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Highlighting the Importance of the Pyrolysis Step on Dust Explosions

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In order to highlight the influence of the pyrolysis step in organic dusts explosions, experiments have been carried out on wheat starch powders and on their pyrolysis gases. Starch pyrolysis has been studied and a representative composition of the pyrolysis gases has been used for explosion tests. Both the particle size distribution and the presence of few percents of pyrolysis gases, as low as 1 %v., induces changes in the rate-limiting step of the combustion reaction, which implies a significant decrease of the minimum ignition energy (MIE) and an explosivity increase. Moreover, the influences of pyrolysis gases are effective both on the combustion kinetics, but also on the flame hydrodynamics. A model based on the flash pyrolysis of organic compounds has been developed and validated by using gas chromatography.

1. Introduction

The explosion of an organic dust suspension can be represented by three successive steps: the particle heating, its devolatilization/pyrolysis and then, the homogeneous oxidation of the pyrolysis gases. Understanding the importance of the rate-determining step of the whole combustion process is obviously a key to develop adequate prevention and protection measures (Dufaud et al., 2010).

Studies have already been carried out in order to underline the impact of pyrolysis on dust explosion (Di Benedetto and Russo, 2007). For instance, Hertzberg et al. (1987) have particularly demonstrated that, notably for coal particles, the combustion is controlled by the gas phase combustion for small particles and low dust concentrations; whereas for high dust concentrations and large particles, the combustion is controlled by the pyrolysis step. Thus, the particle size strongly influences the devolatilization rate and a particle size limit exists, below which the pyrolysis reaction is not the slowest step anymore. For polyethylene, this limit has been set at 80 μm (Di Benedetto et al., 2010a) and 50 μm for coal particles, whereas diameters as low as 10 μm have been proposed for natural organic compounds such as starch (Eckhoff, 2003).

When the devolatilization occurs in the preheating zone, pyrolysis gases and dusts form a combustible mixture, which can be considered as a hybrid mixture of gases and solids. Characterizing the mechanisms of the pyrolysis step, the gases composition and their impact on the dust cloud ignition and on the flame propagation is possible to produce models that predict the explosivities of organic dusts, but also to better understand the specificities of hybrid mixtures explosions. In this article, the peculiar case of wheat starch has been studied.

2. Materials and methods

Wheat starch was provided by Sigma-Aldrich Co. Particle-size distributions measurements have been performed in isopropanol by a laser diffraction analyzer (Mastersizer, Malvern Instrument Ltd.). The parameters d_{10} , d_{50} , and d_{90} which are the quantiles of the volumetric distribution and the Sauter diameter ($d_{3,2}$), are respectively of 16, 35, 76, and 28 μm . The raw starch sample has been sieved to obtain five different granulometric classes with the following diameters d_{50} : 10, 22, 36, 45 and 70 μm .

A Godbert-Greenwald furnace, conventionally used to determine the minimum ignition temperature of a dust cloud, has been modified to produce and analyze the pyrolysis gases by gas chromatography (Dufaud et al., 2011). Pyrolysis experiments were performed at various reactor temperatures, but always greater than 550 $^{\circ}\text{C}$, to enhance the external heat transfer from the reactor to the particles. The relative influences of the residence time, the temperature and the particle size on the gas composition have been studied in order to obtain gas mixtures representative of those obtained during the pyrolysis phase of a dust explosion.

Based on such experiments, a gas mixture has then been prepared in order to represent the pyrolysis gases of starch (Dufaud et al., 2011). The chemical composition of such mixture is given on Table 1.

Table 1: Chemical composition of the pyrolysis gases

Gases	CO	CO ₂	CH ₄	C ₂ H ₄	C ₃ H ₆	H ₂	others
Composition (wt %)	60	30	3	3	2	1	1

The minimum ignition temperature energy (MIE) has been determined with a modified Hartmann tube according to the EN 13821 standard. Modifications have been provided to the apparatus in order to obtain a vacuum-proof system and test hybrid mixtures of gas and dusts.

