Modeling Industrial Crystallizers

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One of the main challenges in industrial crystallizers is to control the crystal size distribution (CSD). CSD control is important to ensure product quality and successful operation of a crystallizer. The final size distribution often affects downstream processing such as filtration, centrifugation, milling etc. Additionally the product purity and quality is directly related to CSD. In spite of its importance, the behavior of crystallizers and characterizing CSD for most processes is not well understood. Part of the complexity is that the size distribution varies in space and time in a crystallizer due to non-ideal flow patterns and heat transfer and is coupled to solution thermodynamics and crystallization phenomena such as nucleation, growth, aggregation and breakage.

One of the ways of understanding crystallization behavior is through modeling. In the past, simple models such as Mixed-Suspension Mixed-Product Removal (MSMPR) models were developed. These models predicted the crystal size distribution assuming that the crystallizer is well-mixed and the hydrodynamic effects were neglected. This greatly limited the use of these models. Nevertheless the models have been extensively used in designing crystallizers. In fact, such rough designs have made the design of crystallizers extremely conservative and they are not optimized for yield or for operation. In pharmaceutical crystallization, the problems are even worse because new drugs are made in existing stirred tanks that limit changes to operation profile and no design modifications. The lack of understanding of the flow characteristics and crystallization kinetics make process development and scale-up or scale-down a time consuming process.

By better understanding the interactive effects of mixing, fluid mechanics, solid and liquid chemical-physical properties, and the overall supersaturation profile, it is then possible to control the crystal size distribution and understand the crystallization behavior for scale-up or scale-down. A simulation model of a crystallizer that attempts to predict crystal size distribution therefore must account for the coupled effects of fluid mechanics and crystallization phenomena in a crystallizer.

The effect of fluid mechanics and non-ideal mixing is generally studied using computational fluid mechanics (CFD). CFD is an established technology that can predict the fluid flow and mixing characteristics in a wide range of applications. However, to be able to include the crystallization phenomena, it is required to solve the population balance equation that has the capability to address changes in particle population.

Population balance is a salient component in the modeling of crystallization processes. Fluid flow occurs in conjunction with the evolutionary processes such as nucleation and growth producing the crystalline phase. It is the capacity of population balance to address the evolutionary aspects of the crystallization phase that makes it indispensable. The population balance equation accounts for various ways in which particles of a specific state can form, migrate to another state, or disappear from the system. Typically, these ways are nucleation, growth, dissolution, aggregation and breakage. Together, these processes are called crystallization phenomena. The population balance equation is coupled with the flow, energy and species (mass balance) equations through the convective terms and the local values of velocity, turbulence, temperature etc. in different parts of the crystallizer. The population is described usually by number density of particles and the usual conservation law can be written for the number density which includes birth and death terms due to the above processes.

There are two approaches of solving population balance equations in CFD. They are the discrete method and the quadrature method of moments. In the discrete method, the particle population is discretized into a finite number of size intervals. This approach can be computationally expensive for crystallization applications as the particle size varies widely. Nucleation occurs in small scales. Aggregation and Growth can yield larger particles and the size distribution can span two or three orders of magnitude.

The Quadrature Method of Moments (QMOM) is an attractive approach, as it allows modeling arbitrary kinetics involving nucleation, growth, aggregation and breakage. In addition, one can recover the crystal size distribution using available numerical techniques to invert the moments.

An example of a batch crystallization problem with potassium chloride in water is shown with the Quadrature Method of Moments.

