

## Organic Dust Explosions: Is It All Just About Pyrolysis?

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Several phenomena occur during a dust explosion and they can impact the overall kinetics: external convection, internal particle heating, pyrolysis reaction and gaseous-phase combustion. According to the particle size distribution, the powder nature, the external temperature and heating rate, any of these steps can be rate-limiting and must therefore be detailed in order to serve as a basis for the explosion modelling. But under which conditions the pyrolysis reaction can be considered as the rate-limiting step of the global phenomenon? For this study, a Godbert-Greenwald furnace was modified to ensure its airtightness and cellulose samples were dispersed through the heated chamber by argon pulses. At the outlet, pyrolysis products were collected and analysed. These tests led to the formulation of a representative gas composition produced by the pyrolysis of cellulose. This representative model gas was then used for explosions tests. The hybrid mixtures of cellulose and pyrolysis gas showed a peculiar behaviour: as the dust-to-gas ratio increased, maximum rate of pressure rise initially increased, then it decreased, while the maximum explosion pressure did not vary significantly. The powder boosting effect on the rate of pressure rise was thus observed. Therefore, the study of the radiative heat transfer mode by adding biochar enlightened a major dependency of the flame propagation on the radiation. In fact, small amounts of char (higher emissivity than cellulose) were enough to significantly increase the rate of pressure rise, with a small influence on the maximum pressure. The pyrolysis step must be considered as a major rate-limiting step in a dust explosion phenomenon, but other ones may play an important role, such as the radiative heat transfer to the particle and the particle heating step. In such a way, these phenomena seemed to control and to determine the flammability and explosibility characteristic of a powder.

### 1. Introduction

Dust explosions are the ultimate result of the mutual interaction of several parameters: chemical composition, particle size, dispersion characteristics, ignition mode and flame propagation phenomena may be considered the major ones. For this reason, to model a dust explosion it is necessary to choose a degree of simplification, in order to reduce the number of variables involved in the system. It is especially true during the CFD simulation of such reactive flows: a fine modeling of flow physics should often be combined to lumped chemical mechanisms. The phenomenon can be then disassembled in four bricks: heating of the particle, pyrolysis reactions, oxidation of the gaseous products and flame propagation.

This work is centered on the determination of the pyrolysis step role in a dust explosion. A focus was also made on the influence of the radiative heat transfer during the flame propagation. With the aim to represent the gaseous products released during the pyrolysis step, various gas blends were prepared. Hybrid mixtures were exploited to achieve the objective: mixtures of cellulose, char, water and the pyrolysis gases were used to enlighten the role of each step and to compare them, in order to identify the rate-limiting phenomenon.

### 2. Materials and Methods

#### 2.1 Powder samples

Microcrystalline cellulose (Avicel ph 101) was selected for this study as it is one of the main components of wood and represents from 35 to 50 % of the terrestrial biomass. Its chemical structure is characterized by high regularity and its strong hydrogen bond pattern, stiffening its chains resulting in mechanically stable insoluble

fibers. If its pyrolysis mechanism has been widely studied, it was mainly through experiments on large pieces of wood or on cellulose fixed bed of particles; conditions which do not correspond to those encountered during a dust explosion.

The thermochemical conversion of dispersed cellulose in the absence of oxygen resulted in solid residues (char), tar and permanent gases production. The solid residue obtained by pyrolysis was represented by a char collected from a bag filter of a wood/biomass gasification process. This char was chosen because it has the same particle size distribution (PSD) as the solid residues collected (in very small quantities) during pyrolysis tests of Avicel ph 101. The characteristic diameters of the cellulose and of the char are reported in Table 1 ( $d_x$  is the diameter below which x percent of the volume distribution lies and  $d_{3,2}$  is the Sauter mean diameter).

*Table 1: Characteristic diameters of the powder samples*

	$d_{10}$ , $\mu\text{m}$	$d_{50}$ , $\mu\text{m}$	$d_{90}$ , $\mu\text{m}$	$d_{3,2}$ , $\mu\text{m}$
Cellulose	22.2	67.9	140.2	41.3
Char	7.8	24.7	120.4	16.3

