen and Hydrogen ratios (Fig. 3) (Van Krevelen, 1950). For each sample, both H/C and O/C increase can be observed, moving from low values characteristic of fresher biomass with high lignin content (black square) to higher values of aged biomass more similar to cellulose (green rhombus).

Furthermore, ATR-FTIR spectra are qualitatively affected by ageing (not reported). Indeed, spectra have the same fingerprint after ageing as the original samples, but the peak intensities are different, particularly those relative to hemicellulose and lignin components. These peaks show a reduced intensity after ageing, likely due to reduced contents of the key components.

#### 3.3. Combustion behaviour and pseudo-components variation

Fig. S2 shows the DTG curves as a function of temperature for the TG/DSC analysis in  $N_2$  flow (left) and airflow (right). For all the samples, the trends were quite similar in quality, while the quantitative effects were highlighted by evaluating the characteristic temperatures and the amount of lignocellulosic components (Table 4). All samples exhibit the reduction of lignin and hemicellulose content and the increase of the cellulose content. The increase in the cellulose content can explain an increase in the reactivity in the homogeneous phase of the samples as its decomposition occurs at intermediate temperatures (about 320 °C) with the formation of flammable gases (especially CO). In the case of sample I, the maximum mass loss is anticipated at lower temperatures (i.e., low MWLT) which could explain a greater flammable character.

Proximate analysis results provide an overview of the share of each

**Table 3**

All samples' volume-weighted mean diameters (pre- and post-dispersion).

Sample	D(4,3) ( $\mu\text{m}$ )	D(4,3) Post Dispersion ( $\mu\text{m}$ )	$\Delta D(4,3)$ % due to Dispersion	$\Delta D(4,3)$ due to Ageing
I	77.6	78.7	+1%	+18%
I aged	91.5	76.3	-17%	
II	125.4	131.5	+5%	NA
II aged	>2000	>2000	NA	
III	311.1	335.4	+8%	-12%
III aged	274.7	298.9	+9%	
IV	225.6	225.8	0	+51%
IV aged	340.9	321.5	-6%	
V	208	324	+56%	+1%
V aged	211	254	+20%	

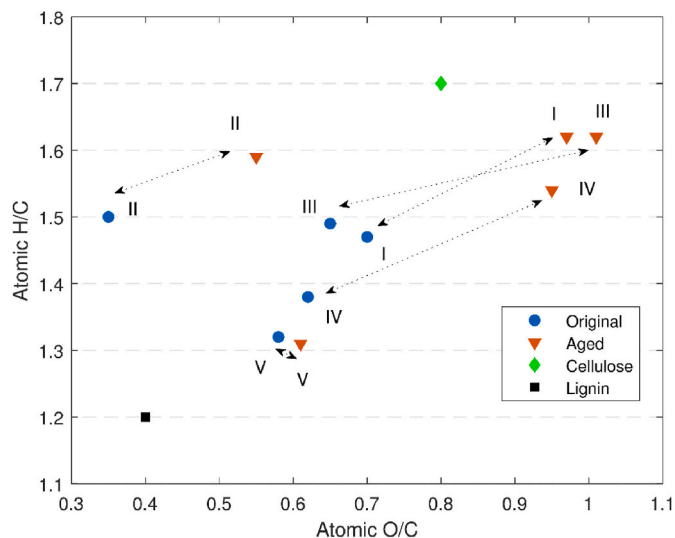


Fig. 3. Van Krevelen plot for the sample tested (original and aged), compared to pure cellulose and lignin.

Table 4  
MWLT, IET, FET and lignocellulosic components.

Sample	MWLT (°C)	IET (°C)	FET (°C)	Hemicellulose %	Cellulose %	Lignin %
I	310	203	500	58	15	27
I aged	287	206	500	19	72	9
II	413	270	458	18	58	24
II aged	410	244	489	10	70	20
III	354	268	442	59	36	5
III aged	354	275	414	44	53	3
IV	350	284	530	6	67	27
IV aged	360	294	530	0	72	27
V	320	240	460	31	14	55
V aged	330	250	481	29	23	48

material that could favour combustion (volatiles and carbon matter with respect to ashes). As shown in Table 5, samples I, II and IV show a reduction in the content of volatile components and an increase in the ash content, while other samples show an increase in the volatile content. In any case, the aged samples are drier than the original samples. It is worth noting that due to the increase in cellulose content, it is likely that volatile components are more flammable than the original samples.

