Some Key Considerations when Evaluating Explosion Severity of Nanopowders

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Protection from explosion events requires the determination of key safety parameters like lower explosion limit, maximum explosion over-pressure, and maximum rate of pressure rise. These parameters are routinely obtained through standard tests performed typically either in a 20 L sphere or a 1 m^3 container. But several aspects are worth a closer investigation. Firstly, the test apparatus must be able to disperse a fairly uniform dust cloud. However, previous investigations showed that actually the current dispersion system can be improved. Indeed, as a function of the sample and the dispersion conditions, the dust concentration in the ignition zone can be significantly different from the nominal dust concentration. Moreover, due to agglomeration/fragmentation phenomena, the particle size distribution can greatly evolve during dust injection. Secondly, the influence of humidity on the explosivity is not considered in current standards. It is just stated that the relative humidity should be checked and noted down, though some provisions exist in American standards. Even when performing the powder injection with synthetic air, the water contained in the residual air of the sphere can impact the chemical reactions occurring during the explosion. Thirdly, the ignition delay time is sometimes modified to study the impact of the dust cloud turbulence on flame propagation but is often misunderstood. For instance, by decreasing the ignition delay time, the injection time of the powder becomes shorter for the same pressure difference. This modifies the dispersion kinetics and can change the particle size distribution. Finally, for very sensitive powders, pre-ignition can occur or the ignition energy sets at 10kJ can lead to an overdriving phenomenon. Maybe these aspects have not been thoroughly considered for micron powders. However, in the case of nanopowders, the importance of these influencing factors was shown in order to duly evaluate explosion parameters. Experimental evidences confirm these aspects and alternative solutions will be presented.

1. Introduction

In 2012, CEN, CENELEC and ETSI have received a mandate by European Commission to provide standardisation deliverables regarding nanotechnologies and nanomaterials. Through resolution BTC 98/2010, CEN Technical Board accepted M/461 Standardization Mandate to CEN, CENLEC and ETSI for standardisation activities regarding nanotechnologies and nanomaterials to take the specific properties of nanomaterials into account. Through M/461, the European Commission requested CEN/TC 352 to publish a Technical specification (TS) entitled "Protocols for determining the explosivity and flammability of nanopowders (for transport, handling and storage)" by the end of 2018. The EU project group (PG) reviewed the available investigations on the explosivity of nanomaterials and agreed that the current approaches could support the production of relevant data for the loss prevention engineers, though some questions are still pending on the interpretation of these results and their extrapolation at large scale. In that context, the PG proposed some additional provisions so that the physico-chemical properties of the powders are characterized further on a systematic routine in order that future standardization work can rely on a compendium of fully

reliable data. Beyond this current consensus, it is however necessary to enlighten the current bottlenecks on the specific behaviour of nanomaterials in order to ensure that explosivity data can provide a representative picture of the industrial worst-case scenario. In this paper, the main parameters of importance to assess dust explosivity are briefly reviewed and recent work that highlights the need to be careful while assessing explosivity of nanomaterials is presented.

2. Standards and beyond

Explosion behaviour characteristics can be determined in Europe according to EN ISO/IEC 80079-20-2:2016 (EN, 2017) and more conventionally according to EN 14034 standards, using a 20 L sphere or a 1 m^3 vessel. Moreover, in order to perform the tests in a due manner, it is also necessary to rely on the guidelines of the standard manufacturer (Cesana and Siwek, 2016). These documents specify various aspects related to the type of nozzle, the ignition delay time, the level of ignition energy, the dispersion procedure, the type of air that should be injected, the importance of humidity and so on. However, it should be noted that some provisions in these guidelines are not reported in the EN 14034 standards. These statements show clearly that several questions are still pending and that there is still no full consensus on what the best experimental conditions are to assess explosivity of a dust. For instance, a powerful 10 kJ ignition source is routinely used to do the tests whereas it is acknowledged that such a strong ignition source is not likely to be found in a plant and tend to overdrive the explosion. The influence of water content is not discussed as well whereas it can either hinder or enhance explosion severity through heat sinking effect, water vaporization, specific reactions with the powder and no recommendations are provided contrary to ASTM 1226-12a. The impact of the nozzle on the dispersion of the nanopowders such as melting effects, irreversible breakage of fibers and impact on the turbulence level along the time, requires further discussion. Finally, it is often considered for practical reasons that tests under air are the most conservative but decreasing the content of oxygen in air could either decrease or increase the explosion severity depending on the nature of the products. These different aspects are investigated in more details in the following sections and specific statements are highlighted for nanopowders.