## 2.2 Pyrolysis experiments

With the aim to represent the cellulose pyrolysis step during a dust explosion, the gaseous products generated by a fast pyrolysis under argon were characterized. For this purpose, a Godbert-Greenwald (GG) furnace was modified, as described by Pietraccini et al. (2021), in order to collect and analyze the products generated: thermogravimetric experiments were conducted on the solid residues (cellulose), tars were analyzed with a GC/MS and the permanent gases were determined by micro-gas chromatography (SRA 3000, Agilent). Two temperature levels were chosen for the tests: 700 and 900°C. It should be stressed that these values correspond to the temperature of the oven, but not necessary to the temperature of the particles undergoing the pyrolysis reactions, which will vary as a function of their residence time and thermal properties. 700°C is the minimal temperature at which sufficient quantities of pyrolysis gases were collected; 900°C is the maximal temperature of the oven. Both temperatures are of interest with regard to dust explosion: 700°C is closer to the minimum ignition temperature of a cellulose dust cloud (around 550°C) but 900°C is more consistent with the flame temperature reached during the flame propagation phase and will lead to a higher cellulose conversion.

## 2.3 Explosion severity

A standard 20L spherical vessel equipped with a rebound nozzle was used for the explosion tests. In order to limit potential overdriving phenomenon, the ignition source was set at 100 J (Sobbe chemical igniters). The sphere was externally cooled with water at a temperature ranging between 20 and 30°C. The procedure was adapted to hybrid mixtures, even for the tests performed on the pure gases: i) the sphere was vacuumed down to 20 mbar, ii) the gas mixture was injected, iii) if necessary, air was added up to 400 mbar, iv) the dust container was pressurized at 20 bar to inject air or, if needed, dust and air, through the outlet valve and the rebound nozzle, v) after 60 ms, the chemical igniters were triggered.

The maximum pressure  $P_m$  and maximum rate of pressure rise,  $dP/dt_m$ , were determined for each test. The maxima of these parameters over a wide range of concentration will be called  $P_{max}$  and  $dP/dt_{max}$ . Applying the 'cube-root law', the Kst (or Kg for pure gases) parameter will be deduced. Tests were divided into three parts, which consisted in the determination of the explosion severity of 1) the powder samples (cellulose and char), 2) the gaseous blend (composition based on the pyrolysis experiment) alone and 3) the hybrid mixtures.

## 3. Results and Discussion

Firstly, the results obtained from pyrolysis tests will be described and a gaseous mixture representative from explosion conditions will be chosen. In a second step, the influences of the fuel nature, the presence of char and the addition of water vapor in the reaction medium will be discussed.

### 3.1 Choice of a pyrolysis gas composition

The proportions of the main permanent gases generated by the pyrolysis of a cellulose cloud at 700 and 900°C are presented in Table 2 (on a nitrogen-, oxygen- and argon-free basis). Values are of the same order of magnitude as those in Graham et al. (1984) and Funazukuri et al. (1986), whose works were performed with similar reactor temperatures.  $H_2$ ,  $CH_4$ , CO and  $CO_2$  were the most abundant species. Small amounts of ethylene, acetylene and benzene were also identified (< 0.3 wt%) but were considered negligible. It can be noted that CO,  $H_2$  and  $CH_4$  concentrations were higher at 900 than at 700°C. This is consistent with a higher secondary conversion of volatiles to produce  $H_2$  and  $CH_4$ .  $CO_2$  follows the opposite trend. It may be due to the higher global

particle temperature reached within the dust cloud, which translates in a higher global conversion degree. Moreover, it should be highlighted that the CO/CO<sub>2</sub> ratio increased significantly when the furnace temperature is increased from 700 to 900°C. At higher reactor temperature, secondary reactions such as Boudouard, gasification and reverse water gas shift reactions are likely to occur, causing CO<sub>2</sub> conversion to CO. Finally, 2 cylinders of synthetic gases corresponding to the two compositions described in Table 2 were ordered. First, this study will focus on the composition obtained at 700°C. Finally, the explosion of gas obtained at 900°C will be compared to ones at 700°C

Table 2: Composition of the cellulose pyrolysis gas mixes used for the hybrid mixture tests

Species	H <sub>2</sub>	CH <sub>4</sub>	CO	CO <sub>2</sub>
Composition (wt%) at 700°C	< 1	≈ 2	50	47
Composition (wt%) at 900°C	2	6	60	32

### 3.2 Explosion severity of pure fuels

Preliminary tests were performed on the cellulose and on the pyrolysis gases. Firstly, it should be noted that the maximum explosion severity was not fully reached for the pyrolysis gases as not all air/gas concentration ranges could be studied. Indeed, due to the experimental procedure, which should be similar for the gases and the powders, the maximum achievable concentration of combustible gas in the sphere is 38%v (i.e. 380 mbar). However, this has no impact on the tests carried out on hybrid mixtures. Figure 1 shows that if the values of  $P_{max}$  is of the same order of magnitude for both fuels, 7.0 and 6.2 bars for the cellulose and the pyrolysis gases, respectively, their maximum deflagration indexes  $K_g/K_{st}$  are significantly different (76 bar.m/s for the powder and 242 bar.m/s for the gases). These results mean that while the combustion of both fuels releases a similar amount of energy, which leads to a similar  $P_{max}$ , the characteristic kinetics are not comparable.

