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1	Fast and tiny : A model for the flame propagation of nanopowders
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7	
8	Abstract
9	To avoid the influence of external parameters, such as the vessel volume or the initial turbulence, the
10	explosion severity should be determined from intrinsic properties of the fuel-air mixture. Therefore,
11	the flame propagation of gaseous mixtures is often studied in order to estimate their laminar burning
12	velocity, which is both independent of external factors and a useful input for CFD simulation.
13	Experimentally, this parameter is difficult to evaluate when it comes to dust explosion, due to the
14	inherent turbulence during the dispersion of the cloud. However, the low inertia of nanoparticles
15	allows performing tests at very low turbulence without sedimentation. Knowledge on flame
16	propagation concerning nanoparticles may then be modelled and, under certain conditions,
17	extrapolated to microparticles, for which an experimental measurement is a delicate task. This work
18	focuses on a nanocellulose with primary fiber dimensions of 3 nm width and 70 nm length. A one-
19	dimensional model was developed to estimate the flame velocity of a nanocellulose explosion, based
20	on an existing model already validated for hybrid mixtures of gas and carbonaceous nanopowders
21	similar to soot. Assuming the fast devolatilization of organic nanopowders, the chemical reactions
22	considered are limited to the combustion of the pyrolysis gases. The finite volume method was used
23	to solve the mass and energy balances equations and mass reactions rates constituting the numerical
24	system. Finally, the radiative heat transfer was also considered, highlighting the influence of the total
25	surface area of the particles on the thermal radiation. Flame velocities of nanocellulose from 17.5 to
26	20.8 cm/s were obtained numerically depending on the radiative heat transfer, which proves a good

- agreement with the values around 21 cm/s measured experimentally by flame visualization and allows
- 28 the validation of the model for nanoparticles.
- 29 Keywords: dust explosion, flame propagation, nanoparticles, modeling
- 30

31 **1. Introduction**

32 Safety barriers, such as explosion venting or suppression systems (Fauske and Clouthier, 2015) need 33 to be designed by considering the experimental characteristics of the dust explosibility. These 34 characteristics are routinely determined in a 20 L sphere (Zalosh, 2019) according to well established standards like EN 14034-1 (2004) and EN 14034-2 (2006). This approach only holds by assuming 35 36 that dust explosibility can be represented by the maximum explosion overpressure value P_{max} and the K_{st} index, deduced from the maximum rate of pressure rise dP/dt_{max}. However, it needs to be further 37 38 guestioned as the measurement of dust explosion severity is actually influenced by several parameters 39 such as the initial turbulence (Amyotte et al., 1988; Zhen and Leuckel, 1997), the ignition energy 40 (Zhen and Leuckel, 1997), the moisture content of the powder (Traoré et al., 2009) and the type of dispersion nozzle (Dahoe et al., 2001; Murillo et al., 2018; Yao et al., 2020). Beyond these main 41 42 influential factors, the validity of the so-called 'cubic law' (Dahoe et al., 2001) commonly used to 43 extrapolate results obtained in a confined volume to another volume (Eckhoff, 2003) is also 44 questioned.

Standard conditions were initially defined to evaluate the explosion severity of microparticles, but when it comes to nanoparticles, potential discrepancies can arise. Indeed, their small size induces a high specific area and new properties, which can lead to modifications in the combustion kinetics (Bouillard et al., 2010; Dufaud et al., 2011) along with extremely high ignition sensitivity, especially for metallic nanopowders that can spontaneously ignite when exposed to air (Boilard et al., 2013; Krietsch et al., 2015). An evaluation of the adequacy of the current standards for the assessment of the explosion severity of nanoparticles is then necessary (Santandrea et al., 2019b). 52 To overcome the identified limitations, direct investigation of the flame propagation could be useful so as to provide fundamental inputs in advanced simulations (CFD or phenomenological approach). 53 An essential parameter is then the laminar burning velocity, which is an intrinsic property of the fuel-54 55 air mixture (Belerrajoul, 2019; Dahoe et al., 2002) that can be used in such simulations to evaluate the consequences of an explosion scenario in specific conditions (Skiold, 2003). The existence of a 56 laminar burning velocity of dusts is difficult to define due to the inherent turbulence related to the 57 58 dispersion of the powder but such an approach was already proposed 30 years ago by Bradley and 59 Lee (1984), though it proved itself challenging when it comes to dusts. Nevertheless, the low inertia 60 and sedimentation rate of nanoparticles enable to investigate flame propagation in very low turbulent 61 conditions (Santandrea et al., 2020).

In this paper, a one-dimensional model initially conceived and validated for hybrid mixtures of gas and combustible dust (Torrado et al., 2018) has been modified and adapted to predict the laminar flame velocity of nanocellulose. Results of simulations are then compared to the experimental values measured on nanocellulose using a flame propagation tube and a vented explosion sphere (Santandrea et al., 2020). The consistency of a correlation established by Silvestrini et al. (2008) to predict laminar flame velocity of micropowders based on the knowledge of their explosion severity was also analyzed for nanocellulose.

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70 **2. Material and experimental method**

71 2.1 Flame propagation observation

Nanocellulose powder, or more precisely a cellulose nanocrystals powder NCC (CelluForce), is composed of primary fibers, whose dimensions are 70 nm length and 3 nm width. The flame propagation of nanocellulose was studied at low turbulence by Santandrea et al. (2020) in a flame propagation tube (Cuervo et al., 2017) and in a vented visualization 20 L sphere, as summarized in Figure 1. Due to a difficult visualization of the flame kernel at high concentration, a concentration of 500 g/m³ was chosen, as it is higher than the minimum explosible concentration, i.e. 125 g/m³, to

ensure an ignition at low ignition energy. It is greater than 225 g/m^3 , the theoretical stoichiometric 78 79 concentration, and rather close to the experimental optimal concentration, i.e. 750 g/m³. The particle 80 size distribution of nanocellulose dispersed in both setups was determined in situ using a laser 81 diffraction sensor (Helos - Sympatec). It appears that the mean surface diameter in the 20L sphere 82 reaches 10 µm, 60 ms after the beginning of the dispersion. However, by applying lower dispersion 83 stresses, e.g. by sedimentation, agglomerates ranging from a few micrometers up to 60 µm are formed 84 in the powder. This does not exclude the presence of nanoparticles (from 100 nm to 300 nm) in the 85 dust cloud as demonstrated by using a Fast Mobility Particle Sizer (FMPS) and a Scanning Mobility 86 (Santandrea et al., 2020).