### 3.4. Ignition energy

After the ageing treatment, some variations in the ignition sensitivity to electric spark could be observed when measuring MIE in the modified Hartman tube. Results are reported in Table 6. Less reactive original samples (I and V) showed increased sensitivity to ignition, with hotspots

Table 5  
Proximate analysis results.

Sample	M %	V %	A %	FC %
I	7.2	70.1	16.5	6.2
I aged	4.6 (-2.6)	67.9 (-2.2)	20.8 (+4.3)	6.7 (+0.5)
II	3.4	86.1	10.5	0
II aged	3.6 (+0.2)	76.4 (-9.7)	19.5 (+9.0)	0.5 (+0.5)
III	7.1	75.2	15.6	2.0
III aged	6.6 (-0.5)	76.9 (+1.7)	16.5 (+0.9)	0.0 (-2.0)
IV	5.4	69.6	20.3	4.8
IV aged	5.1 (-0.3)	68.1 (-1.5)	21.7 (+1.4)	5.1 (+0.3)
V	5.6	67.4	21.3	5.7
V aged	≈0 (-5.6)	70.1 (+2.7)	24.9 (+3.6)	5.0 (-0.7)

and sparks generations at each test condition, although no flame propagation was observed. Sample V sensitivity is enhanced after ageing since its MIE is reduced by 26%. This result is coherent with the moisture reduction due to drying (as seen in TG analysis) and to a visible (from optical microscope analysis) change in morphology, where quasi-spherical agglomerates are observed in the aged samples at the expense of flake-like particles. Original more reactive samples (II, III, IV) behave conversely: MIE is raised by ageing for samples II to IV, by 15% and 85%. This effect could be explained by the passivation of the outer particle surface during ageing, which prevents the sample from igniting at lower energies. This result can be observed in Fig. 2 (IV) for sample IV. Sample II undergoes a marked agglomeration process, resulting in the aged sample not being tested for MIE since PSD is too coarse for testing in the Hartman device ( $D(4,3) > 2000 \mu\text{m}$ ).

Table 7 illustrates the effect of the ageing process on the measured parameters: the arrows indicate the effect of ageing on each measured variable (the green colour indicates a variation towards a safer condition, while the red colour indicates a variation that determines the increase of the risk). The results of this work suggest that if the dust explosion risk has to be assessed in biomass power plants and facilities, dust ageing must be considered. This work proposes a complete procedure, including chemico-physical characterization and thermal screening, to get insight into the effect of lignocellulosic components content variation on explosion risk.

In order to rationalize the results obtained, reference is made below to dimensionless variables that consider the chemical-physical properties of the materials, such as  $D/D_{\text{post}}$ ,  $(O/C)/(H/C)$ ,  $\% \text{cellulose}/\% \text{lignin}$  and  $VM/M$ . The dependence of the minimum ignition energy value on each dimensionless variable is shown in Fig. 4. As can be seen, for each parameter are two clusters of data for  $\text{MIE} < 500 \text{ mJ}$  and  $\text{MIE} > 500 \text{ mJ}$ . It is important to note that an MIE value of 1000 mJ was established to account for materials characterized by low susceptibility to ignition by electrical discharge. As Fig. 4a shows, MIE for both clusters decreases with increasing  $D/D_{\text{post}}$ , i.e. the powder's tendency to fragment during dispersion and produce finer particles, but more so for the group where the MIE is below 500 mJ. Similarly, as the  $VM/M$  ratio increases, i.e. as the amount of volatiles increases or the moisture in the sample decreases (Fig. 4d). Surprisingly, the analysis of the MIE behaviour considering only the  $\% \text{cell}/\% \text{lignin}$  ratio shows a slight increase in the minimum ignition energy with increasing ratio (Fig. 4c), although the lignocellulosic fraction with a lower decomposition temperature associated with the production of combustible material increases. In the case of the ratio  $(O/C)/(H/C)$  (Fig. 4b), the trend differs depending on the data cluster considered. In particular, in the case of  $\text{MIE} > 500 \text{ mJ}$ , the MIE decreases as the ratio increases, whereas it increases in the case of  $\text{MIE} < 500 \text{ mJ}$ .

