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Biomass from Winery Waste: Evaluation of Dust Explosion Hazards

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Food and drink supply chains have significant environmental impacts due to their use of resources, emissions, and waste production. An efficient method to reduce this impact is the valorisation of biomass waste through energy recovery by using it as a source of heat. The European energy system faces several fundamental challenges being currently the largest emitter of greenhouse gases due to its large dependence on fossil fuels (mostly natural gas). Therefore, the energy sector's decarbonization will play a central role in achieving a climate‑neutral economy in Europe. Identifying the suitable material for biofuel is basically focused on the amount of energy that the material stores, availability, and logistic considerations. Sawdust and wood chips have been extensively used as biofuel in recent years, but other promising raw and waste materials could be adopted (with the positive effect of reducing the impact on forestry soil and the food chain). Novel materials bring consequently novel challenges, also regarding their safe use. As an example, a relevant waste flow is produced from wine manufacturing. A solid with high moisture content is obtained from grapes pressing, and it could be reused to produce distillates. The obtained exhausted pomace could be considered among the materials potentially involved in energy recovery. It is also carrying dust explosion hazard, as solid residues could be present in the form of coarse and fine powders.

In this work, grape pomace is examined: its explosion safety-related properties are evaluated to define the severity of events in which this material could be ignited. Minimum Ignition Energy (MIE), explosion pressure peak (P_{max}), deflagration severity index (K_{St}), autoignition temperature (MIT), and Volatile Point (VP) are measured according to standard procedures. This material's thermal susceptibility and ignition sensitivity are studied and compared with biomasses from different sources (ligneo-cellulosic and herbaceous).

1. Introduction

The wine production chain generates a relevant amount of waste, both in the form of liquid and solid materials. Solid wastes and wastewater are generated mainly during the harvesting stage: from one ton of grapes, 0.13 ton of merc, 0.06 of lees, 0.03 of stalks, and 1.65 m^3 of wastewater (Oliviera and Duarte, 2016). Only in Italy (among the largest world producers together with Spain and France) about 8.4 Mton of grapes are processed each year (OIV, 2020): this will lead to approximately one million tons of grape merc to be disposed of. Currently, winery solid wastes are treated by distillation, composting, or sent to landfills. According to European Council Regulation (EC) No 491/2009, grape merc has to be sent to alcohol distillery facilities, where exhausted grape and vinasse (liquid waste) are generated; exhausted grape has the same disposal issues as the non-distilled material (Zhang et al., 2017). Besides this, storage of this material is also not easily practicable because of fermentation reaction which could undergo into the mass bulk, giving undesired products or even self-heating issues, that could degenerate into fires (EPA, 2001).

The EU approach to waste management is addressed to prioritize prevention, reuse, recycling, and recovery with respect to landfill disposal, which is the worst environmental option (General Union environment action

program to 2020). In this context, the winery solid waste becomes a valuable material if different approaches are targeted: beyond distillation, grape pomace could be processed for animal feeding industry, extraction of valuable molecules for pharmaceutical and fine chemicals products (such as polyphenols), and to recover energy. This last option is considered due to the energetic residual content of pomace associated with sugars, mainly polysaccharides (cellulose), which could be converted through combustion processes. Its calorific power, lower with respect to hydrocarbons, and its relatively high CO_2 production in combustion could be seen as disadvantages, though its low cost and its carbon-neutral nature could overcome these adverse effects. The most promising transformation for grape pomace could be pyrolysis treatment (Marculescu & Ciuta, 2013) since it does not require thermic input (the process is only slightly endothermic), but also the pelletization of grape pomace is considered recently as a viable alternative to forest residues (Burg et al., 2017). All these applications are relatively recent and still require improvements in process efficiency. Simultaneously, the safety concerns need to be considered carefully: grape pomace stockpiles could self-ignite, and even dust explosion hazards could arise since grape pomace residues (from the exhausted waste of distillery) are present in the form of coarse and fine particles. This work presents the thermal characterization and explosibility of a grape pomace sample, trying to underline the safety key parameters to monitor and analyze the potential hazards of this type of material compared with other biomass-derived dust (Table 1).

