

New Pyrolysis Mechanisms for Dust Explosion Simulation

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Numerical simulation of dust explosions can be used for intensive, multi-parameter sensitivity studies, reducing the number of experimental tests required. Nevertheless, to develop such approaches, it is imperative to collect reliable input data beforehand. Preliminary tests show that particular attention needs to be paid to developing new flash pyrolysis mechanisms. Indeed, simple devolatilization reactions (polymer into monomer conversion) are not suitable, and the chemical species to be considered are far more numerous than in the case of lighter chemical compounds or shorter chains. On the other hand, the mechanical properties of synthetic polymers seem to limit their fragmentation in the 20L sphere, which could simplify the simulation approach by neglecting particle sizes modification.

1. Introduction

The experimental determination of explosion severity parameters is based on international standards, which generally set arbitrarily the test conditions. However, these conditions are not always those encountered in industrial processes (e.g. high ignition energy and turbulence, particle size distribution (PSD) changes due to powder dispersion in the explosion vessels...) and although the test results are generally conservative, the consequences of this deviation from reality need to be assessed. It should be noted that the term "reality" is certainly inappropriate, as it covers a wide variety of situations that can arise on the same industrial site. In this case, it is more appropriate to describe a range of realistic conditions considered during major risk assessment. Then, the process safety expert has several options: a) From among all probable situations, to determine the most conservative conditions and carry out tests based on these parameters only; This is often the case when the powder is sieved, dried and tested at high ignition energies; b) To carry out an extensive sensitivity study to determine the influence of variations in operating parameters, which requires a very large number of experiments, and is therefore time-consuming and costly; c) To acquire in-depth knowledge of the phenomenon and use numerical simulation to test all the effects of such variations, but this solution cannot be implemented on its own without a preliminary experimental validation.

In this work, the latter approach was favoured and both Computational Fluid Dynamics (CFD) simulation and experimental approach were combined to represent the explosion of organic powders. Several articles were already published on this subject (Islas et al., 2023; Portarapillo et al., 2021; Zhang et al., 2024) but most of the studies combining CFD and dust explosion only consider the powder dispersion stage, without simulating the reaction stages of pyrolysis, oxidation/combustion, and flame propagation within the 20L sphere (Pico et al., 2020). In parallel, numerous studies were focused on determining the reaction mechanisms describing the pyrolysis and/or combustion phases of organic compounds. However, it is rare to obtain this information under the specific conditions of a dust explosion. Indeed, experimental characterizations based on objects of different sizes (millimetre range powders, polymer slabs...), low temperature ramps or oxidation/pyrolysis conditions different from those observed during an explosion, although useful, cannot be directly used within the framework of a numerical simulation.

The aim of this work is to propose lumped mechanisms for the pyrolysis of synthetic or natural organic powders, so that they can be incorporated into CFD simulations of a dust explosion. Indeed, both identifying pyrolysis gases and proposing pyrolysis mechanism is a key-point in modelling a dust explosion (Jiang et al, 2024). Such

development will provide insights, either into predicting the severity of a dust explosion within a 20L vessel, based on the powder properties, or into predicting the potential consequences of a dust explosion in a complex industrial configuration, based on empirical data obtained using a 20L sphere. Knowledge of pyrolysis mechanisms will also be useful for thermal conversion processes of polymers (e.g. waste plastics) and will improve the adjustment of safety parameters for powders at high temperatures. This article presents a state of the art, the methodology and preliminary work carried out on two powders (polyethylene and polystyrene).

2. State of the art

This section will be devoted to a brief bibliographical survey of the state of the art in relation to the CFD of dust explosions, mainly in 20L spheres. The second section will highlight the importance of the reaction mechanisms considered for the simulation.

2.1 CFD simulation of dust dispersion at laboratory scale

The dynamics of dust dispersion in the 20-L test sphere has already been thoroughly studied (Table 1). The influence of various parameters including nozzle geometry, ignition delay time and particle size distribution have been considered. The first challenge of a dust dispersion in the 20L sphere is to ensure a uniform dissemination of the dust inside the vessel. A uniform distribution theoretically guarantees the consistency and reproducibility of the test, but sedimentation and certain physical properties such as a wide PSD, shapes or density may cause heterogeneities (Li et al., 2020; Ray et al., 2020). The second challenge is the control of the dust cloud turbulence, which has a significant effect on the explosion severity and flame propagation (Islas et al., 2022). To improve dust dispersion, different types of nozzles can be designed (Pico et al., 2020). The third challenge is to take account of the ignition phase and its instability, which is, by their very nature, a transient phenomenon (Portarapillo et al., 2021). Finally, correctly describing the reaction kinetics of the powder (heating, pyrolysis/devolatilization, gas oxidation) is a major challenge (Bind et al., 2012; Islas et al., 2022; Pico et al., 2020; Wang et al., 2020) (Table 1).

