



HAL
open science

Nanopowders explosion : influence of the dispersion characteristics

Audrey Santandrea, Stéphanie Pacault, Laurent Perrin, Alexis Vignes, Olivier Dufaud

► **To cite this version:**

Audrey Santandrea, Stéphanie Pacault, Laurent Perrin, Alexis Vignes, Olivier Dufaud. Nanopowders explosion : influence of the dispersion characteristics. 12. International symposium on hazards, prevention, and mitigation of industrial explosions (ISHPMIE), Aug 2018, Kansas City, United States. ineris-01875968

HAL Id: ineris-01875968

<https://ineris.hal.science/ineris-01875968v1>

Submitted on 18 Sep 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Nanopowders explosion: influence of the dispersion characteristics

A. Santandrea^a, S. Pacault^a, L. Perrin^a, A. Vignes^b & O. Dufaud^a

E-mail: olivier.dufaud@univ-lorraine.fr

^aLRGP - Reaction and Chemical Engineering Laboratory, Université de Lorraine, CNRS, LRGP, F-54000 Nancy, France

^bINERIS, Parc Technologique ALATA, BP 2, F-60550, Verneuil-en-Halatte, France

Abstract

This work aims to study the influence of the dispersion conditions in a standard 20L sphere on the explosibility of a nanopowder. Even more than for micropowders, the dispersion conditions have a strong impact on the dust cloud homogeneity and its particle size distribution (PSD). Due to their high surface energy, nanoparticles are prone to agglomeration, but such structures can be broken during the dispersion process. Varying the dispersion pressure, the ignition delay time and even the nozzle type (rebound or symmetric) leads to modifications of the dust specific surface area, and thus of its reactivity. Tests were performed on aluminum and carbon black nanopowders. They were characterized before and during their dispersion in the sphere, notably using in situ laser PSD measurement. The initial turbulence level of the dust cloud was determined by particle image velocimetry. It appears that using the symmetric nozzle, less fragmentation occurs due to a lower shear stress exerted on the agglomerates. This results in a decrease in the explosion severity and an improved experimental reproducibility. Because pre-ignition phenomenon was observed for aluminum nanopowders during their injection through the electrovalve, the dust dispersion by dust lifting was experimented. With regard to the standard procedure, the maximum rate of pressure rise decreased by approximately 30% whereas the maximum overpressure remains nearly unchanged. It means that the same amount of dust reacts in both kinds of experiments but that less fragmentation occurs, which is confirmed by PSD measurements. This work brings some questions about the interpretation of the explosivity results related to nanopowders and highlights the potential need to introduce recommendations in the current standards.

Keywords: *dust explosion, nanopowders, agglomeration, 20L sphere*

1. Introduction

Feedback on accidents involving nanopowders explosions is still rare. However, some accidents involving nanometric powders have already been identified for aluminum in attrition millers (Wu et al., 2010a) or in a Taiwanese laboratory when handling 75 nm titanium particles (Wu et al., 2014). As for micron-sized particles, a quantitative risk analysis must be conducted in order to propose appropriate prevention and protection means. However, transposing directly knowledge and practices acquired with microparticles to nanopowders may be questionable. An accurate risk assessment requires consideration of industrial conditions, whereas standardization implies the use of normalized test conditions, which are often different from the

former ones. The determination of dust explosibility characteristics is no exception of the rule and it is especially true for nanopowders. Indeed, these powders exhibit specific properties that can challenge the application of the standards and the use of conventional scaling law such as the cube-root law.

Previous results show that the ignitability and explosivity of nanopowders vary as a function of the particles physico-chemical properties. Nevertheless, it generally appears that an increase in specific surface area leads to an increase in the ignition sensitivity but causes no significant change on the explosion severity (Bouillard et al., 2010; Holbrow et al., 2010). In the case of metal nanopowders, minimum ignition energies lower than 1 mJ were determined for nano-iron, aluminum and titanium (Dufaud et al., 2011; Wu et al., 2009; Wu, 2017). Pyrophoric behaviours can even be observed for iron or aluminum nanopowders, notably as a function of the testing procedures (Krietsch et al., 2014, 2015; Mohan et al., 2012; Sundaram et al., 2013). Moreover, several studies demonstrated that a significant increase in explosion severity occurs as the particle size decreases in micron size, but showed a plateau for smaller particle sizes (Boillard et al., 2013; Bouillard et al., 2010; Dastidar et al., 2013; Mittal, 2014; Vignes et al., 2012). For carbonaceous compounds of nanosize, their explosibility were found to be rather close to that of micropowders (Holbrow et al., 2010; Turkevitch et al., 2016). Similarly, when determining the minimum ignition energy (MIE), the minimum explosive concentration (MEC) and minimum ignition temperature (MIT) of carbonaceous nanoparticles, Turkevitch et al. (2015) found that their explosion parameters were similar to those of coals and usual carbon blacks. More precisely, Bouillard et al. (2010) showed that the MIT of carbon blacks decreases with decreasing particle size but increases when the primary diameter (diameter of an individual particle) of the powder reaches the nano-size range, which is related to very strong inter-particle cohesion forces (Eckhoff, 2012).

Several hypotheses have been put forward to explain these observations: i) as the specific surface area increases, nanoparticles tend to agglomerate which reduces the reactive active surface with oxygen and decreases the explosivity (Eckhoff, 2011; Wu et al., 2010a); ii) the evolution of the particle size distribution (PSD) of the nanoparticles impacts the heat transfer phenomena, especially radiative, taking place upstream of the flame front (Dufaud et al., 2011; Kosinski et al., 2013; Sundaram et al., 2013); iii) in the case of metal nanopowders, the passivation of the surface can be enhanced with regard to the microparticles (Eckhoff, 2012; Sundaram et al., 2013); iv) the rate-determining step of the combustion reaction differs from micro to nanopowders (Bouillard et al., 2010); v) flame stretching effects, which can be observed for large non-volatile particles, are unlikely to be observed for pure nanos (Cuervo et al., 2017).

The unique characteristics of nanopowders were also underlined by studying the explosivity of gas/nanoparticles hybrid mixtures. For instance, Torrado et al. (2017a) demonstrated that the addition of carbonaceous nanopowders to methane does not only impact the oxidation kinetics, but also the heat transfer and, to a lesser extent, the flame stretching. As a consequence, for fuel lean mixtures, the insertion of carbon black nanoparticles to pure gas can increase the explosion pressure (Kosinski et al., 2013) as well as the maximum rate of pressure rise, especially at high initial turbulence levels (Torrado et al., 2017b).

Recent investigations have also highlighted the specific hazard inherent in handling nanoparticles, in terms of chemical reactivity. For instance, Martin et al. (2018) showed that the reaction between sulfuric acid and aluminum powder, which is not considered as highly explosive when performed with microparticles, leads to a violent explosion when a mixture of H_2SO_4 and of Al-nanopowders is ignited by an open flame.

