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Cooling and seeding effect on supersaturation and final crystal size distribution (CSD) of ammonium sulphate in a batch crystallizer

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Abstract

Different cooling policies (natural (NCP), linear (LCP), controlled (CCP), as well as a proposed cooling policy; impulse changes in natural cooling policy (IC-NCP)) and seeding policies (with two different mean seed size and various seed loadings) were employed to investigate the effect of cooling and seeding on the final CSD of ammonium sulphate grown in a batch-cooling crystallizer. The crystallizer was equipped with an on-line density meter for the estimation of supersaturation. By increasing the amount of the seeds, the supersaturation peak was reduced and a uni-modal final CSD was obtained, irrespective of the cooling policy. At high seed loading (C_s), greater than theoretical critical seed loading ($C_{s,c}^{theo}$) predicted by the seed chart, the cooling policy had no significant effect on the final CSD. However, at low C_s, controlled cooling policy was needed in order to ensure uni-modal and narrow final CSD with large mean size. With the help of a simple on-off control, the IC-NCP was applied to overcome the mathematical complexities associated with the controlled cooling policy. All CSD results of the IC-NCP mode were between the linear and controlled cooling policies, and closer to the controlled cooling profile.

Keywords: Batch crystallization; Cooling and seeding policy; Crystal size distribution; Supersaturation; Ammonium sulphate

1. Introduction

The production of a large number of chemicals, pharmaceuticals, and photographics materials is carried out in batch crystallizers. In batch cooling crystallizers, the supersaturation, ΔC, the difference between the actual concentration (C) and the saturated concentration (C^*), is the driving force for both nucleation and growth phenomena. Supersaturation is generated by a solubility decrease due to temperature reduction. In seeded crystallization, the level of supersaturation should be controlled in such a way that the growth rate predominates the secondary nucleation rate to get a usni-modal and narrow CSD with large mean size of the final crystals. These goals can be achieved by proper cooling and seeding.

In natural cooling policy, the simplest and the most common cooling mode with no temperature control, because of high temperature gradient between coolant and solution, a high supersaturation peak is generated at the initial times of the crystallization process. This peak increases the nucleation rate and leads to a bi-modal final CSD. To keep the supersaturation level almost constant and relatively low, the controlled cooling policy (CCP) proposed by Mullin and Nyvlt [18] and modified further by Jones and Mullin [12] and Jones [11] is commonly applied. Another cooling approach to control the level of supersaturation is the linear cooling policy (LCP). Decreasing the temperature at a constant rate is the characteristic of LCP showing a final CSD which is usually superior to the CSD of NCP and closer to the CSD of CCP. Using an on-line turbidity meter to detect the secondary nucleation and a heating cycles to dissolve fine particles due to nucleation, Moscosa-Santillan et al. [17] proposed a new alternate cooling and heating cycles for the crystallization of glycine. The proposed policy showed improved results in comparison with the LCP and CCP. Fujiwara et al. [7] used seeded batch crystallization of paracetamol in water as a model compound, and implemented in situ ATR-FTIR and laser backscattering for the measurement of the solute concentration and the CSD

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to minimize nucleation and agglomeration effects. The controlled variable was chosen to be the concentration of paracetamol close to the metastable zone. Their optimal results indicated a low and almost constant supersaturation level during the crystallization, which was the characteristics of the CCP. The temperature profile was not, however, similar to CCP.

In the presence of seed crystals, secondary nucleation can be suppressed. Increasing seed loading reduces supersaturation for all cooling modes. The amount of required seeds to overcome the secondary nucleation depends on the mean size, quantity and quality of the seeds, as well as the cooling policy. The seed loading (C_s) is generally defined as the ratio of mass of seed crystals (W_s) to the theoretical yield of crystals (W_{theo}). Chivate et al. [2] and Bohlin and Ramuson [1] found out that increasing C_s decreased the nucleation rate. Also the effect of seed size and seed loading on the final CSD of potassium sulphate, ammonium alum and potassium alum was experimentally investigated by Jagadesh et al. [9,10], Doki et al. [4,5], Holzny et al. [8] and Kubota et al. [13]. Kubota et al. [14] showed that the uni-modal CSD could be achieved even with NCP if enough seed were added to the crystallizer. At C_s higher than the theoretical critical seed loading (defined by the seed chart), the cooling policy had no significant effect on the final CSD. Using simulation and optimization methods in a seeded batch crystallizer, Chung et al. [3] showed that optimizing seed characteristics (width of CSD, mass, and mean size of seeds) is more important than optimizing the supersaturation profile.

