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Ignition Temperatures and Flame Velocities of Metallic Nanomaterials

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The production of materials with dimensions in the nanometre range has continued to increase in recent years. In order to ensure safety when handling these products, the hazard potential of such innovative materials must be known. While several studies have already investigated the effects of explosions (such as maximum explosion pressure and maximum pressure rise) of powders with primary particles in the nanometre range, little is known about the ignition temperatures and flame velocities. Therefore, the minimum ignition temperature (MIT) of metallic nano powders (aluminium, iron, copper and zinc) was determined experimentally in a so called Godbert-Greenwald (GG) oven. Furthermore, the flame velocities were determined in a vertical tube. In order to better classify the test results, the tested samples were characterised in detail and the lower explosion limits of the tested dust samples were determined. Values for the burning velocity of aluminium nano powders are higher compared to values of micrometre powders (from literature). While MIT of nanometre aluminium powders is within the range of micrometre samples, MIT of zinc and copper nano powders is lower than values reported in literature for respective micrometre samples.

Keywords: *Dust explosion, Nanomaterials, Minimum ignition temperature (MIT), Flame velocity*

1. Introduction

Over the past years, the use of nanomaterials in industrial applications has grown, going from pharmaceutical and cosmetics fields, to biomedical, electronics, environment and energy (Vignes, et al. 2012). As the use and production of metallic nano powders increases, measures need to be taken to mitigate accidents (fires, explosions etc.) caused by nanomaterials. The progress in the field of prevention of metal dust explosions has been slow, due to the complexity of extracting the fundamental combustion parameters from laboratories, like ignition sensitivity, burning velocity, flame quenching distance or flame structure (Julien, et al., 2015). However, in terms of nano powders some studies have been performed. Krietsch et al. (2015) have tested metallic nanoparticles in the 20 L-sphere (Siwek chamber) to investigate their explosion behaviour. Sun et al. (2018) measured the flame length, flame height, flame propagation and flame velocity of nano-aluminium clouds in a transparent quartz tube for different atmospheres. Another investigation was carried out by Huang et al. (2007) who studied the combustion processes of nano and micro aluminium particles with a type of Bunsen-burner apparatus. The results showed an increase of the flame speed by adding nanoparticles to the fuel (micrometre particles). Dust explosion in the metal processing industry represents a continuous hazard, it is known that some combustible metals can be as energetic and hazardous as organic fuels. In order to determine if the physical and chemical properties of the nano powders cause an increase in the explosion potential, several parameters that affect the explosivity of metallic nanoparticles have been studied, including the maximum explosion overpressure (p_{max}), the maximum pressure rise $(dp/dt)_{max}$ and the minimum ignition energy (MIE). Nevertheless, research on minimum ignition temperature (MIT) of metal nanoparticles has been limited (Yuan, et al., 2014).

Although several studies have been conducted, there is still a need for more information to better understand the explosion behaviour of nanomaterials. The change in the specific properties of nano powders and the need to develop suitable protective measures against dust explosions lead to the following research questions:

- Does the ignition temperature further decrease when the primary particle size is smaller than one micrometre?
- How does the flame of metallic nano powders propagate?
- How does the laminar burning velocity change for primary particles within the nanometre range?

The aim of this paper is to study the influence of the particle size of metallic nano powders on ignition temperatures and the flame propagation. These characteristics will be assessed by determining the minimum ignition temperature (MIT) and evaluating the flame propagation in a vertical tube. A big challenge when conducting dust explosion tests in general is, that the dust must be dispersed before ignition. In this way, a good distribution of the particles in the corresponding test volume is ensured. This results in high turbulence conditions in standard test apparatuses at the time of ignition. The safety parameters determined are therefore strongly dependent on the respective test conditions. Especially for metallic dusts, the so-called cubic law can often not be applied. Therefore, not only from a scientific point of view, it would be desirable to be able to determine the so-called laminar flame propagation velocity in dust clouds without the influence of initial turbulence. This paper presents results of experiments with different metallic materials and particle size distributions. The aim of these experiments was to minimise the turbulence conditions at the time of ignition by means of a special experimental setup. The flame propagation was experimentally investigated in a vertical tube open at the top side. The tube is placed on a metallic base, which simultaneously holds the dust sample and allows air to enter the tube. A porous plate is located inside the metallic base to minimize turbulence in the air flow. The ignition source is provided by a high voltage spark from two electrodes located on one third of the tube length. The dust concentration is measured optically (by light attenuation) with two concentration probes arranged below and above the electrodes. A high-speed camera is used to record the flame propagation. The burning velocity is calculated considering the ratio between the cross-sectional area and the surface area of the flame zone.

2. Characterisation

According to Krietsch et al. (2015), the increase in the specific surface area of the nano powders increases the ignition sensitivity. On the other hand, oxidation reactions may take place on the surface of the particles before testing. This process is known as “passivation”. This may lead to a decrease in the ignition sensitivity compared to not passivated powders. Furthermore moisture, particle size distribution or agglomeration may influence the reactive properties of nanomaterials. In order to be able to better assess experimental results, a precise characterisation is indispensable. For this reason, the dust samples examined were characterised in detail.

2.1 Particle size distribution

In order to have a better overview of the particle size distribution in the gas phase (during flame propagation testing), the particle size distribution was determined in a “dry dispersion unit”. The purpose of the dry dispersion is to overcome the binding forces between agglomerated particles in the micrometre range, as well as optical dilution of the particle collective, to make them measurable by the sensors. However, dry dispersion is not suitable for very fine particles ($< 1 \mu\text{m}$), because it is difficult to overcome the high particle binding forces. In this case, a wet dispersion method can be used as validation. The measurement was done using the unit Mastersizer Sirocco 2000 from Malvern Panalytical GmbH. Results from dry and wet dispersion are given in Table 1. D_{10} , d_{50} and d_{90} signify the point in the particle size distribution, up to and including which, 10%, 50% or 90% of the total volume of material in the sample is ‘contained’.

For the “wet dispersion method”, a dust sample is suspended in a liquid dispersant. The method is based on laser diffraction measurements which produce volume based particle size distributions. The particle size distribution was measured using Mastersizer 2000 from Malvern Panalytical GmbH in accordance with the ISO 13320 (10/2009) standard. For sample preparation, the nano powders are dispersed in a 3 mmol/l tetrasodium diphosphate solution. For dispersing the zinc sample ethanol is used. An external ultrasonic sonotrode is used to disperse the sample until agglomerates have been destroyed. The finest distribution is then the output as the measurement result. During the measurements, the pre-dispersed suspension is added to the dispersion unit and the samples are stirred. After recording the scattered light data, the particle size distribution is calculated using Mie-theory.

Due to the high surface energy of the nano powders, all particles investigated tend to agglomerate. Although the particles were produced in the nanometre range, they can form structures with diameters of far more than 10 micrometres. Under the selected conditions it was not possible to separate the particles down to the specified primary particle size. The particle size of the agglomerates to be expected is much higher than the information given on the label of the manufacturer.