Thus, as it clearly appears that the specificities of the nanopowders can impact their safety parameters, the need to characterize these powders before ignition and to choose wisely the operating conditions of the tests is more and more imperative. Two peculiar cases can be distinguished: that of ignition of sensitive metals which are prone to pyrophoricity and that of carbonaceous compounds which are likely to strongly agglomerate. In the first case, alternative testing modes have notably been proposed by Krietsch et al. (2013) for nano aluminum and iron, by placing directly the dust into the explosion chamber and by avoiding the contact between powder and oxygen before injection. In this paper, the method of dust lifting has been used as well as dust injection by a pressurised container. The efficiencies of the standard rebound nozzle and a symmetric one, developed in a previous study (Murillo et al., 2018), have also been compared in order to break the agglomerates and approach an ‘ideal homogenous dust cloud’, or at least, ensure a better homogeneity. As the dispersion conditions have an impact both on the initial turbulence of the dust cloud and on its particle size distribution, it can be interesting to determine the ‘best ignition delay time’ for each (nanoparticles / operating conditions) couple. The influences of such dispersion conditions on the dust explosivity will be presented for some selected examples based on aluminum and carbon black nanopowders.

2. Nanomaterials and characterization of their dispersion

2.1 Nanomaterials

Two kinds of nanomaterials have been chosen for this study: a carbonaceous powder, Corax N550, and a nano-aluminum with a primary particle diameter of 100 nm. Before dispersing them in the 20L sphere, their particle size distributions were characterized by various means: by wet dispersion in ethanol (Mastersizer, Malvern), by sedimentation in air through in situ granulometric analyses (HelosVario - Sympatec GmbH) or by determining the specific surface area by BET measurements and estimating the ‘BET equivalent’ diameter. Results presented in Table 1 show that measurements carried out in wet dispersion lead to agglomerates diameters much larger than those observed by dry dispersion. Obviously, it is irrelevant to use the PSD of a wet sample to characterize the PSD of a dust cloud. Moreover, without using a dispersion system (by gravity fall), the nanopowders remain agglomerated and their size is far from that of their primary diameter, which is close to BET diameter.

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

Powders	Mean volume diameter d_{50} dry sedimentation (μm)	Mean diameter d_{50} wet dispersion (μm)	BET diameter (nm)
Corax N550	24	333	75
Al-100	2	286	96

Scanning Electron Microscopy observations confirm these results, but also reveal that the size of the agglomerates can also vary as a function of time. Indeed, Figure 1a and 1d show the primary particles of respectively carbon black and aluminum, but both tend to agglomerate as shown notably in Figure 1b for Corax N550. It should be stressed that the agglomeration effect is less visible for aluminum. The comparison between Figures 1b (Corax N550, 2017) and 1c (Corax N550, 2006) is also rich in lessons: this is the same powder that has been stored under air for more than ten years. It is clear that, over this period, the size of the agglomerates has been greatly increased (from 100 μm to 1 mm), which is also visually perceptible. Such phenomenon will lead to a modification of the surface area-to-volume ratio of the nanoparticles and then change their properties (Yeap, 2018). Vacuum drying of the powder at 90°C leads to the breaking of the agglomerates, which confirms that the aging is mainly due to the presence

of humidity. If a similar aging occurs with Al-nanoparticles, it is less perceptible by SEM observations. It is consistent with Kyrnakova et al. (2017) results, who found that aging of metal nanoparticles (iron, zinc, copper) lead to changes in their phase composition but also in their flame propagation velocity; no significant changes in terms of reactivity were observed for Al-nanopowders.

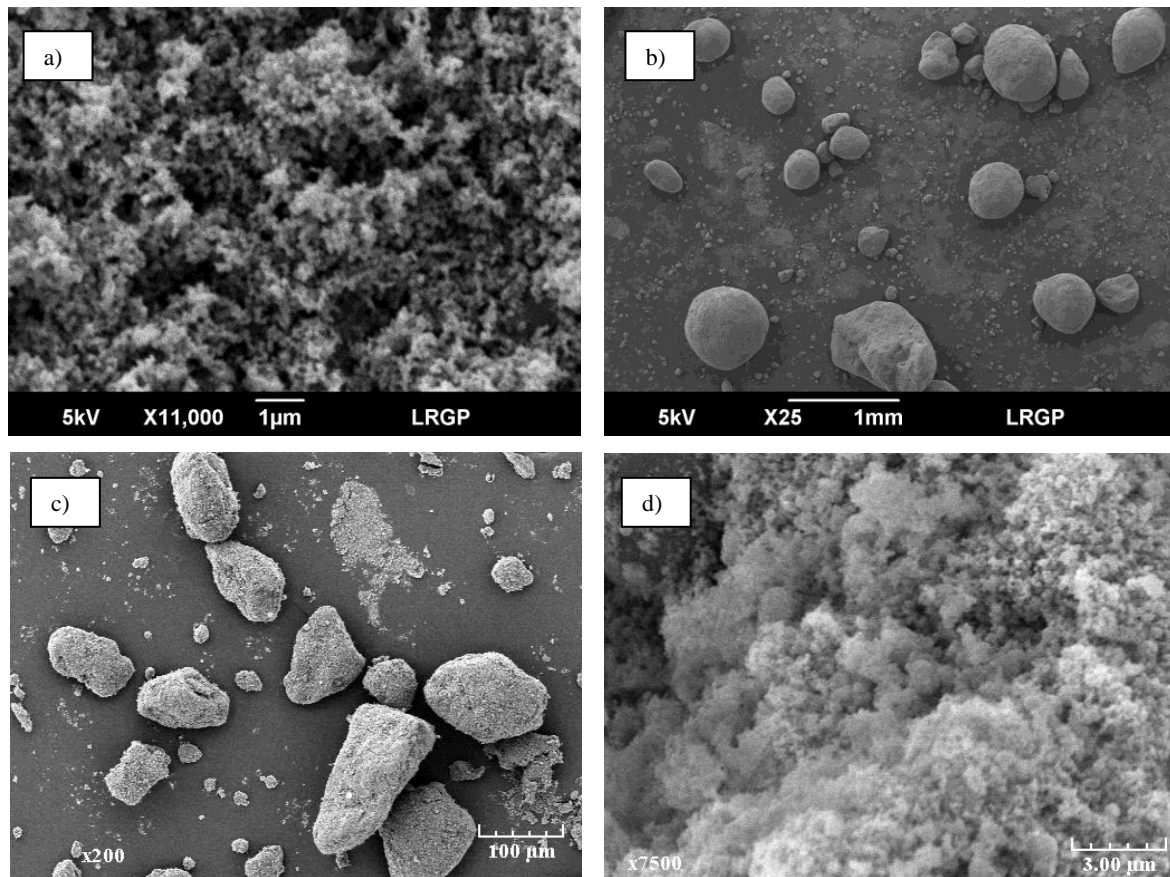


Figure 1: a) Focus on Corax N550 primary particles, b) Carbon black agglomerates – 2017, c) Carbon black agglomerates – 2006, d) Focus on Al-100 primary particles

2.2 Characterization of the dispersed powders

This work aims at determining the influence of the dispersion conditions of the nanopowders on their explosivity. However, two main issues arise. One is related to the metrology of nanoparticles: determining the PSD of nanoparticles over a range from 10 nm (primary particles) to 500 μm (agglomerates), at high concentrations (above the minimum explosive concentration) and with an acquisition frequency of the order of 1 ms is currently technically impossible. Tests have been performed by combining two different techniques: a laser diffraction sensor (Sympatec) for particle size analysis from 0.5 to 175 μm (up to 2 analyses/ms) and a tandem DMA-UCPC for diameters lower than 500 nm (2 min/analysis), Differential Mobility Analyzer (Electrostatic Classifier - TSI 3080) and Ultrafine Condensation Particle Counter (UCPC – TSI 3776) in series (Torrado et al., 2017b). The other issue is due to the interdependence of the dispersion parameters. By modifying the dispersion nozzle/procedure in the 20L sphere, both the PSD and the initial turbulence is modified, the two latter parameters being also linked. Therefore, in order to decouple the influences of turbulence and initial particle size, it is necessary to choose the ignition delay adequately.

