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Industrial batch crystallization of a plate-like organic product. In situ monitoring and 2D-CSD modelling: Part 1: Experimental study

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Abstract

Experimental results obtained during the batch cooling solution crystallization of a fine organic compound in aqueous ethanol solvent are presented. The process monitoring was ensured through in-line, in situ ATR FTIR spectroscopy, providing continuous solute concentration estimates. Off-line image analysis was also performed to yield discrete-time measurements of the 2D-crystal size distribution (CSD) of the platelet-like particles. The decisive effect of secondary nucleation on both the course of supersaturation and CSD was highlighted through the qualitative analysis of selected batch runs, particular attention being focused on the seeds size and weight. At least two nucleation mechanisms allow explaining the experimental results: the introduction of seeds causes a significant burst of surface nucleation and the continuation of the cooling process, through the generation of continuous supersaturation, allows activated secondary nucleation to take place.

Keywords: Batch crystallization; Organic material; Sensors; Nucleation; ATR FTIR spectroscopy; Image analysis

1. Introduction

Crystallization from solution is an important separation and purification unit operation which is more and more expected to yield solid particles exhibiting specific properties such as good filterability, low fines concentration, no caking on storage, good flow ability, etc. The crystallization process requires also to be optimized, which means low energy consumption, volume reduction, easily hand able products, together with on-specification batches.

Generally, batch processes are used for the manufacturing of high-value added fine organic compounds, rather than continuous processes. From an industrial point of view, several desirable features are associated with batch operation: the equipment is rather simple and flexible and requires very low level of maintenance. Moreover, batch operation is suitable to chemical systems exhibiting toxic or viscous features leading to processing difficulties. Also, the design and the development of batch crystallization processes generally require reduced time and investment. Furthermore slowly growing crystals can be obtained with larger sizes through batch processing than through continuous operation (Wey and Kaspinski, 2001).

Nevertheless the in depth analysis of batch crystallization processes is rather difficult due to the transient features of batch processing characterized by temperature profiles, complex time evolutions of supersaturation and increasing mass and surface area of the crystals during the run. As a result, the kinetics of most crystallization mechanisms evolve continuously so that the prediction of the crystal size distribution (CSD) becomes more complex: to develop mechanistic models one needs to consider ordinary and partial differential conservation equations, including population, mass and energy balances (Wey and Kaspinski, 2001).

Moreover, it should be noted that organic crystals usually grown in impure mother liquors exhibit anisotropic habits which cannot satisfactorily be described through one single characteristic size. To investigate the means of ensuring constant end-use solid properties for such organic particles, it is necessary to monitor and control several characteristic crystal sizes and/or internal shape factors.

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The kinetic laws presented in the literature (Mersmann, 2001; Mullin, 2001) allow understanding the effect of key operating parameters on the development of the crystallization process. However, without rigorous kinetic modelling, such understanding remains essentially qualitative as most fundamental crystallization mechanisms occur simultaneously, with complex interactions and in transient mode during batch operations. A possible approach developed for quantitative studies is based upon attempts to separate the occurrence of the various crystallization mechanisms by choosing specific operating conditions such that the intensity of a given mechanism dominates the process. Such kind of approach was applied e.g. to paracetamol in acetone–water mixtures. Crystal growth (Granberg et al., 1999), primary nucleation (Granberg et al., 2001) and agglomeration (Alander and Rasmuson, 2005) were investigated in this way. However, such experimental operating conditions are likely to be observed far from industrial ones. Another possible approach is to describe crystallization processes using the general formalism of population balance equation (PBE) (Randolph and Larson, 1988). Coupled with kinetic laws and mass balance equations, PBEs allow representing the time variations of the particle size(s). Early studies were conducted considering one characteristic size of the particles through mono-dimensional PBE (Franck et al., 1988; Hounslow, 1988; Marchal et al., 1988). This approach was enlarged to two-dimensional PBE accounting for two internal sizes of crystals (Puel et al., 2003): the time variations of both the solute concentration profile and the final two-dimensional CSD of rod-like hydroquinone particles (length and width) were correctly predicted. However, it is clear that the predictive ability of such complex distributed models depends on both the accuracy and the amount of experimental data acquired during the experimental study of the batch process.