Table 1: Summary of relevant CFD studies dealing with dust explosion in a 20L vessel

Reference	Powders	CFD software	Scenario	Turbulence model	Description
Bind et al., 2012	Aluminium and starch	Ansys Fluent	Developing multi-scale (particle and cloud) reaction engineering model	standard k- ϵ model	Combustion at the particle scale for Al and group combustion for starch. Single reaction
Li et al., 2020	Cornstarch	Ansys Fluent	Effects of oxygen, fuel concentration and PSD	standard k- ϵ model	Highlight the influence of flame-turbulence interactions
Islas et al., 2022	Biomass (Pellets Asturias and Cupressus Funebri)	OpenFOAM	Biomass dusts explosion is mainly governed by the characteristics of the cold-flow	Eulerian-Lagrange with 2-way coupling	Moisture evaporation, devolatilization, and char oxidation are considered for the reactions
Pico et al., 2020	Wheat starch	Ansys Fluent	Three different nozzles. Pyrolysis step considered and solid/gas hybrid mixtures	CFD-DPM (Discrete Phase Model) with a Eulerian-Lagrange	Powder dispersion and the pyrolysis/gas oxidation reactions Pyrolysis gases from modified G-G furnace
Portarapillo et al., 2021	Various classes of dusts (A to D)	Ansys Fluent	Comparison between 20L and 1m ³ explosion vessels. Influence of chemical igniters	URANS standard k- ϵ model	Flame propagation and heat transfers generated by pyrotechnic igniters and their impact on different kinds of dusts
Ray et al., 2020	Coal dust	Ansys fluent	Dispersion of coal dust in a 20-L vessel	standard k- ϵ model	Dust dispersion in an 20L explosion chamber
Wang et al., 2020	Corn starch	Ansys Fluent	Three steps-process including devolatilization. 3 ignition modes	standard k- ϵ model	2 pyrolysis reactions, Single gas combustion reaction, and 2 char combustion reactions

CFD corrections can be proposed to take the discrepancies between ‘ideal dispersion’ and reality into account as such variations can lead to a substantially under-prediction of explosion severity for larger particles (Islas et al., 2022). The influence of particle concentration on biomass dust explosion characteristics found significant changes in explosion properties. Low concentration may lead to incomplete burning, while high concentration can increase the flame propagation, and also increases the risk of secondary explosion.

However, excessive turbulence can extinguish the flame prematurely or spread unevenly because turbulence plays a dual role: enhancing both dispersion and combustion efficiency. Pico et al., 2020 explored hybrid dust-gas systems, such as wheat starch and pyrolysis gases. Their results show that interactions between gas-phase reactions and dust combustion can enhance turbulence and explosion intensity. This underscores the importance of considering mixed-phase reactions in explosion modeling.

2.2 Importance of pyrolysis mechanisms

Several authors have attempted to describe the reaction kinetics of powders in a dust explosion by simplifying the various reactions into lumped mechanisms as shown in Table 2. Some authors have considered single steps, either a devolatilization step (Quek et al, 2022) or a reaction step (Bind et al, 2012). Depending on the physico-chemical properties of the powders, or for convenience, it is sometimes appropriate to consider heterogeneous and homogeneous reactions simultaneously (Li et al., 2020). But the stages of an organic dust explosion are invariably the same: heating of the particles, pyrolysis and oxidation of the gases, and neglecting one of these phases can only be justified by determining the rate-limiting step. Therefore, other authors have proposed to develop mechanisms that clearly separate the pyrolysis and oxidation phases (Pico et al., 2020). Islas et al. (2022) have proposed a comprehensive model that also takes into account the particle drying phase. Finally, it should be pointed out that Table 2 is not intended to be exhaustive, and that other reaction models have been proposed, notably for carbonaceous powders (Khan et al., 2024).