87



88

Figure 1. Simplified scheme of the experimental determination of the laminar burning velocity by
flame visualization used by Santandrea et al. (2020)

91

92 Explosion were recorded using a high-speed video camera, and the flame kernel growth was analysed in terms of flame front position and surface area using a model developed by Cuervo (2015) in 93 94 Matlab's Simulink. The equations initially established for gases were then applied to the obtained 95 values, assuming that the devolatilization of organic nanopowders is fast and that, under certain 96 concentration and turbulence conditions, the reaction is then limited by the combustion of the 97 pyrolysis gases (Cuervo, 2015; Di Benedetto and Russo, 2007; Dufaud et al., 2012a). This regime 98 corresponds to small particles for which both heating and pyrolysis steps occur very fast with regard 99 to the gas combustion; i.e. for low pyrolysis time over gas combustion time ratio (Di Benedetto et al.,

100 2010). Thus, the burning velocity was calculated using the spatial velocity S_u , the estimated cross-101 section A_s and the flame surface A_f according to Andrews and Bradley (1972), along with the flame 102 stretching factor K, called Karlovitz factor (Karlovitz et al.,1951). Those parameters were then 103 combined to apply a linear relation linking the burning velocity and the Karlovitz factor K to the 104 laminar burning velocity S_u^0 and the Markstein length δ_M , which is a parameter characterizing the 105 stability of the flame (Clavin, 1985; Markstein, 1964).

106

107 2.2 Pressure-time evolution interpretation

In order to take advantage of the standard explosion tests realized in the 20L sphere, some authors 108 109 such as Silvestrini et al. (2008) developed a correlation between the laminar burning velocity and the 110 parameters P_{max} and K_{St}. Explosions tests were conducted on nanocellulose in the standard 20 L sphere according to international standards (EN 14034-1, 2004; EN 14034-2, 2006), but using 111 112 chemical igniters of 100 J to avoid an overdriving phenomenon, knowing the minimum ignition 113 energy of the dried nanocellulose is 5 mJ (Santandrea et al., 2019b). Since the values of laminar burning velocity obtained by flame propagation observation are available only at 500 g/m³, only the 114 115 results obtained for this concentration are discussed in this work. Nevertheless, tests were performed over a wide range of dust concentration (up to 1250 g/m^3), and the influence of the dust concentration 116 on the laminar burning velocity is discussed by Santandrea et al. (2020). The laminar burning velocity 117 S_u^0 of starch was then calculated from the knowledge of the explosion overpressure P_m and rate of 118 119 pressure rise $(dP/dt)_m$, using the correlation established by Silvestrini et al. (2008):

120
$$S_u^{\ 0} = 0.11 \frac{\left(\frac{dP}{dt}\right)_m V^{1/3}}{P_m \left(\frac{P_m}{P_0}\right)^{0.14} \left(\frac{P_m}{P_0}\right)^{\left(\frac{1}{\gamma}\right)}}$$
(1)

121 where V is the vessel volume, P_0 the atmospheric pressure and γ the ratio of specific heats. This 122 correlation is based on several assumptions, e.g. the flame expansion is spherical, the turbulent length 123 scales are disregarded and the burnt gases remain trapped behind the expanding flame front 124 (Silvestrini et al., 2008).

126 **3.** One-dimensional modelling of flame propagation

127 Complementary to experiments relying on the flame visualization and the pressure-time evolution, 128 the laminar flame velocity was approached using a one-dimension flame propagation model 129 developed by Torrado et al. (2018) and initially designed to describe gas and hybrid mixtures 130 explosions). The model was then adapted to nanocellulose using the same hypothesis than for flame 131 visualization experiments, i.e. considering a fast devolatilization of the dust and a flame propagation 132 kinetically limited by the combustion of the pyrolysis gases. A similar assumption was previously 133 made by several authors, considering that a dust explosion is controlled by homogeneous combustion 134 for diameters lower than 'a critical value' (Eckhoff, 2003; Russo and Di Benedetto, 2013). For 135 instance, based on tests carried out on 110 µm particles, Cashdollar et al. (1989) stated that the 136 explosion of carbonaceous dusts was mainly driven by the gas phase combustion of the volatiles. Di 137 Benedetto and Russo (2007) used this assumption to validate their dust explosion model on 20 µm microcrystalline cellulose. However, it should be clearly stated that this is a strong assumption when 138 139 dealing with organic microparticles as both the pyrolysis reaction and heat transfer can also control 140 the combustion kinetics. By calculating the values of Biot and Py numbers for cellulose particles, Py 141 being defined as the ratio between the pyrolysis time over the characteristic time for heat transfer 142 (Piskorz et al, 1986), it appears that the heat transfer may control the explosion for particles with 143 diameters greater than 200 µm. For smaller dusts, pyrolysis is certainly the rate-limiting step down 144 to a few micrometers, this 'critical limit' being hard to define as it depends on particles properties. 145 While keeping in mind these limitations and preliminary precautions, the assumption of a fast 146 devolatilization of organic nanopowders was made during the model development.

Moreover, since cellulose and starch are both polymers formed of glucose chains, both compounds are assumed to produce the same pyrolysis gases when tested in the same conditions. It is another strong assumption as the physical properties of the powders (particle size distribution, porosity, shape...) play a significant role in their chemical reactivity.