The measurements of dust explosion severity, i.e. P_{max} (maximum overpressure), and $(dP/dt)_{\text{max}}$, (maximum rate of pressure rise), were performed in a 20 L spherical vessel in accordance with the ISO 6184-1 standard. Pyrotechnic igniters of 100 J each were used for the tests in order to avoid the overdriving phenomenon. The influence of the ignition delay t_v , related to the initial turbulence intensity, has also been tested.

3. Results and discussion

After the determination of the main processes of the pyrolysis step, the pyrolysis impacts on the ignition sensitivity and explosion severity of the wheat starch have been studied.

3.1 Characterizing the main processes involved during the fast pyrolysis

Pyrolysis can be controlled by heat transfer, chemical reactions or mass transfer. Various characteristic times, calculated from the experimental data, can be calculated in order to determine the controlling step (Authier et al., 2009). The comparison of these times can be made thanks to dimensionless numbers given in Table 2.

Table 2: Dimensionless number of the main processes involved during pyrolysis

Dimensionless number	Pe (Peclet)	Le (Lewis)	Bi (Biot)	Th (Thiele)
Order of magnitude	10^2	$10^{-3} - 10^{-4}$	$10^{-1} - 10^{-2}$	10^{-1}

As a function of the carrier gas (Ar) overpressure, the residence time ranges from 20 to 50 ms. For particles having a d_{50} of 35 μm , each characteristic transfer time is lower than the latter values, the maximum time being the external heat transfer by radiation and convection, with approximately 15 ms. Pe number is greater than unity, which demonstrates that the pyrolysis gases transfer is limited by convection; however, the influence of internal heat transfer is much greater than the one of mass transfer, as shown by Le number. Bi number is lower than 1, which demonstrates that temperature can

be considered uniform inside the particle. Finally, by using kinetic parameters obtained for cellulose (Dufaud et al., 2011), Th number is lower than 1, showing that the pyrolysis time is probably slower than the heat transfer times (Di Benedetto et al., 2010b). For larger particle sizes, particularly for d_{50} of 70 μm , both internal and external heat transfer times become larger than 20 ms, which strongly modifies the gas composition.

3.2 Influence of the pyrolysis step on the ignition sensitivity

As previously said, the particle size distribution has a direct influence on the rate-limiting step of the dust explosion. By measuring the minimum ignition energies of various starch samples with decreasing mean diameters, the so called “limiting particle size” can be estimated according to Khalili et al. (2011). On Figure 1, it clearly appears that for particles having small diameters - generally much lower than 30 μm , the heating but also the pyrolysis steps are very fast, and the combustion kinetics can be reduced to the oxidation in homogeneous gas phase (reaction-controlled model); whereas, for larger particles, the boundary diffusion limitation remains important. The fact that the MIE still slightly decreases for mean diameters lower than 35 μm demonstrates that a model strictly based on homogeneous gas phase combustion, and as a consequence size-independent, cannot represent properly the experimental trend. Besides, the value of Thiele number calculated in Table 2 shows that, if a diffusion-controlled model is applied for large particles, the influence of the pyrolysis time cannot be neglected.

