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Stronger together? Influence of the agglomeration on nanopowders explosion

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Among the factors influencing dust explosion, the particle size distribution (PSD) is both one of the most important and the most complex to consider. For instance, it is commonly accepted that the explosion sensitivity increases when the particle size decreases. Such an assertion may be questionable for nano-objects which easily agglomerate. However, agglomerates can be broken during the dispersion process. Correlating the explosion parameters to the actual PSD of a dust cloud at the moment of the ignition becomes then essential.
Powders were characterized before and during their dispersion using in situ laser particle size measurement and a fast mobility particle sizer. The turbulence was determined by particle image velocimetry. The explosion severity and sensitivity of nanocellulose was determined under various operating conditions and for wet and dried powders. The impact of the turbulence on the flame kernel growth was highlighted using a flame propagation tube. It appears that the ignition sensitivity of nanocellulose depends on the PSD and on water activity whereas its explosion severity is less modified by the presence of agglomerates in the raw powder.

1. Introduction

If dust explosion risks concerning micron-sized particles can be relatively well estimated, it is not yet the case for nanoparticles. Indeed, the interest in nanotechnologies and in their specific properties due to their small size is quite recent and there are only a few feedbacks on accidental dust explosions involving nanoparticles. Some laboratory tests were already carried out to evaluate the ignition sensitivity and explosivity of nanopowders (Boilard et al., 2013; Holbrow et al., 2010; Krietsch et al., 2015; Wu et al., 2009). It appears that those powders are usually more sensitive to ignition, but no significant variation concerning the explosion severity was observed (Bouillard et al., 2010; Holbrow et al., 2010). The main hypothesis to explain this phenomenon is that Van der Waals cohesion forces tend to form micron-sized agglomerates of nanoparticles, which reduces the reactive surface area and decreases the explosion severity (Eckhoff, 2011; Rumpf, 1962).
For an explosion to occur, some conditions are needed. Among them is the dispersion of the powder, which can break, at least partially, the agglomerates. Since the particle size distribution is a very important parameter influencing dust explosion, it becomes necessary to characterize the dust cloud not only before its dispersion, but also at the exact ignition time. Moreover, it is imperative to choose wisely the operating conditions for the explosion tests, to be sure to evaluate the worst -but realistic- case scenario. Indeed, the standard conditions were established for micron-sized particles and may have to be adapted to nanoparticles, due to their specific properties.
Two of the most important and coupled parameters to consider in dust explosion being the particle size distribution and the initial turbulence, their influence on the explosion severity was evaluated. The initial turbulence was modified by varying the ignition delay time of the test and its influence on the particle size distribution of the dust cloud and its explosivity was studied. In addition, the water content of the powder can

also impact its agglomeration due to the adsorption properties of nanoparticles and capillary forces. Then, explosions tests were performed on nanocellulose before and after drying.

2. Materials and methods

A nanocellulose powder (NCC from Celluforce) with primary fiber dimensions of 3 nm width, an average length of 70 nm and a specific surface area of 400 $m^2.g^{-1}$ was chosen for this study. The ignition sensitivity was measured using a standard modified Hartmann tube according to EN ISO/IEC 80079-20-2:2016/AC (2017). The flame propagation was analyzed in a flame propagation tube of 7 x 7 x 100 cm^3 open at its upper end, connected to the ignition system of the modified Hartmann tube and coupled with a high-speed video camera (Cuervo, 2015).
The explosion severity and minimum explosive concentration tests were performed in a standard 20L sphere according to EN 14034-1&2 (2011). In order to visualize the dust cloud behavior, a new dispersion vessel similar to the 20L sphere but equipped with windows was designed (Vizcaya et al., 2018). The time evolutions of the particle size distribution (PSD) and of the turbulence level were then recorded.
A laser diffraction sensor (Helos - Sympatec) was used to measure PSD on 0.5 to 175 µm (R3 lens) and 0.1 to 35 µm (R1 lens) ranges at 2000 Hz. It was coupled with a Fast Mobility Particle Sizer (FMPS - TSI) measuring particles in the range from 5.6 to 560 nm with 1 Hz time resolution, which gives information on the presence of nanoparticles in the 20L vessel after dispersion. The turbulence level of the dust cloud, represented by the root-mean-square velocity V_{rms}, was evaluated using Particle Image Velocimetry (PIV) (Vizcaya et al., 2018). Different ignition delay times and water activities (Awmeter - Hygrolab) were tested both for the cloud characterization and explosion severity measurements. Since PSD and turbulence are interdependent parameters, they were evaluated in each different condition.