As previously said in introduction, metallic nanopowders which are very sensitive to ignition, cannot be injected through a pressurized reservoir as they can ignite spontaneously due to high shear forces through the injection ducts and outlet valve (Bouillard, 2015). Using such operating procedure may lead to unreliable safety parameters. Consequently, explosion tests have been performed on nanopowders by placing them within the 20L sphere before the gas injection and lifting them through an air pulse. Concurrently, a new nozzle has been proposed in order to improve the homogeneity of the dust cloud and increase the reproducibility of the explosion tests. It is based on the geometry of the standard rebound nozzle for which an axial symmetry has been applied (Murillo et al., 2018).

2.2.1 Particle image velocimetry (PIV) –turbulence

The PIV set-up which was used to determine the turbulence level of the dust clouds in the 20L sphere is described by Vizcaya et al. (2018). The dispersion of dust particles may generate changes in the turbulence of the fluid depending on the diameter of the dust. This influence is determined by the ratio of the turbulence length scale to the particle diameter; hence nanometric dusts do not represent significant variations in macroscopic turbulent flows. However, they cannot be used as tracers and wheat starch particles (10 μm) were used instead. With regard to the time evolution of the flow turbulence, three stages can be identified: from 0 to 40 ms, the bulk of the dust cloud is characterized by a high turbulence; from 40 to 120 ms: a ‘transition’ stage characterized by a decrease of the fluctuations; 120 ms or more: a ‘stability stage’ (Murillo et al., 2018). Then, it appears that the mean horizontal velocity is not affected by a nozzle change. On the contrary, vertical root-mean-square velocity (v_{rms}) is significantly modified and the initial turbulence level of the dust cloud dispersed through a rebound nozzle is twice that obtained with a symmetric one. Nevertheless, between 60 and 80 ms, there is little difference between the two devices. For comparison, the data obtained by Dahoe et al. (2001) for a rebound nozzle have been plotted in the figure 2.

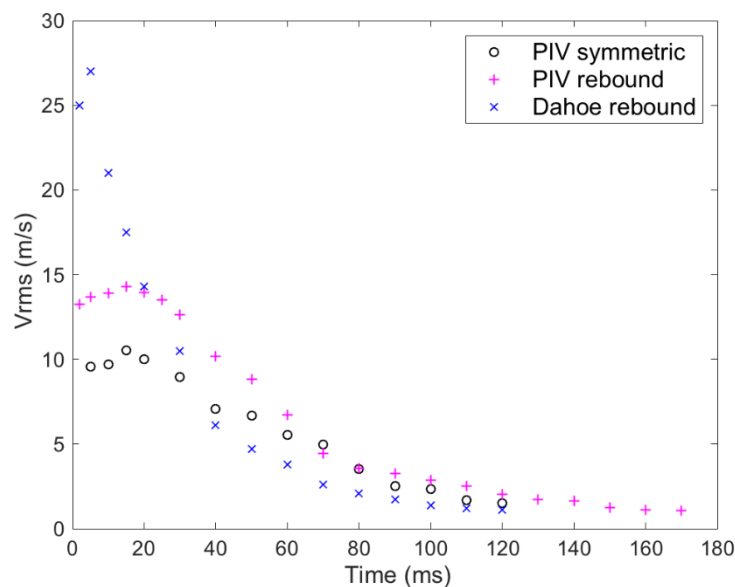


Figure 2: Time evolution of the vertical root-mean-square velocity within the 20L sphere during a standard injection phase – with a rebound nozzle or a symmetric nozzle.

2.2.2 In situ particle size distribution measurements

In view of the PSD obtained by dispersing the particles in a liquid, it is legitimate to ask whether ‘true’ nanoparticles are present in the flow during ignition. Tests performed with DMA-UCPC

demonstrates that 6 minutes after the dispersion of Corax N550, the mean mobility diameter reaches 370 nm and the total concentration is 1.1×10^5 particles/cm³, which confirms that stable nanometric dust cloud is generated during the dispersion phase and is still present a few minutes after the dispersion (Torrado et al., 2017b).

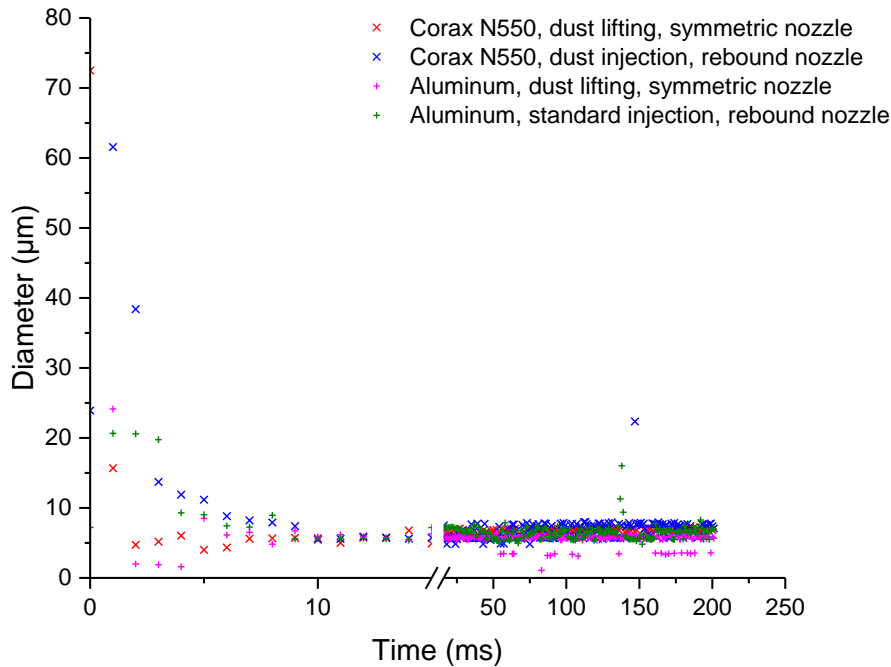


Figure 3: Influence of the injection procedure on the time evolution of the d_{90} during the dispersion of aluminum or carbon black nanoparticles

The time evolution of the PSD of the dust cloud was observed at the center of the 20 L sphere. For Corax N550 as well as for aluminum, the mean diameters observed are of the order of 5 µm. Figure 3 shows a very sharp decrease of the d_{90} –diameter below which 90% of the powder lies - during the first moments of the dust injection. As expected, this evolution is much more marked for the carbonaceous. Moreover, the particle characteristics are more rapidly stable with a symmetrical nozzle and this stability is improved by using dust lifting instead of injection through a reservoir. It should also be underlined that no re-agglomeration phenomenon is visible during the dispersion, neither for aluminum nor for carbon black, which is not the case with powders such as starch (Vizcaya et al., 2018).

