

A Mathematical Model for the Prediction of the K_{St} for Metallic Dusts as a Function of the Particle Size Distribution

Martina Silvia Scotton^a, Marco Barozzi^a, Marco Derudi^b, Sabrina Copelli^{a,*}

^a University of Insubria, Department of Science and High Technology, Via Valleggio 9, 22100, Como, Italy

^b Polytechnic of Milan, Department of Chemistry, Materials and Chemical Engineering,
sabrina.copelli@uninsubria.it

For several years, dust explosions have been one of the major causes of industrial accidents, spanning from metalworking to pharmaceuticals sectors. In accordance with the latest Chemical Safety Board (CSB) investigations, three out of four dust explosions in the United States involved metallic dusts (iron, titanium, zirconium and aluminum). Many chemical processes involve metal powders for their exceptional mechanical, optical and catalytic properties, such as the production of plastics, rubber, paints, coatings, inks, pesticides, detergents and even drugs. The severity of a dust explosion can be defined using experimental parameters such as the maximum explosion pressure (P_{max}), the maximum rate of pressure rise ($(dP/dt)_{max}$) and the deflagration index (K_{St}), which are employed to predict the consequences of a dust explosion for a given scenario. Among these parameters, the deflagration index plays a fundamental role, as it is used for the design of deflagration nozzles aimed to protect industrial equipment and silos from internal dust explosions. The purpose of this work is to develop a mathematical model able to predict the K_{St} value of metal powders as a function of chemical-physical data and the particle size distribution (D_{50} was used as global information). The model structure is based on the writing and resolution of the material and energy balance equations on the single dust particle, also estimating the contribution of oxygen diffusion which, in the case of metal powders, greatly depends on both tortuosity and porosity. The results well agreed with experimental data, providing the basis for the development of more detailed models.

1. Introduction

The value of the deflagration index can be easily calculated through a series of tests carried out in the standard 20-L apparatus. However, considering the intrinsic limits of this approach, the possibility of estimating the K_{St} value through a suitable mathematical model able to overcome at least some of the limits of the experimental approach has been studied in the literature. Indeed, several mathematical models have been proposed to predict the value of K_{St} and other explosion parameters, such as MIE, for organic combustible dusts. Fumagalli et al. (2017) have proposed a simple kinetic free model which used a few information about heat transfer properties of the analyzed dust and a single value of the deflagration index at a reference mean diameter for the evaluation of the deflagration index trend as a function of the mean diameter of the particle. Copelli et. al. (2021) have proposed a mathematical model able to theoretically estimate the MIE value of organic powders using very few easily accessible experimental information, such as granulometric and thermogravimetric analysis (TGA). Therefore, the aim of this work is to develop and validate a mathematical model (based on oxidation reaction kinetics) for the prediction of the K_{St} value for metallic dusts as a function of their mean particle size. Several research have shown that metal dust explosions can be strongly conditioned by both mean diameter and size polydispersity (σ_D) of the dust (Castellanos et al., 2014). The present work considers only the first aspect (that is, the mean diameter), eliminating the polydispersity influence by considering highly peaked granulometric distributions. The model predicts the K_{St} value by solving material and energy balance equations for spherical dust particles wrapped by a single constant temperature fireball (generated by the ignitors explosion inside the 20 L sphere). The model was validated using literature experimental data for aluminum dust, a well-known explosible metal dust.

2. Mathematical Model

For a metal dust explosion, the oxidation mechanism has the greatest impact on the violence of the explosion itself and depends on both the particle temperature and the heterogeneous kinetics (Dufaud et al., 2010). Two different processes are in competition: oxygen diffusion through the oxide/metal layer (variable thickness) within the particle pores and heterogeneous oxidation kinetics. For big dust particles, oxygen diffusion through the pores can be considered as the rate determining step for metal dust explosion and, therefore, it is the main contributor to the deflagration index value. On the contrary, for very small dust particles, the diffusion is very fast, and the oxidation kinetics must be properly taken into account. The stoichiometry of the complete oxidation reaction, starting from pure metal species, M, is schematically described through this equation: $aM + bO_2 \Rightarrow M_aO_{2b}$.

