



# Numerical investigation on new configurations for vapor-phase aerosol reactors

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## ABSTRACT

Non-ideal aerosol reactors for synthesizing nano- and micro-metal-oxide powders can currently be accurately designed by means of computational fluid dynamics (CFD) models instead of an expensive trial-and-error experimental technique. According to a multi-scale approach, fluid dynamics of the reacting volume is modeled by an appropriate population balance equation (PBE) coupled to momentum, energy and chemical species conservative equations. The present work refers to the modeling of non-ideal vapor-phase aerosol reactors, in particular to the numerical investigation on the effects of feeding nozzle arrangement, where the most significant gradients and aerosol phenomena occur. The described aerosol CFD model, which a priori assumes a log-normal particle size distribution (PSD), has been validated against both an experimental and an industrial case, and therefore it has been applied to the study of new reactor configurations. Numerical results show that traditional axial-symmetric and jet-opposed nozzle arrangements can be improved adopting a tangential geometry.

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## 1. Introduction

Producing fine ceramic powders in aerosol reactors by vapor phase represents today a competitive industrial process (Kodas and Hampden-Smith, 1999; Osterwalder et al., 2006). Micro- and nano-metal-oxide powders, like  $\text{TiO}_2$ ,  $\text{ZrO}_2$  or  $\text{SnO}_2$ , due to their chemical, optical and mechanical properties are used in a large range of advanced technological applications, such as components for laser devices, supports for catalysts or material for biomedical implants. For their production, the oxidation of metal-chlorides,  $\text{MeCl}_4$ , is an important synthesis route due to the high reactivity and relative low cost of precursors. High reactivity is determined by a fast chemical kinetics and by strong thermodynamic stability of monomer particles.

Chemical nucleation of ceramic particles is carried out in aerosol reactors where gaseous precursors are fed through separated nozzles. Depending on the fluid dynamics in the reaction volume, reactors may behave like continuous stirred reactors (CSR) or plug flow reactors (PFR). Practically, as the fluid-dynamic regime is typically turbulent, in particular near the nozzle region, their behavior is intermediate between that of the two previously mentioned reactors. This makes industrial aerosol reactor behavior strongly non-ideal and therefore difficult to be accurately designed. On the other

hand, since dimensions and morphological-mechanical properties of metal-oxide particles depend on aerosol phenomena like nucleation and coagulation (i.e., by the local precursors concentration and by the so as-synthesized particles) residence times (i.e., reactor fluid dynamics) must be finely tuned to obtain a final product characterized by the required properties.

Because phenomena occurring at different spatial and time scales must be simultaneously handled, a multi-scale modeling approach is to be adopted. Nanometer dimensions characterize primary particles, whereas meters refer to reactor size: in the middle, there are several other scales, such as those inherent turbulence, micro-particles size and molecular gas path scales. Analogously, with reference to time scales, characteristic times of coagulation, sintering and other particle phenomena may correspond to microseconds, whereas industrial reactor residence times can be of order of seconds. In general, reactor macro-scale parameters, as operating conditions and geometry, must be linked to the chemical and physical phenomena occurring at particle scale.

Several researchers have dedicated works for simplifying and adapting the multi-scale approach to non-ideal reactors. In one of the first works, an isothermal laminar plug-flow reactor was modeled (Pratsinis et al., 1986) showing effects of the velocity profile on the particle concentration and size distribution. In other three pioneering studies (Schild et al., 1999; Tsantilis et al., 1999; Johannessen et al., 2000), the population balance equation (PBE), assuming a mono-dispersed distribution, was integrated by means of a commercial fluid dynamic code over energy and concentration fields for a laminar  $\text{TiO}_2$  flame synthesis hot wall reactor, a palladium

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nano-particle turbulent condenser and for an  $\text{Al}_2\text{O}_3$  flame reactor, respectively. A fully coupled model, where the PBE was rewritten through the particle size distribution (PSD) moments and then was embedded into a commercial computational fluid dynamics (CFD) code, was applied for modeling an un-premixed 2D turbulent jet for the production of  $\text{TiO}_2$  particles from tetra-isopropyl-orthotitanate ( $\text{Ti}(\text{OiPr})_4$ ) (Masi et al., 1999). Advances in aerosol simulation have led to more complex and accurate CFD models, like 3D modeling or application of alternative techniques for describing the particle evolution. Among them, a 3D turbulent mono-disperse model for a carbon black reactor (Skillas et al., 2005) and a quadrature method of moments for soot formation study in turbulent flames (Zucca et al., 2006) were presented.

In this work, a 3D aerosol CFD model, based on a mono-modal method of moments for the PBE and on the assumption of a log-normal PSD, was developed starting from a previous 2D model (Di Muzio et al., 2000). As a case study, the production of metal-oxide powders starting from the oxidation of  $\text{ZrCl}_4$  by  $\text{O}_2$  and  $\text{TiCl}_4$  by  $\text{H}_2\text{O}$  was considered. In order to analyze the non-ideal behavior of relevant synthesis reactors, the aerosol model was coupled to momentum, energy and species balance equations by means of a commercial CFD code based on finite volume (FV) method. Accordingly, the three main statistical moments, the particle concentration, the volume and the spread of distribution, respectively, were embedded into the CFD code as scalar variables, generating three scalar balance equations.