Figure 4 shows the impact of the injection procedure on the particle size distribution of Corax N550. Firstly, it should be stressed that, when using a nozzle, very few agglomerates are observable over the 10-175 µm diameter range. Therefore, it seems that the dispersion procedure is effective since the average diameter measured by sedimentation is 24 µm. This assertion is confirmed by comparing the PSD obtained with or without any nozzle. In the latter case, agglomerates ranging from 40 to 90 µm are clearly visible, which is not the case when a nozzle is used (rebound or symmetric). However, agglomerates greater than 100 µm are scarce, notably when the dust is injected through the reservoir, which suggests that fragmentation also occurs through the injection duct, due to high shear forces. Apart from a slight shift towards the very small diameters, only few significant modifications are observable when the various injection procedures are used for the carbonaceous powder.

Figure 5 confirms that the aluminum particles are less prone to agglomeration than the carbon blacks, which is visible by the absence of agglomerates greater than 10 µm and the presence of ultrafine particles smaller than 1 µm. When aluminum dust is dispersed through the reservoir,

the PSDs are rather similar. Nevertheless, a larger dispersion is visible at 8 ms with the rebound nozzle, which results in the presence of fine particles, with diameters lower than 1 μm , as well as particles greater than 10 μm . On the contrary, the presence of fine particles is more pronounced at 60 ms when a symmetric nozzle is used. When the dust is put within the sphere (dust lifting), two peaks are clearly visible around 2 and 5 μm , which suggest that less fragmentation occurs with this procedure.

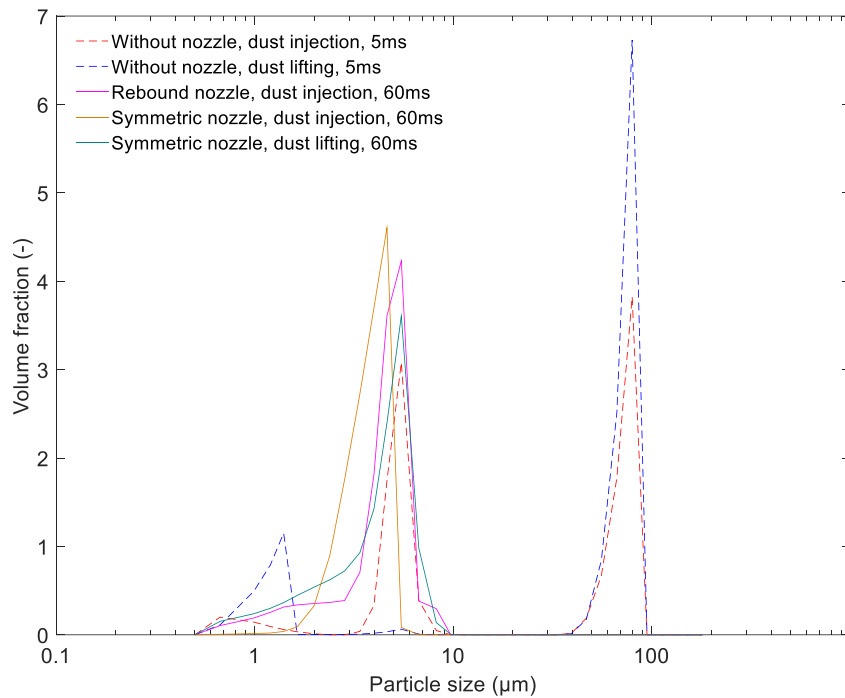


Figure 4: Effect of the injection procedure on the particle size distribution of Corax N550 nanoparticles

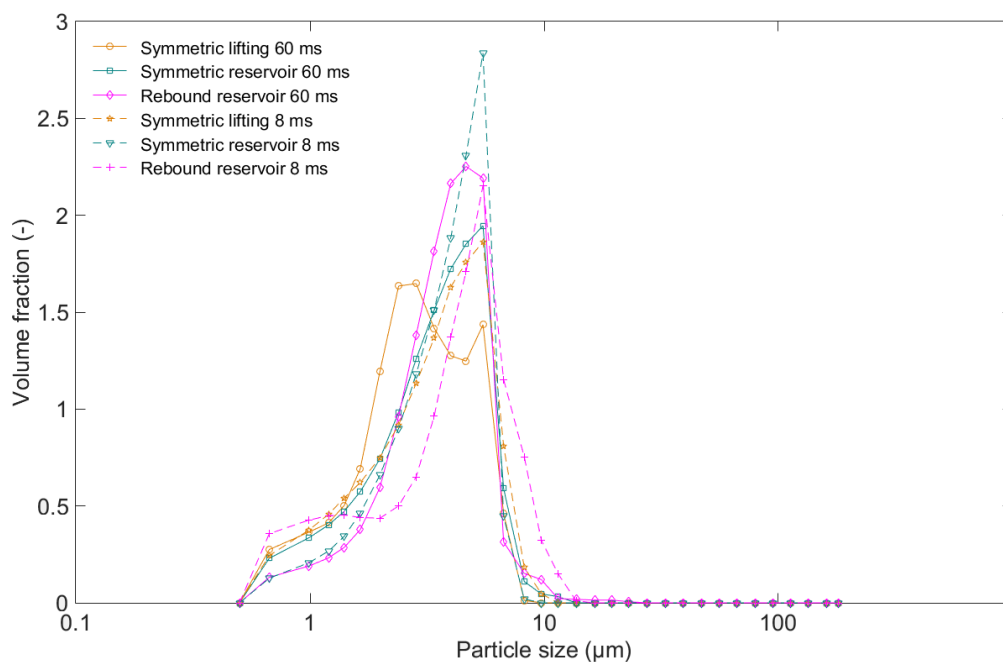


Figure 5: Influence of the injection procedure on the particle size distribution of aluminum nanoparticles

2.2.3 Determination of the dust explosivity

Thanks to PIV and in situ particle size measurement, it is now possible to determine both the turbulence level and the PSD of the dust cloud at any moment of its dispersion and in four cases: the dust dispersion through the reservoir and the 20L sphere equipped with the rebound nozzle or the symmetric one; the dust lifting within the sphere and pure air injection through the rebound nozzle or the symmetric one. Consequently, choosing an ignition delay time (t_v) corresponds to the choice of a couple (PSD, turbulence level). The standards (ASTM E1226-12a, EN 14034 or ISO 6184/1) set a t_v and a dispersion procedure. However, it has been proven, and recalled in the introduction, that such procedures must be reconsidered for the nanoparticles due to their specificities, e.g. strong agglomeration for the carbon blacks and pre-ignition (spontaneous ignition during their injection) for aluminum. Experiences have proven that such phenomena can occur (Figure 6), which makes the standard 20 L protocol questionable, especially for testing highly sensitive nanopowders (Bouillard, 2015).