As a possible answer to this latter problem, in situ spectroscopic sensors were developed during the past decade which allowed the in line acquisition of solute concentration data, easily converted in supersaturation data (Lewiner et al., 2001). Coupling supersaturation measurements with two-dimensional CSD evaluations is then hoped to allow new in-depth evaluation of the kinetics of crystal nucleation and 2D crystal growth during batch operation. Such 2D modelling is expected to allow better understanding of parameters governing the evolution of the particle shape, which is a major issue in the field of industrial crystallization.

2. Objectives of the study

The objective of the present work is twofold. First, batch crystallization of an organic material presenting a platelet habit, is studied experimentally. For the sake of confidentiality, the name of the product in question will not be disclosed. Seeded operations are carried out and monitored using in situ attenuated total reflectance (ATR) mid-infrared spectroscopy. The influence of the cooling rate, the total area of the seeds and of the seeding temperature on both the supersaturation profile and the evolution of CSD is investigated. The habit and the 2D size distribution of the platelet crystals is also investigated. The experimental results provide insights into the secondary nucleation and growth mechanisms involved. Section 3 describes the experimental apparatus and summarizes the main operating conditions. The experimental results are then presented in Section 4. A discussion about secondary nucleation mechanism(s) involved is presented in Section 5. The impact of the growth of the seed particles on the course of supersaturation and the influence of the area of the seeds are also discussed in Section 5.

The second objective is to deduce a model of the batch crystallization in question using a large amount of collected experimental data, notably continuous supersaturation measurements. Such model is expected to predict the evolution of crystal habit as a function of the experimental parameters and will be presented in Part 2 of the present series of papers.

3. Experimental set-up and operating procedure

3.1. Model substance

The organic solid product was supplied by Rhodia (France) as industrial grade quality, and used without further purification. The batch cooling solution crystallization was performed in water/ethanol mixture (80/20 w/w), reagent-grade chemical ethanol was used with deionised water. In this mixture of solvents, the crystals exhibit platelet-like habit, as displayed in Fig. 1. From SEM observations on seed and on final crystals, the thickness of the particles is in the range of 5 to 20 μm and far smaller than the length and the width. The thickness will be assumed constant so that the habit will be described through length L and width L'. An elongation particle shape factor is also defined as the length to width ratio L/L'. Preliminary batch crystallization experiments (Oullion, 2005) have shown

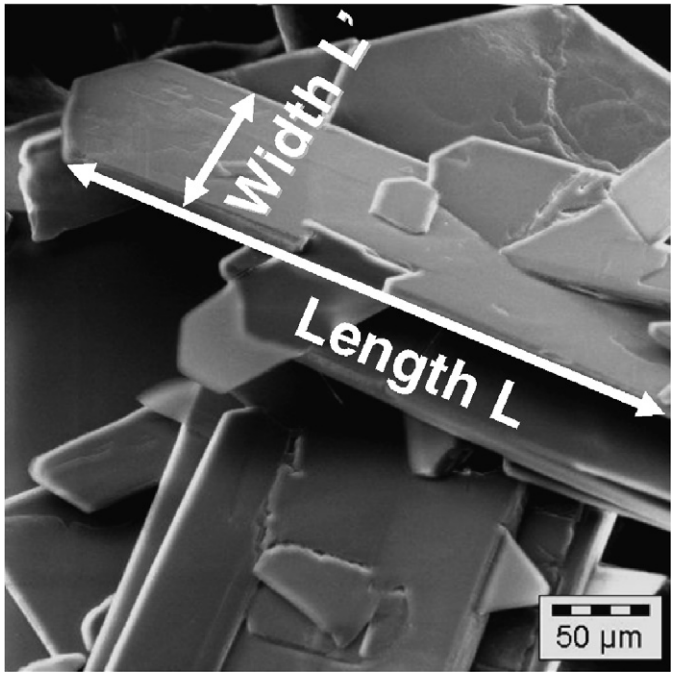

Fig. 1. Environmental SEM picture of crystals of the investigated industrial product.