## 4. Conclusions

Biomass-derived fuels can be stored long before being used in power plants or energy recovery facilities. As a result, ageing may occur in storage facilities. Ageing is a chemical-physical process that can affect the material's chemical composition, morphology and brittleness. The

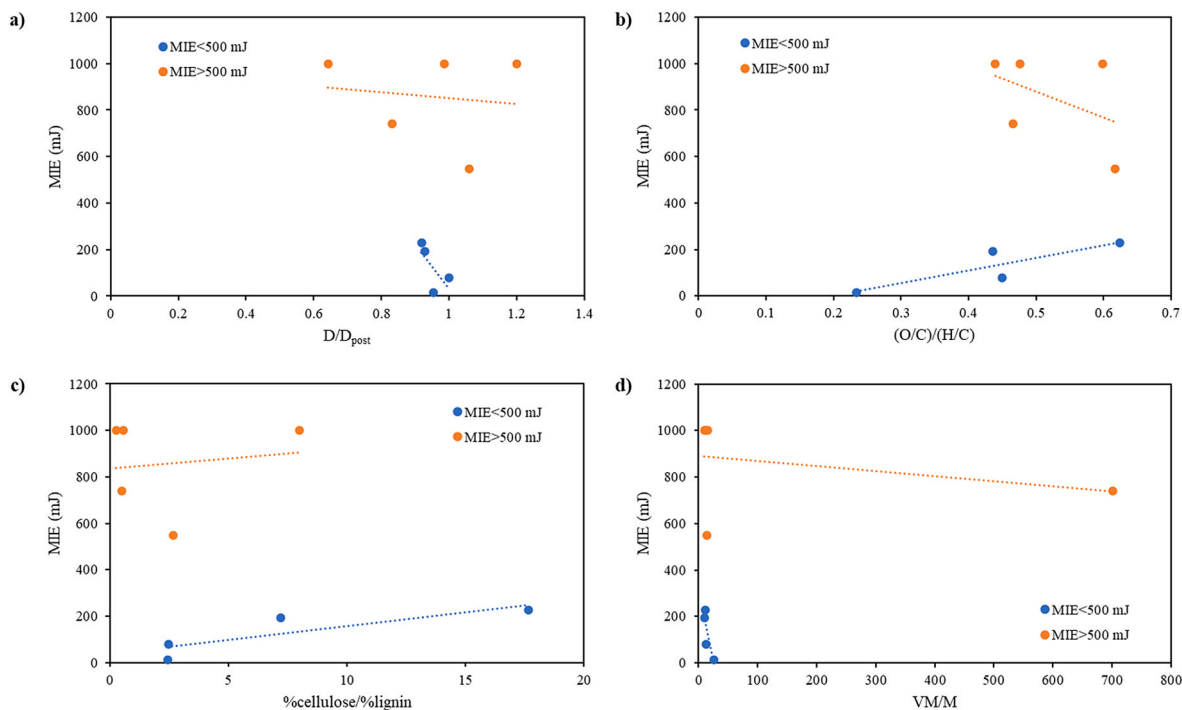
Table 6  
MIE measurements results.

Sample	MIE (mJ)	Comments after ageing
I	>1000	Sparks and hotspots at each concentration
I aged	>1000	
II	13.7	Not possible, $D > 500 \mu\text{m}$ , disk
II aged	Unknown	
III	193.3	-
III aged	227.9	
IV	79	-
IV aged	547.7	
V	>1000	Sparks and hotspots at each concentration
V aged	740	

**Table 7**

Effect of ageing on samples' parameters, where green indicates an expected reduction in ignition sensitivity, while red indicates enhancement of ignition sensitivity.

Sample	Effect of ageing (enhance, reduce, constant ↑ ↓ ≈)								
	D(4,3)	D(4,3) Post Dispersion	O/C	H/C	%cell	%lig	VM%	M%	MIE
I	↑	≈	↑	↑ <sup>a</sup>	↑	↓	↓	↓	↓
II	↑	↑	↑	↑ <sup>a</sup>	↑	↓	↓	≈	ND
III	↓	↓	↑	↑ <sup>a</sup>	↑	↓	↓	↓	↑
IV	↑	↑	↑	↑ <sup>a</sup>	↑	≈	↓	↓	↑
V	≈	↓	≈	≈	↑	↓	↑	↓	↓

<sup>a</sup> See also results from García Torrent et al. (2016) (García Torrent et al., 2016).**Fig. 4.** Measured MIE versus chemical-physical properties of the materials, such as D/Dpost (a), (O/C)/(H/C) (b), %cellulose/%lignin (c) and VM/M (d).

natural consequence is that ageing affects the reactivity and ignitability of these materials. The effects of ageing can vary depending on the material properties. Some materials showed a decrease in overall reactivity, while other samples behaved oppositely. The complex trend is likely due to the interaction of many variables affected by ageing: cellulose to lignin ratio, particle size and brittleness, and moisture content. Further investigations are needed on a larger number of biomass dusts in order to capture all the features and the main trend in function of all the variables.