Table 1: Properties of the nanopowders used in this study.

Powder	Primary particle size (nm)	Specific surface area ($m^2.g^{-1}$)	Mean volume diameter d_{50} by sedimentation (µm)	Mean volume diameter d_{50} after dispersion (µm)
Carbon black	75	40	24	4
Aluminium	96	23	4	3
Nanocellulose	3 nm width, 70 nm length	400	41	13

The previously mentioned parameters can affect the explosion severity depending on the nature of the powder and its properties. Thereby, the 'more suitable' operating conditions can vary as a function of the nature of the dust. Three powders, representing carbonaceous, metallic and organic compounds, were characterized before and after dispersion in the 20 L sphere. Their explosion severities were measured under various experimental conditions, including standard ones (Table 1). The ignition delay time (tv) was varied from 20 ms to 120 ms to highlight the influence of turbulence on explosion severity and flame propagation; 60 ms being the standard value. The influence of the relative humidity was also studied by analysing the composition of the combustion gases by gas chromatography. Moreover, tests were carried out with a new symmetric nozzle to evaluate the breakage of the agglomerates and the homogeneity of the dust cloud (Murillo et al., 2018). Finally, both 100 J and 10 kJ chemical igniters were used to highlight the impact of ignition energy on the explosion severity of nanopowders.

3. Results: nano changes, big differences?

3.1 Dispersion nozzle: chaos from symmetry?

Two standard nozzles can be used to disperse a dust in the 20 L sphere: a perforated annular nozzle and a rebound nozzle. Nevertheless, several alternative proposals were done by other authors to disperse the powder adequately and reduce the heterogeneity of the dust cloud (Dahoe, 2000; Krietsch et al., 2015). More recently, a new symmetric nozzle was proposed to improve the experimental reproducibility by increasing the temporal stability of the nominal dust concentration (Murillo et al., 2018). Explosion tests with various nanopowders were carried out in the 20 L sphere. The rebound nozzle or the symmetric one were used with a 60 ms ignition delay time. Figure 1 shows that the maximum explosion pressure is not modified by changing the dispersion nozzle, and thus is not affected by the dust cloud turbulence. However, the dust deflagration

index K_{St} of carbon nanoparticles greatly varies as a function of the nozzle. The K_{St} parameter is increased by using a rebound nozzle, which generates a greater level of turbulence. Consequently, the rebound nozzle seems to deliver most conservative results though results can be quite poorly reproducible. The experimental reproductibility can however be much improved by dispersing the powder through a symmetric nozzle, as previously observed (Murillo et al., 2018).