The measurement results in Table 1 show a large difference between dry and wet dispersion for all samples except iron. For the dry dispersion method, it can be observed that the aluminium samples show bigger agglomerate sizes. However, this feature is not seen on the wet method. Even though the wet dispersion method is more suitable for nanoparticles, the use of both methods is required because the conditions during the flame propagation test are more similar to the dry method. From this evaluation it can be predicted that a homogeneous dispersion of the particles in the vertical tube will be difficult to achieve, as the distribution of the agglomerates varies from less than one micrometre to more than 100 micrometres in the case of aluminium 200 nm.

Table 1: Particle size distribution measurements

Sample	Dry dispersion			Wet dispersion		
	Particle size distribution [µm]			Particle size distribution [µm]		
	d ₁₀	d ₅₀	d ₉₀	d ₁₀	d ₅₀	d ₉₀
Aluminium 18 nm	1.6	7.8	18.6	0.1	0.8	3.5
Aluminium 40–60 nm	0.9	7.2	22.5	0.2	0.4	0.8
Aluminium 50–70 nm	0.7	2.6	10.3	0.2	0.7	3.4
Aluminium 90-110 nm	0.8	6.4	26.2	0.2	0.7	3.6
Aluminium 130 nm	0.7	4.5	24.7	0.2	0.9	5.8
Aluminium 200 nm	0.8	6.5	119.2	0.4	1.9	11.0
Iron 50–70nm	0.4	1.1	8.0	0.5	1.0	3.3
Iron 90-110 nm	0.4	1.2	6.9	0.5	1.3	6.1
Copper 50–70 nm	0.5	2.0	14.7	0.3	1.2	9.3
Zinc 40–60 nm	0.5	1.6	10.2	0.7	3.7	18.5

2.2 Specific surface area and True density

The absolute density was determined by helium pycnometer (AccuPyc 1340 II) according to DIN 66137-2(03/2019). A 10 cm³ stainless steel cup was used. For the sample preparation, drying was carried out in an oven at 80°C for 3 hours. Results are shown in Table 4.

The measurement for the specific surface area was carried on as double determination, using NOVA 2200 from Quantachrome. The method is based on the BET determination (Brunauer, Emmett and Teller), the specific surface area is determined by physical adsorption of a gas on the surface of the particles, and by calculating the amount of adsorbate gas corresponding to a monolayer on the surface. Physical adsorption results from van der Waals forces between the adsorbate gas molecules and the adsorbent surface of the particles. The measurement was carried out based on DIN ISO 9277 (01/2014) and DIN EN ISO 18757 (01/2006). In each case, 5 points of the adsorption isotherm in the range of the relative pressure p/p_0 from 0.05 to 0.3 (BET range) were used for evaluation. The samples were heated in a degasser at 100 °C in nitrogen steam for a period of 2 hours.

Table 2 shows a summary of all measurement results. Aluminium particles have smaller density values than iron, copper and zinc. On the other hand, the specific surface area is bigger. However, the determination shows smaller values than expected. The relatively small specific surface areas of iron, copper and zinc as well as the broader particle size distributions, indicate not only agglomerates but also solid aggregates.

The results show that the samples with the smaller primary particle sizes have the larger specific surface area.

The true density of aluminium samples is close to the values reported in the literature (2.7 g/cm³), except for Al 18 nm and Al 50-70 nm. The increase in the density of the aluminium samples may indicate an oxide layer (Al₂O₃), on the other hand, a lower value can be due to a layer of aluminium hydroxide (Al(OH)₃). The density values for iron, copper and zinc are below the respective literature values for the pure metal. From this, the conclusion can be drawn that the particles are surrounded by an oxide layer.

Table 2: True density and specific surface area (BET)

Sample	True density [g/cm ³]	Specific surface area (BET) [m ² /g]	Moisture content [%]
Aluminium 18 nm	2.89	23.53	1.6
Aluminium 40–60 nm	2.67	24.08	2.1
Aluminium 50–70 nm	2.58	14.82	1.8
Aluminium 90-110 nm	2.67	11.92	1.6
Aluminium 130 nm	2.67	14.05	1.2
Aluminium 200 nm	2.69	9.44	0.9
Iron 50–70nm	7.15	5.77	-
Iron 90-110 nm	7.12	5.79	-
Copper 50–70 nm	7.83	6.30	0.7
Zinc 40–60 nm	6.06	5.18	0.2

2.3 Moisture content

Moisture content in the metallic nano powders was determined by gravimetric analysis. As it was mentioned before, this parameter has a direct influence on the explosion behaviour. Results are also listed in Table 2. Because the analysis involves drying, it was not possible to determine the moisture content of the iron samples due to the decomposition and burning presented during the test, which resulted in an erroneous measurement. The highest value was determined for aluminium 40-60 nm with a water content of 2.1 %. It is expected that the experimental results are not much influenced by moisture content, since all samples showed values around or below 2%.

3. Experimental

Within the framework of the experimental work, the minimum ignition temperature and flame propagation of the metallic nanomaterials mentioned above were investigated. In the following, the respective experimental setups and the investigation procedures are briefly described.

3.1 Minimum ignition temperature

The MIT of a dust cloud in a hot furnace is defined as “the lowest temperature of a hot surface on which the most ignitable mixture of the dust with air is ignited under specified test conditions” (ISO/IEC 80079-20-2, 2016). At this temperature, the heat produced by a chemical reaction exceeds the loss of heat to the surroundings. The MIT is a useful tool to assess the risk of ignition of a dust cloud from different sources especially like hot surfaces. An overview of the experimental setup is illustrated in Figure 1.

