

Experimental Study and Modelling of the Pyrolysis of Organic Dusts: Application to Dust Explosions

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Pyrolysis gases have been obtained by heating wheat starch thanks to a modified Godbert-Greenwald oven under argon atmosphere. The gases have been analyzed by micro-gas chromatography. The explosivity of both starch and pyrolysis gases have been compared. Totally different explosive behaviours have been observed for the gases and for pure dusts, which highlights the influence of the pyrolysis step on the explosivity of organic particles with diameters greater than 30 μm . However, tests carried out with pyrolysis gases and glass beads mixtures also demonstrate that the impacts of heat transfer and turbulence/combustion interactions should not be neglected.

In addition, a one dimensional finite-volume scheme has been developed to represent the pyrolysis of a single starch particle. The model has been validated for particles exposed rapidly at high temperatures (1,000 K). The characteristic times of the pyrolysis have then been determined, which confirms the importance of the primary gasification of the particle in the rate-limiting step of the dust explosion.

These results also provide a perspective for understanding the specific behaviour of gas/dust hybrid mixtures towards explosion.

1. Introduction

During the explosion of an organic dust cloud, different successive steps occur: the particle heating, its devolatilization/pyrolysis and then, the oxidation of the pyrolysis gases. The characteristic times of these phenomena can be greatly different, and a rate-limiting step can then be defined. For small particles with diameters lower than 10 to 30 μm , the pyrolysis step is fast, and the combustion kinetics can be reduced to the oxidation phase as it has been previously shown by Hertzberg et al. (1987) and Di Benedetto and Russo (2007). This is not the case for larger particles and the heat transfer or the oxygen diffusion can become rate-limiting. Understanding and underlining the role of the pyrolysis step in organic dusts explosions have several aims: i) the results will be used as input into a predictive model based on a simplified kinetic scheme representing the pyrolysis and the oxidation, ii) increasing the effect of the rate-limiting step can lead to the development of adequate protective measures (Dufaud et al., 2010), iii) the study of the combustion process is compulsory to understand the turbulence/combustion interactions in the front flame (influence of the Lewis number, presence of flame pockets...), iv) Amyotte et al. (1993) and later Dufaud et al. (2008) have pointed that the mixture of pyrolysis gases and dusts can be regarded as a hybrid mixture and these results will be extended to such explosive atmospheres.

This paper will describe the approach which has been followed in order to highlight the influence of the pyrolysis step on the explosion of organic dusts. Firstly, the experimental setup which has been developed to synthesize and analyze the pyrolysis gases will be briefly presented. Based on these experiments, the explosive behaviour of organic dust (here, wheat starch), its pyrolysis gases and their mixtures has been studied. In addition, a one dimensional finite-volume scheme has been developed to represent the pyrolysis of a single starch particle. Both experimental and computational results have led to the improvement of a global model representing the explosivity of dusts and gas/dusts hybrid mixtures.

2. Generation of pyrolysis gases and model proposal

In this study, wheat starch (Sigma-Aldrich Co) has been chosen as the organic dust. The characteristic diameters of the powder d_{10} , d_{50} , and d_{90} are respectively of 16, 35, 76 μm . A Godbert-Greenwald furnace has been modified to produce, under argon atmosphere, and analyze the pyrolysis gases by gas chromatography. The whole experimental procedure has been described in previous papers (Dufaud et al., 2012a). If the influences of various parameters, such as the particle size distributions and the oven temperature have been tested, the main parameter which has been adjusted was the residence time. Indeed, it was important to have a sufficiently short residence time, which could be compared to the reaction time of a dust explosion, but also sufficiently long to generate enough pyrolysis gases. At 833 K, the temperature being moderate, the proportion of tar generated during the pyrolysis is approximately 3 to 4 times greater than the gas proportion for residence times lower than a second: this is the domain of 'fast pyrolysis'. The chemical composition of gases obtained under such conditions (notably 60 % CO, 30 % CO₂, 4 % CH₄) have been detailed by Dufaud et al. (2012a). A more complete gasification is obtained at 1000 K, with 80 to 90 % wt. of starch pyrolysed, some chars remaining at the bottom of the oven.

The pyrolysis model chosen in this study describes the pyrolysis of a single starch particle in suspension at 1 bar and 1,000 K. Starch pyrolysis follows the same pyrolysis model than the one proposed by Scott and Piskorz (2009). Three different reactions have been taken into account: the thermal decomposition of starch directly into pyrolysis gases (R1), the generation of tar (R2) and the secondary reaction of tar gasification into pyrolysis gases (R3). Due to the small proportions of char observed during the pyrolysis experiments carried out at high temperatures, char production has been deliberately neglected.