It is also worth noting that the nozzle geometry has not only an influence on the turbulence, but also on the dust fragmentation. The latter effect is probably more pronounced for nanoparticles than for microparticles due to their high propensity to agglomerate (Table 1). Tests were also performed without nozzle and show that the fragmentation phenomenon also occurs in these conditions. Other injection methods may be considered for nanopowders, such as dust lifting, i.e. the dust is placed at the bottom of the nozzle and is lifted by an air pulse. However, the efficiency of the dust dispersion greatly varies as a function of the dust density and agglomeration level, which usually makes this procedure less reliable.
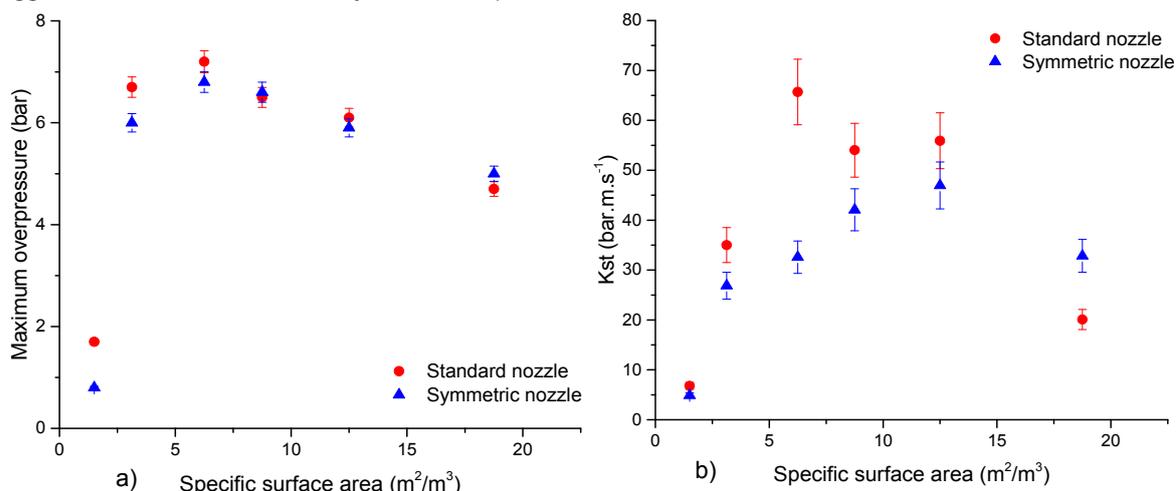
Figure 1: (a-left) Maximum overpressure and (b-right) dust deflagration index K_{St} of carbon black nanoparticles with two different nozzles as a function of the total surface area of particles per cubic meter of cloud

3.2 Not too late: the importance of the ignition delay time

As previously mentioned, 60 ms is considered as the standard ignition delay time. However, it clearly appears that, due to the great variability of the powders density and particle size distribution, a single standard tv will not lead to the same dust cloud distribution within the sphere. Several experimental and numerical studies have demonstrated that the turbulence of the dust cloud evolves temporally in three phases (Dahoe, 2000; Murillo et al., 2018). The second phase, a transition phase from 40 to 120 ms (including 60 ms), is characterised by a significant decrease of the velocity fluctuations.
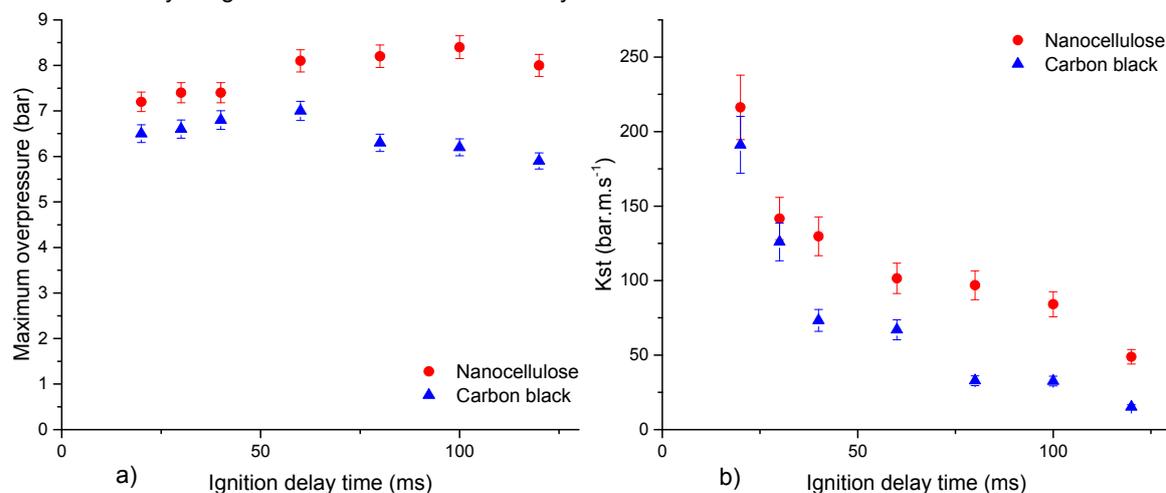
Figure 2: Evolution of (a-left) the maximum overpressure and (b-right) the deflagration index K_{St} of nanocellulose (750 g.m^{-3}) and carbon black (250 g.m^{-3}) as a function of the ignition delay time