Table 1: Explosibility of different biomass dust samples

Sample	Type	d_{10} [um]	K_{St} [bar m/s]	Reference
Olive pomace	Fruity	43	45	Pietraccini et al., 2021
Olive pomace	Fruity	19	70	Pietraccini et al., 2021
Grape pomace	Fruity	69.6	57.8	This work
Southern pine	Woody	28.4	105	H. Medina et al., 2015
Northern pine	Woody	25.4	95	H. Medina et al., 2015
Dalbergia Cochinchinensis	Woody	38.3[1]	217.5	Liu et al., 2019
Pine sawdust	Woody	36.5[1]	194.4	Liu et al., 2019
Cupressus Funebris	Woody	32.5[1]	206.3	Liu et al., 2019

[1] Values refer to d_{50}

2. Grape pomace sample characterization and thermal behavior

Laser diffraction granulometry was used to characterize the granulometric distribution of grape pomace dust. From the optical microscopy, it is possible to analyze the sample's morphology, its shape heterogeneity, such as fibers, flakes of different sizes, and smaller aggregates. This heterogeneity could play an essential role in the sample's explosive behavior: different shapes can be generated by handling and processing the original material, which behaves differently due to its "resistance" to grinding and crushing actions. Likely, parts of the original sample with different chemical nature (grape skins, seeds, and other residues) generate particles with different shapes and, consequently, different sensitivity to ignition (the same applies for other biomass heterogeneous samples as in Pietraccini et al., 2020). In this case, lignin is likely the main component of flakes, thus significantly influencing the explosion reaction. During this work, different analytical techniques were employed to verify this assumption, from FTIR analysis to thermal characterization of the sample through proximate analysis, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). FTIR analysis was carried out in transmission mode in the range 400–4000 cm^{-1} using KBr disks prepared by mixing 2 mg of sample and 200 mg of KBr. This technique was used to confirm the sample's chemical nature (i.e., lignocellulosic biomass) and, given the spectrum, to compare it with those typical of lignin, hemicellulose, and cellulose. TGA/DSC TA Instrument Q600SDT was used to perform TGA/DSC and proximate analysis, following the ASTM D5142-09 method (ASTM, 2009). Briefly, a 10 mg sample was placed in an alumina crucible and heated up to 1000 °C (heating rate: 10 °C/min) under a nitrogen flow (0.1 l(STP)/min). If the first derivative of the thermogravimetric (TG) curve is calculated, a second curve called DTG is obtained. This second curve provides relevant data such as the maximum weight loss temperature (MWL), which is the temperature at which the highest decrease of weight occurs (i.e., the temperature of the inflection point of weight loss and maximum value of DTG). Moreover, it can be used to estimate the main components of lignocellulosic materials by calculating the deconvolution of the DTG curve. The pseudo-components obtained will be cellulose, hemicellulose, and lignin, and the area beneath those curves will represent the percentage of each component. Different deconvolution methods are present in the literature (Jankovic et al., 2019; Perejon et al., 2011; Sronsi and Boonchom, 2018). In this study, Fraser-Suzuki deconvolution (Hu et al., 2016) was used, and the approach was considered good enough (R^2 equal to 0.99). Moreover, TGA/DSC analyses were

performed in oxidative atmosphere: the sample was heated up to 1000 °C (heating rate: 10 °C/min) under airflow (0.1 l(STP)/min). In this case, two important parameters are obtained directly from the DTG curve: Initial Exothermic reaction Temperature (IET), which is the temperature at which the exothermic process begins, and Final Exothermic reaction Temperature (FET), which is the temperature at which the exothermic reaction ends. Minimum Ignition Energy (MIE), explosion pressure (P_{max}), deflagration severity index (K_{St}), autoignition temperature (MIT), and Volatile Point (VP) are measured according to standard procedures (EN 14034-1 to 4, 2011; ISO 80079-20:2016; Sanchirico et al., 2018).