#### CRedit authorship contribution statement

**Enrico Danzi:** Methodology, Investigation, Writing – original draft, Writing – review & editing. **Maria Portarapillo:** Methodology, Investigation, Writing – original draft, Writing – review & editing. **Almerinda Di Benedetto:** Conceptualization, Writing – review & editing, Supervision. **Roberto Sanchirico:** Writing – review & editing, Supervision. **Luca Marmo:** Writing – review & editing, Supervision.

#### 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

No data was used for the research described in the article.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jlp.2023.105157>.

#### References

- Adamski, R., Siuta, D., Kukfisz, B., Mitkowski, P.T., Szaferski, W., 2021. Influence of process parameters in superheated steam drying on fire and explosion parameters of woody biomass. *Fuel Process. Technol.* 211, 106597 <https://doi.org/10.1016/j.fuproc.2020.106597>.
- Amoyte, P., Khan, F., Boilard, S., Iarossi, I., Cloney, C., Dastidar, A., Eckhoff, R., Marmo, L., Ripley, R., 2012. Explosibility of nontraditional dusts: experimental and modeling challenges. *Inst. Chem. Eng. Symp. Ser.* 83–90.

- Andrews, G.E., 2014. Pulverised biomass flame propagation and explosion characteristics: problems and solutions. In: *Proceedings of the Meeting on Biomass Dust Explosions*. University of Leeds, Leeds, UK.
- ASTM D3176 - 15, 2015. Standard Practice for Ultimate Analysis of Coal and Coke. ASTM Int. West, Conshohocken, PA. <https://doi.org/10.1520/D3176-15.2>.
- ASTM D7582-15, 2009. Standard Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis. ASTM Int. West, Conshohocken, PA.
- Berrocal, A., Baeza, J., Rodríguez, J., Espinosa, M., Freer, J., 2004. Effect of tree age on variation of pinus radiata D. Don chemical composition. *J. Chil. Chem. Soc.* 49, 251–256. <https://doi.org/10.4067/s0717-97072004000300012>.
- Bs En 13821:2002, 2003. Potentially Explosive Atmospheres, Explosion Prevention and Protection, Determination of Minimum Ignition Energy of Dust/air Mixtures. European Standard EN 13821 3.
- Bs En Iso 17225-1:2021, 2021. Solid Biofuels—Fuel Specifications and Classes—Part 1: General Requirements.
- Castells, B., Amez, I., Medic, L., Garcia-torrent, J., 2020. Preliminary Study of Lignocellulosic Biomass Ignition Properties Estimation from Thermogravimetric Analysis 434–445. <https://doi.org/10.7795/810.20200724>.
- Centrella, L., Portarapillo, M., Luciani, G., Sanchirico, R., Di Benedetto, A., 2020. Synergistic behavior of flammable dust mixtures: a novel classification. *J. Hazard Mater.* 397, 122784 <https://doi.org/10.1016/j.jhazmat.2020.122784>.
- Cloney, C., 2021. 2020 Combustible Dust Incident Report - Version #1. DustEx Res. Ltd [WWW Document]. [www.dustsafetyscience.com](http://www.dustsafetyscience.com).
- Danzi, E., Di Benedetto, A., Sanchirico, R., Portarapillo, M., Marmo, L., 2021. Biomass from winery waste : evaluation of dust explosion hazards. *Chem. Eng. Trans.* 86, 301–306.
- Di Sarli, V., Danzi, E., Marmo, L., Sanchirico, R., Di Benedetto, A., 2019. CFD simulation of turbulent flow field, feeding and dispersion of non-spherical dust particles in the standard 20 L sphere. *J. Loss Prev. Process. Ind.* 62, 103983 <https://doi.org/10.1016/j.jlp.2019.103983>.
- Endo, K., Obataya, E., Zeniya, N., Matsuo, M., 2016. Effects of heating humidity on the physical properties of hydrothermally treated spruce wood. *Wood Sci. Technol.* 50, 1161–1179. <https://doi.org/10.1007/s00226-016-0822-4>.