Figure 6: Injection reservoir covered with alumina after the pre-ignition of nano-aluminum

With regard to their Minimum Ignition Energies (MIE) (Bouillard et al., 2010), explosion tests have been performed in the 20L sphere with 10 kJ chemical igniters for Corax N550 (MIE > 100 J) and 100J chemical igniters for aluminum (MIE < 1 mJ). In addition to the classical safety parameters (P_{max} , dP/dt_{max} , Kst), the combustion gases were analysed by micro-gas chromatography and solid combustion residues were characterized.

3. Nanopowders explosion: beyond the standards

3.1 Explosion of carbon nanoparticles

3.1.1 Aging effect

As shown by Figure 1, the particle size distribution of the Corax N550 was apparently modified when stored under air for more than 10 years. A first set of explosion tests was realized under the same standard conditions at 11 years apart (Figure 7). The maximum explosion overpressure of carbon nanoparticles is not significantly modified by aging. However, the maximum rate of pressure rise is greatly decreased by the aging of the particles: dP/dt_{max} drops from $503 \text{ bar}\cdot\text{s}^{-1}$ (Bouillard et al., 2010) to $242 \text{ bar}\cdot\text{s}^{-1}$, which is probably due to a change in the PSD. Unfortunately, no in situ measurements were performed in 2006 and it is not possible to compare directly the PSD of the dust cloud at 60 ms, before and after aging. Nevertheless, it can be argued that, as the agglomerates do not fragment completely during their injection (section 2.2.2) (Yeap, 2018), the presence of bigger agglomerates still impacts the final PSD of the carbon nanoparticles in the sphere and thus, reduces the overall surface/volume ratio of the powder and its reactivity. It is consistent with the results presented in Figure 7 as the evolution of the P_m shows that the same amount of powder reacts, but with slower kinetics (dP/dt_m). The

explosion severity of nanopowders is then governed by their primary particle size and tendency to agglomerate, which is a noticeable difference from micropowders (Bouillard, 2015).

3.1.2 Influence of the dispersion characteristics

Four different configurations, described in 2.2.3. have been tested. Note that dust lifting with the rebound nozzle will not be shown here for the sake of conciseness. At first, it should be noticed that the explosion overpressures are not significantly modified by a change in the injection procedure (Figure 8). The maximum P_{\max} is obtained for the standard injection procedure (rebound nozzle, reservoir) and the most notable variations are visible for concentrations greater than stoichiometry.

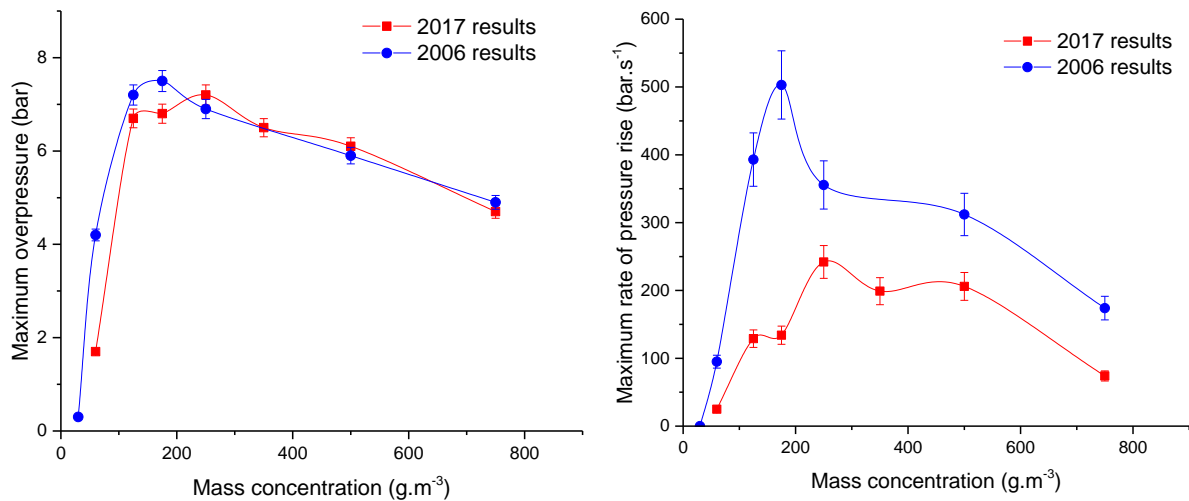


Figure 7: Maximum overpressure (left) and maximum rate of pressure rise (right) for Corax N550 powder in 2006 and 2017 – $t_v = 60$ ms

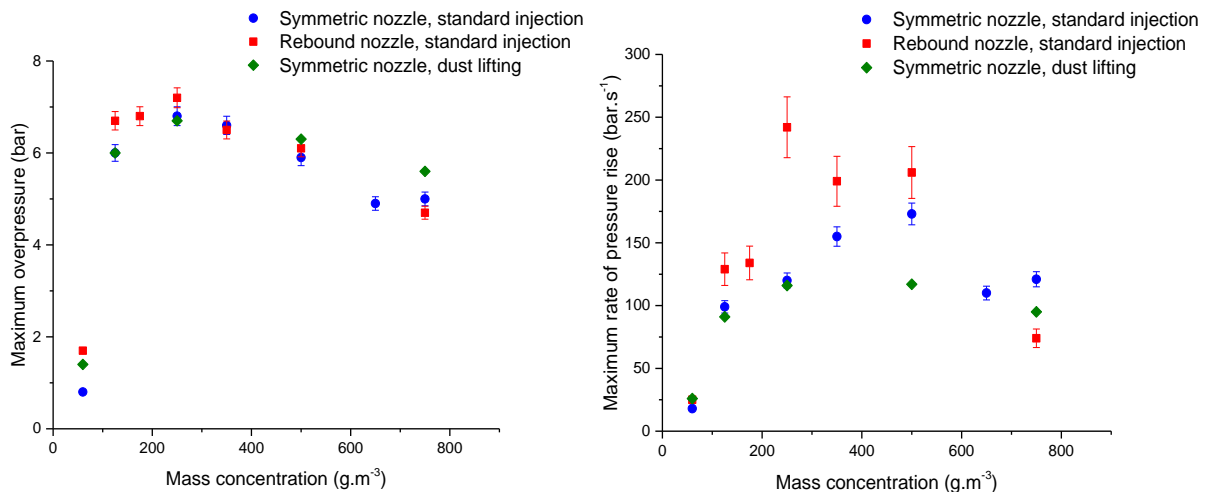


Figure 8: Maximum overpressure (left) and maximum rate of pressure rise (right) for Corax N550 powder – various injection procedures – $t_v = 60$ ms