To validate the model against experimental data, a laboratory scale  $\text{ZrO}_2$  reactor and an industrial scale  $\text{TiO}_2$  reactor were simulated to verify how simulations matched the as-synthesized particle size distribution. Because strong concentration and temperature gradients and consequently the most significant aerosol phenomena occur in the nozzle region, the CFD numerical investigations were focused on the nozzle configuration and on its impact on the final product quality. Modifying the arrangement of inlets, the nucleation and coagulation parameters change and consequently the aerosol evolution is modified. The impact of these reactor parameters were not investigated before in the literature. Numerical results showed that traditional axial-symmetric and jet-opposed nozzles may be characterized by a strong re-circulation. Accordingly, those inlets lead to a larger PSD than to the one that it could be obtained by a new, tangential arrangement where nozzle back-mixing phenomena are limited. This last configuration is firstly analyzed in this work.

## 2. Formulation of the aerosol CFD model

The population balance equation for an aerosol system in steady-state conditions is given by Eq. (1), where convective and diffusive particle transport, and nucleation and coagulation phenomena are represented by left-hand side and right-hand side terms, respectively (Friedlander, 1977; Ramkrishna, 2000). Other phenomena such as growth, sintering and breakage of particles are considered negligible in this work as particle surface reactions or gas condensation are not promoted in the investigated systems, sintering time is much longer than coagulation time and particles are of hard-agglomerate type, that is they do not experience breakage:

$$\mathbf{u} \cdot \nabla f(v) - \nabla \cdot (D_p \nabla f(v)) = N + \frac{1}{2} \int_0^v \beta(v-v', v') f(v-v') f(v') dv' - \int_0^v \beta(v, v') f(v) f(v') dv' \quad (1)$$

The quantity  $f(v)$  is the PSD based on the volume, representing the number of particles of volume  $v$  per unit of the reactor volume,  $\beta(v, v')$  is the coagulation coefficient involving particles of volume  $v$

and  $v'$  and  $N$  is the nucleation rate. The second and the third term in the right-hand side of Eq. (1) are the gain and loss of particles due to coagulation, respectively. The most critical parameter to be defined is the coagulation coefficient as it depends on coagulation mechanism and on the particle transport regime. In case of binary interactions only and of Brownian diffusion, particle interactions can occur in two different regimes, free-molecular ( $Kn \gg 1$ ,  $Kn$  = Knudsen number) or continuum ( $Kn \ll 1$ ) regime, which expressions are given correspondingly in Eqs. (2) and (3) (Landgrebe and Pratsinis, 1989):

$$\beta_{FM}(v, v') = \left(\frac{3}{4\pi}\right)^{1/6} \left[ \frac{6k_B T}{\rho_p} \left(\frac{1}{v} + \frac{1}{v'}\right) \right]^{1/2} (v^{1/3} + v'^{1/3})^2 \quad (2)$$

$$\beta_C(v, v') = \frac{2k_B T}{3\mu} \left[ \frac{C_C(v)}{v^{1/3}} + \frac{C_C(v')}{v'^{1/3}} \right]^{1/2} (v^{1/3} + v'^{1/3}) \quad (3)$$

In the investigated systems, the mean particle diameter may fall within 0.1–0.3  $\mu\text{m}$ : as it corresponds to a Knudsen's number close to unity, intermediate regimes may coexist and therefore an asymptotic combination of free-molecular and continuum boundary is usually adopted (Seinfeld, 1986). Furthermore, in turbulent fluid-dynamic regimes, where particle diameter is at least one order of magnitude larger than vortex diameter, the coagulation coefficient  $\beta$  is determined by the sum of Brownian and turbulent coagulation (Xiong and Pratsinis 1993a,b), that is  $\beta = \beta_B + \beta_T$ , where  $\beta_T$  is given by the following equation:

$$\beta_T(v, v') = 2.3 \left(\frac{3}{4\pi}\right) \sqrt{\frac{\varepsilon \rho}{\mu}} (v^{1/3} + v'^{1/3})^3 \quad (4)$$

In Eqs. (1)–(4)  $k_B$ ,  $T$ ,  $\rho$ ,  $\mu$ ,  $\varepsilon$  are, respectively, the Boltzmann's constant, temperature, mass density, dynamic viscosity and turbulent dissipation rate of the process fluid,  $\rho_p$  is the particle density at the fluid temperature, and  $C_C$  and  $D_p$  are the Cunningham's factor and the particle diffusion coefficient, respectively (Hinds, 1982):

$$C_C(v) = 1 + 2.257 \cdot \left(\frac{k_B T}{\sqrt{2\pi} P d_c^2}\right) \cdot d_{gs}^{-1} \quad (5)$$

$$D_p = \frac{k_B T C_C}{3\pi\mu} \quad (6)$$

In vapor-phase oxidation of metal-chlorides, the particle nucleation rate  $N$ , coincides with the chemical reaction rate,  $R$ . Since  $\text{TiO}_2$  and  $\text{ZrO}_2$  metal-oxides are characterized by a very low vapor pressure and synthesized monomer particles present a diameter larger than the Kelvin's critical diameter (Friedlander, 1977), monomers can be considered thermodynamically stable (Ulrich et al., 1980). Describing the number of monomer particles of volume  $v_0$  by a Dirac's function,  $\delta$ , centered on  $v_0$ , the nucleation rate can be expressed as follows:

$$N(v) = N_{Av} R \delta(v - v_0) \quad (7)$$

where  $N_{Av}$  stays for the Avogadro's number.

The above equations enclose several variables and chemical-physical quantities. The gas velocity vector,  $\mathbf{u}$ , appears in the PBE, whereas Eqs. (2)–(6) depend on the operating conditions (temperature and pressure) and on the chemical-physical properties of the carrier fluid. Eq. (4) contains also a quantity related to turbulence. Finally, the expression of the chemical reaction rate,  $R$ , includes precursor concentrations. Consequently, it is necessary to link the PBE to relevant conservation equations for mass, momentum, energy and chemical species and to constitutive equations for other quantities. Considering Newtonian fluids and negligible pressure work and gravity field, conservation equations for a stationary system are

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