In Figure 2a, the maximum overpressure shows a maximum both for nanocellulose and carbon black. A low tv, i.e. a high turbulence will lead to flame quenching phenomena on a local scale, whereas a moderate turbulence tends to enhance the flame propagation by increasing the flame stretching and improving the mass transfers. Figure 2b underlines the positive impact of the turbulence on the combustion kinetics, which is consistent with results shown in Figure 1. Indeed, different rate-limiting steps can be encountered during the dust combustion. When the diffusion through the gas film is significant, a higher turbulence may improve the mass transfer coefficient and consequently the dust explosivity. When surface reaction is the rate-limiting step, a shift in the particle size distribution due to agglomerates fragmentation should also be considered. In the specific case of nanopowders, diffusional limitation is unlikely but such limitation is expected for agglomerates. It should also be highlighted that nanoparticles can be considered as tracers of the gas flow, unlike most of the micropowders. However, as the nanopowders are heavily agglomerated, they are also sensitive to high shear stress of the turbulent gas flow and then to variation of the ignition delay time. Finally, the dustiness of nanopowders has also a strong impact on the flame propagation and notably on the radiative heat transfer ahead of the flame front (Torrado et al., 2016).

3.3 Water to fire

The influence of water on dust explosions, although often not well developed by current standards, can be important. It can either be the moisture content of the powders or the water vapour present in the explosive atmosphere. Experiments carried out recently on carbon nanopowders stored under air for more than ten years clearly demonstrated that their moisture content was increased. Such phenomenon tends to agglomerate the nanoparticles and significantly reduces their explosion severity (Santandrea et al., 2018). Indeed, the agglomerates cannot be entirely broken up during the dust dispersion process, which limits the reactive surface area. The influence of water adsorbed onto particles should also be considered, especially for powders with a high specific surface area, such as nanoparticles. Similar explosion tests were also performed on dry nanopowders. Figure 3 shows the influence of the ignition delay time on the composition of the burnt gases generated by the explosion of the carbon black at 250 g.m^{-3}. If the evolution of the carbon monoxide and dioxide contents are easily understandable due to the presence of flame quenching and incomplete combustion at very high turbulence levels, the presence of hydrogen can be surprising. Indeed, the combustion of pure carbon must obviously not lead to the generation of compounds containing hydrogen.
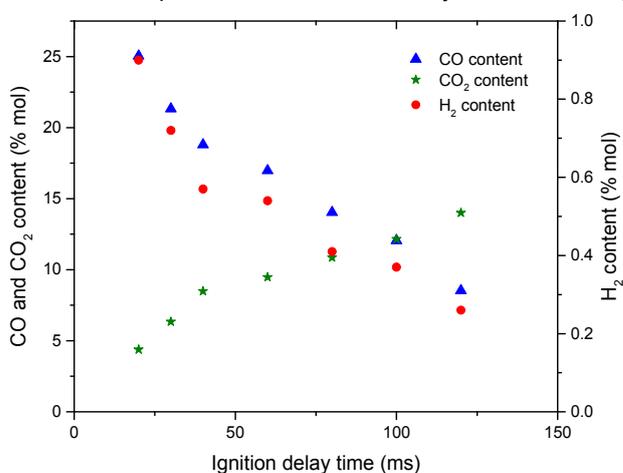
Figure 3: Evolution of the hydrogen, carbon monoxide and carbon dioxide content after combustion of carbon black nanopowders as a function of the ignition delay time

However, it should be reminded that, before the dust injection, the 20 L sphere is vacuumed at 0.4 bara. The remaining water vapour can reach approximately 0.4%. By considering the reaction between water and carbon monoxide at high temperature and the generation of carbon dioxide and hydrogen, it was demonstrated that the hydrogen content observed in Figure 3 was consistent with such amount of residual water (Santandrea et al., 2018). Therefore, even when performing the powder injection with synthetic air, the water contained in the residual air of the sphere can impact the chemical reactions occurring during the explosion. This statement is especially true if the particles react directly with water (for instance, hydrogen generation with metals by water reduction) and if their specific surface area is large, which is the case of nanopowders. Therefore, as water can, depending on the nature of the powder, enhance or hinder the explosion severity, its influence should be further considered by the current European standards.