- Ennis, T., 2016. Fire and explosion hazards in the biomass industries. *Inst. Chem. Eng. Symp. Ser.* 2016-Janua 1–9.
- European Environment Agency, 2019. *Adaptation Challenges and Opportunities for the European Energy System EEA Report No. 01/2019*.
- Fernandez-Anez, N., Slatte, D., Saeed, M.A., Phylaktou, H.N., Andrews, G.E., García Torrent, J., 2015. Ignition Sensitivity of Coal/Waste/Biomass Mixtures IGNITION SENSITIVITY OF COAL. WASTE/BIO MASS MIXTURES, Seep2015.
- García Torrent, J., Ramírez-Gómez, A., Fernandez-Anez, N., Medic Pejic, L., Tascón, A., 2016. Influence of the composition of solid biomass in the flammability and susceptibility to spontaneous combustion. *Fuel* 184, 503–511. <https://doi.org/10.1016/j.fuel.2016.07.045>.
- Hedlund, F.H., 2018. Carbon dioxide not suitable for extinguishment of smouldering silo fires: static electricity may cause silo explosion. *Biomass Bioenergy* 108, 113–119. <https://doi.org/10.1016/j.biombioe.2017.11.009>.
- Hu, M., Chen, Z., Wang, S., Guo, D., Ma, C., Zhou, Y., Chen, J., Laghari, M., Fazal, S., Xiao, B., Zhang, B., Ma, S., 2016. Thermogravimetric kinetics of lignocellulosic biomass slow pyrolysis using distributed activation energy model, Fraser-Suzuki deconvolution, and iso-conversional method. *Energy Convers. Manag.* 118, 1–11. <https://doi.org/10.1016/j.enconman.2016.03.058>.
- Huésca Medina, C., Maccotir, B., Sattar, H., Slatte, D.J.F., Phylaktou, H.N., Andrews, G.E., Gibbs, B.M., 2015. Comparison of the explosion characteristics and flame speeds of pulverised coals and biomass in the ISO standard 1 m3 dust explosion equipment. *Fuel* 151, 91–101. <https://doi.org/10.1016/j.fuel.2015.01.009>.
- IEA, 2022a. World energy outlook 2022 [WWW Document]. URL. <https://www.iea.org/reports/world-energy-outlook-2022/>.
- IEA, 2022b. Bioenergy [WWW Document]. URL. <https://www.iea.org/reports/bioenergy>.
- IEA Bioenergy, 2013. *Health and Safety Aspects of Solid Biomass Storage. Transportation and Feeding*.
- Islas, A., Fernández, A.R., Betegón, C., Martínez-Pañeda, E., Pandal, A., 2023. Biomass dust explosions: CFD simulations and venting experiments in a 1 m3 silo. *Process Saf. Environ. Protect.* 176, 1048–1062. <https://doi.org/10.1016/j.psep.2023.06.074>.
- Islas, A., Fernández, A.R., Betegón, C., Martínez-Pañeda, E., Pandal, A., 2022. Computational assessment of biomass dust explosions in the 20L sphere. *Process Saf. Environ. Protect.* 165, 791–814. <https://doi.org/10.1016/j.psep.2022.07.029>.
- Joint Research Centre European Commission, 2019. *Brief on Biomass for Energy in the European Union*.
- Krause, U., 2009. *Fires in silos*. In: *Hazards, Prevention, and Fire Fighting*. WILEY-VCH Verlag GmbH & Co. KgaA, Weinheim, Germany.
- Kukfisz, B., 2018. The potential fire and explosion hazards in biomass co-firing with conventional fossil fuels based on data obtained during testing. *E3S Web Conf* 45. <https://doi.org/10.1051/e3sconf/20184500039>.
- Lee, J.S., Sokhansanj, S., Lau, A.K., Jim Lim, C., Bi, X.T., Basset, V., Yazdanpanah, F., Melin, S.O., 2015. The effects of storage on the net calorific value of wood pellets. *Can. Biosyst. Eng./Le Genie des Biosyst. au Canada* 57, 8.5-8.8.12.
