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Profiles of temperature, concentration and supersaturation within atomized droplets during flash-crystallization

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ABSTRACT

Flash-crystallization is a suspension crystallization process to produce small, fine crystals ($L_{50,3}$ = 20–90 μm) of substances which are well soluble. A hot and undersaturated solution is atomized into a low vacuum. The small droplets generated partially evaporate and cool down until thermal and mechanical equilibrium is reached. Consequently, they are highly supersaturated in a controlled manner and, thus, enable high nucleation rates. Experiments show that only certain solute–solvent combinations exhibit the high nucleation rates required and, thus, are suitable for flash-crystallization. We show that this observation is not caused solely by the buildup rate of supersaturation, but also by nucleation and growth kinetics. This is concluded by a comparison between the time of flight τ_f of the droplets in the crystallizer and the buildup time τ_b needed for the evolution of temperature and concentration profiles inside each droplet. The buildup time of supersaturation τ_b is negligibly short compared to the time of flight of the droplet. Thus, the driving force for nucleation and growth rate is present during virtually the entire time of flight, and therefore, slow nucleation and growth kinetics are the reason for the behavior observed. The model proposed is in good agreement with data measured.

1. Introduction

The process of flash-crystallization aims at producing small ($L_{50,3}$ = 20–90 μm) and pure crystals from a solution of well soluble substances [1–4]. In conventional evaporation or cooling crystallization processes, such substances are crystallized to a considerably coarser product ($L_{50,3}$ = 150–1000 μm) at low supersaturations [5]. Production of such fine particles requires high nucleation rates. This is realized by atomizing the undersaturated feed solution, which is superheated with respect to the operating pressure p^C of the flash-crystallizer; see Fig. 1 left side. Only a fraction of the solvent is evaporated and, according to the operating conditions, a solids content of ζ = 10–30% by weight is achieved in the suspension. The suspension of crystals produced is collected in the bottom of the crystallizer (sump) to allow for depletion of the residual supersaturation of the droplets. Impurities remain dissolved in the mother liquor and are separated from the crystals by conventional solid–liquid separation, i.e., centrifugation or filtration.

Flash-crystallization may be applied either in the field of product design or in the field of crystallizer control and stabilization. For product design applications, Kaiser [1–3] proved the suitability of flash-crystallization as the first unit of a process chain which further comprises a solid–liquid separation step and agglomeration step to produce large particles (~5 mm). A wide range of specific properties (e.g., size, size-distribution, density, porosity and coating) of the agglomerates may be achieved according to the setting of the various process conditions in the chain. By contrast, submicron particles (500 nm) of the compound RDX were produced by flash-crystallization with an orifice of extra thin inner diameter [6]. Furthermore, flash-crystallization may be used to produce seeds for controlling and stabilizing batch or continuously operated suspension crystallizers [7].

A basic requirement for successful flash-crystallization processes is nucleation within the droplets before mixing with the suspension present in the sump of the crystallizer or in the film draining off from the crystallizer wall. There, the supersaturation will be quickly depleted by the growth of existing crystals and further nucleation will be disabled. Fig. 1 (right side) shows the development of supersaturation expected during the flight of a droplet after atomization. At first, the droplet partly evaporates and cools down to equilibrium temperature $\vartheta^C = \vartheta^*(p^C, x_2)$ and, thus, builds up a supersaturation. After the induction time τ_{ind}, nucleation occurs and the nuclei grow into crystals. The timely

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Nomenclature

A	Surface (m^2)
d	Diameter (μm)
D	Mass diffusion coefficient (m^2/s)
h	Heat transfer coefficient ($W/m^2 K$)
$H, \dot{H}$	Enthalpy, enthalpy flow (kJ, kW)
H	Height (mm)
$M, \dot{M}$	Mass, mass flow (kg, kg/s)
p	Pressure (bar)
$Q, \dot{Q}$	Heat (kJ, kW)
$L_{50,3}$	Median volumetric particle size (μm)
R	Radius (mm)
s	Depth of crystallizer, distance (mm)
t	Time (s)
T	Temperature in Kelvin (K)
u	Velocity (m/s)
W	Shortest distance to wall or sump (mm)
x	Mass fraction of anhydrate in solution (-)
y,z,r	Measurement position (mm)
γ	Activity coefficient (-)
Δh^V	Enthalpy of vaporization (kJ/kg)
θ	Spray angle (°)
$\Theta = (\vartheta^L - \vartheta^C)/(\vartheta_0^L - \vartheta^C)$	dimensionless quantity
ρ	Density (kg/m^3)
κ	Thermal diffusivity (m^2/s)
λ	Thermal conductivity (W/mK)
Λ	Mean free path of vapor molecule (m)
ν	Kinematic viscosity (m^2/s)
ϑ	Temperature in Celsius (°C)
$\zeta = \dot{M}_2/\dot{M}^L$	Solid content (%)
τ	Characteristic time (s)

