Growth Rate Dispersion in Seeded Batch Sucrose Crystallization

B. M. Liang, R. W. Hartel, K. A. Berglund
Departments of Chemical and Agricultural Engineering
Michigan State University
East Lansing, MI 48824

In a previous paper (Liang et al., 1987), growth rate dispersion (GRD) and contact nucleation of sucrose crystals were studied in a photomicroscopic cell. Several hundred nuclei were formed with a gentle sliding contact of a parent crystal over a glass cover slip, indicating that contact nucleation occurred at low contact energy levels. Photomicroscopic observation of the subsequent growth of these nuclei indicated that while all of the nuclei grew at a constant rate, their inherent growth rates were not the same. That is, the nuclei exhibited growth rate dispersion, yet each individual nucleus followed the constant crystal growth (CCG) model of GRD. These results are consistent with previous work (Shanks and Berglund, 1985).

The effects of GRD and contact nucleation are of commercial importance in suspension crystallizers. Several studies have been performed to investigate these effects in both batch and continuous suspension crystallizers. White and Wright (1971) and Berglund (1980) observed a general widening of a growing sucrose seed distribution under nonnucleating conditions. This widening of the distribution was attributed to growth rate dispersion. In the continuous crystallization of sucrose both GRD and contact nucleation were found to be present in the nucleating region of supersaturation (Hartel, 1980). However, the effects of these phenomena on the crystal size distribution (CSD) were not investigated.

The object of this study was to compare the results of batch suspension and photomicroscopic cell experiments on growth rate dispersion of sucrose seed crystals to determine the relative effects of GRD in the two different environments. This was done by observing the change in CSD of the seed distribution in the batch suspension crystallizer, while simultaneously monitoring the individual growth rates of an identical seed sample in the photomicroscopic cell.

B. M. Liang is currently at the Department of Chemical Engineering, Beijing Institute of Light Industry, Beijing, China.
R. W. Hartel is currently at the Department of Food Science, University of Wisconsin, Madison, WI 53706.

Experimental Method

The growth of sucrose seed crystals was observed in the photomicroscopic cell used previously for contact nucleation studies (Liang et al., 1987). The seed crystals ranged from 90×10^{-6} to 125×10^{-6} m with an average size of 129×10^{-6} m as determined by a Coulter Electronics model Z_{B1} particle counter. Samples were carefully inserted into the cell and crystal growth rates at various supersaturations were followed by time-lapse photography. The change in seed size with time was determined using image analysis of the photographic slides. Growth rates based on equivalent circular area were found in this way. The area-based measurements were converted to a volume base by converting the mean size as found by image analysis to an equivalent mean size based on equivalent spherical diameter. This was done by analyzing the original seed distribution by both image analysis and particle counter and determining the ratio of the area-based mean size to the volume-based mean size. Growth rate results are here reported in volume-based units unless otherwise stated.

Batch suspension crystal growth experiments were performed in a glass resin kettle. Stirring was provided by a two-bladed paddle impeller, which maintained good circulation around a stainless steel draft tube. The working volume of the crystallizer was 650 mL. Constant temperature was maintained by immersion of the kettle into a constant-temperature water bath.

Approximately 1.7 g of the seed were added to the supersaturated solution at the appropriate conditions. The seeds were allowed to grow for 30 to 90 min, depending on the growth rate. The batch experiment was terminated before the solution concentration changed significantly, so constant supersaturation was assumed. Samples were periodically pipeted from the crystallizer and analyzed for size distribution on the particle counter. The resulting size distributions were analyzed to yield the mean crystal size and the variance of the size distribution. The change in mean crystal size with time was taken as the average growth rate of the CSD, and the variance of the growth rate distribution was found from the change in variance of the CSD with time squared (Ramanarayanan et al., 1985).

Average growth rates and the variances of the growth rate distributions were determined for each reactor as functions of temperature (313, 323, and 333 K) and supersaturation (0.33 to 2.05 kg sucrose/100 kg solution).

Results and Discussion

Although insufficient data were generated to yield accurate growth kinetic information, the anticipated trends were observed. Average growth rates found in the suspension crystallizer were nearly a factor of two greater than those found in the photomicroscopic cell. This was due to the greater mass transfer resistance to crystal growth under the stagnant conditions existing in the photomicroscopic cell. Kinetic analyses also corroborated this observation in that the activation energy for growth in the cell was significantly lower than that found for growth in the suspension crystallizer. It was then concluded that growth of sucrose crystals in the photomicroscopic cell had a markedly increased resistance due to the decreased mass transfer rate. However, crystals grown in both environments exhibited growth data dispersion.