3.4 Ignition energy: need for a new spark?

Previous experimental results have highlighted the strong impact of the specific surface area on the ignition sensitivity of the powders, by demonstrating that nano-sized powders are more easily ignited than micron-sized (Bouillard et al., 2010; Holbrow et al., 2010). When it comes to metal nanoparticles, the minimum ignition energy may even be lower than 1 mJ (Wu et al., 2010), which poses both problems in terms of ignition prevention but also in terms of experimental characterisation of the explosion severity due to potential pre-ignition phenomena during dust injection. Beyond these practical concerns, another overlooked issue is related to overdriving phenomenon. Indeed, the nanocellulose powder considered in this study has a minimum ignition energy of 5 mJ when dried under vacuum, and of 16 mJ when not treated, which is very low compared to that of microcrystalline cellulose, i.e. 590 mJ. Moreover, the standard ignition energy for explosion tests is 10 kJ, which is much higher than the minimum ignition energy of the powder. This additional amount of energy can lead to an overdriving phenomenon. Therefore, the pressure evolution measured by the sensors is not only due to the explosion itself, but also to the energy released by the chemical ignitors, which induces an overestimation of the explosion severity (Figure 4). This effect is clearly visible at low dust concentration and can lead to misestimate of the lower explosion limit (determined at 2 kJ). Moreover, such phenomenon can impact the flame propagation and stretching, so the results will be less consistent with industrial situations. This behaviour was already observed for micron-sized powders (Zhen and Leuckel, 1997) but are even more pronounced for nanopowders, due to their lower minimum ignition energy.
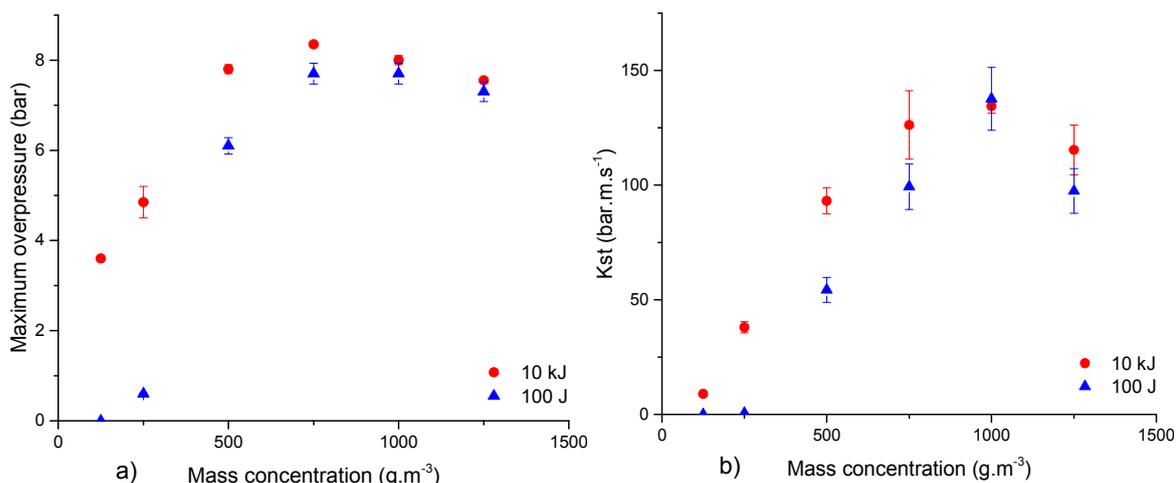
Figure 4: Influence of the ignition energy (10 kJ and 10 J) on (a-left) the maximum overpressure and (b-right) the deflagration index of nanocellulose