Table 2: Summary of some CFD studies of dust explosion – focus on the reaction mechanisms

Reference	Pyrolysis gases	Reaction mechanisms	Model validation
Bind et al. 2012	No	Single combustion reaction for starch: CO ₂ and H ₂ O generation Beckstead combustion time correlation for Al: single reaction	Pressure-time curves from simulation and experimental results, with flame propagation speeds and temperature profiles.
Islas A. 2022	CO, CO ₂ , CH ₄ , and H ₂	Moisture evaporation rate Devolatilization (SFOM & BioCPD) Surface reaction (C + O ₂)	Pressure-time curves from simulation and experimental results, peak pressures
Li et al., 2020	Volatiles CO, H ₂ , CH ₄ , C ₂ H ₄	Combination of heterogeneous combustion of C (with O ₂ or H ₂ O) and oxidation of the so-called volatiles	Pressure-time curves, flame characteristics (flame length, spatial velocity)
Pico P. 2020	Pyrolysis gases (CO, CH ₄ , C ₂ H ₄ and H ₂) + tar (C ₂ H ₄ O)	4 steps pyrolysis, gas oxidation, turbulence-chemistry interactions, and a combination of gas- and solid-phase reactions	Validated with experimental data from pressure-time curves and pyrolysis gases determined from micro-gas chromatography
Quek et al., 2022	C ₂ H ₄	Devolatilization of PE into C ₂ H ₄ and “heterogeneous reaction of LDPE and C ₂ H ₄ ”	Pressure-time curves. Literature data from LDPE/C ₂ H ₄ explosion

3. Materials and methods

CFD simulations require both input data, describing for instance the initial particle size distribution of the powders and the pyrolysis and oxidation mechanisms, and validation data sets of explosion severity parameters.

2.3 Powders

Two kinds of powders were used in this study: natural polymers, such as cellulose, lignin or starch and synthetic polymers, as polyethylene, polypropylene, poly(methyl methacrylate), polylactic acid or polystyrene. Powders were selected for their composition (low additive content) and their fine PSD. Indeed, grinding of polymers, especially those exhibiting good plastic or elastic properties, was avoided as heat modifies their surface properties. The particle size distribution was determined both ex-situ and in-situ, i.e. in the 20L sphere during

the powder injection phase. As stated in introduction, this article focuses on polystyrene (PS) and polyethylene (PE 35-50 μm from VWR).

2.4 Pyrolysis gases and mechanisms determination

In order to reproduce as much as possible the conditions of a dust explosion, the pyrolysis mechanisms must be determined for a powder dispersed in air, undergoing a rapid rise in temperature from ambient temperature to pyrolysis temperature (generally, greater than 350-450°C at the surface of the polymer). Residence times should be short, on the order of a few tens of milliseconds to 200 ms, and the oven temperature should reach 500 to 1000°C. Therefore, a modified Godbert-Greenwald furnace was used to analyze the gaseous compounds generated by the flash pyrolysis of the polymers. The furnace was made air-proof inserting an inner Inconel cylinder. The entire set-up was flushed with argon during 15 to 30 minutes before injecting the powder (0.2 to 0.5 g) with the same gas at pressures ranging from 0.1 to 0.5 barg. The pyrolysis gases collected in a Tedlar bag were analyzed by gas chromatography GC (SRA 3000 μGC with a TCD detector - 3 ways). Permanent gases (e.g. H_2 , CO , CO_2 , CH_4 , C_2H_2 , C_2H_4 , C_2H_6) were measured, as well as aromatic compounds (benzene, xylene...). Additional calibrations may be necessary to identify unknown compounds.

2.5 20L spheres: dust cloud properties and explosion severity

Explosion severity, characterized by the maximum explosion pressure p_m and maximum rate of pressure rise dp/dt_m , was determined in a standard 20L sphere according to EN 14034 series. The ignition energy and ignition delay time were set at 10 kJ and 60 ms, respectively. The dust dispersion is ensured by using a rebound nozzle. The PSD of the dust cloud was determined in-situ at the centre of the 20L sphere as a function of time. A replica of the standard 20L sphere, equipped with 4 windows and with the same dust dispersion system (dust canister, inlet valve, rebound nozzle), was used jointly with a laser diffraction sensor (Helos - Sympatec). The acquisition frequency was set at 5 ms and the analysis range extended from 0.5 to 175 μm .

Particle Image Velocimetry (PIV) will also be applied to the same vessel to characterize the initial turbulence of the dust cloud. Root-mean-square (RMS) velocity of around 5 $\text{m}\cdot\text{s}^{-1}$ are expected at ignition time (Murillo, 2016).