151 Pyrolysis experiments were conducted on wheat starch ($d_{50} = 22 \mu m$) in a Godbert-Greenwald oven 152 modified according to Dufaud et al. (2012b) to collect the post-pyrolysis gases. Oven temperature was modified over a range of 973 to 1173 K. It should be noted that the minimum ignition temperature 153 154 (MIT) of cellulose powder is approximately 773K, value depending on the particle size distribution. Due to short residence times, and considering the particle external and internal heat transfers, 155 temperatures lower than 973K will lead to low pyrolysis conversion and to gas amount too low to be 156 analysed correctly. The maximum oven temperature is 1223K and a temperature too different from 157 158 the MIT would not make it possible to obtain gases representative of those generated during the first phases of ignition (in the preheating zone before their combustion). Therefore, the gas composition 159 160 obtained for a concentration of approximately 500 g/m^3 and a temperature of 973 K was then used as 161 the initial composition of the fuel (Figure 2) in the model for a numerical determination of the laminar flame velocity of nanocellulose. The mass fraction of the species generated by the pyrolysis of the 162 163 powder are also given above the bars in Figure 2. It should be emphasized that a different temperature 164 would lead to a different gas composition, especially considering that the carbon dioxide content would decrease and hydrogen and methane concentrations would increase as the temperature rises. 165 166 Furthermore, such flash-pyrolysis experiments were performed for lean fuel mixtures and the gas composition shown in Figure 2 would not be suitable for fuel rich mixtures (above 750 g/m³ as stated 167 in 2.1). As a consequence, if the model developed in this work can be very useful to give a first 168 estimate a laminar burning velocity, it would be mistaken to believe that a single composition of 169 170 pyrolysis gases would be representative of what occurs at every point of the dust cloud and at every 171 moment during a dust explosion.



Figure 2. Initial composition of the nanocellulose pyrolysis gases/air mixture considered in the
flame propagation model for 500 g/m³ of nanocellulose

172

176 The simulation domain is constituted of a tube with a numerical length of 5 cm involving two parallels walls divided into three distinct zones: preheat, reaction and post-flame, knowing that the flame 177 propagates from the post-flame zone to the preheat zone. Mass, species and energy balances, notably 178 179 based on the properties of the considered chemical species, were then expressed in the simulation 180 domain. Since the main chemical species constituting the pyrolysis gases of nanocellulose are the 181 same than the species initially considered in the model for the flame propagation of a methane/air 182 flame (Torrado et al., 2018), similar reaction mechanisms were used. However, since the pyrolysis step mainly produced carbon monoxide, a reversible oxidation reaction of this gas to produce carbon 183 184 dioxide was added (Table 1, reactions 7 and -7). Reactions involving radicals H, OH and O were also 185 considered to improve the prediction of the flame temperature (Frassoldati et al., 2009). The mass reaction rate of a component depends on its molecular weight and the rate of the reactions in which 186 187 it is involved. The rate of each reaction r_i was then expressed as:

188 $r_i = k \prod \varphi^{n_i} \tag{2}$

189 where φ is the mole concentration and n_i the reaction order of the component i in the reaction j. The 190 reaction constant is assumed to follow an Arrhenius law and is defined as:

191
$$k_j = A_i T^\beta \exp\left(\frac{-E_i}{RT}\right)$$
 (3)

192 where A_i is the pre-exponential factor, E_i is the activation energy and β , a temperature exponent.

193

194 Table 1: Reaction mechanisms considered for the combustion of the pyrolysis gases
195 (Units in cal, mol, m, s)

#	Reaction	A_i	β	E_i	Reaction order	Reference
1	$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$	2.45 x 10 ⁹	0	3 x 10 ⁴	[CH4] ^{0.5} [O ₂] ^{1.25}	(Jones and
						Lindstedt, 1988)
2	$CH_4 + H_2O \rightarrow CO + 3H_2$	3 x 10 ⁵	0	3 x 10 ⁴	[CH ₄] [H ₂ O]	(Jones and
						Lindstedt, 1988)
3	$CO + H_2O \rightarrow CO_2 + H_2$	2.75 x 10 ⁶	0	2 x 10 ⁴	[CO] [H ₂ O]	(Jones and
						Lindstedt, 1988)
-3	$CO_2 + H_2 \rightarrow CO + H_2O$	9 x 10 ⁷	0	2.8 x 10 ⁴	[CO ₂] [H ₂]	(Torrado et al.,
						2018)
4	$H_2 + 0.5O_2 \rightarrow H_2O$	3.85 x 10 ¹³	-1	4 x 10 ⁴	$[H_2]^{0.25} [O_2]^{1.50}$	(Jones and
						Lindstedt, 1988)
	$\mathrm{H_{2}O} \rightarrow \mathrm{H_{2}} + 0.5\mathrm{O_{2}}$	9.27 x 10 ¹⁸	0.88	9.8 x 10 ⁴	[H ₂ O] [H ₂] ^{-0.75}	(Andersen et al.,
					[O ₂]	2009)
5	$O_2 \rightarrow 2O$	1.5 x 10 ⁹	0	1.13 x 10 ⁵	[O ₂]	(Frassoldati et
						al., 2009)
6	$H_2O \rightarrow H \cdot + OH \cdot$	2.3 x 10 ²²	-3	1.2 x 10 ⁵	[H ₂ O]	(Frassoldati et
						al., 2009)
7	$CO + 0.5O_2 \rightarrow CO_2$	1.26 x 10 ⁴	0	10 x 10 ³	$[CO] [O_2]^{0.25}$	(Andersen et al.,
					$[H_2O]^{0.5}$	2009)

-		1.0.5 1.0.12			$[CO_2] [H_2O]^{0.5}$	(Andersen et al.,
-'/	$CO_2 \rightarrow CO + 0.5O_2$	1.95 x 10 ¹²	-0.97	78.4 x 10 ³	[O ₂] ^{-0.25}	2009)

197 The calculation of the flame velocity then relies on the numerical integration of the differential198 equations of mass, species and energy:

199
$$\frac{\partial \rho}{\partial t} + div(\rho u) = 0 \quad (4)$$

200
$$\frac{\partial}{\partial t}(\rho y_i) + div(\rho y_i u) + div(j_i) = \dot{\omega}_i \quad (5)$$

where j_i , ρ , y_i and u are respectively the mass diffusion flux, the mixture density, the mass fraction of the ith component, and the velocity. The reaction rate of the component i, depends on the molecular weight W_i and on the stoichiometric coefficient of the component i in the reaction j:

204
$$\dot{\omega}_i = W_i \sum_{i=1}^{N_r} v_{i,i} r_i$$
 (6)

The energy balance is developed as follows, assuming a constant pressure and negligible viscous
forces (Torrado et al., 2018):

207
$$\sum_{i=1}^{N} C_{p,i}[\rho y_i \partial_t(T) + \rho y_i u div(T) + j_i div(T)] = -\dot{\omega}_i \left[\sum_{i=1}^{Nspecies} \left[h_{f,i}^0 + C_{p,i}T \right] \right] + div(\lambda \nabla T) + Q_{rad} \quad (7)$$

209 The radiation term Q_{rad} will be developed in section 4.2.

The space derivatives were discretized using the finite volume method with 160 control volumes to obtain a system of ordinary differential equations, which was solved using the integration functions ODE (ordinary differential equations) in Matlab. A mesh independence study was carry out by beginning with 40 control volumes and increasing progressively the mesh resolution by 1.2. The expression of the mass and species balance, the mass diffusion fluxes and the energy balance, along with the numerical resolution, are properly described by Torrado et al. (2018).

The resolution of the ordinary differential equations requires an initial value of the temperature and mass fractions of all the considered species in every numerical domain. The composition in the preheat zone, which represents 25% of the numerical domain, is defined by the mass fractions of the considered mixture in laboratory conditions. As a first approximation, the mass fractions and 220 temperature are assumed to evolve linearly in the reaction zone, implying those values are known if the initial and final conditions are fixed. To estimate the conditions in the post-flame zone (70% of 221 222 the considered distance), the adiabatic temperature and mass fraction of the burnt gases for a steady 223 flame were calculated using PREMIX program (Kee et al., 1993). This approach, represented in Figure 3, was used to reduce the calculation time and to improve the convergence of the program, by 224 initializing all the conditions close to a stable solution. Since this numerical model also aims at 225 226 considering the radiative heat transfer induced by the presence of nanoparticles in the mixture, which 227 is not the case of the PREMIX program, this latter was not considered as a suitable method to 228 determine the laminar burning velocity of nanopowders.



229

Figure 3. Schema of the initial conditions of the temperature and fuel fraction in each zone of theflame

232

The system previously defined was then analyzed considering a distance L of 5 cm and an integration time of 50 ms. In order to show an example of raw results obtained by a simulation, the evolution of the temperature with time is presented in Figure 4 for an initial fuel concentration of 500 g/m³. The different positions indicated in Figure 4 correspond to various zones: i) the temperature evolution in the preheat zone is represented by the curves at 0.66 and 0.91 cm, ii) the flame boundaries are located at 1.22 cm and 1.45 cm (including 1.25 cm), and iii) the time-evolution of the temperature in the postflame zone is given at 5 cm. It appears that, in the post-flame zone (5 cm), the temperature is constant with time, since the reaction already occurred. Then, a fast increase of the temperature after a few milliseconds is visible in the reaction zone, especially at 1.22 and 1.25 cm. The thermal wave progressively shifts toward the preheat zone with time, describing the propagation of the flame.

The 1D model was previously validated on methane/air mixtures (Torrado et al., 2018) as it gives a laminar burning velocity of 34 cm/s, which is close to the experimental values of methane/air burning velocity from 34 to 38 cm/s (Dirrenberger et al., 2011; Proust, 2006). Moreover, the model shows a good agreement with commercial software (PREMIX program) to estimate the mass fraction of burnt gases and the final temperature; for instance, the flame temperature of a stoichiometric CH₄/air mixture obtained by the 1D model is 2271 K compared to a theoretical adiabatic temperature of 2236 K.



250



253

254 **4. Results and discussion**

255 *4.1 Combustion of the pyrolysis gases*

256 The position of the flame front, assimilated to the position of the highest temperature, was recorded for each integration time and is presented in Figure 4. It should be reminded that the reaction zone 257 258 was initially located between 1.25 cm and 1.5 cm. However, before 1 ms, a very fast displacement of 259 the flame is observed, preventing a clear determination of the flame front position between 1.4 and 1.5 cm. Nevertheless, a linear evolution of the flame position with time can be observed from 1 ms 260 to 50 ms. A laminar flame velocity of 17.5 cm/s, represented by the slope of the linear regression, 261 262 was then obtained for the combustion of nanocellulose. It should be stressed that this value should be 263 viewed with caution as the pyrolysis step has been considered as very fast with regard to the combustion of the pyrolysis gases, which is a strong assumption only validated form very small 264 265 particles.

The flame velocity calculated using the flame propagation model was then compared to the values 266 experimentally obtained by Santandrea et al. (2020) (Table 2). The value determined numerically 267 268 appears to be of the same order of magnitude than the experimental ones (from 16.9 to 23.5 cm/s), with a maximum difference of 22% with regard to the laminar flame velocity measured in the flame 269 propagation tube. This value is also consistent with laminar flame velocity of "wood gas" at the 270 271 stoichiometry mentioned in the literature by Mollenhauer and Tschöke (2010) and Przybyla et al. (2008), reaching around 14 cm/s and 20 cm/s respectively. Moreover, these results are also in 272 agreement with the flame velocities of dusts, i.e. from 15 to 30 cm/s for the unstretched laminar 273 burning velocity of cornstarch (Dahoe et al., 2002) and from 15 to 55 cm/s, proposed by Sattar et al. 274 (2014) for various powders such as lycopodium, coal and walnut shells. Nevertheless, the difference 275 276 between experimental and numerical values can obviously come from experimental uncertainties, but 277 can also be due to the omission of both the contribution of the radiative heat transfer to the flame 278 propagation or of the pyrolysis reaction. Indeed, if the pyrolysis step can decrease the flame velocity 279 due to a kinetic limitation, the fresh or unburnt remaining particles can also improve the flame propagation through a heat transfer modification in the preheat zone. Such impacts on the radiative 280 281 transfers and on the flame speed were notably observed in the visible spectrum when combustible or

even inert particles (carbon black or alumina) were added to methane (Torrado et al., 2017). To numerically evaluate this influence, the contribution of the radiative heat transfer, added to the flame propagation model by Torrado et al. (2018) and based on the work of Haghiri and Bidabadi (2010), will be now considered during the combustion of the pyrolysis gases of nanocellulose.