3.5 Need some air?

Nanoparticles, especially metal ones, being more sensitive to ignition, the friction generated by the dust injection through the pressurised container can be sufficient to ignite the powder, leading to a pre-ignition phenomenon (Krietsch et al., 2015; Wu et al., 2010). It was the case for the tested aluminium powder that pre-ignited in the dust container for concentrations greater than 500 g.m^{-3}. This phenomenon leads to several issues (Hossain et al., 2013). First, the pressure elevation in the dust container is not measured by the pressure sensors, which leads to an underestimated value of explosion severity. Secondly, the container and outlet valve are not designed to support explosions and can be damaged. Finally, if the metal is oxidized before its injection, the overall quantity of reactant available in the 20 L sphere is artificially decreased and, due to the presence of a thick oxide layer, the powder reactivity can be affected. To avoid such phenomenon, tests were performed by injecting the powder with nitrogen (Figure 5). In order to reproduce atmospheric conditions at the time of the ignition, the air within the sphere was enriched with oxygen. No pre-ignition was observed with the nitrogen injection. However, explosion severity is increased by this procedure, which confirms the previous assumptions: when nanopowders ignite in the dust container, less powder reacts in the sphere, decreasing the maximum overpressure. Moreover, due to the presence of the oxide layer, the reaction is diffusion-controlled as the oxide layer limits the oxygen accessibility to the aluminium surface (Sundaram, 2016). Then, pre-ignition has an influence both on thermodynamic and combustion kinetic and can sensibly affect the explosion severity. In addition, since the storage conditions and time have a direct impact on the formation of the oxide layer, a specific attention should also be given to the powder storage.
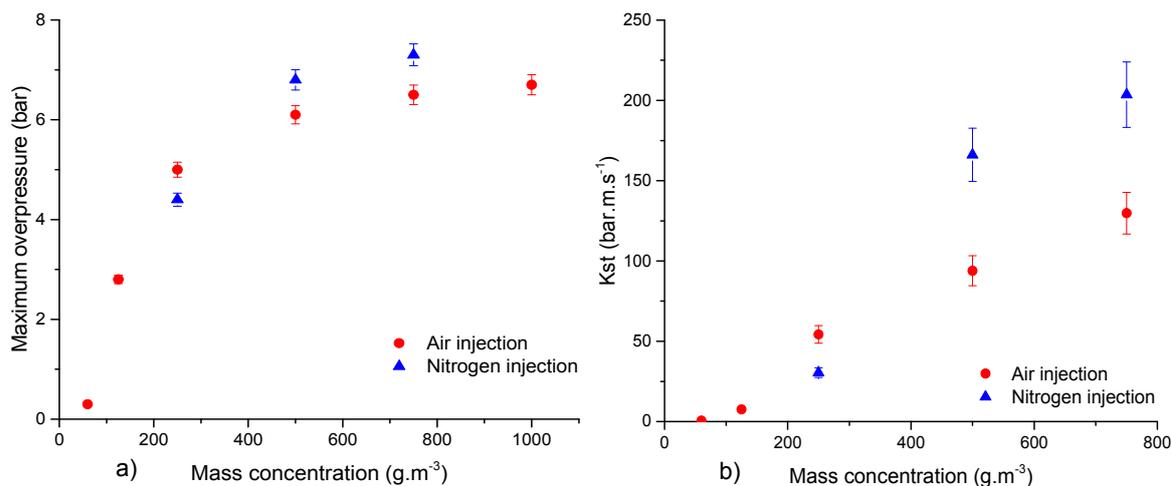
Figure 5: Influence of nitrogen injection on (a-left) the maximum overpressure (b-right) deflagration index K_{St} of aluminium nanopowders

4. Conclusions: Standards are not forever!

Standards are essential landmarks: in view of the multiplicity of industrial situations, they are necessary reference points and are not intended to represent identically the potential explosion under real conditions. Due to their specificities (e.g. high surface area, agglomeration, high sensitivity to ignition, low sedimentation rate etc.), nanopowders exhibit explosive behaviours which can be misinterpreted in light of current standards. Standards are not forever but needs for improvements are!

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