2.6 Numerical simulation

CFD simulation of dust dispersion and flame propagation in a 20 L sphere was carried out using a Euler-Lagrange method (Ansys Fluent). Spatial discretization uses the finite volume method (polyhedral and prismatic cells). Various fluid properties, including the pressure field, velocity field, turbulence intensity, and degree of particle dispersion (spatial repartition of the dust cloud), were obtained and compared with the experimental results. The combustion reaction of the powders was considered via two main steps: the generation of pyrolysis gases followed by their oxidation.

For simulation purposes, the explosion vessel was divided into three parts: a 20L sphere, a standard nozzle, and a dust container, all treated as internal walls without any inlet or outlet conditions in this geometry. All internal walls are defined with a no-slip condition for the gas flow. The calculation parameters of the CFD simulation are defined as a two-phase flow and analyzed with an implicit unsteady formulation. The two-way coupling treats the particles carried by the fluid in a Eulerian-Lagrangian approach, so that the equations of the dust phase are set to a group of particles (or parcel) sharing the same properties.

Spatiotemporal discretization uses a hybrid scheme that blends pure central differencing with the second-order upwind scheme, guided by the Detached Eddy Simulation model for turbulence evolution. Mesh generation was done with a maximum growth rate of 1.3. The edge size ranges from 0.5 mm (near the nozzle) to 16 mm, with a total number of cells kept between 1 and 2,000,000 to ensure manageable computation time. Calculations were done using a server equipped with an Intel Xeon W7-3545 processor at 2.71 GHz and 512 GB of RAM.

Pyrolysis reactions were taken from a simplified global mechanism based on experimental data collected with the Godbert-Greenwald furnace. The oxidation step of the pyrolysis gases was modelled by the CHEMKIN interface. The methodology couples CFD with detailed chemical kinetics. The fluid flow and dispersion dynamics within the 20 L sphere are simulated, and Fluent solves the Navier-Stokes equations, tracking reactant dispersion and evolving concentration fields. Integration of a new pyrolysis mechanism is made via CHEMKIN files, incorporating species transport, reaction rates, and thermal feedback. This coupling predicts species concentrations, temperature profiles, and reaction rates over time. Parametric studies will assess the effects of varying initial conditions, such as fuel concentration and PSD.

Initial simulations confirm the non-uniform nature of the powder dispersion in the sphere and highlight the impact of the powder (PSD, concentration) on turbulence before and after ignition (Murillo, 2016; Pico et al., 2020).

One of the main limitations of using CFD is its computational cost. In this study, simplifications will be necessary in order to limit the computation time, such as the assumption of a constant PSD (section 3.1), the use of lumped kinetic models or the fact of neglecting the deformation of the nozzle during injection. The effects of flame quenching at the wall (particularly radical terminations) are also delicate points to consider.

3. Results

Preliminary tests were performed on polystyrene and polyethylene dusts.

3.1 In-situ particle size distribution

Knowledge of the PSD of the dust cloud before its ignition is essential as it can be strongly different from that determined by dry or wet ex-situ particle size measurement. Figure 1 shows that the PSD of polystyrene significantly changes during its injection in the sphere. Given the difficulty of grinding this type of material, it is unlikely that powder fragmentation can be envisaged. However, the detachment of fine particles attached by electrostatic forces to the primary powders or a change in the powder shape must be considered. Polyethylene being finer, with a primary PSD ranging from 35 to 50 μm , the time-evolution of its PSD is less noticeable. However, the presence of finer particles ($< 20 \mu\text{m}$) should be highlighted.