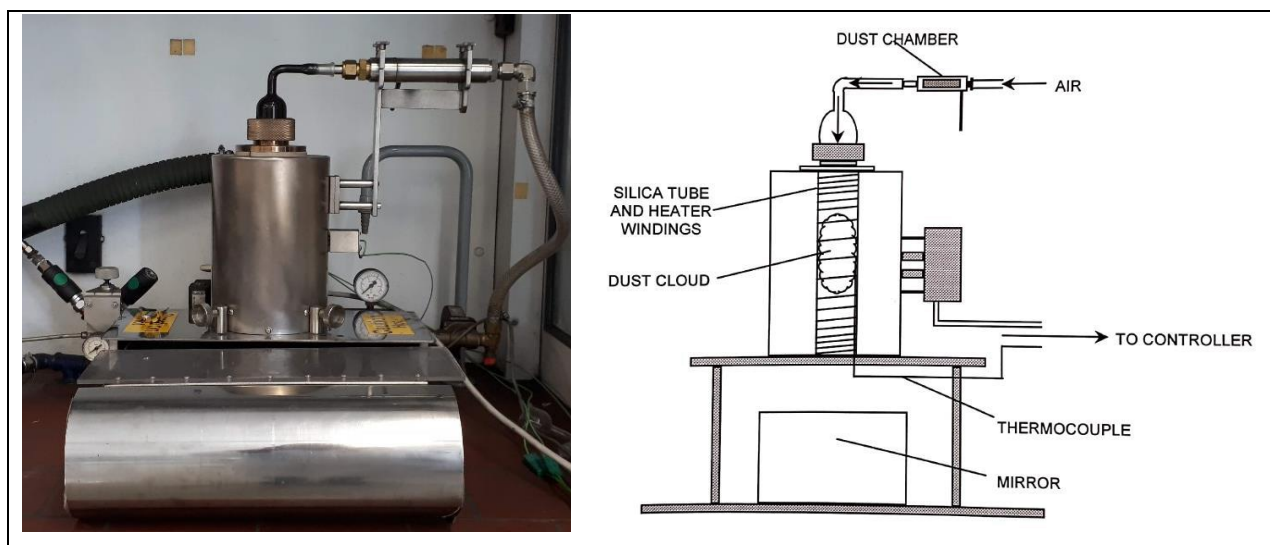


Fig. 1. GG oven experimental setup

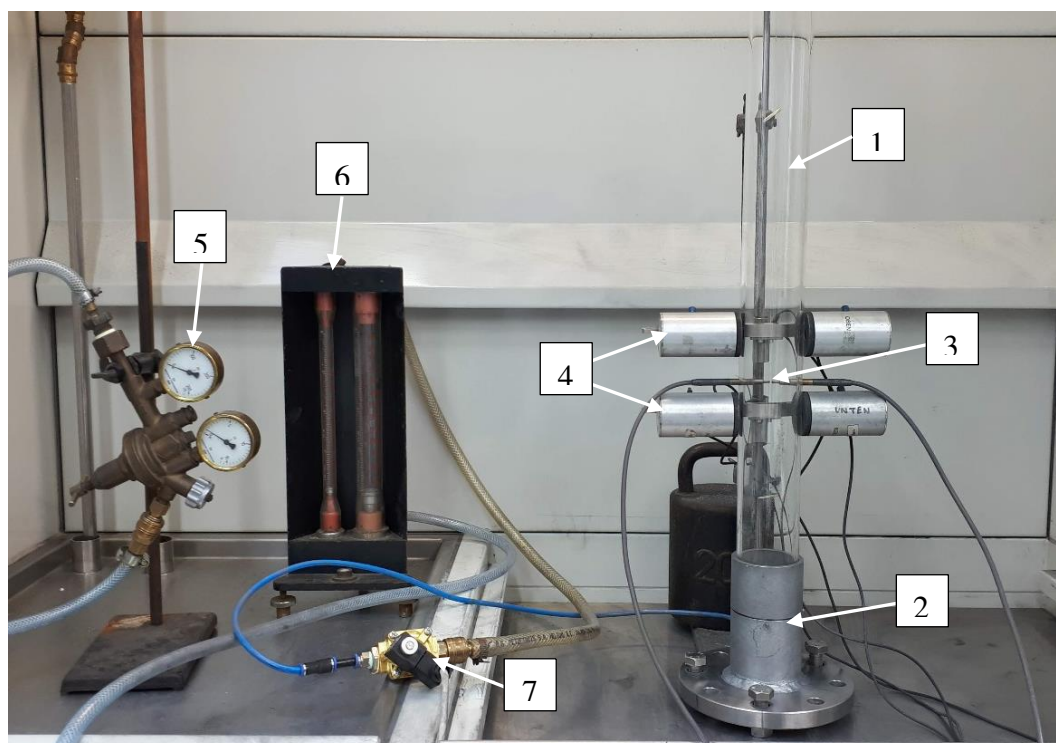
The determination of the MIT for metallic nano powders was performed in the standardised Godbert-Greenwald (GG) oven. The furnace consists of a vertical silica tube of 23 cm long and 3,6 cm internal diameter. Beneath the furnace, a mirror is located for observation of ignition inside the tube. According to the standardised test method the sample is placed into the storage container and then dispersed into the oven by an air blast through the heated vertical tube and the ignition is detected visually, when a flame is observed (outside the oven). For high-density materials, such as metals, the dust quantity is varied from 1 g to 5 g, and the dust is dispersed with air at different overpressures between 0.1 barg and 0.7 barg (10 kPa to 70 kPa). The MIT is the lowest temperature of the wall furnace at which ignition was observed by the above procedure minus a safety margin of 20 K for temperatures above 300 °C and minus 10 K for temperatures at or below 300 °C. A more detailed description of the test procedure can be found in ISO/IEC 80079-20-2 (2016).

3.2 Vertical tube apparatus

The flame propagation of metallic nano powders was studied in the experimental setup shown in Figure 2. The equipment consists of a vertical tube made of acrylic glass with an inner diameter of 60 mm, an outer diameter of 70 mm and a length of 1 m. The tube is placed on a metallic base that provides support and at the same time it contains the dust sample and allows the air supply into the tube. A porous plate is located inside of the metallic base to reduce the turbulence in the air flow. The ignition source is provided by a high-voltage spark from two electrodes located at one-third of the length of the tube (from the bottom).

The dust concentration is measured optically (by light attenuation) with two concentration probes which are positioned beneath the electrodes (lower) and above them (upper). The distance between the two measurement probes is equal to 10 cm. A pressure reducer connected to a flow meter and a

solenoid valve allow the air-flow control. It is worth to mention that the pressurized air is fed into a dryer before to get into the tube. Flame propagation behaviour is observed by the high-speed camera FASTCAM APX RS of 17500 frames per second (FPS). A more detailed description of the experimental setup is presented in Reyes Rodriguez (2019).



1: Vertical tube 3: Electrodes 5: Pressure reducer 7: Solenoid valve
2: Metallic base 4: Concentration probes 6: Flow meter

Fig. 2. Vertical tube experimental setup

Dust concentration has a major impact on the evaluation of the explosion characteristics. Therefore, to analyse the flame propagation, it is crucial to know the concentration of the dust-air mixture at the moment of the ignition. For this reason, two concentration probes (placed above and below the ignition source) were used. The measurement principle is based on the Beer-Lambert law (Eq. 1), which states that the absorbance of the light in a sample is proportional to the concentration of the attenuating species existing.

$$I = I_0 \cdot e^{-klc} \quad (1)$$

Where I is the intensity reduced, I_0 is the initial intensity, k is the extinction coefficient of the material, l is the measurement distance and c is the dust concentration. For the calibration of the concentration probes, a container filled with water is used. Calibration is performed by adding portions of dust to the liquid and mixing with a magnetic stirrer. Since the volume of the liquid and the mass of the dust are known, the concentration can be determined. Each measurement from the concentration probes [mV] is assigned to a specific concentration, then an extinction curve is created for each sample. In order to calculate the concentration at the ignition time, the measurement from the concentration probes is recorded. To make a comparison between each test, it is necessary to linearise the extinction curve using the natural logarithm and expressing it as the proportional change in the light attenuation [%] versus the dust concentration [g/m³]. Figure 3 shows the calibration line and equation for aluminium 90-110 nm.