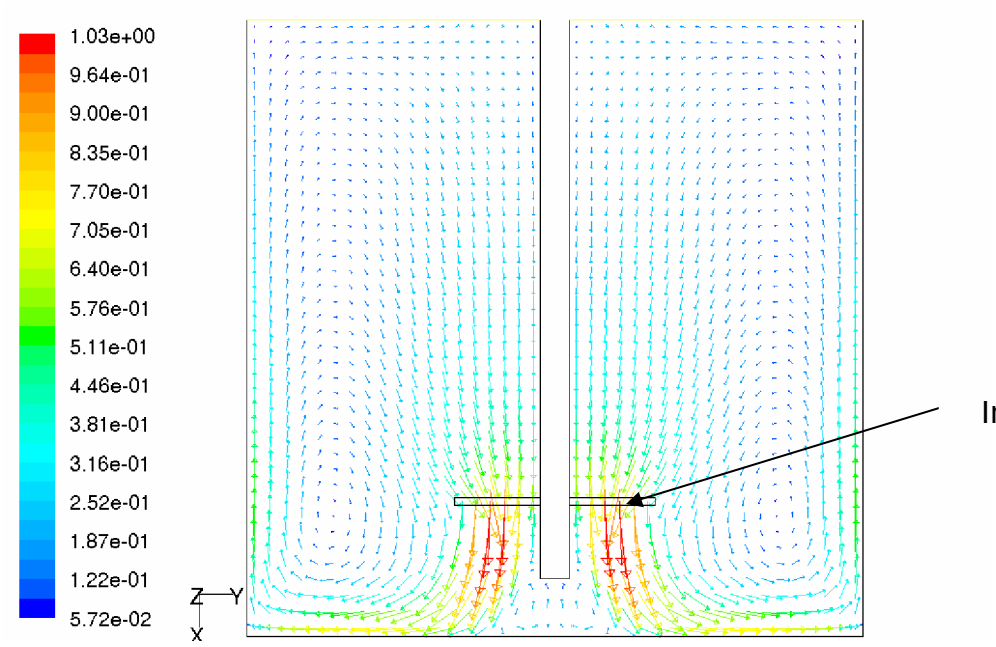

Figure 1. Velocity Vectors in a batch crystallizer.

The mixture is initially at a temperature of 353 K and the walls are cooled at 298 K. The supersaturation ratio is defined as the ratio of concentration of KCl in solution to its solubility. The solubility curve of KCl in water exhibits a linear dependency on temperature in the operating range. The growth (G) and nucleation (B^o) kinetics are based on power-law kernels as:

$$G = K_g (S-1)^{n_g}$$

$$B^o = K_N (S-1)^{n_N}$$

The analysis predicted the moments. From the moments, the crystal size distribution at final state was obtained and is shown below.