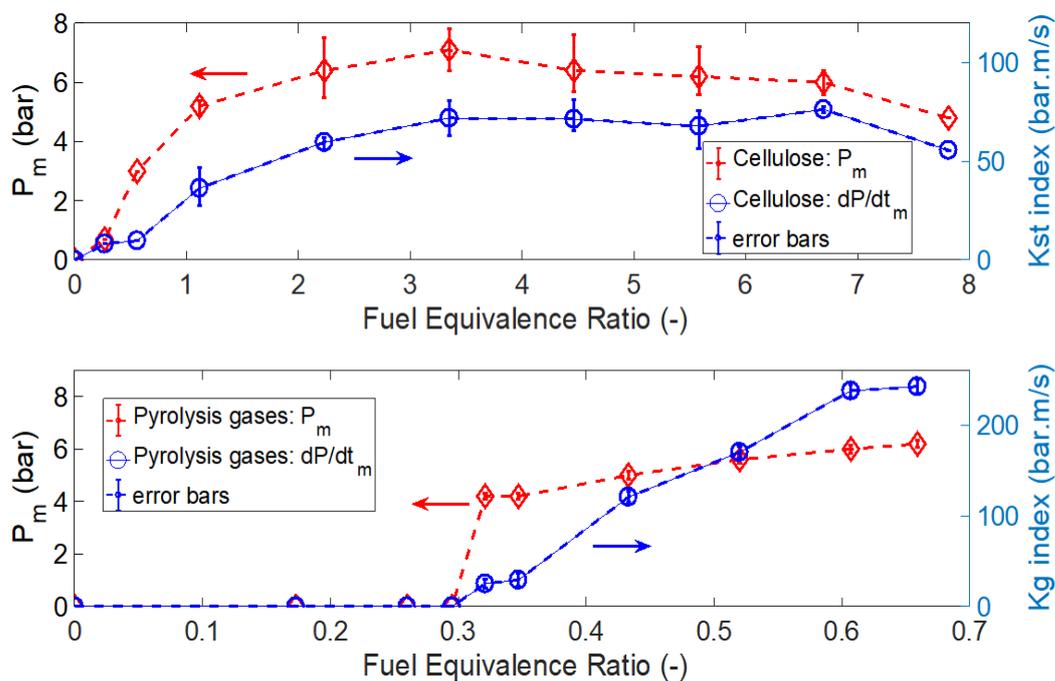


Figure 1: Maximum explosion pressure  $P_m$  and explosion index ( $K_g$  or  $K_{st}$ ) of cellulose and its pyrolysis gases collected at 700°C

It should also be noticed that the fuel equivalence ratio (FER, defined as the ratio of the fuel-to-oxygen ratio to the stoichiometric fuel-to-oxygen ratio) at which the maximum values are observed is greatly different for both fuels. It is particularly noteworthy that the maximum explosion severity is obtained for a FER of 3.3 (i.e. 750 g/m<sup>3</sup>), i.e. for a large excess of cellulose. As the maximum gas concentration is 38 %v., most of the tests performed on hybrid mixtures were based on this value. Theoretically, by neglecting the presence of water vapor, this amount of gases would be generated by the total pyrolysis of 10 g of cellulose, i.e. a concentration

of 500 g/m<sup>3</sup> in the 20L sphere or a FER of 2.2. Further tests were then carried out with 38%v. of pyrolysis gases and 10 g of cellulose as references.

### 3.3 Explosion severity of hybrid mixtures of pyrolysis gases and cellulose

As explained in the introduction, the explosion of organic particles can be decomposed into four main steps, including their pyrolysis and the oxidation of the gaseous products. In order to demonstrate that the latter phase was not the rate limiting step of a cellulose explosion, reactive mixtures of cellulose and pyrolysis gases were chosen in such a way that the oxygen quantity consumed remained theoretically the same for every composition. In other words, the fuel equivalence ratio was set at approximately 0.7. Calculations were based on the complete combustion equations for carbon monoxide, hydrogen, methane and cellulose and on the oxygen amount consumed for the combustion of 38%v. of pyrolysis gases (or 3.2 g of cellulose).