3. Results

Grape pomace dust analyzed here has a broad Particle Size Distribution (PSD), with a 90th percentile equal to 633.7 um and a 10th percentile of 69.6 um (Figure 1, left). Its fine fraction, i.e., lower to 500 μm, is about 71.3%.
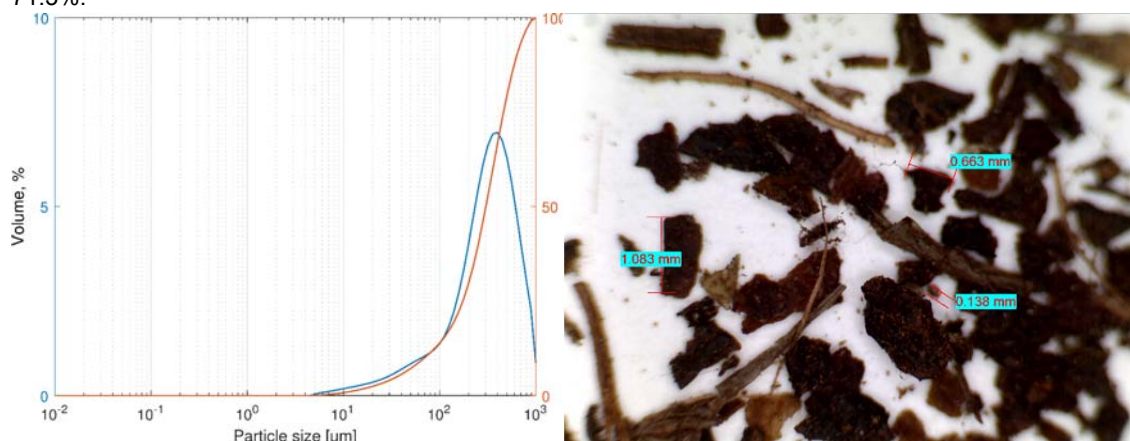

Figure 1: Grape pomace dust (PSD) (left) and Grape pomace dust optical microscope image (right)

Figure 1, right, represents the grape pomace dust seen at the optical microscope. The sample's morphology is complex: particle shape is heterogeneous as fibers, flakes of different sizes, smaller aggregates (with one size minor than approximately 100 um) are present. Figure 2 shows the FTIR spectrum as measured for the grape pomace dust. The peaks are those typical of a lignocellulosic biomass: 3389, 2922, 2860, 1740, 1650, 1510, 1451, 1420, 1365, 1320, 1244, 1161, 1120, and 890 cm^{-1}. Moreover, the spectrum shows the typical (Galletti et al., 2015) lignin fingerprint (1000-2000 cm^{-1}), qualitatively confirming the assumption above reported.
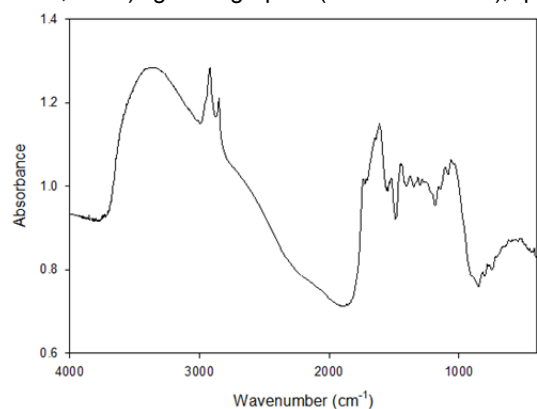