The explosion model is developed under the following assumptions: (1) one-dimensional, spherically symmetric dust particle whose volume element is equal to $\partial V = r^2 \cdot \sin \theta \cdot \partial r \cdot \partial \theta \cdot \partial \varphi$, and surface element is equal to $\partial S = r^2 \cdot \sin \theta \cdot \partial \theta \cdot \partial \varphi$; (2) negligible resistance to mass transfer; (3) no secondary reactions of the oxides produced; (4) local thermal equilibrium; (5) unsteady-state assumption for the gaseous phase and negligible convective fluxes (only diffusive fluxes are taken into account in the case of metal powders); (6) particles with constant total volume, V_t (presence of a metallic skeleton with a constant density ρ_M , non-constant porosity ε because of the reduction of the pores diameter due to the formation of oxide layers onto the metallic skeleton - conversely to what happens for organic particles for which the porosity increases). Basing on the last assumption (6), it is necessary to write material balances for both the metallic phase (M) and the gaseous oxygen; obviously a certain amount of metallic particle could not react with oxygen.

2.1 Material balance equations on the metallic phase

The material balance equation on the metallic phase can be written as:

$$\frac{\partial n_M}{\partial t} = -a \cdot k \cdot c_{M,app} \cdot c_{O_2,app} \cdot V_t \quad \text{where:} \quad \begin{cases} c_{M,app} = \frac{n_M}{V_t} \\ c_{O_2,app} = \frac{n_{O_2}}{V_t} \end{cases} \quad (1)$$

where the apparent concentrations of metal and oxygen ($c_{M,app} = n_M/V_t$ and $c_{O_2,app} = n_{O_2}/V_t$, respectively) were introduced referring to the total volume of the particle (i.e., including empty and full spaces).

Considering assumption (6), Eq.(1) can be re-written as:

$$\left\{ \begin{array}{l} \frac{\partial c_{M,app}}{\partial t} = -a \cdot k \cdot c_{M,app} \cdot c_{O_2,app} \\ I.C. \quad t = 0 \quad c_{M,app,0} = \frac{\rho_M}{PM_M} \cdot (1 - \varepsilon_0) \end{array} \right. \quad (2)$$

where $\varepsilon = (V_t - V_S)/V_t$ is the porosity of the dust particle (variable during the process), ε_0 is the initial porosity of the dust particle (which is constant), and V_S is the volume occupied by the metal/oxides phase. It is possible to make dimensionless Eq. (1) by introducing the following dimensionless variables $\mu = c_{M,app}/c_{M,app,0}$ and $\eta = c_{O_2,app}/c_{O_2,S}$; where the first is the apparent dimensionless metal concentration and the second is the apparent dimensionless oxygen concentration. Finally, the dimensionless material balance on the solid phase results:

$$\left\{ \begin{array}{l} \frac{\partial \mu}{\partial t} = -\alpha \cdot C_{O_{2,S}} \cdot k \cdot \mu \cdot \eta \\ I.C. \quad t = 0 \quad \mu = 1 \end{array} \right. \quad (3)$$

2.2 Material balance equation on oxygen

In order to write the indefinite material balance equation on the oxygen present in the gas phase of the dust particle, it is necessary to define the apparent oxygen concentration as $c_{O_2,app} = c_{O_2} \cdot \varepsilon$ and, then, it is possible to insert such a definition in the complete oxygen balance equation.

Moreover, considering both under unsteady state conditions and negligible convective fluxes for the gaseous phase (hp: (5)), it is possible to obtain:

$$\left\{ \begin{array}{l} \frac{\partial c_{O_2,app}}{\partial t} = \wp \cdot \frac{\partial}{\partial x} \left(\frac{\partial c_{O_2,app}}{\partial x} \right) - \beta \cdot k \cdot c_{M,app} \cdot c_{O_2,app} \\ \text{I. C. } t = 0, \quad c_{O_2,app} = 0 \\ \text{B. C. } x = 0, \quad \left. \frac{\partial c_{O_2,app}}{\partial x} \right|_{x=0,t} = 0 \\ x = R, \quad c_{O_2,app}(t, x = R) = c_{O_2,S} \end{array} \right. \quad (4)$$

Such an equation must be made dimensionless and transferred in a spherical coordinates system before being solved with Eq. (3). Finally, it results:

$$\left\{ \begin{array}{l} \frac{\partial \eta}{\partial t} = \wp \cdot \left(\frac{\partial^2 \eta}{\partial r^2} + \frac{2}{r} \cdot \left(\frac{\partial \eta}{\partial r} \right) \right) - \beta \cdot k \cdot c_{M,app,0} \cdot \mu \cdot \eta \\ \text{I. C. } t = 0, \quad \eta = 0 \\ \text{B. C. } r = 0, \quad \left. \frac{\partial \eta}{\partial r} \right|_{r=0,t} = 0 \\ r = R, \quad \eta(t, r = R) = 1 \end{array} \right. \quad (5)$$

As it is possible to notice, Eq. (5) considers only the oxygen diffusion within the dust particle and the reactive term due to the aluminum oxidation: the convective fluxes were not considered because the high tortuosity of the intraparticle environment.