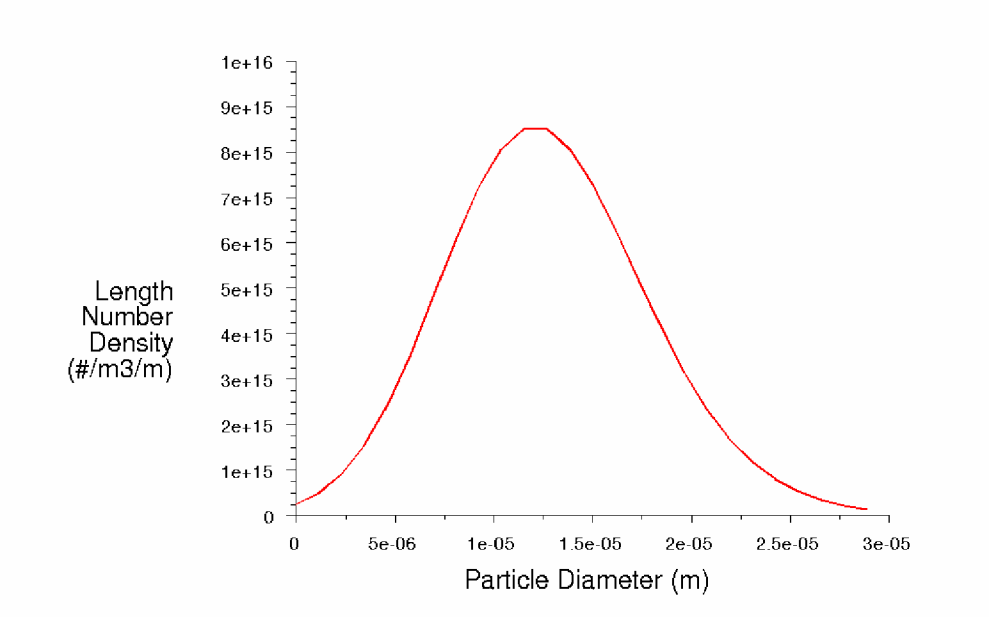

Figure 2. Crystal Size Distribution averaged over the entire crystallizer volume.

Based on the above concepts, Fluent, Dow Chemical, and the University of Utah have been working together to model a crystallizer that is in operation on a pilot scale at Dow's Ludington facility. This effort was part of a funded project from the Department of Energy (DOE) that concluded in June of this year. The physical process is to enrich and purify a stream that is rich in calcium chloride (CaCl) and potassium chloride (KCl) by crystallization of sodium chloride (NaCl), which is considered an impurity. The inlet composition of the solution mixture is about 45% KCl, 20% CaCl, and 1% NaCl. The inlet stream contains 2.7% NaCl solids with an average size of 122 microns. The objective is to reduce the NaCl in the solution further to about 0.5%. The jacketed reactor is cooled to 300 K with the inlet stream at approximately 325 K. The solubility curve of NaCl, which is linear with temperature, was obtained using *StreamAnalyzer* from OLI Systems.

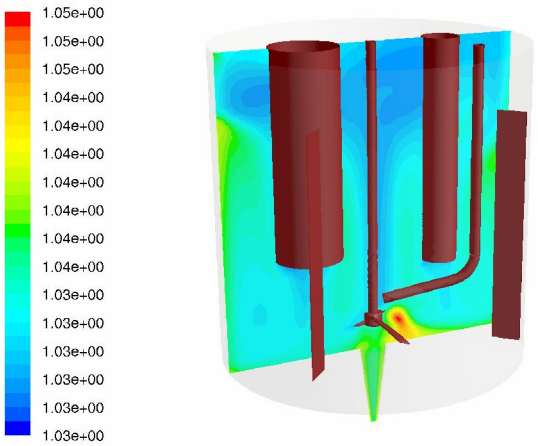

Figure 3. Supersaturation Profile at a vertical cross-section. The supersaturation ratio is higher near the inlet where there is ample supply of the solute.

The Eulerian granular multiphase model in FLUENT was used with the population balance solver on a 3D mesh of 400,000 cells. The rotation of the impeller was simulated using the multiple reference frames (MRF) approach. The constituents NaCl, CaCl, and KCl in water were each modeled as a species in the primary phase.