Super- and subscripts

0	Initial, feed
1	Solvent
2	Solute
b	Buildup of supersaturation
C	Crystallizer
f	Flight
G	Gaseous
ind	Induction time
L	Liquid
O	Orifice
R	Radial
V	Vapor
z	Axial direction
^	Non-dimensional
*	Equilibrium

Dimensionless quantity

Reynolds number	$Re = (u \times d)/\nu$
Knudsen number	$Kn = \Lambda/d$
Supersaturation	$S = x_2/x_2^*$
Degree of superheat	$S_D = p^*(\vartheta_0^L)/p^C$
Flash number	$Fl = (\tau_f - \tau_b)/\tau_{ind}$
Dimensionless temperature	$\Theta = (\vartheta^L - \vartheta^C)/(\vartheta_0^L - \vartheta^C)$

distinction between the different steps is not clear-cut and they overlap, therefore, in Fig. 1, we mark transition areas with a diffuse gray area. Kaiser [3] already estimated roughly the duration of the buildup and the droplet velocity. His approach is explained in detail in the respective sections to contextualize this study. However, the question remains whether the sum of the buildup time of supersaturation τ_b and induction time τ_{ind} is shorter than the time of flight of the droplets τ_f given by the dimensions of the apparatus. We define this relation with the ratio (Eq. (1))

$$\frac{\tau_f - \tau_b}{\tau_{ind}} = Fl \quad (1)$$

which we call a Flash (Fl) number. Only when $Fl \geq 1$, flash-crystallization will lead to the fine product desired.

In the following, we estimate the characteristic times τ_f and τ_b and their impact on the Fl number. In the first part, the time of flight of the droplets in the flash-crystallizer before hitting its sump or wall is assessed. In the second part, we estimate the buildup time of supersaturation. It is governed by the evaporation rate of the solvent, which, in turn, depends on the temperature of the droplets. Therefore, we model the evolution of the temperature profiles inside the droplets during evaporation. The results are compared to temperature measurements of the spray using an IR (infrared) camera. Temperature and mass concentration profiles inside the droplets are calculated for two cases: a well mixed droplet and an unmixed droplet, where we consider heat conduction and diffusion. The timely development of these profiles corresponds to the buildup time of supersaturation τ_b within the droplet. The characteristic times τ_f and τ_b calculated can be applied to the Fl number (Eq. (1)) and it will give the maximum allowable value for the induction time τ_{ind}.

2. Time of flight τ_f

The time of flight of the droplets is the residence time inside the crystallizer between leaving the atomizer (here, hollow cone nozzles) and hitting the sump or the wall. Generally, a long time of flight would enable solute–solvent combinations with slow nucleation kinetics to be successfully flash-crystallized. This time can be increased, for instance, by larger crystallizer dimensions or slower entrance velocity. τ_f of a droplet of initial size d_0 and velocity $u_0 = (u_{y,0}; u_{z,0})$ can be estimated by solving its momentum balance. The velocity decreases with time due to drag forces acting on the droplet (Eq. (2)). Thereby, the gravity term in this equation occurs just in the vertical direction z and disappears for the velocity in the radial direction y [8].

$$\frac{du}{dt} = \left(1 - \frac{\rho^G}{\rho^L}\right) \times g - c_w(Re) \times \frac{\rho^G}{\rho^L} \times \frac{3}{4d}|u| \times u \quad (2)$$

The drag coefficient c_w of droplets for different Reynolds (Re) numbers is taken from literature [9,10]. The velocity $u(t) = (u_y; u_z)$ and the distance of the droplet traveled $s(t)$ determine the time of flight τ_f of the droplets inside the crystallizer.

Kaiser [3] calculated the initial droplet velocity using Bernoulli's principle for incompressible fluids and with this boundary condition he solved Eq. (2) in axial direction z. Initial droplet velocities of $u_{z,0}$ = 25–35 m/s were received for a pressure difference of Δp = 4–6 bar. In contrary, we calculate the velocities in axial and radial direction to consider the spray angle θ (see Fig. 1). Laser Doppler anemometry measurements in a vertical distance of z = 15 mm to the nozzle serve as an initial condition for our calculations [4]. Conditions for a typical flash-crystallization process are characterized by a superheating of the feed of $\Delta\vartheta = \vartheta_0^L - \vartheta^C = 80K$, which corresponds to a degree of superheating of $S_D = p^*(\vartheta^L)/p^C = 10.1$ for the system potassium nitrate