3. Effects of water content

Some of the nanocellulose powder was dried at 90°C under vacuum to be compared with a non-treated 'wet powder'. The water activity of the powder as well as its mean volume diameter d_{50}, determined by sedimentation in air and after dispersion in the sphere are given in Table 1. Minimum ignition energies of both samples are also presented. Firstly, it can be observed that, due to Van der Waals forces, the nanoparticles are agglomerated up to a microscale. It should be noted that the presence of water tends to enhance agglomeration. However, during the dispersion procedure, agglomerates are partially broken and both samples, wet or dried, have similar PSD at the ignition time on the 0.5 - 175 µm range. Tests performed with the R1 lens and with FMPS confirms that part of the nanocellulose remains at the nanoscale (100 to 200 nm) and is still dispersed within the sphere even 1 second after dispersion. Primary agglomerates of a few particles are obviously more difficult to break than larger agglomerates of 41 or 65 µm (Table 1) and such polydispersity will have an influence on the ignition and explosion parameters. As the PSD only slightly differs between the wet and dried dispersed powder, an influence of the water activity on the minimum ignition energy of the nanocellulose can be noticed. A similar influence was highlighted by Traoré et al. (2009) on magnesium stearate. It should be highlighted that the minimum ignition energy of the dried nanocellulose is very low, notably compared to that of microcrystalline cellulose (590 mJ).

Table 1: Influence of water activity on the particle size distribution and on the minimum ignition energy of nanocellulose

Powder	Water Activity (Aw)	Mean volume diameter d_{50} sedimentation (µm)	Mean volume diameter d_{50} after dispersion in the 20L sphere (µm)	Minimum Ignition Energy (mJ)
Wet	0.23	65	11	16
Dried	0.03	41	13	5

Explosion tests realized in the standard closed 20L sphere confirm that drying the powder leads to an increase of its ignition sensitivity. Indeed, it can be observed in Figure 1 that the minimum explosive concentration (MEC) of the powder is shifted from 250 $g.m^{-3}$ for the wet sample to 125 $g.m^{-3}$ for the dried one. Figure 1a shows that the maximum overpressure appears to be independent of the water content of the sample, which tends to indicate that the same amount of powder is involved in the reaction. An alternative will be to consider that water modify the sequence of reactions, without changing significantly the maximum explosion pressure. Such hypothesis will be discussed in the light of the analysis of the combustion gases. The maximum rate of pressure rise $(dP/dt)_m$, a parameter related to the combustion kinetics, is slightly modified by the humidity, the explosivity of the wet powder is always lower than that of the dry powder (Figure 1b). For instance, the maximum value of $(dP/dt)_m$ reaches 496 $bar.s^{-1}$ for the dry powder and 435 $bar.s^{-1}$ for the wet sample. This variation can notably

be attributed to a heat sink effect due to water vaporization. It should be kept in mind that such inhibiting effect will not be encountered for metal powders for which the presence of humidity can lead to hydrogen generation by water reduction (Traoré et al., 2009). The burnt gases were analyzed to determine the impact of water on the combustion.