When the carbonaceous powder is injected through the reservoir (standard injection), the maximum rate of pressure rise decreases significantly, from 242 to 173 bar.s⁻¹, using the symmetric nozzle rather than the rebound nozzle. In addition, a shift of the maximum is observable from 250 to 500 g.m⁻³. In parallel, as shown by Murillo et al. (2018), the

reproducibility of the explosion tests is greatly increased by the symmetric nozzle. These changes can be correlated to both an increase of the turbulence level and to a slight decrease of the particle size when a rebound nozzle is used. Indeed, Figure 4 shows that finer particles are present at 60 ms when a standard injection procedure is followed. However, it should be stressed that the PSD shown in this figure correspond to a specific location (at the centre of the sphere) and a specific time, and that the PSD as well as the local dust concentration vary greatly as a function of time in the case of the rebound nozzle (Murillo et al., 2018). As the maximum explosion pressure does not vary much, the shift of the $(dP/dt)_{max}$ cannot be due to a decrease of the fuel conversion rate but may be attributed to both PSD and turbulence alterations (Figure 2). Figure 8 also demonstrates that significant changes are noticeable when using different injection procedures with the same nozzle, e.g. the symmetric one. As the turbulence level is not affected by the injection of the powder through the reservoir or the dust lifting (nanoparticles and their agglomerates can be considered as tracers) and as the maximum explosion pressures are not significantly modified, it seems that the PSD evolution is one of the main cause of the explosivity changes. This is partially shown in Figure 4 at the sphere centre, and it is particularly visible by integrating the data over the entire duration of the dispersion. A slight shift in the PSD of the dust cloud can affect both the reaction kinetics (modification of the specific surface area and oxygen accessibility) and the radiative transfer through a dust cloud (Cassel et al., 1957), especially when considering the nanoparticles agglomerates.

3.2 Explosion of aluminum nanoparticles

The same tests performed on the carbonaceous compounds were performed on aluminum nanoparticles, using the four different configurations of powder injection. In Figure 9, it is clearly visible that, whatever the configuration tested and the concentration, the standard procedure (rebound nozzle and standard injection) always leads to the most important explosion characteristics. However, it should be highlighted that, when the concentration exceeds 750 g.m^{-3} , this procedure systematically leads to powder ignition within the reservoir, which obviously modifies the reactivity of the dust during its ignition within the sphere.

Contrary to the Corax N550, the maximum overpressure of the Al nanoparticles varies as a function of the injection mode, which raises the question of the full conversion of the powder. Especially in the case of dust lifting with the symmetric nozzle, P_m decreases at 5.4 bars whereas it reaches 6.5 bars at 750 g.m^{-3} when the standard procedure is applied. This assertion is confirmed by collecting the dust after combustion at the bottom of the 20 L sphere, where grey crusts composed of both alumina and aluminum can be observed. It is worth noting that the Minimum Explosive Concentration is not significantly modified by the various procedures.

Concerning the maximum rate of pressure rise, the difference between the standard procedures and the other injection modes seems to be increased as the dust concentration increases. It should be underlined that the $(dP/dt)_{max}$ was not identified over the chosen concentration range, whereas the stoichiometry (by considering only the oxidation of aluminum in alumina) is reached at 315 g.m^{-3} . Other reactions should then be considered such as the nitration of aluminum at high temperature, which is confirmed by measuring the pressure drop in the 20L sphere after explosion and cooling. Thus, at high dust concentrations, the final pressure is lower than the one obtained by only removing the oxygen, which is due to nitrogen consumption and the generation of aluminum nitride (Loryan & Borovinskaya, 2003). SEM observations combined with EDX (energy dispersive X-ray spectrometry) performed on the oxidation residues confirm these results. Moreover, dust lifting leads to lower explosivity than with the standard injection procedure. Finally, even if only slight PSD changes occur by using various nozzles and injection procedures with the aluminum powders (Figure 5), significant variations of the dust explosivity are observed. It is consistent with the results obtained by Wu et al.

(2010), who found that if the particle sizes of 35 nm and 100 nm of aluminum powders were comparable after agglomeration, yet their explosive parameters were different. The following assumptions can be proposed: i) the slight PSD modifications and notably the presence of fine particles with diameters lower than 1 μm have a noticeable impact on the evolution of the specific surface area (note that no precise PSD can be given for particle diameter lower than 0.5 μm at such concentrations), ii) the same modification have also an effect on the particles emissivity, which diminishes as the PSD decreases to nanosizes (Sundaram et al., 2013; 2016), iii) the injection procedure changes the dust repartition within the sphere, which can influence the flame propagation and the radiative transfer (Cassel et al., 1957), iv) the use of different nozzles implies changes in the initial turbulence level (Figure 2), parameter impacting the flame kernel growth and flame front propagation (Proust, 2006). This last hypothesis was tested by modifying the ignition delay time.

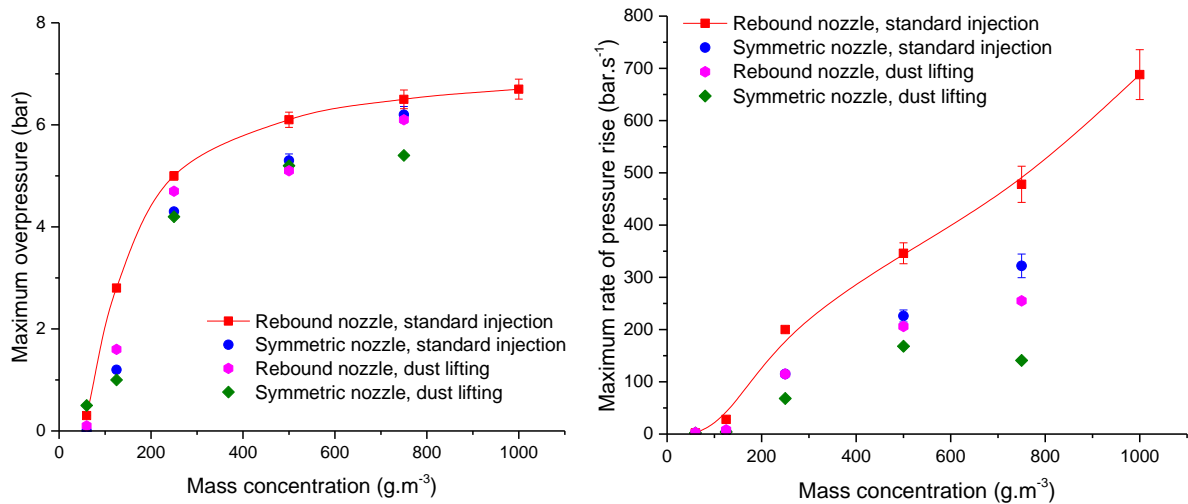


Figure 9: Maximum overpressure (left) and maximum rate of pressure rise (right) for aluminum powder– various injection procedures – $t_v = 60 \text{ ms}$

3.3 Influence of ignition delay time

Figure 10 shows the evolution of the maximum rate of pressure rise of carbon black (Corax N550) at the optimum concentration, i.e. 250 g.m^{-3} , as a function of the parameter t_v . For each test, the combustion gases were collected and analysed by gas chromatography; the ratio CO/CO_2 and hydrogen were specifically studied. At first glance, the presence of hydrogen in the combustion gases may seem surprising when it comes to the oxidation of pure carbon. It should not be forgotten that, during the injection procedure, the 20L is initially vacuumed at 0.4 bar absolute. Hence, for a relative humidity of 0.4, the initial molar percentage of water in the sphere is 0.36%. By considering that water reacts with carbon monoxide at high temperature to generate carbon dioxide and hydrogen, and by using the adequate equilibrium constants (Wagman et al., 1945), the hydrogen concentration can be calculated as a function of the reaction temperature. Conversely, using the hydrogen content and the CO/CO_2 ratio determined by chromatography and the calculated H_2O content, it is possible to evaluate the equilibrium constant and estimate the corresponding reaction temperature. The results of these calculations are presented in Table 2, as well as the carbon monoxide content. It appears that the greater the turbulence level (low ignition delay time), the greater the carbon monoxide concentration. This might be explained by the heterogeneous repartition of the fuel within the sphere at low t_v , which leads to zones at high local fuel equivalent ratio and quenching due to intense turbulence, both phenomena tending to increase the CO content. It should also be kept in mind that the

CO/CO₂ equilibrium will be shifted to the direction of CO formation when the temperature increases (Table 2).