One of the most important parameters to be determined with a quite high degree of accuracy is the oxygen diffusion coefficients within the dust particle, \wp . Such a parameter can be calculated considering the combined contribution of molecular and Knudsen diffusion inside the particle.

Particularly, knowing the specific surface area of the particles, a_s , and assuming the presence of a single equivalent cylindrical pore of diameter d_p , it is possible to write the following system of algebraic equations:

$$\left\{ \begin{array}{l} a_s = \frac{\pi d_p L}{\rho(1-\varepsilon)V_t} \\ \varepsilon V_t = \frac{\pi d_p^2}{4} \cdot L \end{array} \right. \quad (5b)$$

The resulting equivalent diameter of the single pore is:

$$d_p = \frac{4\varepsilon}{a_s \rho(1-\varepsilon)} \quad (5c)$$

Such a value can be considered representative for the calculation of the Knudsen diffusion of oxygen inside the particle.

2.3 Energy balance equation on the solid particle

The energy balance equation for a single dust particle is referred to its total volume, V_t . Hypothesizing that the heat capacity of the solid phase (S) is constant and much greater than that one of the gaseous phase (oxygen), it is possible to obtain the general form:

$$\rho_{M,app} \cdot c_{p,M} \frac{\partial T}{\partial t} = -\nabla \times (h \cdot \vec{v} + \vec{q}) + \Delta H_{ox} \cdot \tau_{ox} \quad (6)$$

where: $\rho_{M,app} = \rho_M \cdot (1 - \varepsilon)$ is an effective particle density taking into account that the porosity is varying from an initial value to a smaller one; $h = \rho_{O_2,app} \cdot c_{p,O_2} \cdot T$ is the enthalpy of the volatiles per unit of volume (we refer only to the gaseous phase because the solid phase can not be subjected to convective fluxes), J/m^3 ; $\vec{q} = -\bar{\lambda} \cdot \nabla T$ is the conductive heat flux, W/m^2 (not only associated with temperature gradients); $\bar{\lambda}$ is the effective thermal conductivity of the system, $W/(m \cdot K)$; ΔH_{ox} is the exothermic reaction enthalpy for the oxidation reaction, $[J/kmol]$ or $[J/kg]$. Inserting the previous definitions, developing all the terms considering hp (5) and considering constant the thermal conductivity, it results (in spherical coordinates):

$$\left\{ \begin{array}{l} \rho_M \cdot (1 - \bar{\varepsilon}) \cdot c_{p,M} \cdot \frac{\partial T}{\partial t} = \bar{\lambda} \frac{\partial^2 T}{\partial r^2} + \frac{2 \cdot \bar{\lambda}}{r} \cdot \frac{\partial T}{\partial r} + \Delta H_{ox} \cdot r_{ox} \\ \text{I.C. } t = 0, \quad T = T_0 \\ \text{B.C. } r = 0, \quad \bar{\lambda} \cdot \frac{\partial T}{\partial r} \Big|_{r=0} = 0 \\ r = R, \quad \bar{\lambda} \cdot \frac{\partial T}{\partial r} \Big|_{r=R} = -h_c \cdot (T|_{r=R} - T_{ext}) - \varepsilon \cdot \sigma \cdot (T^4|_{r=R} - T_{ext}^4) \end{array} \right. \quad (6b)$$

where $\bar{\lambda} = \lambda \cdot (1 - \bar{\varepsilon})$ (since the porosity of the particle varies during time, it was necessary to introduce $\bar{\varepsilon}$ which is a mean porosity). As the porosity tends to decrease during the oxidation process, $\bar{\varepsilon}$ can be considered equal to 0 as a first approximation. Introducing all the variables, the following system is obtained:

$$\left\{ \begin{array}{l} \frac{\partial T}{\partial t} = \frac{\lambda}{\rho_M \cdot c_{p,M}} \cdot \left(\frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial T}{\partial r} \right) + \frac{\Delta H_{ox}}{\rho_M \cdot c_{p,M} \cdot (1 - \bar{\varepsilon})} \cdot k \cdot c_{M,app} \cdot c_{O_2,app} \\ \text{I.C. } t = 0, \quad T = T_0 \\ \text{B.C. } r = 0, \quad \lambda \cdot \frac{\partial T}{\partial r} \Big|_{r=0} = 0 \\ r = R, \quad \lambda \cdot \frac{\partial T}{\partial r} \Big|_{r=R} = -h_c \cdot (T|_{r=R} - T_{ext}) - \varepsilon \cdot \sigma \cdot (T^4|_{r=R} - T_{ext}^4) \end{array} \right. \quad (7)$$