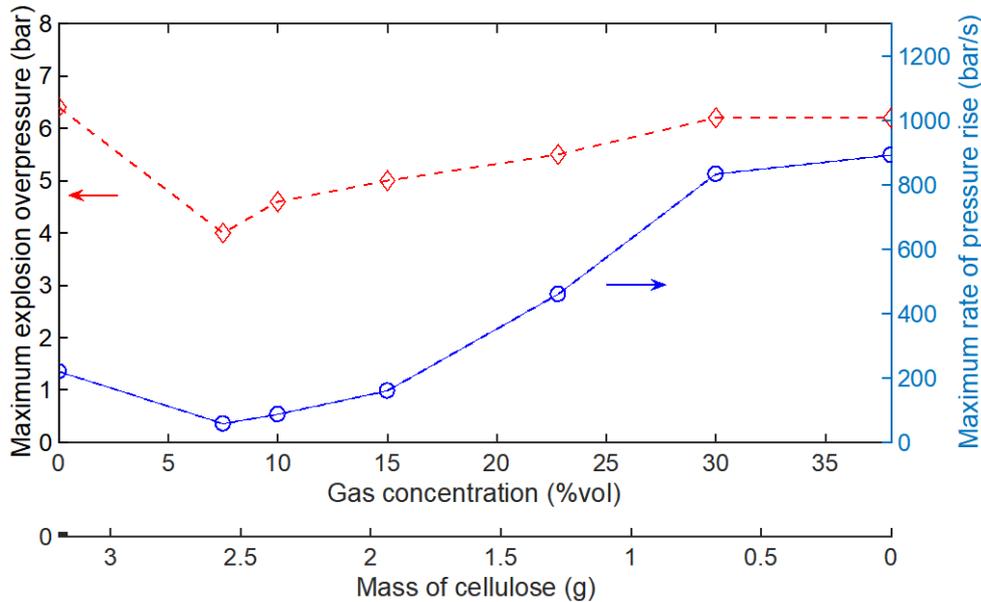


Figure 2: Maximum explosion pressure  $P_m$  and maximum rate of pressure rise of cellulose/pyrolysis gases mixtures - at constant theoretical oxygen consumption (FER = 0.7)

The evolution of the maximum explosion pressure shown in Figure 2 clearly demonstrates that such an approach is not suitable to represent the combustion of cellulose during an explosion as neither the maximum explosion pressure nor the maximum rate of pressure rise remain constant. The fact that carbon dioxide and water vapor (inert gases) are released during the pyrolysis makes the assumption of a constant FER inadequate.

A second approach based on the hypothesis that a given mass of cellulose will be pyrolyzed into the same mass of permanent gases was explored. It was then considered that 10 g of cellulose would decompose into 10 g of the mix of pyrolysis gases defined in Table 1, and that, as an example, an energy-equivalent reaction mixture would be composed of 6 g of cellulose and 15%v. of pyrolysis gases (4 g). Figure 3 demonstrates that, from a thermodynamic point of view, the energy released by such mixtures do not vary much, as the maximum explosion pressure varies from 6.2 to 6.7 barg. However, the combustion kinetics is strongly affected by the nature of the fuel, even for a constant mass of reactants: the maximum rate of pressure rise drops from 892 to 220 bar/s when the permanent gases are progressively replaced by the same mass of cellulose. If the pyrolysis step was negligible and the gas phase oxidation was the limiting step, such a severe discrepancy would not be observable.

It should be highlighted that for a mixture composed of 1 g of cellulose and 9 g of pyrolysis gases,  $(dP/dt)_m$  increases significantly with regard to the pure gases and reaches 1165 bar/s. A similar but less pronounced trend is also observable for 2 g of cellulose. As previously said, the overall combustion kinetics of the powder is slower than that of the pyrolysis gases, because the powder undergoes first a pyrolysis step (thermal or chemical regime as a function of the PSD) to produce the pyrolysis gas. If the increase of  $(dP/dt)_m$  is not related to kinetics, it can be due to the hydrodynamics perturbations of the flame due to the presence of powders (flame stretching) or to the modification of the radiative transfer. An estimation of the pyrolysis  $Py''$  and Biot numbers (Pietraccini et al., 2021) illustrates that, for small cellulose particles, the pyrolysis cannot be neglected with respect to the

external convection and the internal conduction; but also that their pyrolysis is likely to occur before the flame will reach them. As a consequence, the influence of radiation has to be discussed.