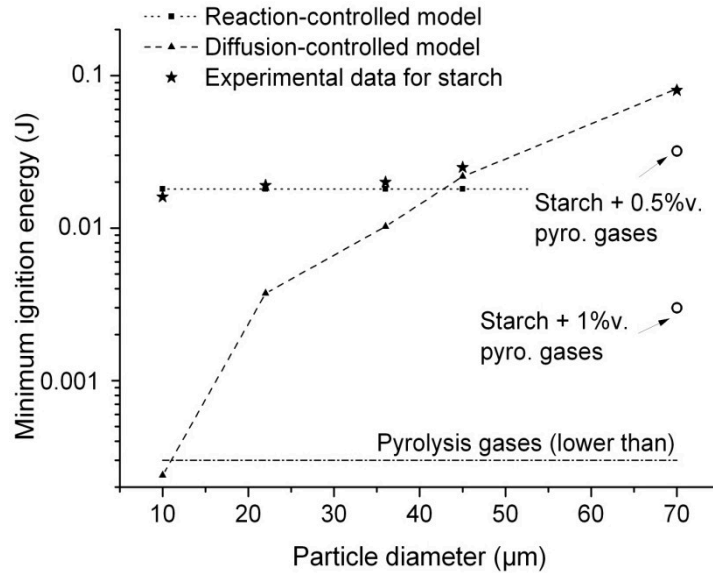


Figure 1: Influence of the mean particle size on the minimum ignition energies of starch and pyrolysis gases-starch mixtures

In fact, the devolatilization of the solid particles mainly becomes rate controlling at high dust loadings and for large particle sizes. It should also be remarked that the introduction of few percents of pyrolysis gases to the dust suspensions, as low as 1 or 2 % vol., also induces changes in the rate-limiting step of the combustion reaction and implies a drastic decrease of the MIE down to 3 mJ at 1 % v.

Introducing the Spalding thermal number B_T , defined by Equation 1, is useful to link the ignition sensitivity of the starch particles and the one of their pyrolysis gases and hybrid mixtures from a thermal point of view:

$$B_T = \frac{q_{st}H + C_{pa}(T_g - T_v)}{L + C_{ps}(T_b - T_s)} \quad (1)$$

where q_{st} is the mass ratio of fuel to air, C_{pa} and C_{ps} are respectively the specific heat of the air and of the solid, H is the heat of combustion and L , the heat of vaporization/gasification and T_g , T_b and T_s are respectively the temperatures of the gas, the boiling point and the temperature of the surface of the

fuel. It represents the ratio of the heat released by the combustion to the heat required to gasify and heat the fuel to ignition. For the starch particles, B_T is slightly greater than 1, whereas it tends to much larger values for gases such as carbon monoxide, methane or other permanent gases. By adding or generating small amounts of pyrolysis gases, B_T increases by decreasing the heat necessary to gasify enough fuel to reach the lower explosion limit. The relationship between the MIE and B_T being a decreasing exponential function (Mannan and Lees, 2005), only a few percents of gases are necessary to obtain a decrease of the MIE from 80 to 3 mJ, which is consistent with the results on Figure 1.

3.3 Effect of the pyrolysis step on the explosion severity

In order to highlight the impact of the pyrolysis step on the dust explosion severity, the maximum rates of pressure rise of both starch and pyrolysis gases have been compared on Figure 2. Totally different behaviours have been observed for the gases and for pure dusts. For instance, the maximum rate of pressure rise of the pyrolysis gases reaches 2830 bar.s^{-1} , whereas it remains lower than 400 bar.s^{-1} for the starch at the stoichiometric concentration. Such difference can notably be explained by the importance of the pyrolysis step on the dust explosion kinetics. However, it should be kept in mind that, by directly testing the pyrolysis gases, and thus bypassing the pyrolysis step, other parameters such as the thermal transfer upstream from the flame and the initial turbulence intensity are also modified.

The evolution of the parameter $(dP/dt)_{\max}$ of hybrid mixtures of starch and pyrolysis gases (at constant fuel equivalence ratio $\Phi = 1$) has also been compared with the previous sets of data. It should be noted that, for gas concentrations greater than approximately 12 %v., the explosive behaviour of such mixtures is close to the one of the pure gas.