Figure 2: Grape pomace dust FTIR spectra

Figure 3, left, shows the weight percentage and DTG curves as a function of temperature for TG/DSC analysis in N_2 flow. DTG curve exhibits two peaks: the former at low temperature is related to the moisture loss while the latter to the pyrolysis of lignocellulosic components. Following the standard test method, we carried out the proximate analysis from the weight loss curve, which results are given in Table 2. It is worth noting that the volatile content is very high, so it is reasonable to assume that the sample, if dispersed in air, will be subject to homogeneous combustion controlled by the devotatilization process. However, it is worth noting that the peak

temperature corresponding to the pyrolysis step's activation is very high (about 380°C). This data suggests that the onset of the pyrolysis could control the explosion.
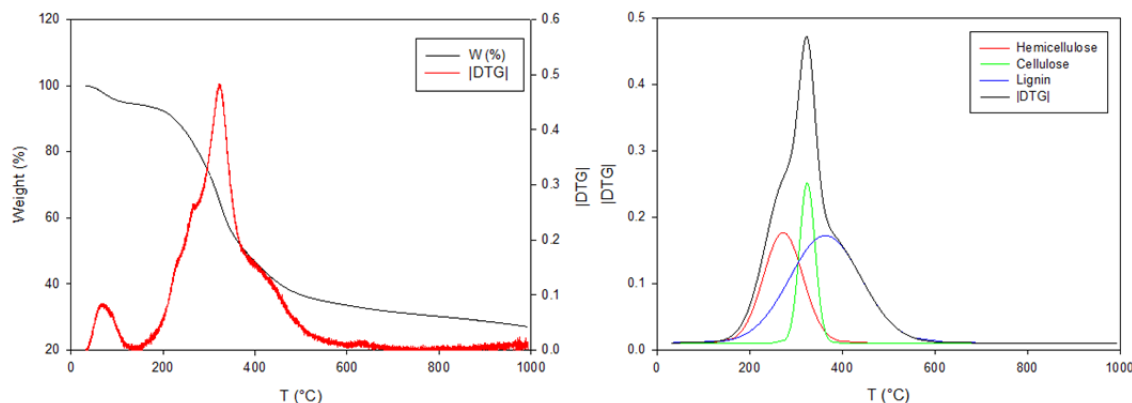

Figure 3: Weight percentage and DTG curves as a function of temperature, TG/DSC analysis, 10 °C/min, N_2 flow (left), and deconvolution through Fraser-Suzuki equation of DTG curve (right).

Table 2: Grape pomace dust proximate analysis

Proximate analysis	Percentage (%)
Moisture	5.6
Volatile	67.4
Ash	26.9
Fixed carbon	5.7

Figure 3, right, shows the DTG and the hemicellulose, cellulose, and lignin peaks as a temperature function, as obtained through the Fraser-Suzuki equation. The amount of each component and the deconvolution parameters are reported in Table 3. As qualitatively observed from the FTIR spectrum, the sample mainly consists of lignin (55.2 %) and contains a small amount of cellulose (14.3 %).

Table 3: Grape pomace dust thermal characterization, TG/DSC analysis, 10 °C/min, N_2 flow and Fraser-Suzuki deconvolution parameters (R^2=0.99)

Parameters	Value	Parameters	Hemicellulose peak	Cellulose peak	Lignin peak
		Fraser-Suzuki deconvolution parameters			
Maximum weight loss temperature (MWL)	320 °C	Xc [°C]	272.3	324.4	363.7
Hemicellulose content	30.5 %	A [NU]	26.9	12.6	48.5
Cellulose content	14.3 %	Sig [NU]	64.5	20.8	119.8
Lignin content	55.2 %				

Figure 4 shows the weight percentage and DTG curves as a function of temperature for TG/DSC analysis in airflow. In this case, the DTG curve exhibits three marked peaks. The first peak is relative to the hemicellulose exothermic reaction (peak temperature 300 °C). The second is very sharp and is related to cellulose combustion (peak temperature 426 °C) while the last to lignin reaction (peak temperature 460 °C). From this result, the effect of the relative content of the three components, which have different reaction temperatures, on the flammability/explosibility parameters is more understandable. The exothermic process starts at 200 °C (IET) and finishes 525 °C (FET), with a final solid residual equal to 10 %, attributable to char.