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- 287

Table 2: Numerical and experimental values of laminar flame velocity of nanocellulose

Determination method	Laminar flame velocity (cm/s)
Flame propagation model	17.5
Flame visualization: propagation tube	21.4 ± 1
Flame visualization: vented sphere	20.5 ± 3
20L sphere: application of Silvestrini et al. (2008) correlation	19.9 ± 3

288



289

290 Figure 4. Evolution of the flame front position with time during the combustion of nanocellulose

- 291 *pyrolysis gases*
- 292
- 293 4.2 Influence of the radiative heat transfer

294 Since the pyrolysis of nanocellulose particles and the combustion of the pyrolysis gases happen simultaneously, the unburnt particles can impact the flame propagation by variations of the heat 295 296 transfer. However, the remaining dust can hardly be quantified and characterized for each integration 297 time without taking the pyrolysis kinetics into account. Thus, several dust concentrations, assumed constant with time, were tested. The dust clouds were supposed to be homogeneous over the 298 299 simulation domain and constituted of monodispersed spherical particles. Moreover, due to the 300 agglomeration of the nanoparticles, the particle size after dispersion must be considered (Santandrea 301 et al., 2019a). As described in section 2.1, particle size distribution measurements after dispersion of nanocellulose in the 20L sphere led to a mean value of 10 µm (Santandrea et al., 2020). This value 302 303 was then chosen as a reference for the calculation, along with 100 nm, to represent the primary particles, and 60 µm, which is the mean diameter of nanocellulose agglomerates before dispersion, 304 i.e. the agglomerates not broken by the dispersion process. In this model, Mie scattering, valid for 305 306 micron particles, was then used to define the radiative heat transfer. It should be noted that Rayleigh 307 scattering, encountered for particles smaller than 100 nm, do not contribute significantly to the flame expansion due to the emission in every direction (Hong and Winter, 2006). Thus, decreasing the 308 309 particle size below this size would only decrease the radiative heat transfer contributing to the flame 310 propagation, and so the flame velocity. The concentration of dust that did not react during the combustion of the 500 g/m³ of nanocellulose was varied from 2.5 g/m³ to 100 g/m³. These values 311 were chosen as orders of magnitude to represent the radiative heat transfer at the beginning and at the 312 313 end of the reaction. The radiative heat transfer was then added to the energy balance, and the heat 314 capacity of the dust was then taken into account during the calculation of the mean heat capacity of 315 the mixture. Due to the assumption of a fast pyrolysis, the heterogeneous reactions involving the solid 316 particles were not considered in the model. However, it should be noted that Torrado et al. (2018) 317 evidenced that the contribution of the chemical reactions of the powder is negligible with regard to the contribution of the radiative heat transfer at low concentrations (2.5 g/m^3) . 318



Figure 6. Numerical values of the laminar flame velocity of a mixture of nanocellulose pyrolysis gases (500 g/m^3) and inert particles considered for the radiative heat transfer: influence of the inert particle

322 diameter at 2.5 and 100 g/m^3 .



324 Figure 7. Numerical values of the laminar flame velocity of a mixture of nanocellulose pyrolysis gases

325 (500 g/m^3) and inert particles considered for the radiative heat transfer: influence of the inert powder

326 concentration for particle diameters of 5, 10 and 60 μ m.

Figure 6 confirms that the laminar flame velocity obviously varies as a function of the particle size 328 329 distribution (Ghaffari et al., 2019) and of the dust concentration. In Figure 6, it also appears that small 330 particles contribute more to the radiative heat transfer than bigger particles in the micro-range. Indeed, particles of 60 µm bring similar contribution to the flame acceleration, i.e. around 0.5 cm/s, at 2.5 331 g/m³ and 100 g/m³, whereas 100 g/m³ of 5 µm particles lead to a flame velocity of 20 cm/s, i.e. 14% 332 333 higher than the flame velocity of the pyrolysis gases. At this point, it should be stressed that for large 334 particles, the assumption of a fast pyrolysis with regard to the combustion reaction is certainly not 335 valid and that simulations presented for powders having a mean diameter larger than 10 µm are only 336 given as an indication. It should also be underlined that the contribution of particles of 100 nm to the 337 radiative heat transfer may be overestimated since Mie scattering was considered for the calculation whereas Rayleigh scattering is more representative of the heat transfer of nanoparticles. In Figure 7, 338 it appears that a dust concentration of 2.5 g/m^3 leads to a mean flame velocity of around 17.8 cm/s 339 340 for particles between 5 and 60 µm. Therefore, increasing the concentration also increases the 341 contribution of the radiative heat transfer to the flame propagation, reaching 20.0 cm/s when 342 considering 100 g/m³ of particles of 5 μ m.

