Controlling aerosol processes for synthesis of ceramic powders

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Several ceramic powders for advanced applications involving catalysis, electronics or bio-engineering, such as fumed silica, TiO_2 and ZrO_2, are produced via aerosol processes. Synthesising nano- and micro-ceramic particles of uniform diameter and shape is fundamental to meet product specifications, which are typically stringent. In this paper, an example of process control applied to a TiO_2, perfectly stirred, aerosol reactor is described for the special case of a flow rate variation.

1. Introduction

Aerosol synthesis of nano- and micro-ceramic powders used as high-engineered materials in advanced technological applications is nowadays a competitive process. For instance, production of fumed silica for optical fibres, TiO_2 for pigments and ZrO_2 for medical prosthesis are today well-run, industrial scale aerosol processes. On the other hand, advanced applications require a final product characterised by stringent quality, mainly defined by geometrical dimension, morphology and chemical composition of the particles. For this reason, it is fundamental to have an accurate control of the synthesis process, that is, of the relevant reactor. Typically, a multi-scale approach is adopted for modelling aerosol reactors: a Population Balance Equation (PBE), accounting for particle-scale phenomena as nucleation and coagulation, is coupled to macro-scale balance equations for continuity and momentum (Kodas, 1999). As the resulting model is computationally heavy, the PBE is usually processed by means of the Method of Moments (MoM). The case described in this study refers to a TiO_2 aerosol synthesis, via $TiCl_4$ oxidation. The reactor model expressed by MoM has been reduced to a system of ordinary differential equations considering a continuous, perfectly stirred aerosol reactor. By doing so, a process control for the special case of precursor flow rate variation can be effectively applied for reducing the width of particle size distribution. The simultaneous presence of different scales and of complex coupled phenomena make hard to guarantee on-spec productions when operating variations happen, consequently searching for efficient process control solutions is the aim of present research. In literature, other researchers have focused their attention on aerosol controllability through conventional systems, Semino and Ray (1995), and, recently, on the adoption of more efficient nonlinear feedback controllers, Kalani and Christofides (1999), Chiu

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et al. (2000). In this framework, process sensitivity analysis and development of a control loop are essential for achieving a final high quality product in terms of average particle size and standard deviation. Reactor modelling is described in next paragraph. Section 3 deals with sensitivity analysis of the aerosol process and possible control approaches. Preliminary results are reported in section 4.

2. Aerosol Reactor Modelling

For modelling aerosol reactors, a multi-scale approach is applied in order to handle large spatial-temporal scale ranges, for instance from particle-scale to reactor-scale. Phenomena involved in particle evolution are taken into account through the PBE that, for the system here considered, where phenomena are limited to nucleation and coagulation, can be defined as (Friedlander, 1977):

$$\frac{\partial f(v)}{\partial t} = N + \frac{1}{2}\int_0^v \beta(v - v', v')f(v - v')f(v')dv' - f(v)\int_0^\infty \beta(v, v')f(v')dv' \tag{1}$$

where f(v) is the particle distribution function based on volume, representing the number of particles of volume v per unit reactor volume, β(v,v') is the coagulation coefficient involving particles of volume v and v', and N is the nucleation rate. R.h.s terms represent the nucleation, the gain and loss of particles due to coagulation, respectively. Assuming the typical log-normal shape for the PBE and rewriting it through the first three statistical moments $M_{0,1,2}$ (Manenti et al., 2006) equation (1) is replaced by:

$$\dot{M}_0 = N + \Omega M_0^2 \tag{2}$$

$$\dot{M}_1 = v_0 N \tag{3}$$

$$\dot{M}_2 = v_0^2 N + \Psi M_1^2 \tag{4}$$

where l.h.s terms stand for temporal variations, v_0 is the volume of the primary particle, and Ω and Ψ, assuming Brownian coagulation, represent the harmonic average of relevant coefficients for continuum and free molecular regime. Starting from important properties represented by moments M_0, M_1 and M_2, that is the particle concentration number, the total particle volume and the polydispersity respectively, one can characterize the ceramic powder by its geometric average diameter (d_g) and its geometric standard deviation (σ_g). Coupling equations (2), (3) and (4) to material and thermal balances over a CSTR reactor, expressed by equations (5) and (6), the aerosol model is carried out:

$$\dot{C}_i = -N \tag{5}$$

$$\dot{T}\left(\rho C_p\right) = N\Delta H_r(T) - (T\text{-}T_w)U/D \tag{6}$$

where subscript "i" refers to the chemical species, ρ and C_p are the density and specific heat of the carrier gas (Ar), ΔH_r is the chemical reaction enthalpy, and U, D and T_w are the thermal exchange coefficient, the diameter and the wall temperature respectively of the aerosol reactor. For the case of TiO_2, which particles are characterised by a very low vapour pressure, the nucleation rate N corresponds to the chemical reaction rate. The reaction $TiCl_{4\,(g)} + O_{2\,(g)} \rightarrow TiO_{2\,(s)} + 2Cl_{2\,(g)}$ can be assumed single step and of one order with regards to the $TiCl_4$ in case of excess in O_2 (Pratsinis et al., 1990), that is $N= k \cdot \exp[-E/RT] \cdot C_{TiCl4}$, where k, E and R represents the kinetic constant, the activation energy and the universal constant for gas. Main process parameters used in the model are reported in table 1.