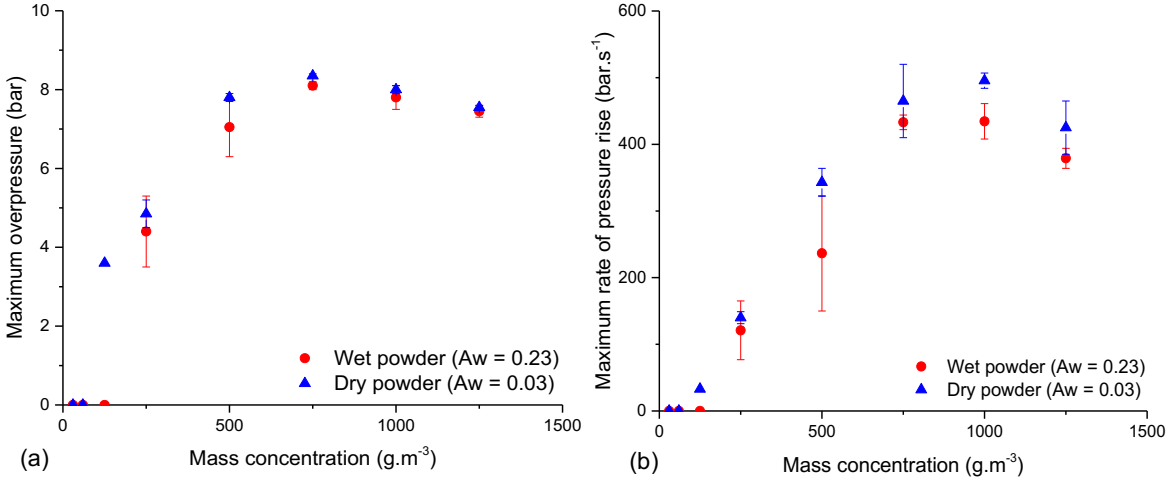


Figure 1a) Maximum overpressure, b) maximum rate of pressure rise for wet and dry nanocellulose

The combustion gases were collected after each explosion test by gas chromatography. The analysis of the oxygen content in the burnt gases allows the determination of the experimental stoichiometry. By considering a simple combustion reaction between cellulose and oxygen to form carbon dioxide and water, the stoichiometric concentration is obtained for approximately 250 g.m^{-3}. In practice, there is always a slight shift between the theoretical stoichiometry and the experimental one, due to the heterogeneity of the cloud. Figure 2a shows this shift, as there is still oxygen within the sphere at 250 g.m^{-3}, whereas a negligible oxygen concentration is obtained at 500 g.m^{-3}. However, the maximum overpressure is obtained at 750 g.m^{-3} and the maximum rate of pressure rise at 1000 g.m^{-3}.

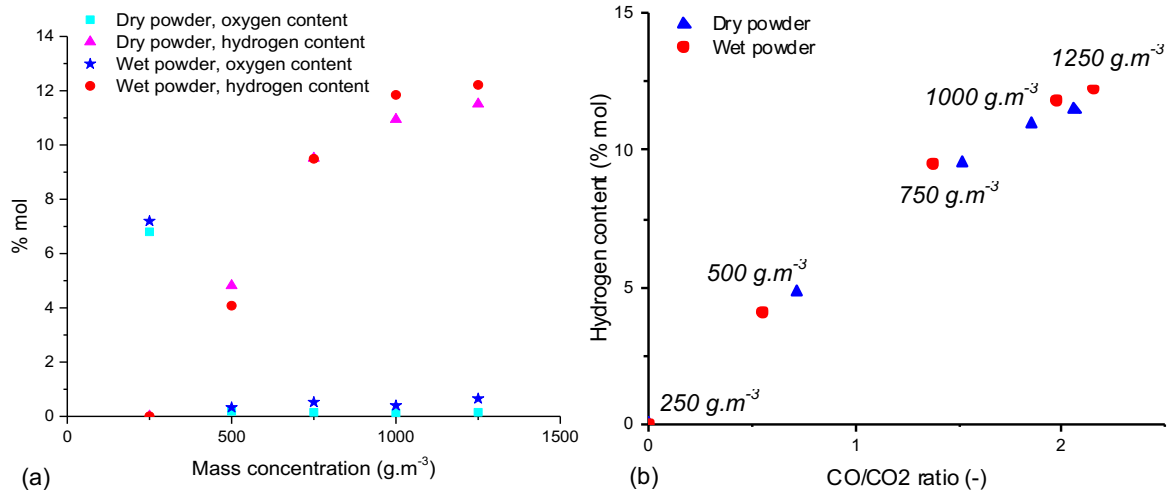


Figure 2: Influence of nanocellulose concentration and water activity on the composition of the combustion gases (a) O_2 and H_2 molar concentration (b) CO/CO_2 ratio and H_2 content

Such a deviation can be notably explained by a much more complex combustion reaction than that previously considered. Indeed, Figure 2 illustrates that hydrogen and carbon monoxide are also generated during the explosion. More specifically, Figure 2b also shows a linear correlation between the hydrogen content in the sphere and the CO/CO_2 ratio, meaning that both hydrogen and carbon monoxide concentration rise with the dust concentration. Obviously, carbon monoxide is mainly formed for fuel rich mixtures; but its generation is also enhanced by a temperature increase due to Boudouard equilibrium. At high temperatures (i.e. high pressures in the sphere), chars or soot can then react with CO_2 in absence of oxygen. Agglomeration tends to promote

such phenomenon by limiting the oxygen accessibility to the dust surface and favoring oxygen-diffusion limitation with respect to chemical reaction limitation. Figure 2 also shows that the influence of the water content of the powder on the burnt gases composition is negligible. As a consequence, the variations of the ignition sensitivity and of the dust explosivity (Figure 1b) cannot be related to a change in combustion kinetics, but more likely to thermal sink effect, radicals capture and water vaporization. However, the fact that the drying step induces slight changes in the PSD by enhancing the agglomerates breakage cannot be neglected.