Seeds growing in the photomicroscopic cell were found to exhibit the same growth behavior as contact nuclei growing in the same environment (Liang et al., 1987). That is, plots of the rate of change in time of the crystal sizes resulted in straight lines with varying slopes, as shown in Figure 1. This indicates that growth rate dispersion exists for these seeds and that the CCG model is followed. In addition, a plot of the growth rate vs. each initial seed size resulted in such great scatter that no correlation could be ascertained. This is similar to the contact nuclei results. The growth rate distribution found in this way was found to fit both the normal and gamma distributions equally well.

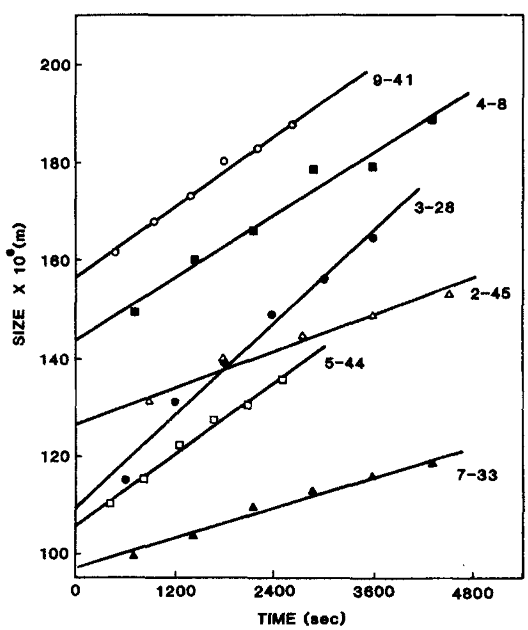

Figure 1. Characteristic size (volume-based) vs time for individual seed crystal growing in photomicroscopic cell.

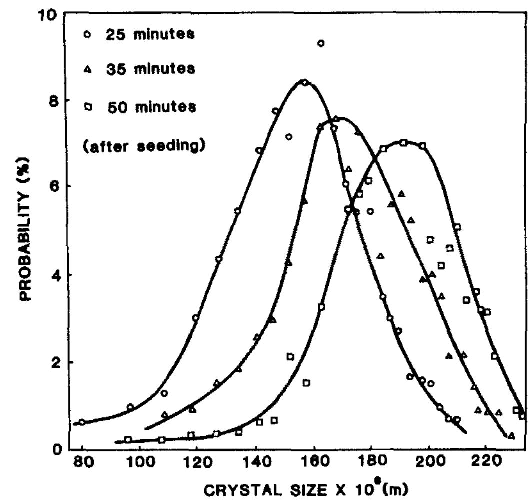

Figure 2. Change in sucrose crystal size distribution with time in suspension crystallizer.

Growth rate dispersion was also exhibited in the batch suspension crystal growth experiments, as shown in Figure 2. The increasing variance of the CSD with time indicates that the seeds were growing at varying rates. These results are similar to those found by White and Wright (1971) and Berglund (1980).

The variance of the growth rate distribution, σ_G^2, was correlated to the mean growth rate of the distribution using a power law model of the form

$$\sigma_G^2 = a\bar{G}^b \quad (1)$$

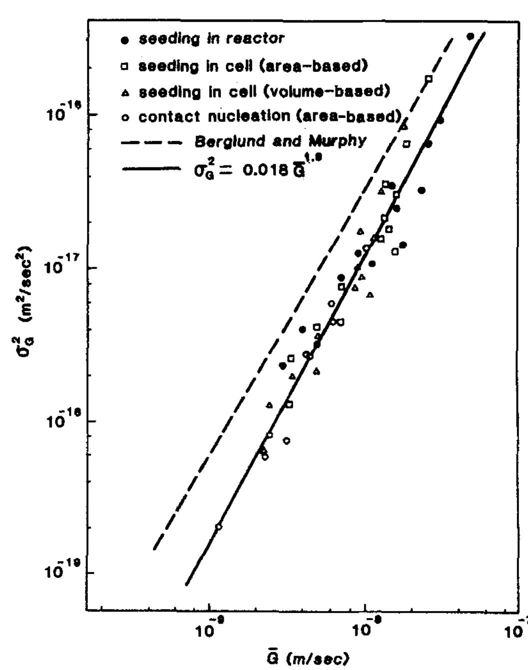

Figure 3. Relationship between variance of growth rate distribution and mean growth rate for various growth conditions.

