

# Finite Element Analysis for a Supercritical Particulate Process

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## ABSTRACT

Collocation and Galerkin finite element algorithms are developed to solve the steady state population balance equation. Unlike previously proposed schemes, the algorithms are derived over an unscaled domain which permits accurate prediction of both the moments and the density distribution over domains large enough to reduce finite domain errors to negligibly small values. The utilization of supercritical fluids (SCFs) for the processing of several products has attracted considerable interest in recent years as an emerging “green” technology. Particle formation using SCFs can be carried out according to several different techniques, including antisolvent techniques such as the supercritical antisolvent (SAS) process. However, depending on the considered particle formation mechanism, population balance model of SAS process may include phenomena such as primary nucleation, secondary nucleation, crystal growth, as well as agglomeration and/or breakage (attrition) of crystals. The resulting equation is often of the integro-partial differential form. A powerful numerical algorithm for the treatment of the implemented population balance model structures was applied in this work. Algorithm simulations were performed for changes in the main SAS process operating parameters, i.e., the antisolvent addition rate and saturation level.

**Keywords:** population balance, crystallization kinetics, numerical algorithm, SAS.

## 1 INTRODUCTION

Nonconventional processing methods can lead to the development of materials with unique chemical, physical or mechanical characteristics that make them suitable for specialized applications. One such method is crystallization with SCFs, where the unique fluid characteristics and solvent properties of supercritical fluids are utilized. The utilization of SCFs for the processing of pharmaceuticals, nutraceuticals and other products has attracted considerable interest in recent years as an emerging “green” technology [1], [2]. Crystallization using SCFs have several advantages over conventional liquid solvents/antisolvents crystallization as their physical properties such as density and solubility can be “tuned” within a wide range of

processing conditions by varying both temperature and pressure.

Supercritical antisolvent techniques are considered highly effective for producing superior products of fine and uniform particles [2]. Moreover, SCFs can be easily separated from both organic cosolvents and solid products, providing a potentially clean, recyclable, and environmentally friendly technology [1]. Antisolvent techniques such as the supercritical antisolvent (SAS) process exploit the low solubility of most compounds in the antisolvent, in particular CO<sub>2</sub>, which has to be miscible with the organic solvent. In the SAS process, high pressure CO<sub>2</sub> is injected into the liquid phase solution, which causes a sharp reduction of the solute solubility in the expanded liquid phase. As a result, precipitation of the dissolved compound occurs. The potential advantages of the SAS crystallization process lies in the possibility of obtaining solvent free, micrometer and submicrometer particles with a narrow size distribution [3]. By varying the process parameters, the particle size, size distribution and morphology can be “tuned” to produce a product with desirable qualities. This makes the SAS technique attractive for the micronization of high-valued products, such as pharmaceuticals [4].

Although SAS experimental investigations cover a rather wide range of promising applications, only a few modeling studies have been embarked to advance the understanding, and to accomplish a quantitative characterization of the process. The modeling work that have addressed the antisolvent processes initially have comprised of thermodynamics and phase behavior investigations. In the study of Muhrer et al. [5], a model which rationalize solution thermodynamics and particle formation and growth were proposed. The model addresses and illustrates the effect of the antisolvent addition rate on the average particle size, and the particle size distribution. Their modeling work established the possibility of adapting the antisolvent addition rate to the final product characteristics. The model was successfully able to represent the experimental observations phenomenologically.

## 2 THEORY

The driving force for crystallization is the supersaturation of the solute. In the SAS process, supersaturation increases due to the antisolvent action and decreases because of the precipitation. The nucleation and growth of the particles in the SAS process is described

using the population balance equation, which describes the evolution of the particle size distribution with time. A proposed model by Muhrer et al. [5], was employed to fill the gap between the experimental results obtained from the SAS crystallization of phenanthrene from toluene using CO<sub>2</sub> as antisolvent, and the theoretical understanding of the particles formation mechanisms and the influence of the process parameters in the SAS process. The population balance technique parallels other balance approaches such as material. However, what is different in the population balance is the accounting for both the size and number of particles. A number balance over a size range  $L$  and  $L + dL$  over an increment of time  $dt$  is given as [6]:

$$\frac{\partial n}{\partial t} + \frac{\partial(nG)}{\partial L} + \frac{n}{\tau} = B(L) - D(L) \quad (1)$$

where ' $n$ ' represents the population density of the crystals at time ' $t$ ' of a given size ' $L$ ' per unit mass of solvent per unit size,  $G$  represents the growth rate of particles,  $B(L)$  represents the birth function of particles of size  $L$  at any instant by means of agglomeration and breakage,  $D(L)$  is the death function representing the death of particles of size  $L$  by means of breakage at any instant. The implementation of the combined Collocation and Galerkin method [7] requires the finite representation of the differential equations, which is accomplished through the construction of a Jacobi Matrix, representing the finite version. This defining step in the applied method requires numerical integration which is achieved using the Gaussian quadrature method. These integrals terms are implemented for every crystallization phenomena such as primary nucleation, secondary nucleation, and crystal growth. The material balance on the antisolvent in the crystallizer is given by:

$$\frac{d(N_L x_A + N_V y_A)}{dt} = Q_A \quad (2)$$

where  $Q_A$  is the molar flow rate of antisolvent, and  $N_L$ ,  $N_V$ , are the molar hold-ups of the liquid and the SAS phase in the crystallizer, and  $x_A$ ,  $y_A$ , are the mole fractions of the antisolvent in the liquid and the SAS phase, respectively.

