



# Experimental screening method for flash-crystallization



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## HIGHLIGHTS

- Introduction of process diagrams to perform flash-crystallization experiments.
- Droplet size correlates with the crystal sizes produced.
- Mother liquor in sump and crystal size indicate successful nucleation and growth in the droplets during their flight period.
- Estimation of median crystal sizes for flash-crystallization.

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## ABSTRACT

Flash-crystallization is a process to produce small, fine crystals ( $L_{50,3} = 30\text{--}90\ \mu\text{m}$ ) from solutions of substances which are well soluble. Such substances tend to crystallize readily at low supersaturations to rather coarse size ranges above  $200\ \mu\text{m}$  (Mersmann and Kind, 1988). For such substances, the feasibility of the flash-crystallization process has been well examined on a laboratory scale and on a pilot plant scale. It is ready to be transferred to production scale. However, not all combinations of solute and solvent can be flash-crystallized. Nucleation and growth kinetics must allow for the fast formation of crystals. Here, we introduce an experimental screening method for a fast but reliable determination of the general suitability of any so far untested solute–solvent combination for the flash-crystallization process. It is found that the particle size of the product and residual supersaturation after flash-crystallization are key indicators for a successful nucleation in the droplets. Offline investigation of atomized droplets shows that one droplet carries approximately one nucleus and crystal. Additionally, this allows us to estimate the median particle size of so far untested solute–solvent combinations. They are in good agreement with measured particle sizes.

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## 1. Introduction

The flash-crystallization process produces rather small ( $L_{50,3} = 30\text{--}90\ \mu\text{m}$ ) and pure crystals from the solution of well soluble substances. In general, their volumetric size distribution is rather narrow. In conventional crystallization processes such substances tend to crystallize readily at low supersaturations to rather coarse size ranges above  $200\ \mu\text{m}$  (Mersmann and Kind, 1988). Production of such fine particles requires high nucleation rates. This is realized by atomizing an undersaturated feed solution into the flash-crystallizer, which is superheated in reference to the pressure in the crystallizer (see Fig. 1: left side). Only 10–30% by weight of the solvent is evaporated, depending on the operational conditions. The suspension of crystals produced is collected in the bottom of the crystallizer (sump). Impurities remain dissolved in the mother liquor and are

separated from the crystals by conventional solid–liquid separation, i. e. centrifugation or filtration. The product suspension contains 10 to 30% by weight of crystal mass depending on the supersaturation and solute–solvent combination.

Flash-crystallization has recently been reported to be applied either in the field of product design or in the field of crystallizer control and stabilization. For product design applications, Kaiser and Kind (2007, 2009) and Kabelac (2009) proved the suitability of flash-crystallization as the first unit of a process chain which is further comprised of solid–liquid separation and agglomeration. A wide range of specific agglomerated properties (size, size-distribution, density, porosity, coating, etc.) may be achieved according to the setting of the various process conditions in the chain. Large particles ( $\cong 5\ \text{mm}$ ) may be produced with this process chain, whereas Risse et al. (2012) produced sub-micron particles (500 nm) for the compound RDX. They used a nozzle with an extra thin inner diameter to do this. Flash-crystallization may also be used as a means to seed crystallizers either in batches or in continuous mode for crystallizer control and stabilization (Wood, 2011).

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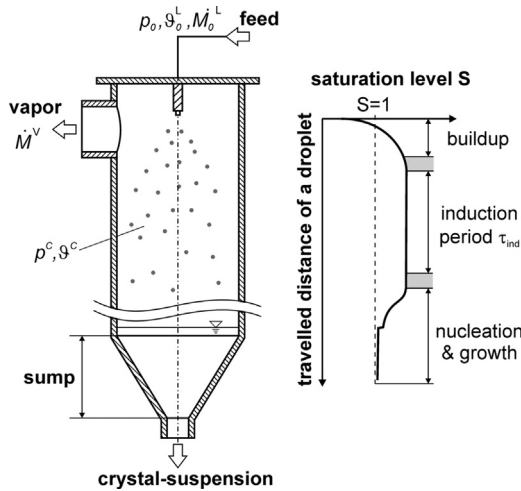


Fig. 1. Flash-crystallizer and development of saturation level in a droplet during flight.

The basic requirement for the stable operation of a flash-crystallization process is the successful nucleation within the droplets before they hit the wall or fall into the sump of the crystallizer. There, they are mixed with crystal suspension or coalesce and the supersaturation will be depleted quickly, disabling further nucleation. The scheme in Fig. 1 (right side) shows the expected development of the saturation level during the flight of a droplet after atomization. At first, the droplet partly evaporates, cools down and builds up a supersaturation. After a certain time, the so-called induction time  $\tau_{ind}$ , nucleation occurs and the nuclei grow to crystals.

The estimated time of flight for droplets in the range of  $d = 50\text{--}100\ \mu\text{m}$  is  $\tau_f = 10\text{--}25\ \text{ms}$ , depending on the size of the crystallizer (Gebauer et al., 2012). Basic calculations for the flash-evaporation of single droplets show that the buildup of supersaturation occurs almost instantaneously within 1 ms (Gebauer, 2013; Kabelac, 2009). Thus, the limiting part for a successful flash-crystallization process is the induction time  $\tau_{ind}$ . It is a crucial physicochemical property of a given solute–solvent combination for its successful application in flash-crystallization. Induction time measurements in the scale of milliseconds for supersaturations which occur in flash-crystallization ( $S = 1.05\text{--}3$ ) have not been reported in the literature yet. A promising approach is to correlate and extrapolate induction times received from turbidity measurements into supersaturated regions of the flash-crystallizer as reported (Gebauer, 2013).