A 1D finite volume method with a constant mesh size has been applied to a spherical particle of 30 μm diameter. The equations representing the mass, energy and momentum balances have been discretized and then solved using Matlab[®] (2011b). An upwind scheme has been used for the discretization of the convection terms. The particle core shrinking has been taken into account by eliminating the volumes having porosities greater than 75 %. Reynolds number of the flow has been considered as constant, and it has been assumed that the exhaust gases do not affect the convection at the particle surface. The orders of the reaction have been set at one, with constants following an Arrhenius' law.

3. Dust, pyrolysis gases and hybrid mixtures explosions: experiments

Based on the previous experiments, a gas mixture has then been prepared in order to represent the pyrolysis gases of starch (Dufaud et al., 2012a). 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. The lower explosivity limit (LEL) of the gases, the Minimum Explosive Concentration (MEC) of the dust and the explosion severity, i.e. P_{max} (maximum overpressure), and $(dP/dt)_{\text{max}}$ (maximum rate of pressure rise), were measured in a 20 L spherical vessel (Eckhoff, 2003). 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 (Dufaud et al., 2012b). Figure 1 represents the influence of hybrid mixtures on the explosivity limits of starch and pyrolysis gases.

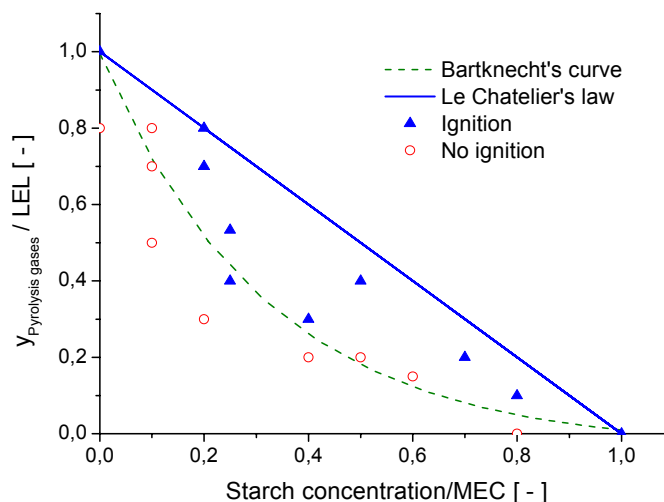


Figure 1: Representation of the explosivity limits of starch/pyrolysis gases hybrid mixtures

As already mentioned by Khalili et al. (2012), Le Chatelier's law is usually not applicable for such hybrid mixture: explosions being observed for concentrations both lower than the MEC and the LEL, the relationship proposed by Barktnecht being more adequate. It should also be noticed that the deviation from Le Chatelier's law is certainly more pronounced for starch with a few percents of pyrolysis gases than when a small proportion of dust is added to pure gases. It seems consistent with the previous observation stating that the presence of few percents of gas/vapors, as low as 1 % vol., induces changes in the rate-limiting step of the dust combustion reaction, from boundary diffusion to homogeneous gas phase reaction (Khalili et al., 2012).

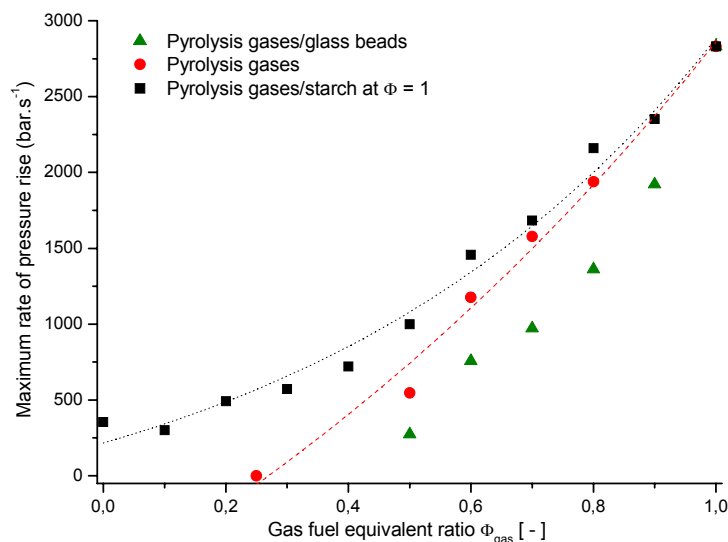


Figure 2: Influences of starch and glass beads addition on the maximum rate of pressure rise of pyrolysis gases