Both the dust concentration and the particle size are thus of great importance when considering the
radiative heat transfer. As proposed by various authors (Haghiri and Bidabadi, 2010; Meinköhn et al.,
2007), the absorbed, emitted and scattered energy in a dust cloud can be expressed as:

346
$$\frac{dI}{dx} = K_a I + K_s I - K_a I_b - \frac{K_s}{4\pi} \int_{4\pi} I(\Omega) P d\Omega \qquad (8)$$

where I and I_b are the thermal intensity and thermal intensity of a black body. An analytical solution of equation 8 was proposed by Haghiri and Bidabadi (2010) for each zone represented in Figure 3. By neglecting the multi-scattering contribution, i.e. for isotropic scattering, the integral term can be removed from equation 8. The absorption coefficient K_a and the scattering coefficient K_s directly depend on the dust concentration, the dust density and the particle size, as follows (Haghiri and Bidabadi, 2010):

$$K_a = \frac{3}{2} \frac{C}{\rho_p \, d_p} \, Q_{abs} \tag{9}$$

$$K_s = \frac{3}{2} \frac{c}{\rho_p \, d_p} \, Q_{sca} \tag{10}$$

where C is the dust concentration, ρ_p the particle density, d_p the particle diameter and $Q_{abs} = \varepsilon_P$ and Q_{sca} = 1- ε_P respectively the absorption and scattering efficiency, and particle emissivity ε_P . In the preheat zone, only the absorption term was considered, whereas both absorption and scattering were considered in the reaction and post-flame zones. The implementation of both equations (9) and (10) in the 1D model was detailed by Torrado et al. (2008). The thermal properties of cellulose powders were considered as inputs.

The absorption and scattering coefficients are then directly proportional to the total surface area (TSA) developed by the particles in the cloud, which can be expressed as follows for spherical particles:

364

$$TSA = \frac{6 C}{\rho_p \, d_p} \tag{11}$$

Once again, simulations were performed by considering the combustion of pyrolysis gases 365 366 representative of the devolatilization of nanocellulose (Figure 2) and at an initial mass concentration 367 of 500 g/m³. In order to consider the radiative contribution of the powder on the flame propagation, 368 particles having the same thermal properties than cellulose were numerically added to the reactive 369 system; however, potential heterogeneous reactions were not taken into account. A linear evolution 370 of the calculated flame velocity with the total surface area developed by the particles considered in 371 the radiative heat transfer appears in Figure 8. It can be observed that the radiative heat transfer generated by particles developing a total surface area lower than 10 m^2/m^3 does not lead to a 372 373 significant increase of the flame velocity, with values between 17.5 and 18 cm/s. However, when considering a total surface area of 100 m²/m³, a flame velocity of 20.8 cm/s is reached, thus proving 374 375 the importance of considering the surface area when analysing dust explosions, instead of focusing 376 only on mass concentration. It should also be noted that increasing the concentration too much would

377 lead to an important increase of absorption, which would hence limit the heat radiation in the preheat





Figure 8. Influence of the total surface area of the particles implied in the radiative heat transfer on
the flame velocity of a mixture of nanocellulose pyrolysis gases (500 g/m³) and inert particles

383

380

384 5. Conclusions

385 The laminar burning velocity of nanocellulose has been determined using a one-dimensional flame propagation model adapted from a model already validated for hybrid mixtures. The numerical 386 system, composed of mass and energy balances equations and of mass reaction rates adapted to the 387 388 combustion reactions, was solved by the finite volume method. Assuming that the devolatilization of organic nanopowders is fast, the chemical reactions were considered limited to the combustion of the 389 pyrolysis gases. A first value of laminar flame velocity of 17.5 cm/s was obtained for 500 g/m³ of 390 391 nanocellulose, which is close to values experimentally measured in a flame propagation tube or a 392 20 L sphere, around 21 cm/s, thus showing a good consistency between the numerical and experimental approaches. 393

394 However, since in practice, the devolatilization of the particles is not instantaneous, the remaining 395 particles can contribute to the radiative heat transfer, which was added to energy balance. Due to the tendency of nanoparticles to agglomerate, different particle diameters and dust concentrations were 396 397 tested. Thus, although the heat transfer of nanoparticles tends to be neglected due to Rayleigh 398 scattering, which does not contribute to the flame propagation, the contribution of the remaining micro-agglomerates after dispersion must be considered. Indeed, the existence of a linear relation 399 400 between the laminar flame velocity and the total surface area developed by the particles implied in 401 the radiative heat transfer was highlighted. A flame velocity reaching 20.8 cm/s for a total surface area of 100 m^2/m^3 considered for the radiative heat transfer was then obtained, showing a strong 402 403 impact of the heat radiation on the flame propagation.

404 Nevertheless, it should be kept in mind that, even if the nanocellulose pyrolysis could be considered 405 as very fast, this assumption is potentially not valid for nanopowders agglomerates and certainly not 406 for larger organic particles. In the latter case, consideration of the pyrolysis kinetics, using for instance 407 a semi-global lumped-reaction system, will be necessary. In any case, this work shows that knowledge 408 of the kinetics of pyrolysis and/or combustion allows the numerical assessment of a laminar flame 409 velocity, provided that the radiative phenomena are also taken into consideration.

410

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415 **References**

Amyotte, P.R., Chippett, S., Pegg, M.J., 1988. Effects of turbulence on dust explosions. Prog. Energy
Combust. Sci. 14, 293–310. https://doi.org/10.1016/0360-1285(88)90016-0

