A Stochastic Approach for Anti-Solvent Addition Policy in Crystallization Operations: An Application to a Bench-Scale Fed-Batch Crystallizer

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Abstract: This work aims a stochastic approach for the calculation of robust anti-solvent addition policies for controlling the mean crystal size (MCS) in fed-batch crystallization operations. The proposed strategy is based-on a non-structured population balance where uncertainties associated with the start-up condition and random fluctuations along the fed-batch operation can be taken into account in a very natural fashion. We include and quantify the effect of the uncertainties by embedding a deterministic crystal growth model into a Fokker-Planck equation (FPE) resulting in a stochastic model for the MCS dynamics. This approach uses the Generalized Logistic equation (GLE) that has an adequate mathematical structure that suits the dynamic characteristic of the crystal growth. Thus, the numerical solution of the FPE provides the most likely MCS evolution for a given anti-solvent flow-rate. The effect of the anti-solvent is incorporated into the parameters of the FPE. The parameters of the FPE are computed as linear piece-wise interpolating functions of the anti-solvent flow-rate. The strategy uses a PID-like regulator in closed-loop fashion with the FPE to compute the anti-solvent addition flow-rates for different set-point targets in the MCS. In order to validate the stochastic model and assess the merits of the proposed strategy, the crystallization of sodium chloride in water using ethanol as anti-solvent is performed in a bench-scale fed-batch crystallizer. The implementation of the calculated anti-solvent policies resulted in a good control of the MCS despite modelling mismatch and uncertainties present during the crystallization operation.

Keywords: Anti-Solvent; Crystallization; Fokker-Planck Equation; Mean Crystal Size; Stochastic.

1. INTRODUCTION

The design of chemical plants endeavors to build equipment that preferably content hazards and make possible the transformation and separation of materials. It also attempts to harness the impact of apparently disordered and erratic phenomena (*e.g.* turbulent flow, pressure and temperature fluctuations, measurement noise, etc.). Fluctuations are a very common element in a large number of chemical, biological and physical phenomena. Practically, all systems are subjected to complicated external or internal influences that are not fully known and that are often termed noise or fluctuations. However, if a sufficiently long record of noisy measurement is analyzed, it may admit a statistical description. This means that it is possible to estimate the probability or likelihood that the process variable will attain in some specified range of values (Feigenbaum, 1980; Risken, 1984).

The study of stochastic system as the Brownian motion resulted in the Fokker-Planck equation (FPE). The FPE is just an equation of motion for the distribution function of fluctuating macroscopic variables. The FPE deals with those fluctuations of systems which stem from many tiny disturbances, each of which changes the variables of the system in an unpredictable but small way. The FPE provides a powerful tool with which the effects of fluctuations close to transition points can be adequately treated and that the approaches based on FPE are superior to other approaches based on Langevin equations (LE). The FPE plays an important role in chemical and biological processes that involve noise.

For many practical applications it is required to have simplified models that group the complexity behind a natural phenomenon and its interactions with its surroundings. For a dynamic system, it means of a set of deterministic differential equations with semi-empirical parameters. When studying chemical processes, these models are the core element for the design of all model-based control and optimization strategies. However, extra care is needed to take into account the no modeled dynamics and unknown exogenous disturbances acting on the process. The FPE is an interesting approach to introduce the robustness feature to the design of prediction, control and optimization tools.

This work describes a novel stochastic approach for the robust prediction of the mean crystal size (MCS) in a bench-scale fed-batch crystallization unit where anti-solvent is added to speed-up the crystal formation process. The crystal growth is modeled by a classic logistic equation of common use in theoretical ecology (May and McLean, 2007; Grosso et al., 2007). In a different fashion, the use of FPE for a monomer particle growth can be found in the literature (Matsoukas and Yulan, 2006). Unknown dynamics, internal and external fluctuations and sensitivity to initial conditions can be taken into account by embedding the logistic equation in the FPE.

2. Mean Crystal Size Estimation for an Anti-Solvent Aided Crystallization Process

Crystallization is a physical process for solid-liquid separation where the solid (solute) is dissolved in the solvent (liquid). The driving force in crystal formation is the super-saturation. The super-saturation condition establishes the thermodynamic equilibrium for the solid-liquid separation and it can be affected by cooling and evaporation. The super-saturation can be also induced by addition of precipitant or anti-solvent to the solution. The anti-solvent reduces the solubility of the solute in the original solvent resulting in super-saturation. The anti-solvent aided crystallization is an advantageous technique of separation where the solute is highly soluble or heat sensitive.