The explosive behaviours of starch and its pyrolysis gases have been compared. At stoichiometric concentration, the maximum rate of pressure rise of pure starch is approximately seven times lower than the one of its pyrolysis gases, which reaches $2,830 \text{ bar.s}^{-1}$. If such difference underlines the importance of the pyrolysis step on the dust explosion process, it should be kept in mind that, by replacing an organic dust by its pyrolysis gases, many parameters are also modified: the initial turbulence intensity, the thermal transfer upstream from the flame... Thus, Figure 2 shows the influence of glass beads ($35 \mu\text{m}$) addition on the explosivity of pyrolysis gases/air mixtures. It clearly demonstrates that, even for a few percents of inert solids, the explosivity of the gases is strongly modified. Explaining the specific explosive behaviour of hybrid mixtures only by considering the modification of the combustion kinetics is then nonsense. Nevertheless, the Figure 2 also shows that the explosivities of the pyrolysis gases and starch/pyrolysis gases mixtures are very similar when the gas concentrations are high. On the contrary, and as already said, the addition (or the generation in the first moments of a dust explosion) of a few percents of pyrolysis gases to an organic dust has a strong impact its explosivity. Previous experiments carried out on starch particles having different particle size distributions have notably demonstrated that this change is more visible for larger particles (Dufaud et al., 2012b), which reinforces the argument that the presence of pyrolysis gases modifies the rate-limiting step of the combustion of particles with diameters larger than $30 \mu\text{m}$.

4. Pyrolysis of a single particle: model

Pyrolysis can be controlled by heat transfer, chemical reactions or mass transfer. The estimation of characteristic times is a useful tool for defining the controlling steps. The characteristic times of the pyrolysis (Authier et al., 2009) have been determined through the model developed for a single particle of starch and have been defined as follows, respectively for the reaction, internal heat transfer by conduction and internal mass transfer by convection:

$$t_{Ri} = \frac{1}{k_i} \tag{1}$$

$$t_{cond} = \frac{L^2 \rho C_p}{\lambda} \tag{2}$$

$$t_{i,conv} = L^2 \mu / (PK) \tag{3}$$

where k_i is the kinetic constant of the reaction i , L is the characteristic length of the system, ρ is the particle density, C_p is the heat capacity, λ is the thermal conductivity, μ is the dynamic viscosity of the gases, ΔP is the pressure gradient and K , the permeability of the particle.

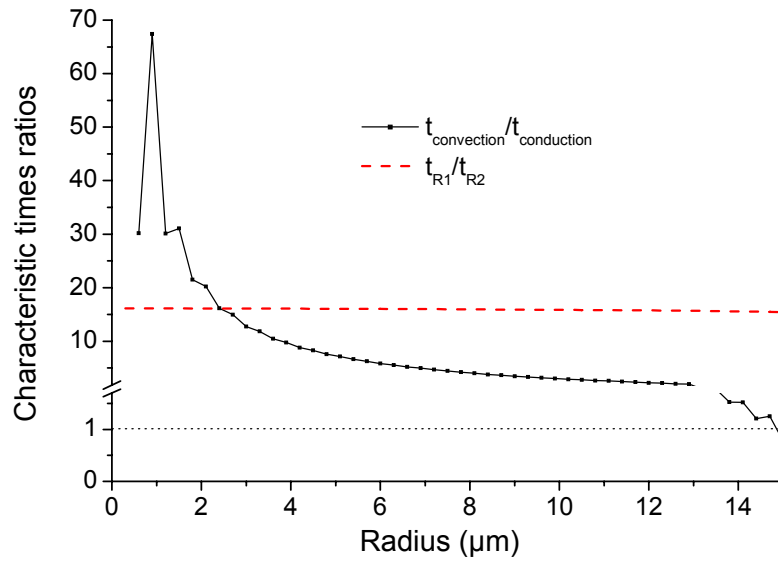


Figure 3: Evolutions of t_{conv}/t_{cond} and t_{R1}/t_{R2} of a single starch particle as a function of its radius. Heating time: 5 ms

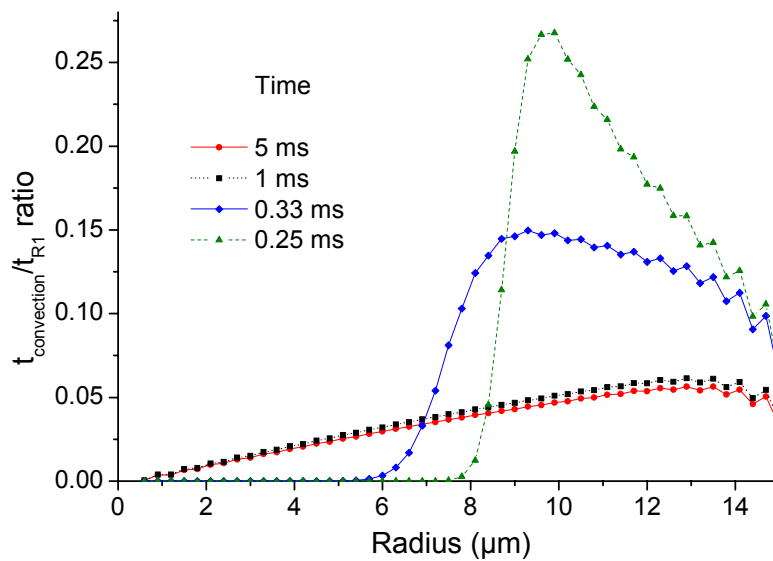


Figure 4: Time evolution of the ratio of the characteristic times related to the internal mass transfer and to the gas generation as a function of the particle radius