### 3.4 Explosion severity of hybrid mixtures of pyrolysis gases and char

The radiative effect of solid particles located in the preheating zone, ahead from the propagating flame, has notably been considered by introducing char in the gaseous fuel mixtures. Char has been selected to be representative of the solid residues generated by the pyrolysis of cellulose. Explosions tests were carried out on the char sample, leading to a maximum explosion pressure of 6.5 bar and a  $K_{St}$  index reaching 70 bar.m/s. However, it should be stressed that the minimum ignition energy of char is greater than 1 J, which means that this powder is rather insensitive to ignition because it does not generate reactive volatiles.

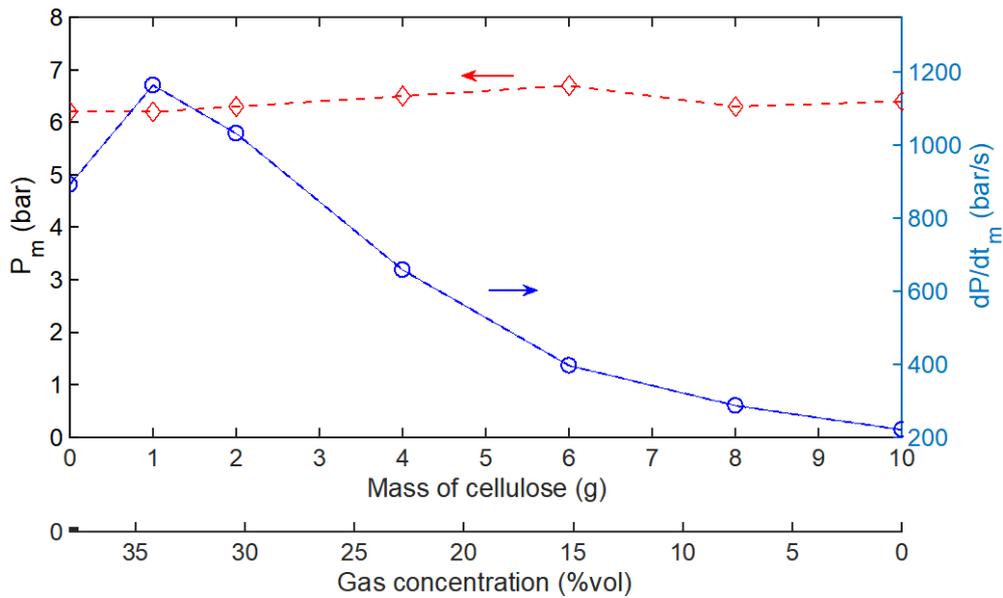


Figure 3: Maximum explosion pressure  $P_m$  and maximum rate of pressure rise  $(dP/dt)_m$  of cellulose/pyrolysis gases mixtures - at mass of permanent gases released/reactants ( $m = 10$  g)