The present work investigates the effects of seeding and cooling policy on the level of supersaturation for the crystallization of ammonium sulphate in a batch crystallizer.

2. Experimental set up

All experiments were carried out in a 1.5-l jacketed-agitated batch crystallizer as shown in Fig. 1. An on-line density meter (MPDS 2000, Anton Paar, Graz, Austria) was used to estimate the actual solution concentration by measuring the solution density and temperature. Two correlations (Eqs. (1) and (2)) calculated by Tadayon et al. [20] were used to relate the actual and saturation concentrations to the density and temperature of the solution.

$$C = \frac{-0.9599\rho[1 + 1.9343 \times 10^{-4}(T - 273)] + 1}{0.5858\rho[1 + 5.4613 \times 10^{4-}(T - 273)] - 1} \qquad (1)$$

$$C^* = 0.708 + 0.0022(T - 273) + 1 \times 10^{-5}(T - 273)^2 - 1 \times 10^{-7}(T - 273)^3 \qquad (2)$$

where T and ρ are in K and kg/m^3, respectively. The solution temperature measured by a thermocouple (J type) was varied by manipulating the temperature of the cooling water through the jacket. Manipulation of the cooling water temperature was achieved by adjusting the set point of a water bath system (RTE220, Nestlab Instruments, Inc., Portsmouth, NH) through a three level cascade control system. Samples were continuously withdrawn from the solution by a pump, passed through the density meter and then recycled to the solution vessel. A LabView (National Instruments, Austin, TX, USA) hardware/software system was employed for data acquisition and control. A typical run was started with the preparation of 1.5-l of saturated solution at 30 °C by dissolving appropriate amounts of ammonium sulphate in de-ionized water. Pre-weighed seed crystals were added to the crystallizer at time zero and the crystallizer temperature was set to follow the set point according to different cooling profiles. The final crystallization temperature was set at 10 °C. All required data were scanned every 10 s during the batch. At the end of each experiment, an appropriate amount of solution was withdrawn, filtered through a 5 μm filter, washed with 2-propanol (EM Science, Merk, Darmtadt, Germany) saturated with ammonium sulphate, and then its size distribution was measured by Malvern Mastersizer 2000 (Malvern Instruments Ltd., Worces Tershine, UK).

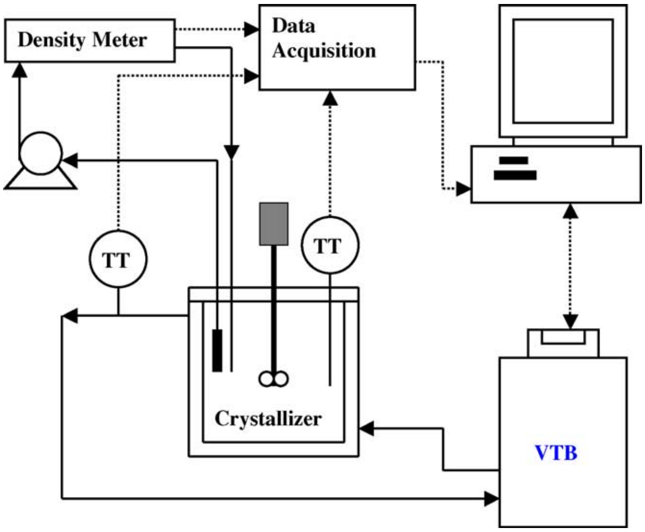

Fig. 1. Experimental set up: TT, Thermocouple; VTB, Variable temperature bath.

2.1. Seed preparation

To prepare seed crystals, commercial grade of ammonium sulphate crystals (BDH Inc., Toronto, Canada) were ground, washed with 2-propanol twice, filtered using a 20-μm filter paper, dried at room temperature for 24-h, and then sieved using Gilsonic Autosiever (Gilsonic Co. Inc., Worthington, OH, USA). Two different volume-weighted mean sizes (VWMS) of seed crystals, 165 μm and 380 μm, were prepared from three adjacent sieves. Suitable amount of the crystals separated using the conning and quartering method were used for measurement of the CSD and VWMS by Malvern Mastersizer.