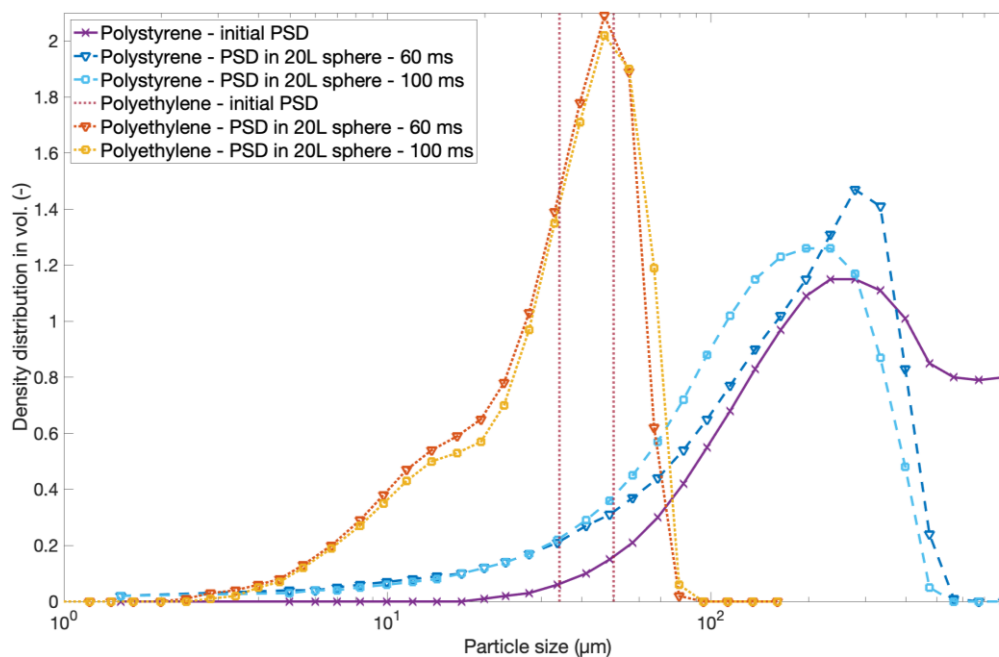


Figure 1: Time-evolution of the PSD of polystyrene and polyethylene powders in the 20L sphere

3.2 Pyrolysis gases of polymers

Table 3 summarizes the gases and aromatic compounds collected at 500°C and identified by chromatography. It is essential to note that the given contents were normalized by removing the values corresponding to argon and residual air, as well as by not considering peaks corresponding to unknown compounds.

Table 3: Gas chromatography analyses of polymer powders pyrolysis (permanent gases and aromatics)

Permanent gases and aromatics	H ₂	CH ₄	CO	CO ₂	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₄	C ₃ H ₈	Aromatics
PS Normalized volume content (vol.%)	2.5	1.9	6.3	3.1	0.6	3.1	0.6	75.2	3.7	3
PE Normalized volume content (vol.%)	0.9	0	11.4	9.5	0.4	4.2	0.5	46.0	3.1	24.1

Low quantities of light permanent gases are generated (H₂, CO, CH₄...), which marks a notable difference with the natural compounds, e.g. starch and cellulose, previously studied by Pietraccini et al. (2023). On the other hand, the C₃ and aromatic contents (e.g. toluene, xylene) are remarkably high. For polystyrene, it should be noted that the microGC was not calibrated to identify neither styrene, nor methylstyrene C₉H₁₂, which are two main products of PS pyrolysis (Artetxe et al., 2015). In the case of polyethylene, the low quantity of ethylene generated is due to the low test-temperature (500 °C). Experiments at higher temperatures show a significant increase in C₂H₄ concentration. However, Table 3 shows that heavier compounds, especially aromatics (here

toluene) should also be considered. Presence of carbon monoxide and dioxide, which can be surprising for PE, is confirmed by other studies and may be due to the presence of additives or adsorbed air (Ouiminga et al., 2009). Despite the large quantities of tar and incondensable compounds, the analysis will mainly focus on lighter species, as such heavy compounds will eventually decompose into light C₁-C₄ gaseous hydrocarbons at higher temperature, e.g. during an explosion (Jiang et al., 2024). By changing both the oven temperature and residence time, lumped pyrolysis mechanisms can be proposed implemented and coupled to oxidation reactions of the pyrolysis gases. Such an approach has already been applied to cellulose and starch (Pietraccini et al., 2023) and will be extended to synthetic polymers.

4. Conclusions

Foundations have been laid for the numerical simulation of polymer powder explosions. In parallel with the development of CFD aspects, the choice of turbulence models and mesh generation, preliminary experiments were done on polystyrene and polyethylene dusts. They suggest that the development of new mechanisms representing the flash pyrolysis of polymer is needed. From a kinetic point of view, the pyrolysis stage cannot be neglected and basic devolatilization reactions (e.g. depolymerization reaction or generation of light gases only) seem inadequate. Indeed, the range of chemical species involved is significantly broader, as demonstrated by flash pyrolysis tests. Nevertheless, there are some simplification possibilities, such as neglecting the fragmentation of polymer powders during their injection in the 20L sphere.

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