On the one hand, the Figure 3 shows that the rate of tar formation is always greater than the rate of gas formation from the primary particle. On the other hand, it can be observed that the characteristic time related to the mass transfer by convection is usually much greater than the heat conduction time. Obviously, notably due to the spatial evolution of the particle porosity, the limitation induced by the mass transfer within the particle is greater at its centre than at its surface, where the t_{conv}/t_{cond} ratio becomes lower than unity. Figure 4 demonstrates that the rate-limiting step is always the pyrolysis reaction leading to gas formation. The time evolution of the ratios observed on Figure 4 is due to the heating and the progression of the thermal wave within the particle.

Figures 3 and 4 confirms that, the generation of pyrolysis gases being the rate-limiting step, the addition of a few percents of gas can accelerate the combustion kinetics during the explosion such an organic dust. Once a sufficient quantity of gases is obtained around the particles, the combustion is certainly governed by the oxidation phase.

5. Dust explosion modelling

The previous results tend to demonstrate that the pyrolysis step is not always negligible when considering the dust explosion kinetics. A model representing a dust explosion in a 20 L sphere, previously developed by our laboratory (Dufaud et al., 2012a), has then been modified in order to introduce the pyrolysis reactions R1, R2 and R3. The model has been tested and validated for pure organic dusts and will be extended to hybrid mixtures and especially methane/starch mixtures, which have already been studied (Khalili et al., 2012).

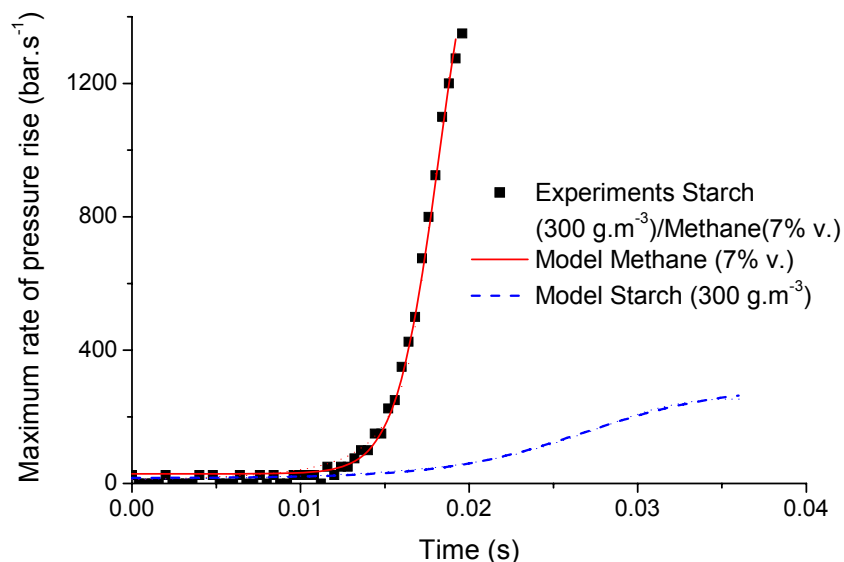


Figure 5: Comparison between models optimized for methane or starch and experiments on starch/methane hybrid mixture

At first, the kinetics constants have been fitted for methane at 7 % v. and starch at 300 g.m^{-3} . Then, the experimental data obtained for a 7 % v. methane/ 300 g.m^{-3} starch mixture have been fitted using either the parameters determined for the pure dust or those obtained for the methane. The results of this comparison are shown on figure 5. It is clearly demonstrated that the combustion parameters used for pure methane are more adapted to the representation of the maximum rate of pressure rise of such mixture than those of starch, the pyrolysis reaction not being the rate-limiting step at such amount of gases. However, tests and simulations confirm that the pyrolysis step becomes significant at lower gas concentrations.

6. Conclusions

As a function of the particle size distribution, the dust explosion phenomenon is governed by different mechanisms. For organic dusts with small diameters, generally lower than 10 to $30 \mu\text{m}$ - more for some polymer, the devolatilization or pyrolysis process is often very fast (Di Benedetto et al., 2010). This is not the case for larger particles for which the primary gasification can be rate-limiting. Nevertheless, it should

be kept in mind that understanding the combustion kinetics of a dust explosion is not sufficient to correctly model such phenomenon and that the influences of thermal radiation upstream of the flame and of combustion/turbulence interactions should also be taken into account (Russo and Di Benedetto, 2007). Finally, the one dimensional model for starch pyrolysis will be extended to a 3D-scale and validated by μ GC measurements at various temperatures.

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