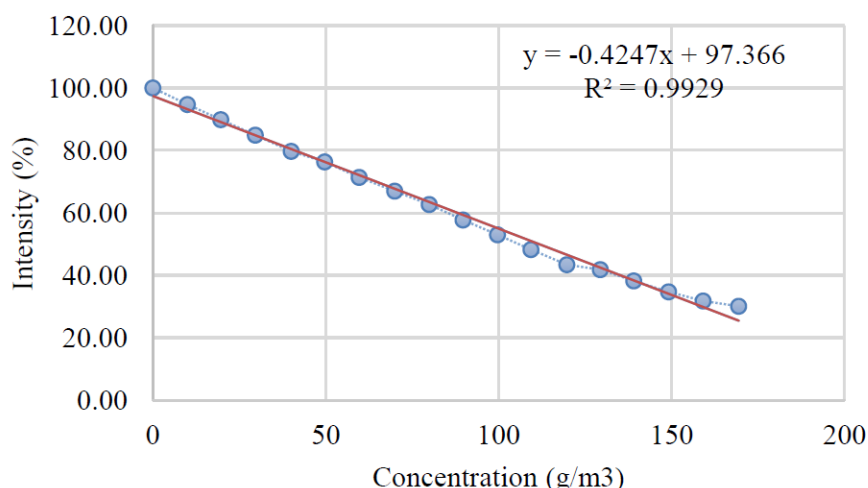


Fig. 3. Calibration result (lower concentration probe) with aluminium 90-110 nm

The test procedure starts with the weighing of the sample. Because of the difference in the density between samples, different quantities of dust were required. For instance, aluminium samples required 2–3 g to have an ignition, contrary to iron samples where 5 g were needed. Once the flow rate has been adjusted at the desired value, the sample is placed in the metallic base. After this, the tube is locked onto the base. The concentration probes must remain in the same place and distance for all tests. The test starts with the input of the uniform air flow, whereby the particles are dispersed slowly. For most of the samples, a flow rate of 3000 l/h is sufficient to create a homogenous cloud within the tube. Before the dust cloud reaches the top of the tube (after a few seconds), the flow is stopped and almost simultaneously the ignition source is triggered. Due to the lack of air flow, the particles no longer rise in the tube. At the same time, the sinking process has not yet begun. Ignition therefore occurs at a moment when the particle velocity or turbulence within the tube is almost zero. At the same moment, the camera is started. For a correct concentration record, the values from the concentration probes are monitored. By doing this, the change in the light attenuation can be analysed after each test.

Figure 4 shows the dispersion of a dust cloud of one of the aluminium samples, the moment of the ignition and the flame expansion.



Fig. 4. Experimental observation of the flame propagation of an aluminium sample

3.3 Determination of quasi laminar (unstretched) flame velocities

The flame velocity S_{fl} is calculated from the video recording. After each test, the high-speed camera creates a file with 7000 pictures. Therefore, a computer program is needed in order to determine the flame front propagation. In this study, a self-created program was used. This program is able to scan the pixels from the pictures and recognise the “flame front”.

Figure 5 shows the distance in pixels of the image, which goes from 0 to 1022 pixels. In the picture, the flame is recognised at the x-value of 207 pixels.

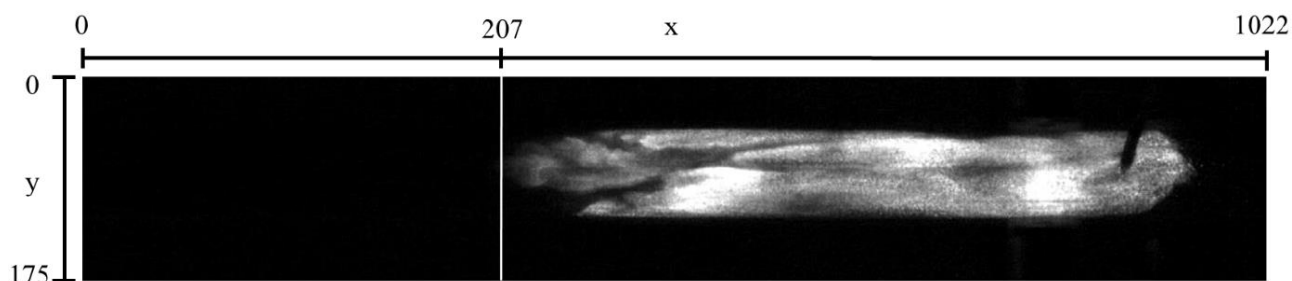


Fig. 5. Determination of the flame front at a specific time

The flame velocity S_{fl} is then determined as the distance travelled by the flame in a certain time interval. It is worth to mention that the flame velocity of every test performed varies depending on the concentration. It is also not constant along the tube (see Figure 6). By knowing the change in the distance travelled by the flame front every millisecond, S_{fl} can be monitored and the highest value of S_{fl} during one test can be determined.

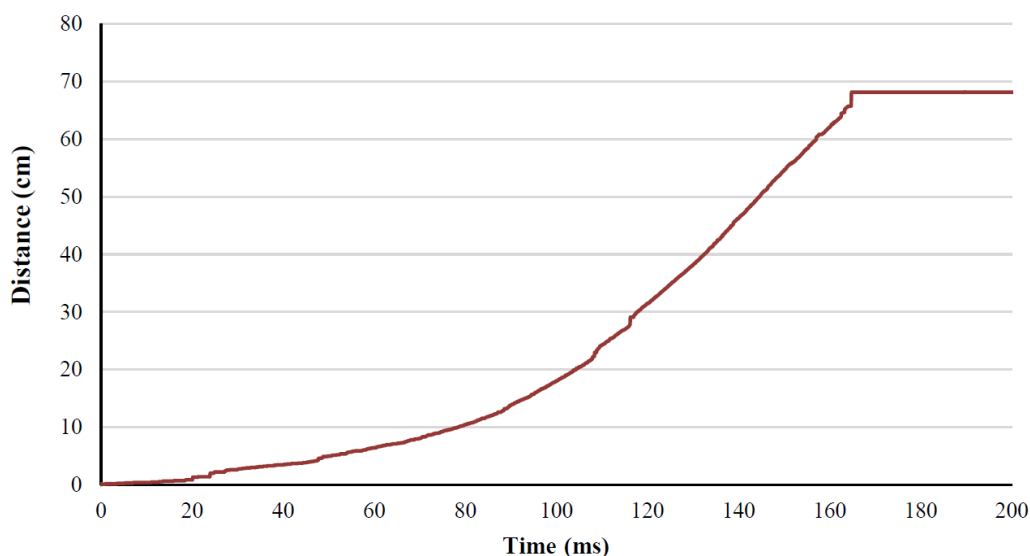


Fig. 6. Flame propagation during a test with iron 90-110 nm

As it can be noticed from Figure 6, there is a “jump” of the flame front after about 115 ms. This can be explained with the presence of combustion gases in the middle of the tube which thrust the flame upwards and therefore increase the flame speed. Therefore, it is important to determine the maximum flame speed of every test before the combustion gases are notably present in the system and consequently the flame lifts off. Figure 6 illustrates that the highest flame velocity during this single test (mean concentration of 324 g/m³) was found after 108 ms.