And, using the previously introduced dimensionless variables:

$$\left\{ \begin{array}{l} \frac{\partial T}{\partial t} = \frac{\lambda}{\rho_M c_{p,M}} \cdot \left(\frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial T}{\partial r} \right) + \frac{\Delta H_{ox}}{\rho_M \cdot c_{p,M} \cdot (1 - \bar{\varepsilon})} k \cdot c_{M,app,0} \cdot c_{O_2,S} \cdot \mu \cdot \eta \\ \text{B.C. } r = 0, \quad \lambda \cdot \frac{\partial T}{\partial r} \Big|_{r=0} = 0 \\ r = R, \quad \lambda \cdot \frac{\partial T}{\partial r} \Big|_{r=R} = -h_c \cdot (T|_{r=R} - T_{ext}) - \varepsilon \cdot \sigma \cdot (T^4|_{r=R} - T_{ext}^4) \end{array} \right. \quad (8)$$

Equations (3), (5) and (8) constitute a system of Partial Differential Equations (PDEs) that must be numerically solved applying suitable mathematical methods. In this work, the Method Of Lines (Schiesser, 1991), which solve systems of partial differential equations where the derivatives with respect to both time and space are present by discretizing the spatial derivatives and solving the resulting differential algebraic equation (DAEs) system, was chosen.

2.4 Deflagration index determination

As a first approximation, it is possible to assume that all the changes in the explosion violence (that is, in the K_{St} value) observed by varying the particles size distribution can be well represented by the maximum rate of temperature rise at the particle boundary.

Such a rate of temperature rise is influenced by different phenomena: 1) the convective heat flux coming from the "fireball" generated by the explosion of the ignitors, which heats the air present into the 20 L sphere; 2) the diffusion of oxygen inside the particle; and, 3) the heterogeneous oxidation reaction taking place into the particle itself.

According to a previously proposed correlation to determine the deflagration index of an organic dust as a function of the mean particle diameter (Copelli et al., 2019), the correlation developed in the present work uses one experimental datum, the K_{St} of a reference particle size distribution of the analyzed dust, together with the maximum rate of temperature rise at the particle boundary for both the reference and the analyzed dust.

The following correlation can be therefore used:

$$K_{St}(D_m) = \frac{\left(\frac{\partial T}{\partial t} \right)_{max}}{\left(\frac{\partial T}{\partial t} \right)_{D_m}} \cdot K_{St}(D_{ref}) \quad (9)$$

where D_{ref} is a reference average diameter, $K_{St}(D_{ref})$ is the experimental value of the deflagration index measured at that average diameter, $\left(\frac{\partial T}{\partial t} \right)_{max}$ is the derivative of the temperature with respect to time at the external boundary of a dust with the granulometric distribution equal to D_{ref} . Likewise, $K_{St}(D_m)$ is the value of the deflagration index predicted for a dust with granulometric distribution equal to D_m and $\left(\frac{\partial T}{\partial t} \right)_{D_m}$ is the derivative of the temperature, with respect to time, at the external boundary of a dust with granulometric distribution equal to D_m . It should be noted that this method, conversely to the previously proposed for organic dusts, do not make possible to completely ignore the information on the chemical kinetics of the process (the heterogeneous oxidation) as they are only partially contained in the experimental value of $K_{St}(D_{ref})$.

In practice, having the experimental value of K_{St} of a metallic powder of known particles size distribution is possible, using Eq. (9), to predict the value of K_{St} of the same powder with different particle size distributions, using only the estimated rate of the maximum heating rate of the particle at its external boundary for both diameters.

3. Validation and discussion

The mathematical model here presented was validated considering different aluminum granulometric distributions and using D_{50} as global information.

This metal, generally, possesses particle size distributions highly peaked around the mean value; therefore, D_{50} can be used to represent the entire particle size distribution with respect to the determination of the deflagration index value.

Six diameters (5, 9, 15, 20, 25 and 30 μm), characterized by σ_D values of 0.95, 1.17, 1.48, 1.87, and 2.51, were tested. For what concerns the last two distributions, it is possible to notice a quite high degree of polydispersity; anyway, it was decided to test them in order to evaluate the limitations of the present model.

It is important to consider that such distributions refer to quite big aluminum particles, therefore the corresponding values of the deflagration index will be quite low and it will be quite difficult to be within the acceptable ranges.