- 418 Andersen, J., Rasmussen, C.L., Giselsson, T., Glarborg, P., 2009. Global Combustion Mechanisms
- 419 for Use in CFD Modeling under Oxy-Fuel Conditions. Energy & Fuels 23, 1379–1389.
 420 https://doi.org/10.1021/ef8003619
- 421 Andrews, G.E., Bradley, D., 1972. Determination of burning velocities: A critical review.
 422 Combustion and Flame 18, 133–153. https://doi.org/10.1016/S0010-2180(72)80234-7
- Belerrajoul, M., 2019. Modélisation multi-échelle de la combustion d'un nuage de particules (PhD
 Thesis). National Polytechnic Institute of Toulouse.
- Boilard, S.P., Amyotte, P.R., Khan, F.I., Dastidar, A.G., Eckhoff, R.K., 2013. Explosibility of
 micron- and nano-size titanium powders. J. Loss Prev. Process Ind. 26, 1646–1654.
 https://doi.org/10.1016/j.jlp.2013.06.003
- Bouillard, J., Vignes, A., Dufaud, O., Perrin, L., Thomas, D., 2010. Ignition and explosion risks of
 nanopowders. Journal of Hazardous Materials 181, 873–880.
 https://doi.org/10.1016/j.jhazmat.2010.05.094
- Bradley, D., Lee, J.H.S., 1984. Proceedings of the first international colloquium on the explosibility
 of industrial dusts 220–223.
- Cashdollar, K.L., Hertzberg, M., Zlochower, I.A., 1989. Effect of volatility on dust flammability
 limits for coals, gilsonite, and polyethylene, Symposium (International) on Combustion, 22,
 1, 1757-1765.
- Clavin, P., 1985. Dynamic behavior of premixed flame fronts in laminar and turbulent flows. Progress
 in Energy and Combustion Science 11, 1–59. https://doi.org/10.1016/0360-1285(85)90012-7
- Cuervo, N., 2015. Influences of turbulence and combustion regimes on explosions of gas-dust hydrid
 mixtures (PhD Thesis). The University of Lorraine, France.
- Cuervo, N., Dufaud, O., Perrin, L. Determination of the burning velocity of gas/dust hybrid mixtures
 (2017) Process Saf. Environ., 109, pp. 704-715. https://doi.org/10.1016/j.psep.2017.06.009

- Dahoe, A.E., Cant, R.S., Scarlett, B., 2001. On the Decay of Turbulence in the 20-Liter Explosion
 Sphere. Flow, Turbulence and Combustion 67, 159–184.
 https://doi.org/10.1023/A:1015099110942
- Dahoe, A.E., Hanjalic, K., Scarlett, B., 2002. Determination of the laminar burning velocity and the
 Markstein length of powder–air flames. Powder Tech., Special issue in Honour of Prof Jimbo
- 447 122, 222–238. https://doi.org/10.1016/S0032-5910(01)00419-3
- Di Benedetto, A., Russo, P., 2007. Thermo-kinetic modelling of dust explosions. J. Loss Prev. Process
 Ind., Selected Papers Presented at the Sixth International Symposium on Hazards, Prevention
 and Mitigation of Industrial Explosions 20, 303–309.
 https://doi.org/10.1016/j.jlp.2007.04.001
- Di Benedetto, A., Russo, P., Amyotte, P., Marchand, N., 2010. Modelling the effect of particle size
 on dust explosions (2010) Chemical Engineering Science, 65 (2), pp. 772-779.
 https://doi.org/10.1016/j.ces.2009.09.029
- Dirrenberger, P., Le Gall, H., Bounaceur, R., Herbinet, O., Glaude, P.-A., Konnov, A., BattinLeclerc, F., 2011. Measurements of Laminar Flame Velocity for Components of Natural Gas.
 Energy Fuels 25, 3875–3884.
- Dufaud, O., Khalili, I., Cuervo-Rodriguez, N., Olcese, R.N., Dufour, A., Perrin, L., Laurent, A.,
 2012a. Highlighting the Importance of the Pyrolysis Step on Dusts Explosions. Chemical
 Engineering Transactions 26, 369–374.
- 461 Dufaud, O., Poupeau, M., Khalili, I., Cuervo, N., Christodoulou, M., Olcese, R., Dufour, A., Perrin,
- 462 L., 2012b. Comparing Pyrolysis Gases and Dusts Explosivities: A Clue to Understanding
 463 Hybrid Mixtures Explosions? Ind. Eng. Chem. Res. 51, 7656–7662.
 464 https://doi.org/10.1021/ie201646s
- 465 Dufaud, O., Vignes, A., Henry, F., Perrin, L., Bouillard, J., 2011. Ignition and explosion of
 466 nanopowders: something new under the dust. Journal of Physics: Conference Series 304,
- 467 012076. https://doi.org/10.1088/1742-6596/304/1/012076

- Eckhoff, R.K., 2003. Dust Explosions in the Process Industries 3rd Edition, 3rd ed. Gulf
 Professional Publishing.
- EN 14034-1, 2004. Determination of explosion characteristics of dust clouds Part 1: Determination
 of the maximum explosion pressure P_{max} of dust clouds.
- 472 EN 14034-2, 2006. Determination of explosion characteristics of dust clouds Part 2: Determination
 473 of the maximum rate of explosion pressure rise (dp/dt)max of dust clouds.
- Fauske, H.K., Clouthier, M.P., 2015. A theoretical-based and generalized method for dust and
 gaseous deflagration Vent sizing. 49th Annual Loss Prevention Symposium 2015, LPS 2015
 Topical Conference at the 2015 AIChE Spring Meeting and 11th Global Congress on Process
 Safety, 573-581.
- 478 Frassoldati, A., Cuoci, A., Faravelli, T., Ranzi, E., Candusso, C., Tolazzi, D., 2009. Simplified kinetic
 479 schemes for oxy-fuel combustion. 1st International Conference on Sustainable Fossil Fuels
 480 for Future Energy S4FE 2009.
- Ghaffari, M., Hoffmann, A.C., Skjold, T., Eckhoff, R.K., van Wingerden, K., 2019. A brief review
 on the effect of particle size on the laminar burning velocity of flammable dust: Application
 in a large-scale CFD tool. J. Loss Prev. Process Ind., 62, art. no.103929.
 https://doi.org/10.1016/j.jlp.2019.103929
- Haghiri, A., Bidabadi, M., 2010. Modeling of laminar flame propagation through organic dust cloud
 with thermal radiation effect. International Journal of Thermal Sciences 49, 1446–1456.
 https://doi.org/10.1016/j.ijthermalsci.2010.03.013
- Hong, S.-H., Winter, J., 2006. Size dependence of optical properties and internal structure of plasma
 grown carbonaceous nanoparticles studied by in situ Rayleigh-Mie scattering ellipsometry.
 Journal of Applied Physics 100, 064303. https://doi.org/10.1063/1.2338132
- Jones, W.P., Lindstedt, R.P., 1988. Global reaction schemes for hydrocarbon combustion.
 Combustion and Flame 73, 233–249. https://doi.org/10.1016/0010-2180(88)90021-1