Since the flame velocity is known, the laminar flame velocity could be determined. However, it should be noted that the propagation of the flame upwards within the tube causes turbulence, cooling effects etc. at its walls. The flame only propagates quasi laminar the first milliseconds from time of ignition at the center until the flame hits the tube wall. Therefore, the term unstretched flame velocity would be more appropriate in this case. For a better comparison, however, the term laminar flame

velocity is used in the following. To determine the laminar flame velocity (S_L), the model of Andrews and Bradley (1972) is used. They calculate the laminar burning velocity S_L by using Equation 2:

$$S_L = \frac{A'}{A_{fl}} (S_{fl} - u) \quad (2)$$

Where S_{fl} is the flame velocity selected at the maximum value reached by the flame front during the test, A' is the flame section at the bottom of the flame zone, A_{fl} is the surface of the flame zone and u is the flow velocity. In this study u is considered as zero because the air flow stops just before ignition, so that the particle velocity is almost zero. The flame velocity S_{fl} in Equation 2 is valid for states where $S_{fl} > S_L$ and $S_{fl} > u$. When the flame is completely developed along the tube, A' should correspond to the cross-sectional area of the tube. On the contrary, when the flame does not occupy the entire section, the dead space near to the tube walls should be taken into account. The surface of the flame zone A_{fl} can be considered as a paraboloid of revolution. Figure 7 illustrates the geometry of the flame shape (Di Benedetto, et al., 2011).

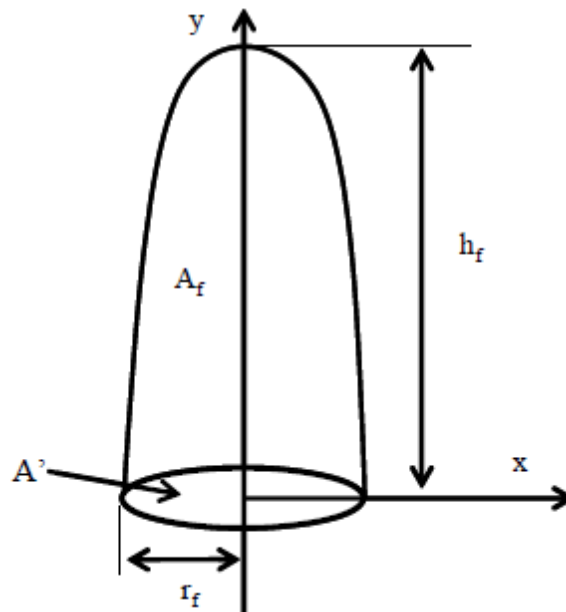


Fig. 7. Geometry of the flame

The surface area of the flame can be calculated by Equation 3 (Perry & Green, 2007)

$$A_{fl} = 2\pi \cdot \left(r_f^2 + \frac{r_f \cdot h_f \cdot a}{e} \right) \quad (3)$$

Where r_f is the flame radius and h_f is the flame height, $a = \arccos(r_f/h_f)$ and $e = \sin(a)$.

For the estimation of the height and the radius of the flame, the program *ImageJ* was used. Once the scale has been established, just by selecting both the diameter and the height on the image, the value in distance scale (m or cm) can be found.

It is assumed that S_L is constant over the entire cross section of the tube and at any time for one specific concentration. In order to verify this, the laminar burning velocity was calculated for time steps of 20 ms during a test with one of the iron samples. Table 3 shows the variation of the S_L within a single test. Contrary to the original assumption, the values are not constant, since the values vary between 0.11 m/s and 0.17 m/s.

Table 3: Calculation of laminar flame velocity during a single test with one of the Iron samples

Time [ms]	Diameter [cm]	Height [cm]	A` [cm ²]	A _n [cm ²]	S _L [m/s]
60	2.52	7.17	4.99	90.36	0.13
80	3.51	11.68	9.68	204.34	0.11
100	4.35	19.84	14.86	428.24	0.13
120	4.81	30.76	18.17	732.22	0.17
140	4.2	44.27	13.85	918.54	0.12

4. Results and discussion

In addition to the investigations on MIT and flame propagation, the lower explosion limit (LEL) of the nano powders was also determined in the 20 L-sphere (Siwek Chamber) according to EN 14034 part 3 (2006). It is equivalent to the Minimum Explosive Concentration (MEC). The LEL is taken as the highest concentration of the dust at which no ignition occurs in three consecutive tests. Table 4 shows the results of the determination. Notice that copper has a value above 1000 g/m³, which makes it difficult to ignite in the vertical tube.

Table 4: LEL, explosion behaviour at lower concentrations and MIT

Sample	LEL [g/cm ³]	Concentration [g/m ³]	p _{ex} [barg]	(dp/dt) _{ex} [barg/s]	MIT [°C]
Aluminium 18 nm	60	125	1	11	440
		250	3.3	53	
Aluminium 40–60 nm	20	125	3.7	106	470
		250	4.9	190	
Aluminium 50–70 nm	30	125	4	102	540
		250	5.7	304	
Aluminium 90-110 nm	30	-	-	-	510
Aluminium 130 nm	30	125	3.9	126	580
		250	5.5	286	
Aluminium 200 nm	30	125	4.7	141	310
		250	7	555	
Iron 50–70nm	60	125	0.4	9	pyrophoric
		250	2.4	74	
Iron 90-110 nm	60	125	3.9	89	pyrophoric
		250	5.3	238	
Copper 50–70 nm	above 1000	-	-	-	250
Zinc 40–60 nm	60	125	0.1	0	300
		250	1.2	27	

The overpressure (p_{ex}) occurring during the explosion of the metallic nano powders and the rate of the explosion pressure rise (dp/dt)_{ex} were also determined in the 20 L-sphere. The determination was made for two main concentrations similar to those existing during the study of flame propagation in the vertical tube. It should be noted that the determination was made for reference purposes, using two chemical igniters of 1 kJ each (2x1 kJ in total). This is different to the standard procedure for determining the maximum overpressure (p_{max}), for which two chemical igniters of 5 kJ each are used, and tests are conducted over a wide range of concentrations. The idea was to keep the overdriving of

the ignition source low and thus possibly better recognize connections between the experiments in the 20 L-sphere (explosion severity) and the vertical tube (flame velocity). Results are shown in Table 4. Copper is excluded from this determination, since its LEL is higher than 1000 g/m³. For nano iron and nano aluminium, it can be observed that p_{ex} and $(dp/dt)_{ex}$ increase as the primary particle size increases from smaller to bigger fractions. In general, aluminium samples created higher pressures, followed by iron.