- Lin, S., Liu, Z., Zhao, E., Qian, J., Li, X., Zhang, Q., Ali, M., 2019. A study on the FTIR spectra of pre- and post-explosion coal dust to evaluate the effect of functional groups on dust explosion. *Process Saf. Environ. Protect.* 130, 48–56. <https://doi.org/10.1016/j.psep.2019.07.018>.
- Liu, A., Chen, J., Lu, X., Li, D., Xu, W., 2021. Influence of components interaction on pyrolysis and explosion of biomass dust. *Process Saf. Environ. Protect.* 154, 384–392. <https://doi.org/10.1016/j.psep.2021.08.032>.
- Marmo, L., Ferri, A., Danzi, E., 2019. Dust explosion hazard in the textile industry. *J. Loss Prev. Process. Ind.* 62, 103935 <https://doi.org/10.1016/J.JLP.2019.103935>.
- Miranda, T., Montero, I., Sepúlveda, F.J., Arranz, J.I., Rojas, C.V., Nogales, S., 2015. A review of pellets from different sources. *Materials* 8, 1413–1427. <https://doi.org/10.3390/ma8041413>.
- Pietraccini, M., 2019. *Explosibility and Flammability of Four Olive Pomace Dust Samples*. Politecnico di Torino.
- Pietraccini, M., Danzi, E., Marmo, L., Addo, A., Amyotte, P., 2021. Effect of particle size distribution, drying and milling technique on explosibility behavior of olive pomace waste. *J. Loss Prev. Process. Ind.* 71, 104423 <https://doi.org/10.1016/j.jlp.2021.104423>.
- Portarapillo, M., Danzi, E., Sanchirico, R., Marmo, L., Di Benedetto, A., 2021a. Energy recovery from winery waste: dust explosion issues. *Appl. Sci.* 11 <https://doi.org/10.3390/app112311188>.
- Portarapillo, M., Luciani, G., Sanchirico, R., Di Benedetto, A., 2020a. Ignition mechanism of flammable dust and dust mixtures: an insight through thermogravimetric/differential scanning calorimetry analysis. *AIChE J.* 66 <https://doi.org/10.1002/aic.16256>.
- Portarapillo, M., Sanchirico, R., Di Benedetto, A., 2021b. On the pyrotechnic ignitors role in dust explosion testing : comparison between 20 L and 1 m 3 explosion vessels. *Process Saf. Prog.* 40, 289–295. <https://doi.org/10.1002/prs.12249>.
- Portarapillo, M., Trofa, M., Sanchirico, R., Di Benedetto, A., 2022. CFD simulation of turbulent fluid flow and dust dispersion in the 1 m3 explosion Vessel equipped with the rebound nozzle. *J. Loss Prev. Process. Ind.* 76, 104755 <https://doi.org/10.1016/j.jlp.2022.104755>.
- Portarapillo, M., Trofa, M., Sanchirico, R., Di Benedetto, A., 2020b. CFD simulations of dust dispersion in the 1 m3 explosion vessel. *J. Loss Prev. Process. Ind.* 68, 104274 <https://doi.org/10.1016/j.jlp.2020.104274>.
- Sanchirico, R., Di Sarli, V., Russo, P., Di Benedetto, A., 2015. Effect of the nozzle type on the integrity of dust particles in standard explosion tests. *Powder Technol.* 279, 203–208. <https://doi.org/10.1016/j.powtec.2015.04.003>.
- Sandberg, D., Haller, P., Navi, P., 2013. Thermo-hydro and thermo-hydro-mechanical wood processing: an opportunity for future environmentally friendly wood products. *Wood Mater. Sci. Eng.* 8, 64–88. <https://doi.org/10.1080/17480272.2012.751935>.
- Van Krevelen, D.W., 1950. Graphical-statistical method for the study of structure and reaction processes of coal. *Fuel* 29, 219–228.
- World Bioenergy Association, 2019. *Global Bioenergy Statistics*.
- Worsfold, S.M., Amyotte, P.R., Khan, F.I., Dastidar, A.G., Eckhoff, R.K., 2012. Review of the explosibility of nontraditional dusts. *Ind. Eng. Chem. Res.* 51, 7651–7655. <https://doi.org/10.1021/ie201614b>.
- Zhao, C., Jiang, E., Chen, A., 2017. Volatile production from pyrolysis of cellulose, hemicellulose and lignin. *J. Energy Inst.* 90, 902–913. <https://doi.org/10.1016/j.joei.2016.08.004>.