The material balance on the solvent in the crystallizer is given by:

$$\frac{d(N_L x_S + N_V y_S)}{dt} = 0 \quad (3)$$

where  $x_S$ ,  $y_S$ , are the mole fractions of the solvent in the liquid and the SAS phase, respectively.

The material balance on the solute, which relates the change in solute concentration to changes in magma density, is given by the following equations:

$$\frac{d(N_L x_P + N_P)}{dt} = 0 \quad (4)$$

$$N_P = \frac{N_L v_L k_v m_3}{v_P} \quad (5)$$

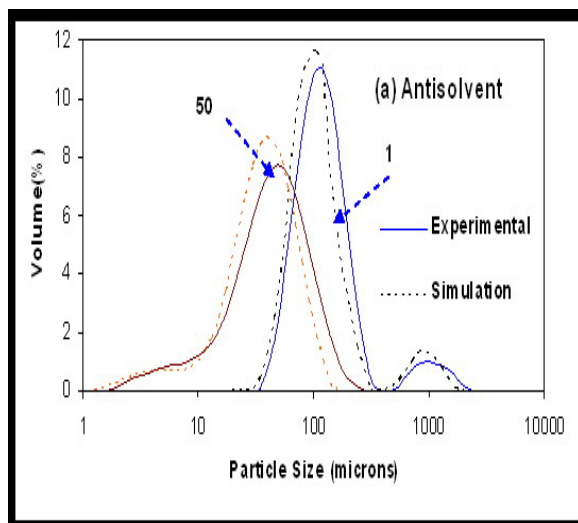
where  $N_P$ ,  $x_P$ ,  $k_v$ ,  $v_P$  and  $m_3$  are the molar hold-up of the solute in the solid phase, the mole fractions of the solute in the liquid phase, the volume shape factor, the molar volume of the solid solute, and the third moment of the population density function, respectively. The third moment of the population density is related to the total weight of crystals in the crystallizer, and is given as:

$$m_i = \int_0^{L_{\max}} L^i n(L) dL; \quad i = 3 \quad (6)$$

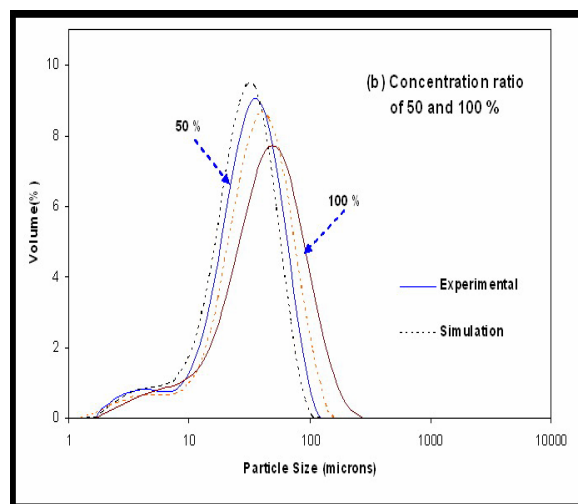
### 3 RESULTS AND DISCUSSION

The nucleation and growth dynamics of the SAS process using phenanthrene-toluene-carbon dioxide as a model system was investigated applying a rigorous mathematical model. This model accounts for the governing physical phenomena, i.e., the thermodynamics of near-critical solutions, and the particle formation process controlled by primary and secondary nucleation, and crystal growth. Simulations were performed for changes in the main operating parameters, i.e., the antisolvent addition rate and saturation level. The simulations were performed at a process temperature of 25°C, while the antisolvent addition rate,  $Q_A$ , was varied between 1 and 100 ml/min, and the initial solute concentration was varied between 25% and 100% of the concentration ratio. The model was successfully able to predict/represent the experimental observations phenomenologically. It was shown that the simulation findings were consistent with the experimental results, and good quantitative agreement was achieved. The population balance model was implemented in a dynamic simulation program that solves complex sets of partial integro-differential equations using a numerical algorithm of a finite-element type, the Collocation and Galerkin method [7]. In the employed population balance model, the secondary nucleation rate effectiveness factor,  $\alpha''$ , was shown to be the only parameter controlling the qualitative effect of the process variables, i.e., the antisolvent addition rate, on the particle size, and size distribution of the final precipitate [5]. Moreover,  $\alpha''$  is the only parameter in the relationships describing nucleation mechanisms that cannot be estimated based on physical properties of the model system. Comparisons between the measured and simulated volume percent particle size distributions, as a function of the antisolvent addition rate, 50 and 1ml/min (100% solute concentration ratio) are displayed in Figure 1. Figure 2 shows the comparisons between the measured and

simulated volume percent particle size distributions at 50 and 100 % solute concentration ratio (50 ml/min antisolvent addition rate). It is evident that the simulated particle size distribution is in a reasonable agreement with experimental data. However, small differences can be observed. The difference between associated plots could be due to the simulation assumptions such as the absence of breakage and agglomeration.



**Figure 1.** Comparison between the experimental and simulated volume percent particle size distributions at the antisolvent addition rate of 50 and 1 ml/min.



**Figure 2.** Comparison between the experimental and simulated volume percent particle size distributions at 50% and 100% solute concentration ratios.

## 4 CONCLUSIONS

The finite element algorithm were found to be capable of making accurate predictions of the number density function and the second moment of the population balance equation using reasonably small numbers of elements. The combined Collocation and Galerkin was successfully able to treat the implemented population balance model structures, producing smooth dynamic and steady state particle size distributions. Moreover, the simulation results were consistent with the experimental results, and good quantitative agreement was achieved. The theoretical findings showed that the observed pattern of behavior could be explained by invoking differences in the relative weight of the primary and of the secondary nucleation rate.

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