4.1 Results of the MIT determination

In this research aluminium, copper and zinc nano powders were tested in the GG oven, following the standardised method from ISO/IEC 80079-20-2:2016. The Iron samples sometimes ignited spontaneously at air without any ignition source and have thus not been tested in the GG oven.

The values obtained with nano powders are within the range of lowest values or lower than those for micrometre powders reported in databases. The German GSBL database (GSBL 2019) reports MIT of micrometre aluminium samples from 440-850 °C. The highest MIT value for nano aluminium samples is 580°C (aluminium 130 nm). With decreasing particle size, MIT of nano aluminium is further decreasing. Aluminium 18 nm has a MIT (440 °C) which is equal to the lowest values reported in the database for micrometre aluminium. However, for aluminium 200 nm the MIT is 330 °C and thus the lowest value of all aluminium samples and even lower than all database values for aluminium.

The copper sample has a MIT equal to 250 °C, which seems to be quite low, considering that there is not a single reported MIT for copper (some samples with no ignition up to 850 °C). The reported values for zinc powder with particle size <10 µm is 570 °C and 830 °C for 160 µm. These values are also above the MIT value determined for zinc 40-60 nm (300°C). In the case of the iron powders, the MIT reported in the literature (BIA 1997) for a particle size equal to 12 µm is 580 °C. As mentioned before, in this research the iron powders in the nanometre range showed a pyrophoric behaviour. For this reason, it was not necessary to determine their MIT.

Investigated nano powders clearly show that the ignitability increases further from the micrometre range to the nanometre range as the particle size decreases. Particularly noteworthy, however, are the results obtained with aluminium 200 nm. Both the explosion pressure, pressure rise and MIT are most critical in comparison to the other aluminium samples. A glance at the characterisation of particle sizes (Table 1) shows that this sample has a very large particle size distribution. This might favour such a behaviour.

4.2 Results of the flame propagation tests

Since one of the aims of the study was to compare the influence of the particle size on the burning characteristics, samples with different particle size were chosen for aluminium. The comparison between different metallic nano powders was also of research interest, therefore nano powders of iron, copper and zinc were tested in the vertical tube apparatus. In the case of the copper sample, the LEL is higher than 1000 g/m³, since ignition was not achieved in the vertical tube. For aluminium 18 nm, the ignition of the dust cloud was also not achieved. Even though the particle size distribution is not that wide (see Table 1). The tendency to form big agglomerations while lifting the particles caused that an adequate cloud not be formed within the LEL. In addition, the smaller particles are attracted to the wall due of the tube immediately after switching on the air flow. Thus, ignition could not be realised.

The dust concentration is a key parameter in the determination of the burning characteristics of a dust sample. Therefore, achieving similar concentrations for all samples was one of the first aims. However, neither changing the amount of dust nor adjusting the air flow had a major impact on the concentration of the cloud at the time of ignition. This may be due to measurement errors but moreover due to the wide particle size distribution of all samples, which is one of the characteristics of nano powders. After a lot of failed tests, when ignition was not achieved with all samples at the same concentration, tests were continued with trying to realise at least comparable concentrations for each sample.

The flame velocities were determined using the procedure described in chapter 3.3. As a result of the data analysis, a velocity profile specific for each test was created. As it can be seen in Figure 8, there are “peaks” in the velocity profile that do not correspond to such a drastic velocity increase. There are jumps where the program is not able to correctly detect the flame front in a series of images.

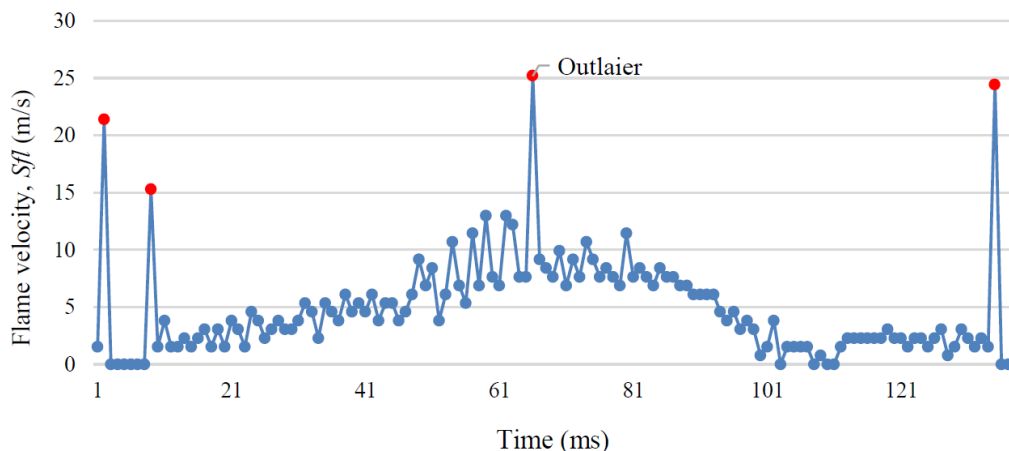


Fig. 8. Flame velocity profile of one test with iron 90-110 nm

In order to determine which velocities were abnormal peaks and which were the highest flame velocities, a graphical analysis of the data was performed to rule out the irregular values. A boxplot is a graphical tool that shows the distribution of the data within a sample. By using the median and the range between the first quartile and the third quartile, the boxplot creates an upper and lower whisker. If a normal distribution is considered, 99.3% of the data should be within the whiskers. Thus, any value below or above the whiskers is considered an outlier, meaning, it is not a representable value of the sample. The boxplot in Figure 9 shows that the outlier values correspond to the peaks in the graph of Figure 8.