Table 2: Estimation of the reaction temperature from the composition of the combustion gases and carbon monoxide content from chromatography measurements for Corax N550 explosion

Ignition delay t_v	20 ms	30 ms	40 ms	60 ms	80 ms	100 ms	120 ms
CO (% mol)	25.0	21.3	18.8	17.0	14.0	12.1	8.5
T_{reaction} (°C)	1072	963	902	853	837	809	751

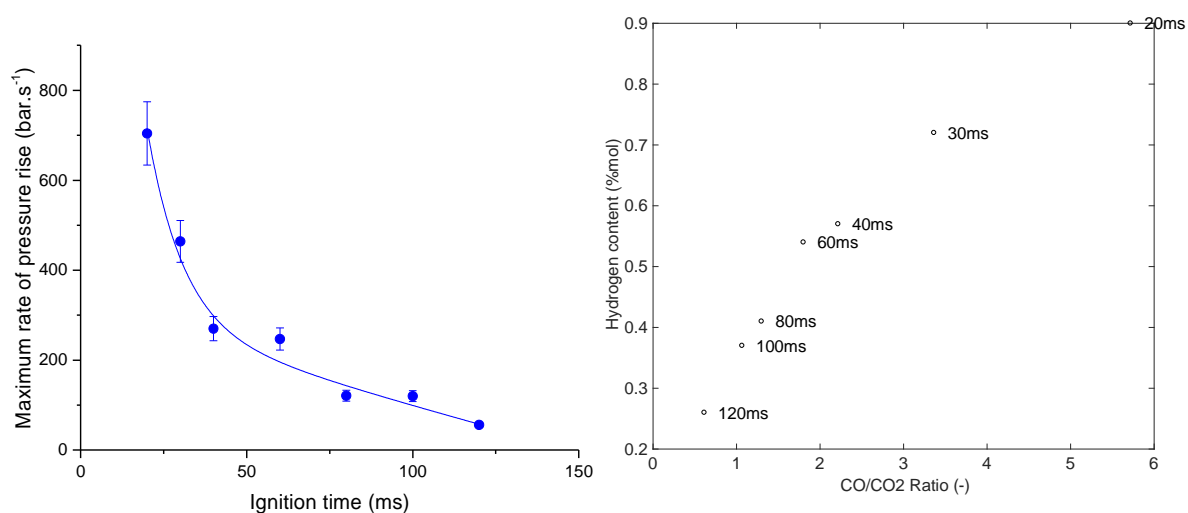


Figure 10: Influence of the ignition delay time on the maximum rate of pressure rise of Corax N550 at 250 g.m⁻³ (left) and on the CO/CO₂ ratio and H₂ content (right)

The maximum rate of pressure rise strongly decreases as the ignition delay time increases, e.g. from 704 bar.s⁻¹ at 20 ms to approximately 50 bar.s⁻¹ at 120 ms (low turbulence levels), which confirms that the reactivity of the dust cloud is still enhanced for t_v as low as 20 ms. However, the reproducibility greatly decreases at low t_v and flame kernel quenching can also occur at very low ignition delay times. Moreover, it should be stressed that the injection of the dust is still in progress at 20 ms. This augmentation of explosivity is probably related to the turbulence increase (Figure 2), which improve the heat and mass transfers, rather than to a PSD variation (Figure 4). The heterogeneity of the dust cloud should also be considered, even if this parameter as not been studied experimentally, its influence was demonstrated by CFD simulations (Vizcaya et al., 2017). Finally, due to their low sedimentation rate and high stability, tests performed at higher t_v could lead to the estimation of explosion characteristics of a ‘quasi-initially quiescent’ dust cloud. By using correlations such as those developed by Silvestrini et al. (2008), ‘unstretched flame velocities’ might then be appraised.

4. Conclusions

Nanopowders have specific characteristics, such as the propensity to agglomeration or to self-ignition or even pyrophoricity for metals compounds, that can have a significant impact on the determination of their explosivity. Standards exist with established procedures, but there are currently no recommendations on how to interpret their results correctly: i) what about the extrapolation of results on an industrial scale (i.e. of the validity of the cubic law)?, ii) how to analyze explosion parameters in the case of pre-ignition phenomenon or how to avoid this phenomenon?, iii) are these results representative of the industrial operating conditions, in terms of turbulence and particle size distribution? As the operating conditions appear to have much

greater influence in the case of nanoparticles than for micropowders, one of the key elements is to know precisely the characteristics of the dust cloud during its dispersion. This knowledge is difficult to achieve because the changes in dispersion conditions have not only an influence on the PSD, but also on initial turbulence level.

From this study, it appears that the particle size distribution of the nanoparticles before and after injection within the 20L sphere are greatly different and that modifications in the dispersion procedure can impact the fragmentation of the nanoparticles agglomerates. Even slight changes in the PSD of a nanoparticles cloud lead to significant modifications of its explosivity. It should also be noticed that changing the dispersion nozzle can improve the reproducibility of the tests and limit the pre-ignition phenomenon. However, the use of a symmetric nozzle instead of a standard rebound nozzle lead to much lower explosivities. A similar finding can be drawn from the replacement of the dust injection through a reservoir by dust lifting. Finally, a peculiar attention should be paid to aging phenomenon of nanoparticles with regard to their safety parameters.

By thoroughly characterizing the dust cloud before ignition, it is then possible to choose a suitable injection procedure and ignition delay time which will correspond to the worst-case scenario or, in a more relevant way, to conditions consistent with the actual industrial processes.

References

- Boilard, S.P., Amyotte, P.R., Khan, F.I., Dastidar, A.G. & Eckhoff, R.K. (2013). Explosibility of micron- and nano-size titanium powders. *Journal of Loss Prevention in the Process Industries*, 26, 1646–1654.
- Bouillard, J., Vignes, A., Dufaud, O., Perrin, L. & Thomas, D. Ignition and explosion risks of nanopowders. *Journal of Hazardous Materials*, 181, 873–880 (2010).
- Bouillard, J.X. (2015). *Nanoengineering*, Global Approaches to Health and Safety Issues, chapter 1.5, 111–148
- Cassel H.M., Liebman I. & Mock W.K. (1957). Radiative transfer in dust flames, *International on Combustion*, 6 (1), 602-605.
- Cuervo, N., Dufaud, O. & Perrin, L. (2017). Determination of the burning velocity of gas/dust hybrid mixtures. *Process Safety and Environmental Protection*, 109, 704-715.
- Dahoe, A., Cant, R. & Scarlett, B. (2011). On the decay of turbulence in the 20-liter explosion sphere, *Flow, Turbulence and Combustion*, 67: 159.
- Dastidar, A., Boilard, S., Amyotte, P.R. & Turkevich, L.A. (2013). Explosibility of nano-sized metal powders, *Proceedings of AIChE Spring Meeting and Global Congress on Process Safety*, Paper No. 47b.
- Dufaud, O., Vignes, A., Henry, F., Perrin, L. & Bouillard, J. (2011). Ignition and explosion of nanopowders: something new under the dust. *Journal of Physics: Conference Series*, 304, 012076.
- Eckhoff, R.K. (2011). Are enhanced dust explosion hazards to be foreseen in production, processing and handling of powders consisting of nano-size particles? *Journal of Physics: Conference Series*, 304, 012075.
- Eckhoff, R.K. (2012). Does the dust explosion risk increase when moving from μm -particle powders to powders of nm-particles? *Journal of Loss Prevention in the Process Industries*, 25, 448–459.