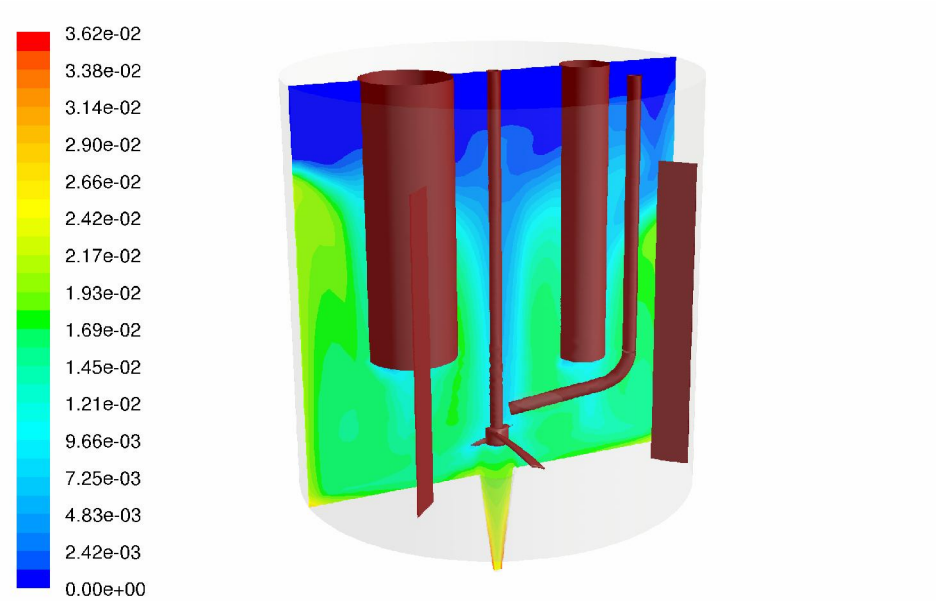

Figure 4: NaCl (solids) volume fraction contours along a vertical cross-section. The solids show some settling.

Results show that as the NaCl solute enters the (cooler) reactor, it is quickly consumed to form crystals. At the outlet, the mass fraction of NaCl in solution is 0.37% compared to 1% at the inlet, indicating a significant purification of the solution. The solids volume fraction shows some settling of the solids. At the outlet at the base of the reactor, the amount of solids is 3% and the average particle size is 133.8 microns, almost 10% larger that the size at the inlet. Results for the total number density of solids shows that the maximum is close to the inlet where there is ample supply of solute and a high supersaturation ratio. The crystal size distribution at the outlet is in good qualitative agreement with observations. Further study is under way for quantitative comparisions.

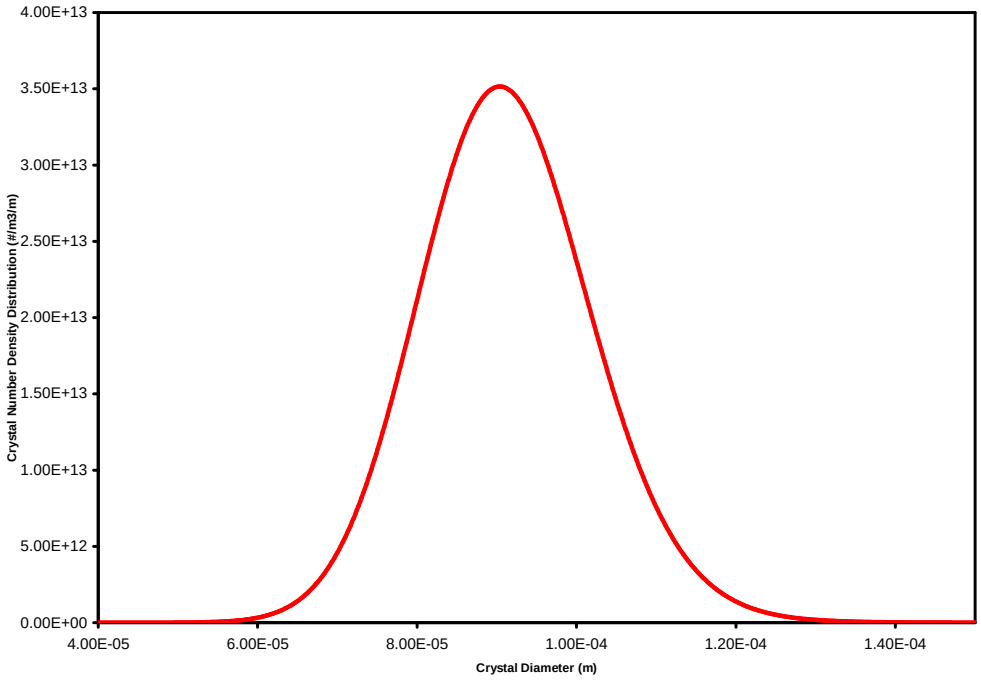

Figure 5: Crystal size distribution at the bottom outlet

In summary, a crystallization model that is predictive must account for the various interactions between hydrodynamics and crystallization phenomena. This is feasible by using population balance equations within a robust CFD framework.