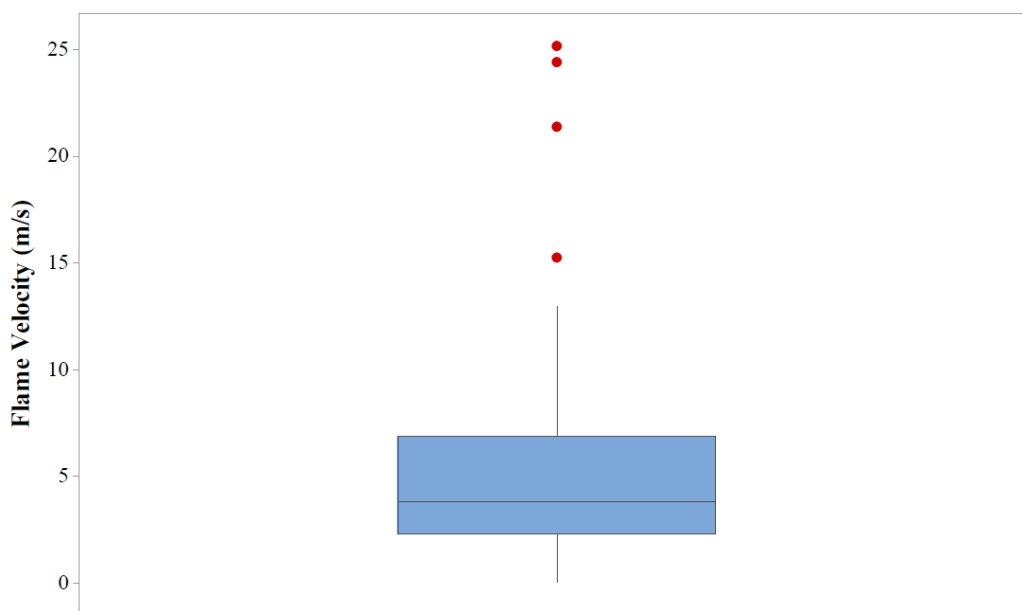


Fig. 9. Boxplot of the one test with iron sample 90-110

This procedure was performed for all successful experiments. The boxplot results were summarised, the resulting S_{fl} evaluated and then the S_L calculated according the described procedure. Table 5 shows the results of all successful tests performed with aluminium 200 nm. The highest S_L (Test 16, 0.52 m/s) is twice the lowest value (Test 5, 0.26 m/s). However, this behaviour is not related to the concentration since other tests have a higher concentration and a lower S_L .

Table 5: Flame velocities of aluminium 200 nm

Sample	Concentration [g/cm ³]	S_{flmax} [m/s]	S_L [m/s]
Test 2	123.9	11.45	0.29
Test 3	146.5	15.26	0.40
Test 5	151.5	11.45	0.26
Test 7	145.6	12.97	0.46
Test 8	162.6	13.74	0.38
Test 9	191.7	7.63	0.27
Test 11	194.8	12.21	0.33
Test 16	141	20.61	0.52
Test 18	142.6	12.21	0.30

The listing of all tables of the values determined with all dusts would go beyond the scope of this article. For this reason, all calculated S_L of the respective successful tests are shown in Figure 10. It displays a comparison of all samples between the laminar burning velocities determined and the corresponding concentration. The zinc sample has higher concentrations, due to the higher density. Therefore, it was necessary to use more material in order to observe the flame propagation in the vertical tube. Despite this, the laminar burning velocity is still in the same range as the other samples.

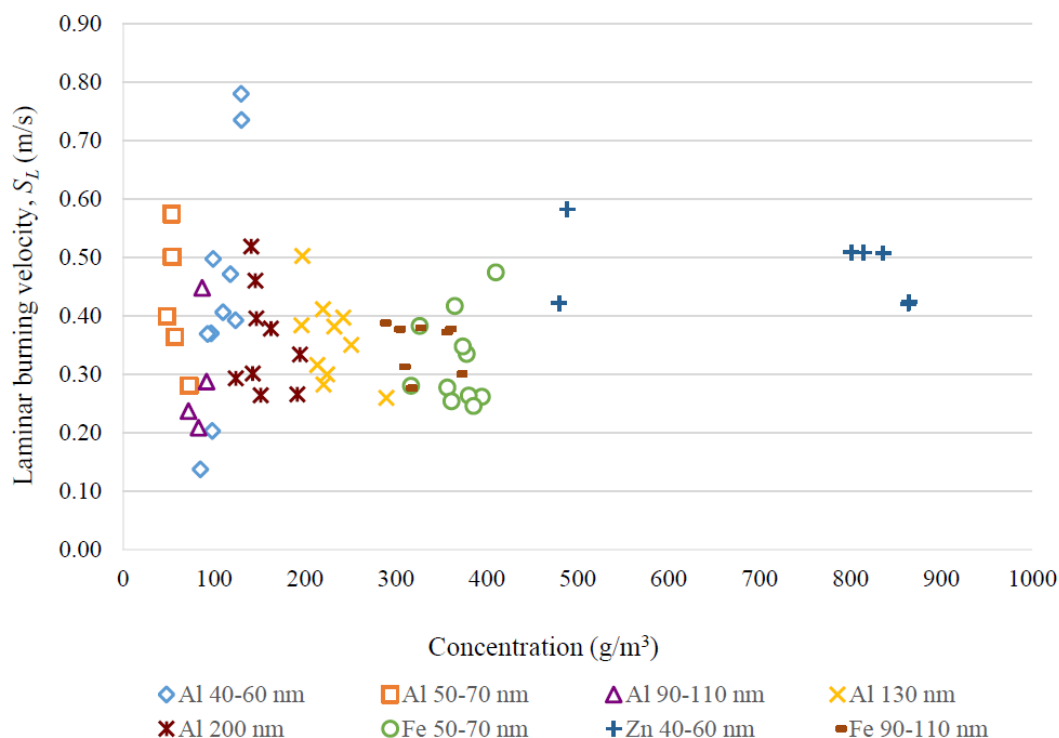


Fig. 10. Comparison of the quasi laminar flame velocity for different metallic nano powders

Data dispersion may be caused by the difficulties experienced in obtaining repeatability in experiments and to the accuracy of dust concentration measurement. Aluminium sample 40-60 nm shows the highest variation as well as the highest value for the S_L . This sample also has the largest specific surface area equal to 24 m²/g and the lowest LEL of 20 g/m³.

The results of this study can be compared with the data reported in the literature on the combustion of aluminium clouds. Figure 11 shows the results reported by Escot Bocanegra et al. (2010). Experimental results show faster flame propagation in nanoparticle clouds compared to microparticle clouds. The experimental set up was also a vertical tube, with the difference that the cloud was ignited at the top and the flame propagation was observed from top to bottom.