- Holbrow, P., Wall, M., Sanderson, E., Bennett, D., Rattigan, W., Bettis, R. & Gregory, D. (2010). *Fire and Explosion Properties of Nanopowders*. UK Health and Safety, Executive. RR782.
- Kosinski, P., Nyheim, R., Asokan, V., & Skjold, T. (2013). Explosions of carbon black and propane hybrid mixtures. *Journal of Loss Prevention in the Process Industries*, 26 (1), 45-51.
- Krietsch, A., Scheid, M. & Schmidt, M. (2014). *Burning and explosion properties of metallic nano powders*, Proceedings of Symposium Series Hazards 24, 159, 1-9.
- Krietsch, A., Scheid, M., Schmidt, M. & Krause, U. Explosion behaviour of metallic nano powders. (2015). *Journal of Loss Prevention in the Process Industries*, 36, 237–243.
- Krietsch A., Romahn, T.-M., Scheid, M., & Krause U. (2013). Modified setup of 20-L-Sphere for the determination of safety characteristics of nano powders, *Chemical Engineering Transactions*, 31, 805-810.
- Kyrmakova, O.S., Sechin, A.I., & Nazarenko O.B. (2017). Influence of long-term storage on fire hazard properties of metal nanopowders, *J. Phys.: Conf. Ser*, 881, 012027.
- Loryan, V.E., Borovinskaya, I.P. (2003). Aluminum combustion in nitrogen, *Combustion, Explosion and Shock Waves*, 39 (5), 525–533.
- Martin, C., Comet, M., Schnell, F., Berthe, J.E. & Spitzer, D. (2018). Aluminum nanopowder: A substance to be handled with care, *Journal of Hazardous Materials*, 342, 347-352.
- Mittal, M. (2014). Explosion characteristics of micron- and nano-size magnesium powders. *Journal of Loss Prevention in the Process Industries*, 27, 55–64.
- Mohan, S., Ermoline, A. & Dreizin, E.L. (2012). Pyrophoricity of nano-sized aluminum particles. *Journal of Nanoparticles Research*, 14:723.
- Murillo, C., Amín, M., Bardin-Monnier, N., Muñoz, F., Pinilla, A., Ratkovich, N., Torrado, D., Vizcaya, D. & Dufaud, O. (2018). Proposal of a new injection nozzle to improve the experimental reproducibility of dust explosion tests. *Powder Technology*, 328, 54-74.
- Proust, C. (2006). Flame propagation and combustion in some dust-air mixtures, *Journal of Loss Prevention in the Process Industries*, 19, 89-100.
- Silvestrini, M., Genova, B. & Leon Trujillo, F.J. (2008). Correlations for flame speed and explosion overpressure of dust clouds inside industrial enclosures. *Journal of Loss Prevention in the Process Industries*, 21, 374–392.
- Sundaram, D.P., Puri, P. & Yang, V. (2013). Pyrophoricity of nascent and passivated aluminum particles. *Combustion and Flame*, 1870-1875.
- Sundaram, D.P., Puri, P. & Yang, V. (2016). A general theory of ignition and combustion of nano- and micron-sized aluminum particles. *Combustion and Flame*, 169, 94–109.
- Torrado, D., Buitrago, V., Glaude, P.A. & Dufaud, O. (2017a). Explosions of methane/air/nanoparticles mixtures: Comparison between carbon black and inert particles. *Process Safety and Environmental Protection*, 110, 77-88.
- Torrado, D., Cuervo, N., Pacault, S., Glaude, P.A. & Dufaud, O. (2017b). Influence of carbon black nanoparticles on the front flame velocity of methane/air explosions. *Journal of Loss Prevention in the Process Industries*, 49, Part B, 919-928.
- Turkevich, L.A., Dastidar, A.G., Hachmeister, Z. & Lim, M. (2015). Potential explosion hazard of carbonaceous nanoparticles: Explosion parameters of selected materials. *Journal of Hazardous Materials*, 295, 97–103.

- Turkevich, L.A., Fernback, J., Dastidar, A.G. & Osterberg, P. (2016). Potential explosion hazard of carbonaceous nanoparticles: screening of allotropes. *Combustion and Flame*, 167, 218–227.
- Vignes, A., Muñoz, F., Bouillard, J., Dufaud, O., Perrin, L., Laurent, A. & Thomas, D. (2012). Risk assessment of the ignitability and explosivity of aluminum nanopowders. *Process Safety and Environmental Protection*, 90, 304–310.
- Vizcaya, D., Pinilla, A., Amín, M., Ratkovich, N., Munoz, F., Murillo, C., Bardin-Monnier, N. & Dufaud, O. (2018), CFD as an approach to understand flammable dust 20 L standard test: Effect of the ignition time on the fluid flow. *AIChE Journal*, 64, 42–54.
- Wagman, D.D., Kilpatrick, J.E., Taylor, W.J., Pitzer, K.S. & Rossini, F.D. (1945). Heats, free energies, and equilibrium constants of some reactions involving O₂, H₂, H₂O, C, CO, CO₂, and CH₄. *Journal of Research of the National Bureau of Standards*, Research paper RP1634, 34, 143-161.
- Wu, H.C., Chang, R.C. & Hsiao, H.C. (2009). Research of minimum ignition energy for nano titanium powder and nano iron powder. *Journal of Loss Prevention in the Process Industries*, 22, 21–24.
- Wu, H.C. (2010). Explosion characteristics of aluminum nanopowders. *Aerosol and Air Quality Research*, 10: 38–42.
- Wu, H.C., Ou H.J., Peng D.J., Hsiao H.C., Gau C.Y. & Shih T.S. (2010a). Dust explosion characteristics of agglomerated 35 nm and 100 nm aluminum particles. *International Journal of Chemical Engineering*, Article ID 941349
- Wu, H.C., Wu, C.W., Ko, & Y.H. (2014). Flame phenomena in nanogrinding process for titanium and iron, *Journal of Loss Prevention in the Process Industries*, 27, 114-118.
- Wu, H.C. (2017). *Fire and explosion risk analysis for nanomaterials*, RSC Detection Science, chapter 32 from *Advanced environmental analysis: applications of nanomaterials*, Vol. 2, 383-396.
- Yeap, S.P. (2018). Permanent agglomerates in powdered nanoparticles: Formation and future prospects, *Powder Technology*, 323, 51-59