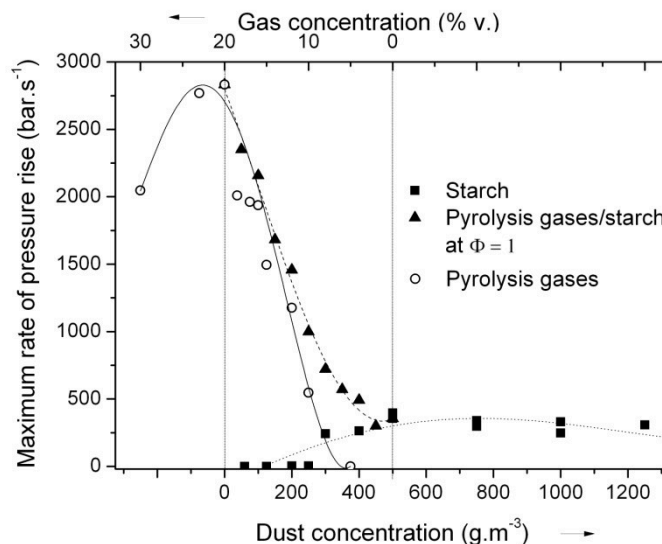


Figure 2: Comparison of the maximum rate of pressure rise of wheat starch, its pyrolysis gases and their hybrid mixtures (fuel equivalent ratio set at 1) - $t_v = 60 \text{ ms}$ - $d_{50} = 35 \mu\text{m}$ - dried powders

Figure 3 demonstrates that, for a constant fuel equivalent ratio, as soon as the gas portion exceeds 20 to 25 %m. (for a dust concentration of $375 - 400 \text{ g.m}^{-3}$), the explosive behavior of the various hybrid mixtures is approximately the same, whatever the particle size distribution is. It is also worth mentioning that, as already stated in paragraph 2.2, adding a few percent of pyrolysis gases to the pure dust probably modifies the rate-limiting step of the combustion. Such a change is more visible on figure 3 for larger particles ($d_{50} = 70 \mu\text{m}$) than for smaller ones ($d_{50} = 45 \mu\text{m}$), which confirms the previous assertion. Indeed, for dust concentrations decreasing from 500 g.m^{-3} to 400 g.m^{-3} , the $(dP/dt)_{\max}$ of such mixtures increases from 115 % to 290 % respectively for $45 \mu\text{m}$ and $70 \mu\text{m}$ particles. The effect of the initial turbulence intensity has also been tested. A strong decrease of the explosivity has been observed for a $70 \mu\text{m}$ starch/pyrolysis gases mixture when the ignition delay t_v increases from 60 to 180 ms. In fact, from a pyrolysis point of view, t_v plays a role on the volatile release and the

mixing step of the emitted volatiles with air (Hertzberg et al., 1987) but it has also an effect on the flame hydrodynamics (notably, see Peclet number on Table 2). Thus, during the explosion of starch cloud, the pyrolysis gases are present simultaneously with the dust, creating a hybrid mixture in the flame front. This mixture burns with a “flamelet” regime: the leading flame has a laminar front (due to the presence of pyrolysis gases) interacting with large eddies (Dufaud et al., 2011; Proust, 2006).

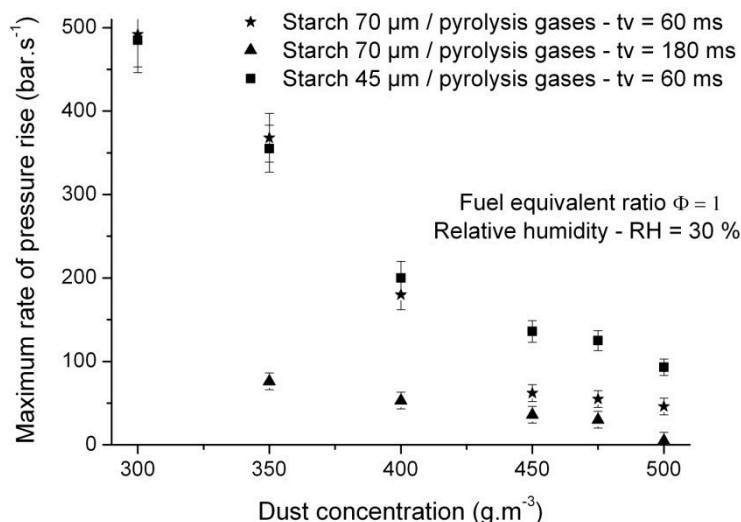


Figure 3: Evolution of the maximum rate of pressure rise of hybrid mixtures of starch and pyrolysis gases for various mean diameters and various ignition delay t_v