Table 1: model parameters.

Parameter	**Value and Unit of measure**
Reaction kinetic constant	$k= 8.26 \cdot 10^4\ s^{-1}$
Reaction activation energy	$E= 88.8 \cdot 10^3\ J\ mol^{-1}$
Precursor concentration	$C_{TiCl4}= 8.0 \cdot 10^{-4}\ mol\ m^{-3}$
Primary particle volume	$v_0= 3.115 \cdot 10^{-29}\ m^{-3}$
Reaction enthalpy	$\Delta H_r= -177.0 \cdot 10^6\ J\ kmol^{-1}$
Thermal exchange coefficient	$U= 400\ W\ m^{-2}\ K^{-1}$
Reactor diameter	$D= 0.01\ m$

3. Control Technique for Particle Size Distribution

Controlling the particle size distribution in aerosol processes is a problem remarkably hard to solve, especially for nonlinearities due to chemical reactions, nucleation and coagulation phenomena, which induce to adopt complex control techniques. In accordance with Kalani and Christofides (2002), a conventional approach may be not able to ensure the control of the system, consequently a nonlinear control or a model predictive control are more appropriate techniques for aerosol systems.

3.1 Sensitivity analysis

Strong nonlinearities embedded in the model require a parametric sensitivity analysis in order to study the reactor behaviour and realize its control. For space reasons, main overall trends are merely reported in this work, in particular the ones relating particle size distribution parameters (i.e. the d_g and σ_g) and aerosol reactor parameters, such as the wall heat exchange coefficient and reactant concentrations. On the other hand, the aerosol system presents a weaker sensitivity against other process parameters. For instance, figure 1 (on the left) shows the diameter growth against the residence time: higher the $TiCl_4$ concentration higher the increment of particle size. Nevertheless, the feeding $TiCl_4$ concentration has an upper limit dependent on the final σ_g, which could be reduced increasing the reactor residence time. The precursor concentration presents also a lower limit to prevent the quenching of the chemical reaction and therefore too low operating temperatures. For these reasons, feeding $TiCl_4$ concentration has been set between $5 \cdot 10^{-4}$ kmol/m^3 and $9 \cdot 10^{-4}$ kmol/m^3. With such constraints, the σ_g reaches an initial peak over 1.50 due to sudden particle nucleation, and then it is lowered till 1.34 at the end of the residence time for the coagulation phenomenon. Nevertheless, for the specific case of flow rate variations, precursor concentration cannot be employed as manipulated variable so another parameter, as the overall thermal exchange coefficient *U*, has to be selected. Figure 2 illustrates dependence of the particle size on the coefficient *U*: at its higher values, reactor temperature decreases and this allows slowly moderating the coagulation effect. As showed in figure 2, *U* has a remarkable effect with a long residence time only (left) and it has in any case a negligible impact on the final particle size variability. In the following description, the coefficient *U* is utilized as the main manipulated variable for controlling the average particle size.

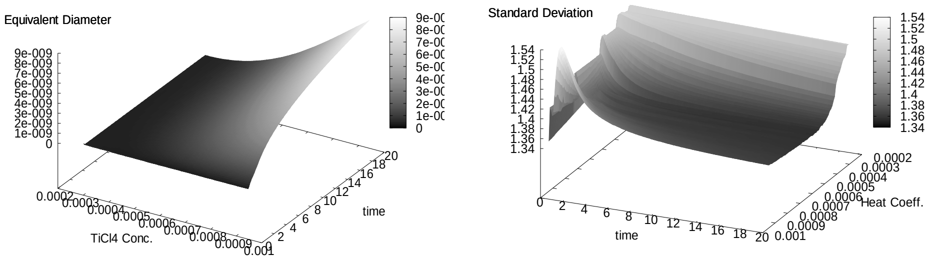

Fig. 1: dependence of geometric average diameter (left) and geometric standard deviation (right) on $TiCl_4$ feed concentration. Units according to table 1.