In order to determine the maximum rates of temperature increase at the boundary of the particles for both the reference and the analyzed dust, Eq. (3), (5) and (8) were solved considering a constant temperature of the gas surrounding the dust particles equal to 500 [K], that is the stoichiometric temperature reached by the air in the 20 L sphere when the ignitors only are burst.

Such an assumption can be justified because the heterogeneous oxidation of aluminum is very fast and highly exothermic and it requires quite low temperatures to be triggered. Moreover, the heat generated by the oxidation quickly rises the temperature of the dust particle, also igniting a strong radiating effect towards the other metallic dusts: this effect was not considered within this preliminary work. Such a piece of information is considered to be summarized in the experimental value of the deflagration index present into Eq. (9).

The results obtained are shown in the parity plot of Figure 1.

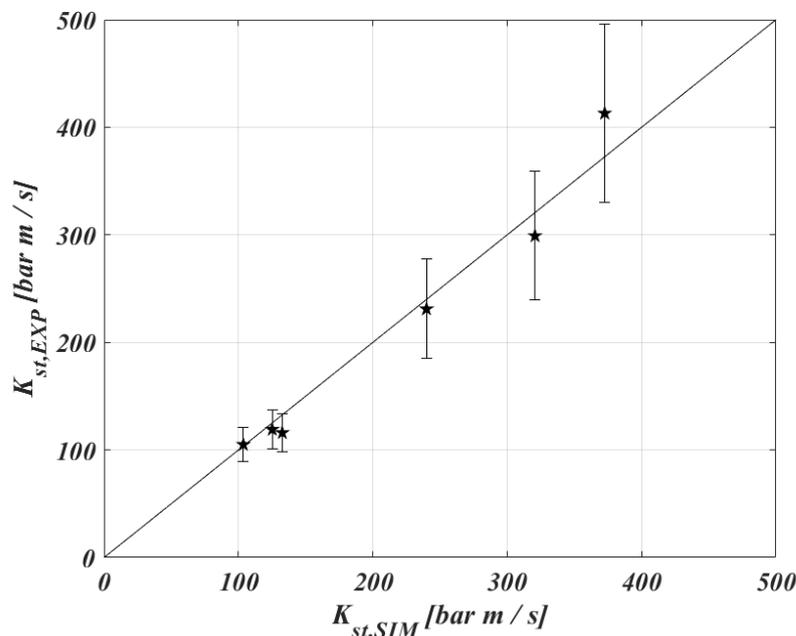


Figure 1: Experimental K_{St} value vs Simulated K_{St} value for aluminum dust

Observing Figure 1, it is possible to notice that all the predicted K_{St} values are quite close to the experimental ones and, in all cases but one, fall within the maximum and minimum acceptable limits, independently on the occurrence of either overestimation or underestimation of the experimental K_{St} .

These inaccuracies in the deflagration index prediction are not a major problem as all the underestimates are acceptable because they perfectly meet the experimental errors; while, the overestimations do not represent a problem from the safety point of view, in fact they lead to conservative predictions. Furthermore, in accordance with all the studies conducted so far, the predicted values also indicate that the increase in the particles size leads to a reduction in the explosion severity.

4. Conclusions

The aim of this work was to develop a mathematical model able to predict the K_{St} value of metal powders as a function of a few chemical-physical data and the particle size distribution (using only D_{50} as global information). The validation of the model was done by comparison among the model estimated values of the deflagration index and the experimental data available in the literature for aluminum dust, which is one of the most used metal powder in the process industries.

As shown by the results, a good degree of accuracy in the prediction of the deflagration index was reached. The comparison among predicted and experimental data demonstrated that the proposed model was able to predict with a good accuracy the value of the deflagration index for aluminum powders having different particle sizes and distributions.

This mathematical model can be considered innovative because it is able to estimate the contribution of diffusion of oxygen inside the particle pores, which, in case of metal powders, greatly depends on tortuosity and porosity. It also considers the kinetics of metal oxidation, and it is able to predict the K_{St} value of a metallic dust with a given particle size distribution, regardless of the powder concentration used, which means a substantial reduction in time and costs related to experimental testing.

One of the criticalities of the model is the underprediction of the deflagration index for very small mean particles diameters, those ones implying the highest values of the K_{St} .

Anyway, preliminary results showed a good agreement between literature K_{St} values and model predictions, as they are always within the acceptability range related to the unavoidable experimental uncertainties.

Such an achievement, once further validated on a wider range of explosive metal dusts, could lead to an improvement in the risk assessment panorama for powder handling operations by making the risk evaluation process quicker and cheaper.

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