3.4 Impacts on the modelling of organic dust explosions

A predictive model based on the flash pyrolysis mechanisms and on a set of differential equations describing the heat and mass balances in the burning dust cloud has been developed by Dufaud et al. (2011). For the pyrolysis step, a simplified kinetic scheme proposed by Varhegyi et al. (1994) has been used. The validity of this model has notably been tested by analyzing the post-combustion gases by micro gas chromatography. Nitrogen introduced in the 20 L sphere has been considered as a reference compound and its ratios with various gaseous compounds (carbon dioxide, methane, oxygen) have been measured and compared with those calculated by using the model. More qualitatively, the observation of the carbon monoxide/carbon dioxide and carbon dioxide/oxygen ratios gives useful information on the combustion kinetics and yield. Moreover, the presence of methane and hydrogen has been noticed and analyzed for high dust loadings and more generally, rich fuel-air mixtures.

As shown on Figure 4, it gives a satisfactory agreement for cellulosic compounds, carbohydrates and more generally for organic dusts (less than 2 % of deviation on the maximum pressure on Figure 4). However, the turbulence/combustion interactions have to be taken into account to improve the model.

4. Conclusions

For organic dusts with diameters greater than “the limiting particle size”, i.e. more than 30 μm for the wheat starch, the pyrolysis step plays an important role in the dust explosion kinetics. Their ignition sensitivity and explosivities are considerably lowered with regard to smaller particles for which the devolatilization is faster and the combustion controlled by the oxidation of the homogeneous gas phase. Understanding the role of the pyrolysis step on the dust explosion allows the development of predictive models taking into account such mechanisms. In terms of prevention and protection, it can also be useful to determine the diameter of the critical ignition kernel and thus to the design of adequate flame arresters (Khalili et al., 2011). The combustion of organic powders leading to the simultaneous presence of a dust cloud and pyrolysis gases, such studies can also have implications on the study of hybrid mixtures explosions.

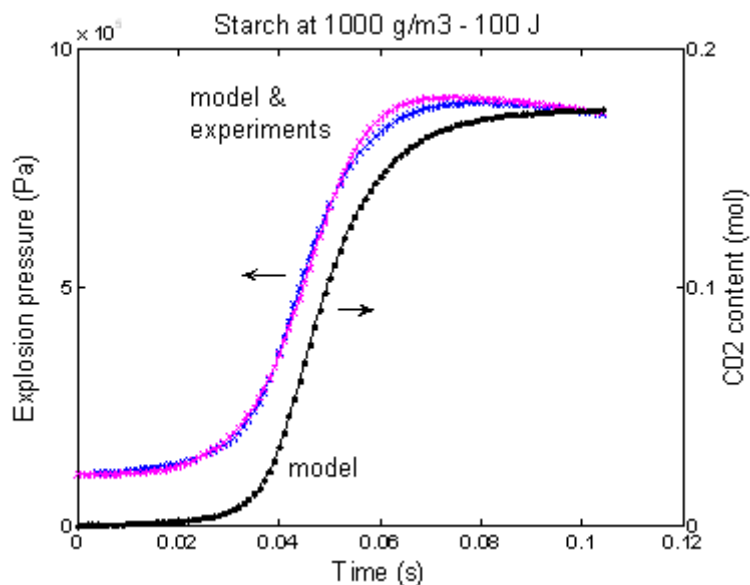


Figure 4: Evolution of the explosion overpressure and the carbon dioxide content as a function of the time for wheat starch – $d_{50} = 35 \mu\text{m}$. Comparison between the model and the experiment at $1000 \text{ g}\cdot\text{m}^{-3}$ and ignition energy $IE = 100 \text{ J}$ in a 20 L apparatus

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