The parameters a and b were determined by linear regression of the logarithmically transformed data. The results for the batch suspension crystallizer were

$$\sigma_G^2 = 8.5 \times 10^{-5}\ \overline{G}^{1.6} \tag{2}$$

with a correlation coefficient of 0.96. For the seeded growth (area-based) in the photomicroscopic cell, the results were

$$\sigma_G^2 = 0.13\ \overline{G}^{2.0} \tag{3}$$

with a correlation coefficient of 0.94. The results compare well with the previous results on growth rate dispersion of contact nuclei reported by Liang et al. (1987) and with the results of Berglund and Murphy (1986) on batch suspension growth. These relations are compared graphically in Figure 3. A statistical t-test on the slopes and intercepts of these various models at the 95% confidence level indicates that these models are identical. This suggests that experiments performed under different conditions (stirred suspension vs. stagnant photomicroscopic cell) and at different crystal sizes (seed crystals vs. contact nuclei) all result in a common form of growth rate dispersion. In other words, the degree of growth rate dispersion is constant for sucrose crystal growth no matter what the origin of the crystals or the growth mechanism. A common model derived from the data at all conditions (including the data on contact nuclei of Liang et al., 1987) yields the following averaged relationship.

$$\sigma_G^2 = 0.018\ \overline{G}^{1.9} \tag{4}$$

Conclusions

1. Seeds growing in the photomicroscopic cell under stagnant conditions exhibit growth rate dispersion (GRD) in the same fashion as contact nuclei under the same conditions. The seeds exhibit constant individual growth rates, with each crystal having a different inherent rate. This is consistent with the constant crystal growth (CCG) model of GRD.

2. Seeds growing in a stirred suspension batch crystallizer also exhibit growth rate dispersion, as evidenced by the increasing width of the CSD with time.

3. Growth rate dispersion, as defined by the increase in the variance of the growth rate distribution with increasing mean growth rate, was found to be identical for growth under a variety of conditions. Seeded crystal growth in both stirred suspension and stagnant cell environments, as well as contact nuclei grown in the stagnant cell all result in a common expression for growth rate dispersion. It was found that the variance changed with approximately the 1.9 power of the mean growth rate under all conditions.

4. It is commonly believed that growth rate dispersion is a surface-induced effect (e.g., caused by a varying dislocation density between crystals) so that crystals growing under a mass-transfer limited mechanism should not exhibit growth rate dispersion or exhibit GRD to a lesser extent. The results presented here, however, contradict this hypothesis.

Notation

$\overline{G}$ = mean growth rate, m/s
σ_G^2 = variance of growth rate distribution, m^2/s^2

Literature Cited

Berglund, K. A., "Growth and Size Dispersion Kinetics for Sucrose Crystals in the Sucrose-Water System," M.S. Thesis, Colorado State Univ., Fort Collins (1980).

Berglund, K. A., and V. G. Murphy, "Modeling Growth Rate Dispersion in a Batch Sucrose Crystallizer," *Ind. Eng. Chem. Fundam.*, **25**(1), 174 (1986).

Hartel, R. W., "A Kinetic Study of the Nucleation and Growth of Sucrose Crystals in a Continuous Cooling Crystallizer," Ph.D. Diss., Colorado State Univ., Fort Collins (1980).

Liang, B. M., R. W. Hartel, and K. A. Berglund, "Contact Nucleation and Growth Kinetics in Sucrose Crystallization," accepted, Chem. Eng. Sci., (1987).

Ramanarayanan, K. A., K. A. Berglund, and M. A. Larson, "Growth Kinetics in the Presence of Growth Rate Dispersion from Batch Crystallizers," *Chem. Eng. Sci.*, **40**(8), 1604 (1985).

Shanks, B. H., and K. A. Berglund, "Contact Nucleation from Aqueous Sucrose Solution," *AIChE J.*, **31**, 152 (1985).

White, E. T., and P. G. Wright, "Magnitude of Size Dispersion Effects in Crystallization," *Chem Eng. Prog. Symp. Ser.*, **67**(110), 81 (1971).

Manuscript received Mar. 10, 1987 and revision received Aug. 3, 1987.