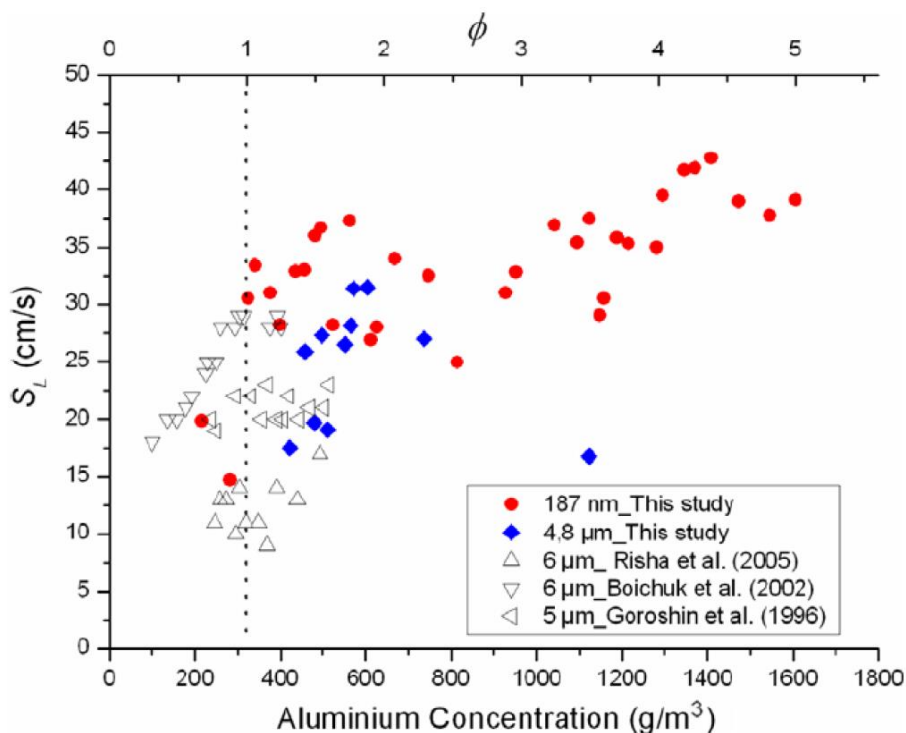


Fig. 11. Laminar flame velocity versus aluminium concentration (Escot Bocanegra, et al., 2010)

5. Conclusions

The aim of this work was to study the influence of the particle size of metallic nano powders on ignition temperatures and the flame propagation. Samples of aluminium with different particle sizes were analysed as well as nano powders of iron, copper and zinc. In total 10 samples were investigated. The particle size is an important parameter for the combustion mechanism. The influence of the heat and mass transfer becomes relevant when the combustion reaction takes place on the particle surface. For nanoparticles in a dust cloud, previous studies (e.g. Huang et al. 2007) have shown that the combustion behaves as kinetic-controlled whereas micrometric particles show diffusion-controlled combustion. This can be directly correlated with the results obtained for the flame propagation test in the vertical tube. Aluminium nanoparticles present higher laminar burning velocities in comparison with micrometric particles reported in the available literature like Escot Bocanegra et al. (2010).

The particle size distribution is one of the main parameters to evaluate and compare the results of the flame propagation tests. Two methods were used, a dry dispersion and a wet dispersion. As a result, all samples showed larger particle sizes than the primary particle sizes given by the manufacturer. In addition, the measurements showed a wide particle size distribution, which hindered the homogeneous dispersion in the vertical tube. The determination of the specific surface area yielded lower values than one would theoretically expect for nanoscale particles. This is due to the much larger agglomerates and aggregates.

Furthermore, most of the aluminium samples showed true density values close to the data reported for pure aluminium, which indicates that the samples did not show a high degree of passivation, except for the 18 nm aluminium sample. This feature contributed to the fact that the 18 nm aluminium sample could not be ignited and analysed for the flame propagation test. As a result of the

determination of the minimum ignition temperature (MIT), it was observed that the ignition temperature decreases for particles smaller than one micrometre. Results of the measurements in the GG oven were compared with data reported for the same method. The tests show that all nano samples studied can have lower MIT than micrometric samples.

The flame propagation of metallic nano powders was observed in a vertical tube. More than one hundred tests were carried out in order to be able to analyse and compare the results. A high-speed camera was used to record the progress of the flame over time. The flame velocity was obtained from the video recordings, as a measure of the distance travelled by the flame front in a time interval of one millisecond. The quasi laminar (unstretched) burning velocity S_L was then calculated. It was found that the values of S_L obtained for nano powders were higher than the values reported in the literature for larger particles (micrometric). The S_L might be an alternative to assess the explosion severity instead of the so-called dust explosion constant K_{St} , which is strongly influenced by turbulent conditions.

References

- Andrews, G. & Bradley, D. (1972). Determination of burning velocities: A critical review. *Combustion and flame*, 18(1), pp. 133-153.
- BIA (1997). *Combustion and explosion characteristics of dust*, s.l.: HVBG (Federation of the statutory accident insurance institutions of the industrial sector).
- Di Benedetto, A. et al. (2011). Flame propagation of dust and gas-air mixtures in a tube. Chia Laguna, Cagliari, Sardinia, Italy, Conference: MCS 7 (Seventh Mediterranean Combustion Symposium).
- EN 14034-3, 2006. Determination of explosion characteristics of dust clouds - Part 3: Determination of the lower explosion limit LEL of dust clouds.
- Escot Bocanegra, P. et al. (2010). Experimental and numerical studies on the burning of aluminum micro and nanoparticle clouds in air. *Experimental thermal and fluid science*, Volume 34, pp. 299-307.
- GSBL (2019). ChemInfo/Gemeinsamer Stoffdatenpool Bund Länder. www.gsbl.de (13.12.2019)
- Huang, Y., Risha, G. A., Yang, V. & Yetter, R. A., (2007). Combustion of bimodal nano/micron - sized aluminum particle dust in air. *Proceedings of the combustion institute*, pp. 2001-2009.
- ISO/IEC 80079-20-2 (2016). International standard: explosive atmospheres- Part 20-2: Material characteristics - Combustible dusts test methods. Geneva: International Electrotechnical Commission.
- Julien, P. et al. (2015). Effect of scale on freely propagating flames in aluminum dust clouds. *Journal of loss prevention in the process industries*, 36 July, pp. 230-236.
- Klippel, A., 2015. Investigation into the influence of dustiness on the course of vented dust explosions, Berlin: Bundesanstalt für Materialforschung und -prüfung.
- Krietsch, A., Scheid, M., Schmidt, M. & Krause, U. (2015). Explosion behaviour of metallic nano powders. *Journal of loss prevention in the process industries*, Volume 36, pp. 237-243.
- Reyes Rodriguez, M. D. (2019). Investigation on ignition temperatures and flame propagation of metallic nanopowders. Master Thesis at Otto-von-Guericke-Universität Magdeburg and Bundesanstalt für Materialforschung und -prüfung (BAM), Germany.
- Sun, Y. et al. (2018). Combustion characteristics on nanoaluminum cloud in different atmospheres. *Industrial & engineering chemistry research*, pp. 129-138.
- Vignes, A. et al. (2012). Risk assessment of the ignitability and explosivity of aluminium nanopowders. *Process safety and environmental protection*, Volume 90, pp. 304-310.
- Yuan, C., Amyotte, P. R., Hossain, M. N. & Li, C. (2014). Minimum ignition temperature of nano and micro Ti powder clouds in the presence of inert nano TiO₂ powder. *Journal of hazardous materials*, Volume 275, pp. 1-9.