Here, we propose another approach comprising several steps. The first step is a general method for estimating the key process parameters which are required to achieve certain process conditions, i.e. supersaturation, suspension density. This is demonstrated for the aqueous solution of potassium nitrate ( $\text{KNO}_3$ ). The second step is carrying out batch flash-crystallization experiments, which either lead to a suspension or not. Thereby, measurements of the supersaturation of the mother liquor in the sump, as a third step, inform about the deviation from thermodynamic equilibrium. This will be shown for the aqueous solutions of sodium chloride ( $\text{NaCl}$ ), potassium chloride ( $\text{KCl}$ ), potassium alum ( $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ) and potassium sulfate ( $\text{K}_2\text{SO}_4$ ). A supersaturated sump indicates long induction time and slow crystal growth. In principle, severely supersaturated mother liquor must be avoided due to loss of yield and incrustation problems in the successive solid–liquid separation. Several means are at hand to reduce such supersaturation of the sump, e.g. providing residence time, elevating the temperature, adding solvent or adding extra solid to the sump. In the case of successful particle production by flash-crystallization, in a fourth step, whether the nuclei of these particles have been formed in the droplets during their flight period or due to long induction time in

the suspension of the sump can be deduced from the mean of the particle size distribution. Additionally, the preservation of atomized droplets in silicon oil and their offline investigation allow the relationship of the droplet sizes to the number of crystals inside the droplets to be examined. An estimation of the crystal sizes produced for solute–solvent combinations, such as urea ( $\text{CH}_4\text{N}_2\text{O}$ ) in water ( $\text{H}_2\text{O}$ ), is possible for the assumption of one nucleus per droplet.

## 2. Materials and methods

### 2.1. Estimation of process parameters

The pressure  $p^C$  of the flash-crystallizer, the temperature  $\vartheta_0^L$  and the initial solute concentration  $x_{2,0}$  of the binary, superheated feed stream are process parameters, which are set by the operator. The total pressure in the flash-crystallizer  $p^C$  is low compared to the vapor–liquid (VL) equilibrium pressure of the superheated feed solution. Upon introduction into the flash-crystallizer isenthalpic flash-evaporation of the feed solution occurs. Thereby, the solvent evaporates if the vapor pressure of the solute is negligible. Evaporation ends when the temperature of the droplet phase has reached the boiling temperature  $\vartheta_b = \vartheta^C = \vartheta^*(p^C, x_2)$  (Stephan et al., 2009). This temperature depends on the total pressure  $p^C$  in the crystallizer and the concentration  $x_2$  of the solute in the concentrated droplet phase (Kaiser and Kind, 2007). In the following, it is assumed that thermodynamic VL equilibrium is attained at the outlet of the evaporation zone of the crystallizer without depletion of solute concentration  $x_2$  in the droplets due to the formation of solids. Furthermore, it is assumed that the droplets are homogeneous in temperature and concentration. Physical properties of supersaturated solutions may be determined by extrapolation from data of undersaturated solutions. Steady state mass-, solute- and energy-balance for the flash-crystallizer are

$$0 = \dot{M}_0^L - \dot{M}^V - \dot{M}^L \quad (1)$$

$$0 = \dot{M}_0^L \cdot x_{2,0} - \dot{M}^L \cdot x_2 \quad (2)$$

$$0 = \dot{H}_0 - \dot{H}^L - \dot{H}^V - \dot{Q} = \dot{M}_0^L \cdot c_{p,0}^L \cdot (\vartheta_0^L - \vartheta^C) - \dot{M}^V \cdot \Delta h^V(\vartheta^C) - \dot{Q} \quad (3)$$

with  $\vartheta^C = \vartheta^*(p^C, x_2)$ . Here, the heat flux  $\dot{Q}$  is defined as heat loss to the environment. Combination of these equations leads to the following implicit equation for the determination of a set of process parameters ( $\vartheta_0^L, x_{2,0}, p^C$ ) as a function of temperature of the crystallizer chosen  $\vartheta^C$  and supersaturation chosen  $S = x_2/x_2^*(\vartheta^C)$ :

$$\vartheta_0^L = \vartheta^C + \Delta h^V(\vartheta^C)/c_{p,0}^L \cdot \left[ 1 - x_{2,0}/S \cdot x_2^*(\vartheta^C) \right] + \dot{Q}/\dot{M}_0^L \cdot c_{p,0}^L \quad (4)$$

The heat of vaporization  $\Delta h^V(\vartheta^C)$  can be calculated according to the Watson equation (Kabelac, 2006). The pressure inside the crystallizer  $p^C$  is set by the condenser and the vacuum system. It is calculated by correlations given in Kabelac (2009) as well as the solubility  $x_2^*(\vartheta)$  and the heat capacity of the solution  $c_p^L$ . The solubility for a certain temperature varies by about  $\Delta x_2^*(\vartheta) = \pm 1\%$ . An intended supersaturation  $S$  and a crystallizer temperature  $\vartheta^C$  are set for the design of a flash-crystallization process, and consequently lead to the required feed temperature  $\vartheta_0^L$  and concentration  $x_{2,0}$ .

### 2.2. Laboratory setup for experimental screening

Fig. 2 depicts a laboratory setup for flash-crystallization. It allows for the screening of so far untested solute–solvent combinations

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