- Karlovitz, B., Denniston, D.W., Wells, F.E., 1951. Investigation of Turbulent Flames. J. Chem. Phys.
 19, 541–547. https://doi.org/10.1063/1.1748289
- Kee, R.J., Grcar, J.F., Smooke, M.D., Miller, J.A., Meeks, E., 1993. PREMIX: A Fortran program
 for modeling steady laminar one-dimensional premixed flames.
- Krietsch, A., Scheid, M., Schmidt, M., Krause, U., 2015. Explosion behaviour of metallic nano
 powders. J. Loss Prev. Process Ind. 36, 237–243. https://doi.org/10.1016/j.jlp.2015.03.016
- 499 Markstein, G.H., 1964. Non-steady flame Propagation. P22, Pergarmon, New York.
- Meinköhn, E., Kanschat, G., Rannacher, R., Wehrse, R., 2007. Numerical methods for
 multidimensional radiative transfer, in: Reactive Flows, Diffusion and Transport. Springer,
 pp. 485–526.
- Mollenhauer, K., Tschöke, H., 2010. Handbook of Diesel Engines. Springer Science & Business
 Media.
- 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 Tech. 328, 54–74.
 https://doi.org/10.1016/j.powtec.2017.12.096
- 509 Piskorz, D., Radlein, A., Scott, D.S., 1986. On the mechanism of the rapid pyrolysis of cellulose,
 510 Journal of Analytical and Applied Pyrolysis, 121-137.
- 511 Proust, C., 2006. Flame propagation and combustion in some dust-air mixtures. J. Loss Prev. Process
 512 Ind. 19, 89–100.
- 513 Przybyla, G., Ziolkowski, L., Szlęk, A., 2008. Performance of SI engine fuelled with LCV gas.
 514 Poland: Institute of Thermal Technology.
- 515 Russo, P., Di Benedetto, A., 2013. Review of a dust explosion modelling, Chemical Engineering
 516 Transactions, 31,955-960.

- Santandrea, A., Gavard, M., Pacault, S., Vignes, A., Perrin, L., Dufaud, O., 2020. 'Knock on
 nanocellulose': Approaching the laminar burning velocity of powder-air flames. Process Saf.
 Environ. 134, 247–259. https://doi.org/10.1016/j.psep.2019.12.018
- Santandrea, A., Pacault, S., Perrin, L., Vignes, A., Dufaud, O., 2019a. Nanopowders explosion:
 Influence of the dispersion characteristics. J. Loss Prev. Process Ind. 62, 103942.
 https://doi.org/10.1016/j.jlp.2019.103942
- Santandrea, A., Vignes, A., Krietsch, A., Perrin, L., Laurent, A., Dufaud, O., 2019b. Some Key
 Considerations when Evaluating Explosion Severity of Nanopowders. Chem. Eng. T. 77,
 235–240. https://doi.org/10.3303/CET1977040
- 526 Sattar, H., Andrews, G.E., Phylaktou, H.N., Gibbs, B.M., 2014. Turbulent flames speeds and laminar
- burning velocities of dusts using the ISO 1 m3 dust explosion method. Ch. Eng. Trans., 36,
 157-162. https://doi.org/10.3303/CET1436027.
- Silvestrini, M., Genova, B., Leon Trujillo, F.J., 2008. Correlations for flame speed and explosion
 overpressure of dust clouds inside industrial enclosures. J. Loss Prev. Process Ind. 21, 374–
 392. https://doi.org/10.1016/j.jlp.2008.01.004
- 532 Skjold, T., 2003. Selected aspects of turbulence and combustion in 20-Litre explosion vessel (Master
 533 thesis). University of Bergen, Norway.
- Torrado, D., Cuervo, N., Pacault, S., Glaude, P.-A., Dufaud, O., 2017. Influence of carbon black
 nanoparticles on the front flame velocity of methane/air explosions. J. Loss Prev. Process Ind.,
 49, pp. 919-928. https://doi.org/10.1016/j.jlp.2017.02.006
- Torrado, D., Pinilla, A., Amin, M., Murillo, C., Munoz, F., Glaude, P.-A., Dufaud, O., 2018.
 Numerical study of the influence of particle reaction and radiative heat transfer on the flame
 velocity of gas/nanoparticles hybrid mixtures. Process Saf. Environ. 118, 211–226.
 https://doi.org/10.1016/j.psep.2018.06.042
- 541 Traoré, M., Dufaud, O., Perrin, L., Chazelet, S., Thomas, D., 2009. Dust explosions: How should the
 542 influence of humidity be taken into account? Process Saf. Environ., 12th International

- 543 Symposium of Loss Prevention and Safety Promotion in the Process Industries 87, 14–20.
 544 https://doi.org/10.1016/j.psep.2008.08.001
- Yao, N., Wang, L., Bai, C., Liu, N., Zhang, B., 2020. Analysis of dispersion behavior of aluminum
 powder in a 20 L chamber with two symmetric nozzles. Process Safety Progress 39.
 https://doi.org/10.1002/prs.12097
- Zalosh, R., 2019. Dust explosions: Regulations, standards, and guidelines, in: Methods in Chemical
 Process Safety. Elsevier, pp. 229–282. https://doi.org/10.1016/bs.mcps.2019.03.003
- 550 Zhen, G., Leuckel, W., 1997. Effects of ignitors and turbulence on dust explosions. J. Loss Prev.
- 551 Process Ind. 10, 317–324. https://doi.org/10.1016/S0950-4230(97)00021-1





 $500 \text{ g.m}^3 - \text{tv} > 300 \text{ ms}$

Video analysis – flame kernel growth Matlab's Simulink – Vision toolbox

















