Kinetics and Modeling of Crystallization in Surfactant-Free Monodisperse Emulsions

Richard D. Dombrowski, Particle and Systems Design Centre, Division of Chemical Engineering, University of Queensland, Brisbane, QLD, Australia
James D. Litster, Particle and Systems Design Centre, Division of Chemical Engineering, University of Queensland, Brisbane, QLD, Australia
Norman J. Wagner, Department of Chemical Engineering, University of Delaware, Newark, DE, USA

Abstract

Solution crystallization from surfactant-free, monodisperse emulsions is investigated as a method for producing crystals of a narrow crystal size distribution (CSD). Within each drop there is a limited amount of material available to crystallize, thus limiting the maximum crystal size. Easily controllable properties such as the drop size, the initial concentration of solute, the concentration of salt or anti-solvent and the temperature profile determine the maximum possible crystal size. In the case of a material that exhibits growth rate dispersion (GRD), a fast-growing crystal will quickly grow to near this maximum size, at which time the supersaturation in the drop will be depleted and growth stops. The cessation of growth of fast-growing crystals due to mass balance considerations allows slower-growing crystals time to "catch-up", leading to a narrower crystal size distribution. A monodisperse drop size distribution ensures that the maximum crystal size is the same for all drops. As an extension of this concept, if the operating conditions are chosen to favor the formation of only one crystal per drop and the crystallization time is sufficiently long to allow the supersaturation to be depleted, then the product crystals will have a narrow size distribution near the maximum size. Figure 1 shows examples of drops containing lactose crystals that satisfy the one crystal per drop condition and have grown to the maximum size.

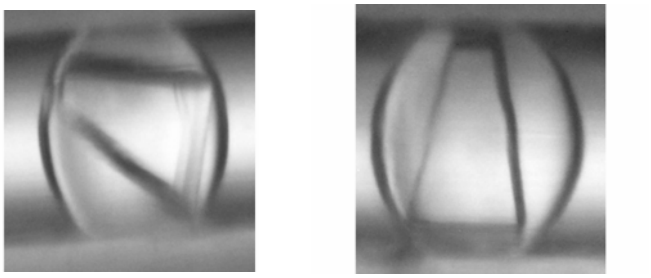

Figure 1. Single crystals of alpha-lactose monohydrate in drops in the microfluidic crystallizer. Drops are approximately 300μm in diameter.

To test the performance of the drop-based crystallization approach, isothermal lactose crystallization experiments were carried out at 20°C, 30°C and 40°C using a microfluidic T-junction to form uniform drops of diameters between 100 to 300 μm, followed by a temperature controlled plug-flow crystallizer to prevent drop coalescence. The number and sizes of crystals in the drops were measured after 24 hours at constant temperature using a Nikon stereomicroscope and ImageJ image analysis software. The maximum fraction of drops containing a single crystal was approximately 35% for each of the temperatures tested. The CSD from drops that contained only one crystal had a coefficient of variation (CV) as low as 7.0%, as compared to 40% obtained from bulk crystallization.[1] The CV of the total crystal population was between 16-20% at the temperatures and supersaturations tested. It is desirable to increase the fraction of drops containing a single crystal beyond the 35% maximum for isothermal crystallization to further narrow the overall CSD.

A population balance model (PBM) incorporating nucleation kinetics and crystal GRD is proposed. The model predicts the number and size of crystals in the drops and the overall CSD. Model predictions are compared against measurements of the time evolution of the CSD for the lactose system using the microfluidic crystallizer. Figure 2 shows a comparison of the model predictions for the mean and CV of the single crystal population compared with experimental results for crystallization at 30°C in 150μm diameter drops with an initial concentration of 76 g lactose/100 g water.

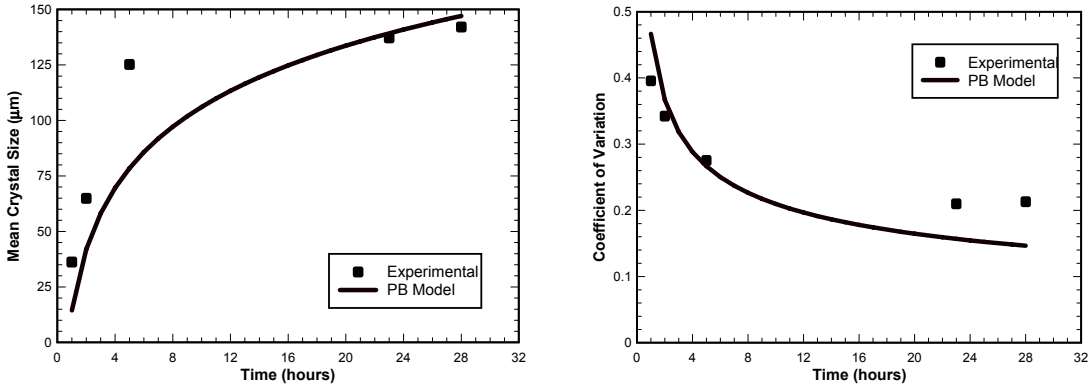

Figure 2. Time evolution of the CSD of lactose crystals compared with model predictions for crystallization in 150μm drops in the microfluidic crystallizer.

The PBM captures the observed dynamics in the microfluidic crystallizer with good quantitative agreement. The model is a useful tool for control and optimization of microfluidic crystallizers.

References

1. Butler, B. *Modeling Industrial Lactose Crystallization.* PhD. Thesis, University of Queensland, 1998