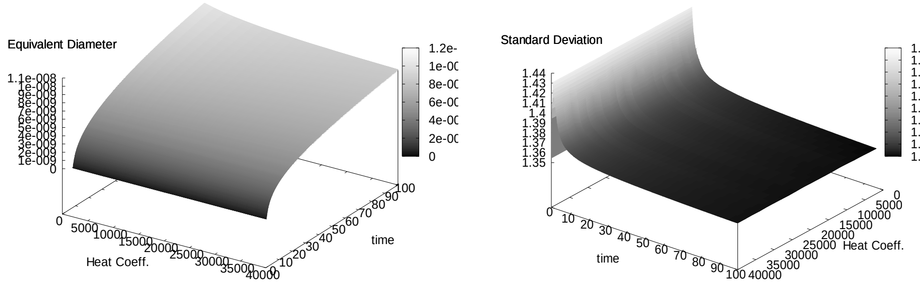

Fig. 2: dependence on average geometric diameter (left) and geometric standard deviation (right) on the overall heat exchange coefficient. Units according to table 1.

3.2 Optimal trajectory as *moving* set point in feedback control

Beyond the control technique type employed, traditional or advanced, linear or nonlinear, the regulation of a generic system requires a controlled variable, which has to be kept as close as possible to its set point, and at least a manipulated variable, which represents the degree of freedom of the problem. The target is to regulate the final particle size with the secondary aim to leave unchanged the particle size distribution, keeping it low. In absence of particle breakage phenomena, the aerosol system is characterised by a continuous and irreversible coagulation of particles, that is by a constant increase in the particle size, without any possibility to reduce the average diameter along the reactor; therefore, there are no traditional (proportional-integral) control schemes able to steer the reactor. As a consequence, the present study implements an optimal trajectory as the *moving* set point of control loop, based on the following values:

$$V_g = \frac{M_1^2}{M_0^{1.5} \cdot M_2^{0.5}} \tag{7}$$

$$\mathrm{d_g} = \left(\frac{6}{\pi \cdot AGVol} \right)^{\frac{1}{3}} \tag{8}$$

representing the average geometrical volume (7) and the average geometrical diameter (8), respectively. The optimal trajectory for the moving set point is obtained by simulating the growth of geometrical diameter under the ideal assumption of unperturbed system.

4. Numerical Results

The first-principles mathematical model has been developed in Fortran90; a Gear BDF method, implemented in IMSL® libraries, has been used for solving the differential system, with a maximum time step of 0.1s. The special case of the flow rate variation has been investigated and the following figure reports temporal evolutions of the average geometrical diameter according to a +10% step disturbance on $TiCl_4$ feed concentration. The final set point of parfticle size is fixed at 10 nm.

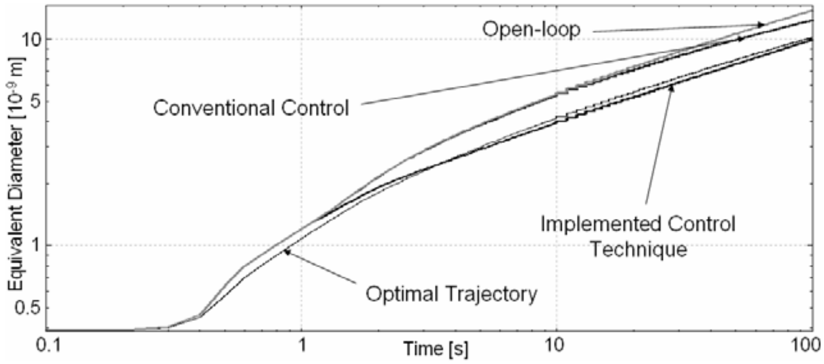

Fig. 3: Temporal profile of average diameter with a step disturbance of the feed precursor concentration. Advantages of the implemented technique compared with conventional control and open-loop simulations.

Figure 3 clearly shows that conventional control trend do not fit well with optimal trajectory and long residence times are required for dampening the initial disturbance; on the contrary, the implemented control loop, characterized by a moving set point, is able to regulate the system by smoothing the disturbance within short time and by guaranteeing the on-spec diameter at the end of the reactor. Any other possible perturbations not reported in the present paper enforce advantages about this technique.

5. Conclusions and Future Development

With the increasing demand of fine ceramic powders, the accurate design and relevant process control of aerosol reactors is nowadays assuming a more and more important role in the industrial field; for its strong nonlinearities, due to special phenomena involved in the particle dynamics, aerosol control modelling represents an actual challenge in the development of control techniques. Essentials of the aerosol mathematical modelling and sensitivity analysis over a TiO_2 perfectly stirred aerosol reactor have been described. Then, a process control technique has been applied in order to synthesize a final product of a specific quality. As shown, traditional controls appear inadequate; consequently an alternative approach (moving set point) for controlling aerosol reactors has been presented. By comparison of such different control schemes, preliminary results are encouraging. Implementation of a predictive control, to achieve a real time management of grade changes in the end product quality, is one of the future developments.

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