It is worth noting that hemicellulose is the major contributor to volatiles. However, it generally gives mainly CO_2. Thus, not really contributing to the propagation of the explosion/flammability process of the dust. Conversely, lignin generates CH_4, and cellulose generates CO (Zhao et al., 2017).
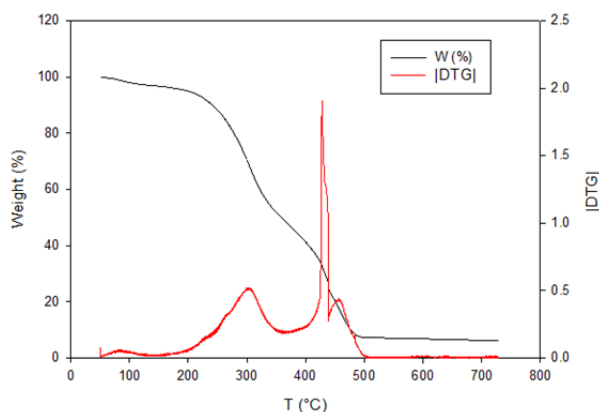
Figure 4: Weight percentage and DTG as a function of temperature, TG/DSC analysis, 10 °C/min, airflow

From Table 4, MIE analysis showed how the sample was not sensitive to be ignited by an electrical spark with associated energy lower than 1 J. Despite the high volatile content, VP (i.e., the temperature at which volatiles are produced from the dust-generating a flammable vapor mixture at LFL) is > 300 ° C. Regarding MIT, no flame instantaneously came out from the apparatus, but instead, the flame appeared after 2-3 seconds from the injection of the powder, maybe due to the off-gases ignition into the chamber (flash fire). Finally, from the explosibility parameters, the dust can be classified in the St-1 class. The high MIT and VP values are related to the nature of the volatiles produced from hemicellulose, cellulose, and lignin. Hemicellulose produced volatiles at low temperature (xc=272.3 °C, Table 3), but mainly CO_2. Conversely, the cellulose and lignin produced flammable volatiles (CO and CH_4, respectively), but their production is activated at much higher temperatures (Table 3). Likely, the pyrolysis/devolatilization step may be the limiting one involved in the dust flame propagation. Even if more prone to volatilisation, hemicellulose fails to enhance the flame propagation due to its decomposition into low reactive volatile gases. These results could arise further studies on the cellulose and lignin influence on explosibility. The lignin effect on MIE is not clear where it seems not to have any impact (as also in Castells et al., 2020). Conversely, MIT is more similar to the AIT of lignin (lignin peak temperature in the oxidative atmosphere is 460°C). G. Torrent et al. (2015) have found some indications that the increasing content of lignin in biomass dust samples seems to affect the self-ignition tendency than the volatile matter content positively.

Table 4: Explosibility properties

Parameters	Value
K_{St}	57.8 bar m/s
P_{max}	6.3 bar
MIT_{Cloud}	480 °C
MIT_{Layer}	290 °C
MIE	>1000 mJ
Volatile Point	>300 °C

4. Conclusions

The figure of solid biomass is increasing in the energy generation overview and, together with it, the potential risks associated with the handling and storage of such material. The authors have identified grape pomace among those dusty materials, which could constitute an explosion hazard if not properly handled or disposed of since its organic characterisation and relatively high content of energetic molecules such as sugar and lignin. Despite this, poor attention is paid to dust explosion hazards in the literature background. In contrast, biomass dust studies only recently had focused their attention not only on "flammability" parameters but also on the thermal behavior, as an indicator of the combustion/pyrolysis reaction role on reactivity. This work underlines thermogravimetric analysis's relevancy to recover information about biomass composition and expected behavior when exposed to temperature increase. From these results, it is suggested that the very high lignin content of grape pomace affects the combustion process, leading to low reactivity. The pyrolysis temperature of lignin is higher than that of other components (thus leading to a likely lower sensitivity to ignition). Grape pomace dust belongs to the St-1 class (K_{St} 57.8 bar m/s and P_{max} 6.3 bar) and exhibits quite a

high cloud autoignition temperature (480 °C) and Minimum Ignition Energy (> 1000 mJ). Further tests will study the sample's elementary composition to compare the C to O and O to H ratios with other biomass dust to define the energetic potential and set it against the explosibility parameters.

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