4. Effects of turbulence

4.1 Influence of the turbulence on nanoparticles explosivity

It is common knowledge that the initial turbulence within the sphere varies as a function of time (Dahoe et al., 2001). Indeed, right after the injection, the turbulence level is high and decreases with time through three stages: high turbulence and heterogeneity of the cloud (from 0 to 45 ms), transition stage (from 45 to 125 ms) and a stability stage from 125 ms (Murillo et al., 2018). This tendency can be outlined from Figure 3 by the red curve. According to EN 14034-1&2 (2011), the standard ignition delay time tv is 60 ms, i.e. ignition occurs 60 ms after the beginning of the injection. The parameter tv can be modified, but it also changes the injection dynamic, as shown in Figure 3b. If the ignition delay time is below 60 ms, the injection is faster, which leads to greater heterogeneities within the cloud and a lower stability. For tv above this value, the injection is still made in 60 ms. Blue points in Figure 3a represent the turbulence level of the cloud at the moment of the ignition for different tv. During the transition stage, for ignition delay times close to 60 ms, there is no significant difference in the turbulence level compared to the standard. However, for the two other stages, there is a slight difference both in the turbulence and heterogeneity of the dust cloud.
The influence of ignition delay time on the PSD was also evaluated, from 20 ms to 120 ms, using the laser granulometer. In all tests, the mean volume diameter d_{50} obtained was approximately the same than the one measured with an injection of 60 ms, i.e. 13 µm. For dry nanocellulose, the influence of ignition delay time on the PSD is then negligible, showing that the agglomerates strength is greater than the shear stress generated by the flow.

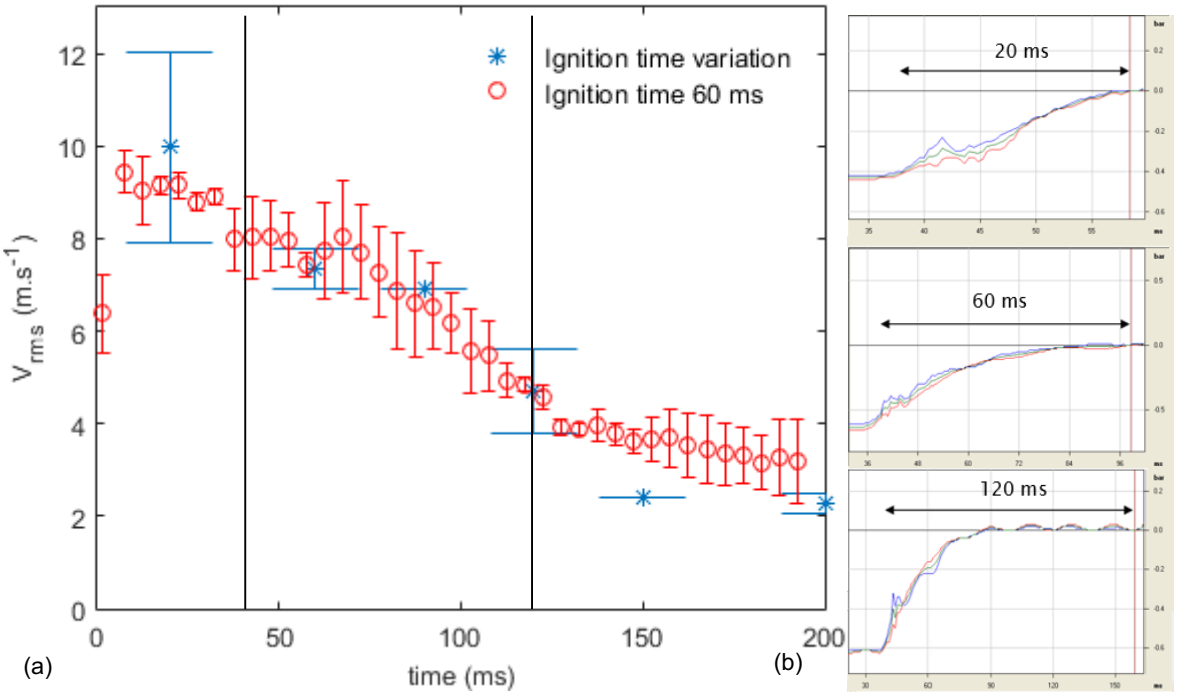


Figure 3: (a) Time evolution of the root-mean-square velocity within the 20L sphere during a standard injection for various ignition delay times (b) Modifications of the injection dynamic for various ignition delay times