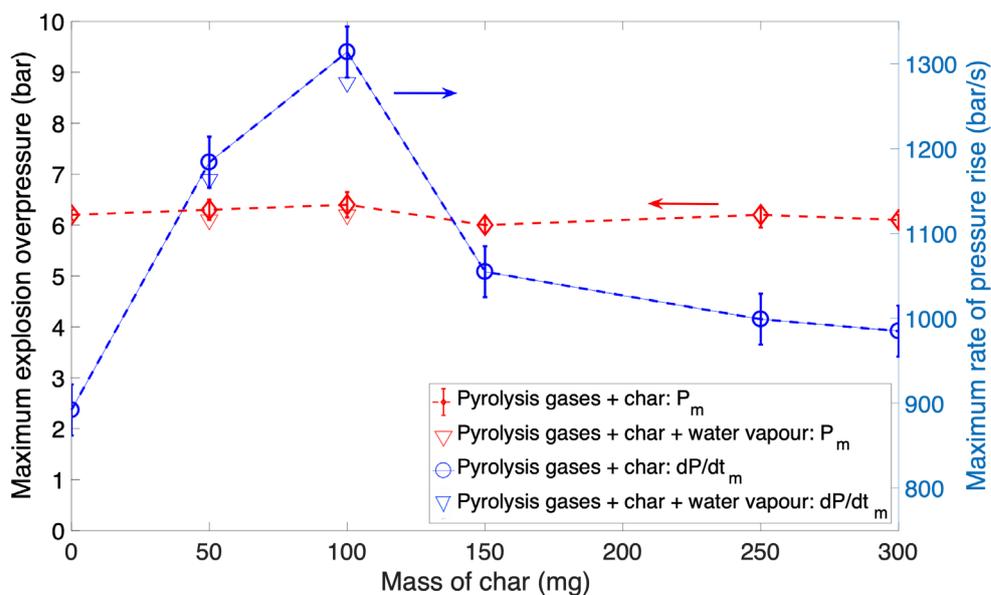


Figure 4: Evolution of the explosion severity of the pyrolysis gases as a function of char and water vapour addition

Pyrolysis tests performed in the Godbert-Greenwald oven showed that the mass of char and solid residues collected ranges between 5 and 10% of the mass of cellulose injected. In order to highlight the influence of solid residues, on the explosion severity, small quantities of char ranging from 50 to 300 mg were added to 38%v. of pyrolysis gases. Given the small amount of fuel added, it is logical that the maximum pressure observed in Figure 4 hardly varies. On the contrary, the maximum rate of pressure rise strongly increases from less than 900 bar/s to 1315 bar/s, which is consistent with the evolution observed in Figure 3 when a few grams of cellulose were added to the pyrolysis gases. This modification of the combustion kinetics is certainly not caused by changes in the chemical reactions, but is more likely to be related to an enhancement of the radiative transfers or particle-turbulent flow interactions (Rockwell and Rangwala, 2013). Furthermore, the promoting effect of the particles on the flame speed is more pronounced for char than for cellulose. As both powders have rather similar particle size distributions (Table 1), it is highly likely that this discrepancy can notably be explained by the different optical properties of both materials. Finally, it should be kept in mind that the explosion severity of hybrid mixtures of dust and gases can be higher than that of pure fuels (Song et al., 2019).

In all the above reasoning, the generation of water vapor by pyrolysis has been neglected, for two main reasons: the analytical quantification of its concentration is difficult; it is a non-permanent 'inert' gas. Moreover, some authors demonstrated that the water production can reach approximately 8 to 10 wt% of the exhaust gases during the pyrolysis of cellulose (Piskorz et al., 2000). By considering these values, 0.8 g of water was vaporized in the 20L sphere before the gas injection. A few experiments were carried out to assess the potential influence of water vapor on the char/pyrolysis gases mixtures. As can be seen in Figure 4, the presence of water vapor tends to slightly decrease both  $P_m$  and  $(dP/dt)_m$ , but the influence of water remains limited under these conditions. Indeed, it is known that water vapor has limited chemical effects for high temperature gas-phase reactions.

Further tests were performed on the pyrolysis gases generated at 900 °C (Table 2) and by combining both cellulose, char, water vapor and pyrolysis gases. It appears that the increased hydrogen content, due to the higher temperature, plays a significant role in the ignition of the mixtures.

#### 4. Conclusions

This work aimed to study the role of the pyrolysis step in an organic dust explosion. By exploiting a modified version of the Godbert-Greenwald oven, it has been possible to obtain a characteristic composition of cellulose pyrolysis gaseous products, which was the key to experimentally simulate the pyrolysis reactions. Through the study of the hybrid mixtures of cellulose and pyrolysis gases, it was possible to conclude that: i) the presence of a small amount of powder can increase the rate of pressure rise, which is likely due to the increase of radiative heat transfers within the dust cloud; ii) however, beyond a certain concentration, the powder reduces the overall rate of the flame propagation, which translates in a lower  $(dP/dt)_m$ ; iii) the char has the same effect as cellulose, but slightly enhanced by the radiative properties of the product itself (higher emissivity); iv) the kinetics appears to be faster for higher concentration of gases, which means that the pyrolysis (i.e. the phenomenon that produces the gaseous products from the solid) is the rate-limiting step of a cellulose dust explosion.

Furthermore, the work showed the interest in using a Godbert-Greenwald oven as a reactor for studying cellulose dust explosions. It allowed to reproduce some of the fundamental characteristics of such phenomenon (dispersion of the powder, high heating rates, short residence times), which is necessary to better understand the role of each step involved.

Additional tests have been performed to investigate the influence of the temperature on the pyrolysis gases and how it is related to the explosion severity.

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