2.1 Mathematical Model

The development of rigorous mathematical models describing the dynamic of crystal growth in crystallization processes are based-on population balances. The idea of population balances has been widely used in theoretical ecology and extended to the modeling of particulate systems in chemical engineering. The population balances can be either structured or unstructured models.

At the core of the structured population dynamics, the number of crystals in a fed-batch crystallizer is increased by nucleation and decreased by dissolution or breakage. Structured population balances models provide detailed information regarding the crystal size distribution in the crystallization unit. However, they demand a great deal of knowledge on the complex thermodynamic associated with the solute and solvent properties to be adequately incorporated in the population balances. Some important contributions in this subject have been reported in the literature (Worlitschek and Mazzotti, 2004; Nagy et al. 2007; Nowee et al., 2007).

Here, we introduce a simple unstructured population model, where the crystals are classified by their size, *L*. The growth of each individual crystal–is supposed to be independent by the other crystals and is governed by the same deterministic model. In order to take into account the growth fluctuations and the unknown dynamics not captured by the deterministic term, a random component can be introduced (Gelb, 1988). The stochastic model can thus be written as a Langevin equation of the following type:

$$\dot{L} = f(L;\vartheta) + \eta(t) \tag{1}$$

In Equation 1, $f(L;\vartheta)$ is the expected rate of growth of L (the deterministic model introduced below), L is the size of the single crystal, t is the time, ϑ is the vector parameter defined in the model, and $\eta(t)$ is a random term assumed as Gaussian additive white noise:

$$\begin{aligned} &E[\eta(t)] = 0 \\ &E[\eta(t)\eta(t+\tau)] = 2D\delta(\tau) \end{aligned} \tag{2}$$

Where D is the additive noise intensity. Equation 1 implies that the crystal size L behaves as a random variable, characterized by a certain probability density function (PDF) $w(L,t)$ depending on the state variables of the system, i.e. the size L and time t. Incidentally, it should be noted that one can regard the probability density $w(L,t)$ as the relative ratio of crystals having a given dimension L, in the limit of infinite observations. Thus, from a practical point of view, it coincides with the Particle Size Distribution experimentally observed.

The new random variable thus can be described in terms of its probability density distribution, $w(L,t)$, at any instant of time t and should follow the linear Fokker-Planck Equation, FPE:

$$\partial_t w + \partial_L [\, f(L;\vartheta(u))w \,] = D(u)\,\partial_{LL} w \tag{3}$$

along with the boundary conditions:

$$f(0)w(0,t) - D(u)\partial_L w(0,t) = 0 \tag{4a}$$

$$\partial_L w(\infty,t) = 0 \tag{4b}$$

The reflecting boundary condition in Equation 4a ensures that the elements of the population will never assume negative values, whereas Equation 4b ensures the decay condition on $w(L,t)$ as L goes to infinity, for any time.

The diffusion coefficient D determines the random motion of the variable L that takes into account the fluctuation in the particle growth process (Randolph and Larson, 1988; Olesen et al, 2005).

Regarding the deterministic part of the model, our purpose is to choose a model as simple as possible, with a parsimonious number of adjustable parameters. To this end, the Generalized Logistic equation (Tsoularis and Wallace, 2002), is possibly the best-known simple sigmoidal asymptotic function used to describe the time dependence of growth processes in an unstructured fashion:

$$f(L;\vartheta) = r\,L^{\alpha}\,[\,1-(L/K)^{\beta}\,]^{\gamma} \tag{5}$$

In Equation 4, L is the size of the single crystal, the crystal growth rate r and the equilibrium mean crystal size K are considered constant for each experimental condition and they are supposed to be only dependent on the anti-solvent flow rate. Moreover, α, β and γ are positive real numbers that regulate the shape of the growing curve. Hereafter we will consider the simple case with $\alpha=\beta=\gamma=1$. With these assumptions, the present growth model can be regarded as the simplest model taking into account mild nonlinearities. In spite of this simplicity, this model provides the main qualitative features of a typical growth process: the growth follows a linear law at low crystal size values and saturates at a higher equilibrium value.

Finally the evolution in time of the probability density is described in terms of a linear, partial differential equation depending on the parameters r (linear Malthusian growth