The evolution of explosion severity as a function of the ignition delay time was evaluated with dry nanocellulose (Aw = 0.03) at 750 g.m^{-3} and is presented in Figure 4. Firstly, it appears that the maximum rate of pressure rise reaches 800 bar.s^{-1} for an ignition delay time of 20 ms (Figure 4b), which corresponds to a root-mean square velocity of around 9 m.s^{-1} and decreases to 200 bar.s^{-1} for a root-mean square velocity of 4.5 m.s^{-1} (120 ms). In

such case, the flame stretching tends to enhance the explosion severity. The maximum rate of pressure rise tends to stabilize after 120 ms, which corresponds to the turbulence 'stability stage'. However, the measurements reproducibility greatly decreases for low tv and local quenching phenomena can occur at very high turbulence. Indeed, the maximum overpressure (Figure 4a) obtained for ignition delay times below 60 ms appears to be reduced. In such cases, the CO content is increased due to local quenching of the flame by high shear stresses (Torrado, 2017). The influence of flame stretching on the explosion severity of nanopowders being highly probable, tests were conducted in the flame propagation tube presented in section 2.

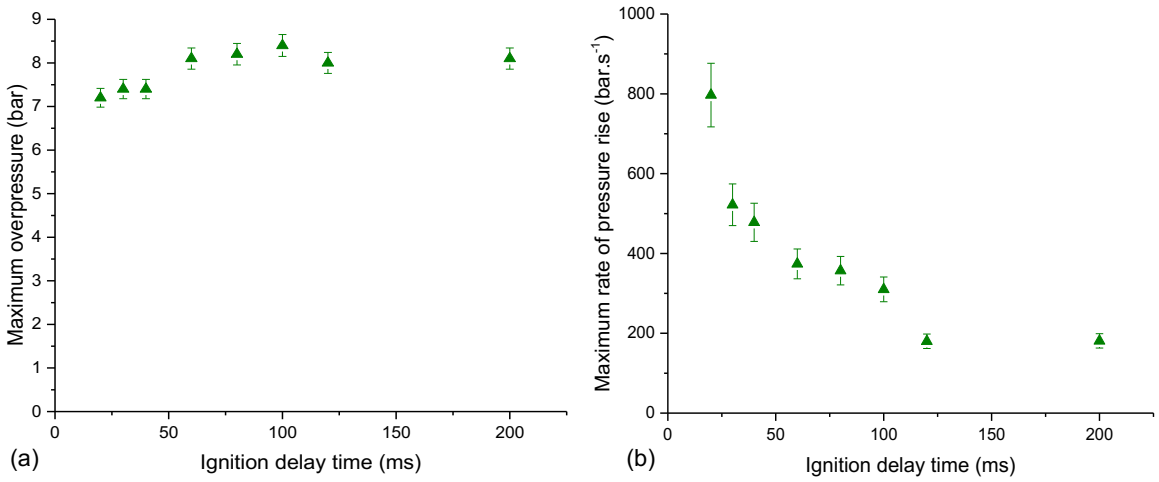
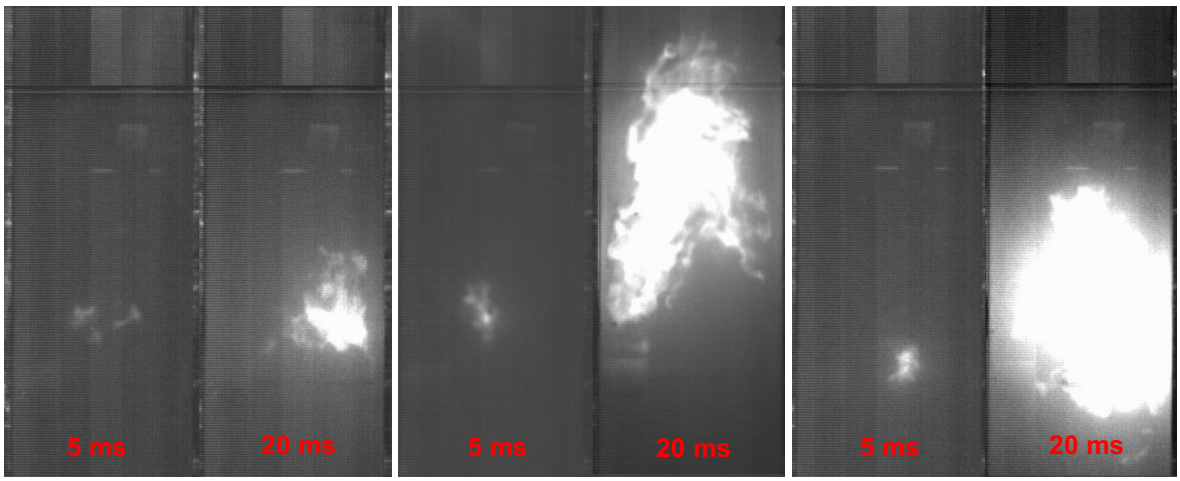


Figure 4: (a) Influence of the ignition delay time on (a) maximum rate of pressure rise (b) maximum overpressure of nanocellulose at 750 g.m^{-3}

4.2 Influence of the turbulence on flame propagation

Flame kernel growth and flame propagation was observed for concentrations of 185 g.m^{-3}. Tests were made in the propagation tube with ignition delay of 60, 130 and 180 ms respectively. Figure 5 shows the flame propagation 5 ms and 20 ms after the dust cloud ignition. It can be outlined from Figure 5a that the high turbulence level due to the low tv enhanced the flame stretching and limits its propagation. Even if the relationships between tv and the turbulence level are different in the tube and in the sphere, these tests confirm the previous hypothesis concerning the flame kernel quenching in the 20L vessel at high turbulence.
On the contrary, when the ignition delay time is increased to 180 ms (Figure 5c), the turbulence level is too low to stretch the flame which remains nearly parabolic. The flame propagation is then improved by moderate flame stretching, i.e. here at 130 ms (Figure 5b).



(a) (b) (c)

Figure 5: Visualization of flame propagation of nanocellulose at 5 ms and 20 ms for ignition delay times of (a) 60 ms (b) 130 ms (c) 180 ms.

The spatial flame velocity was then determined for the flame kernel growth stage (before the interactions with the tube walls). The spatial velocity increases from 5,7 $m.s^{-1}$ to 12,1 $m.s^{-1}$ when the ignition delay time increases from 60 ms to 130 ms, it decreases to 7 $m.s^{-1}$ when tv reaches 180 ms. Obviously, the spatial velocity cannot be directly related to the combustion kinetics, contrary to the laminar burning velocity which is an intrinsic characteristic of the combustible mixture (Cuervo, 2015). Further investigations are needed to determine the unstretched flame velocity for various turbulence and dust cloud composition. As highlighted by other authors (Torrado, 2017), the influence of nanoparticles dispersed upwards from the flame front on the radiative transfer cannot be neglected and the polydispersity of the dust cloud has to be taken into account.

5. Conclusions

The ignition and explosion characteristics of nanocellulose were studied with regard to their water activity and to the turbulence level of the dust cloud. Both parameters can have a strong impact on the particle size distribution of nanoparticles clouds. However, in the case of nanocellulose, it appears that the dispersion process breaks some agglomerates but that their size is only lowered down to approximately 10 µm. It should be stressed that the dust cloud is highly polydispersed and that primary nanoparticles of 10 nm are present as well as primary agglomerates and bigger micrometric structures.

Due to their agglomeration, the explosion severity of nanocellulose particles is comparable to that of cellulosic micro-powders. However, this is not the case for the ignition sensitivity which drops down to 5 mJ for nanocellulose whereas it reaches 590 mJ for microcrystalline cellulose. These results are consistent with those obtained for carbon blacks and some metal nano-powders (Bouillard et al. 2010; Holbrow et al., 2010).

The specificity of the nanopowders lies in their high specific surface area, but in a dust cloud, the whole particle size distribution has to be considered. The presence of nanoparticles can have an influence on the ignition process and these tiny particles can play the role of ignition promoters. But if their proportion is low compared to that of the agglomerates, their influence will be low on the combustion process, except for the potential modification of the radiative transfer. In the case of nanopowder explosions, cohesion seems to be neither an advantage, nor a force!

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