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Production of Sucrose Crystals of Uni-Modal Size Distribution by Seeded Batch Cooling Crystallization

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Abstract

From sucrose aqueous solution of high viscosity, sucrose was crystallized by seeded cooling in a batch crystallizer. At low seed loadings, the product crystal size distribution (CSD) was wide-spread because of enormous secondary and primary nucleation. However, at high seed loadings, it became uni-modal, where the crystallization was dominated by seed growth with practically no secondary nucleation. Enough seeding was thus effective in suppressing nucleation even during batch crystallization with high viscosity solution. The volume mean size of the product crystals obtained at high seed loadings agreed with that calculated by a simple mass balance assuming growth-dominated crystallization with no change in the number of crystals.

Keywords

Batch Cooling Crystallization, Seeding Effect, Sucrose

1. Introduction

Since ancient, batch crystallization is carried out in various systems. The manufacturing of sugar ranks with the manufacturing of salt, and the history is long [1] [2] [3]. However, the theoretical research report example on the manufacturing method of sugar is little, and the process is developed in the know-how accumulated by the experience over the long time in individual enterprise [4]. In the solution of the high viscosity like sugar solution, there seems to be possible to be crystallization behavior unlike the low viscous solution, and there is seldom a view on them. At the present, it is comparatively abounding that the crystallization is done in the solution of which the viscosity is consequentially

high, because the operation in the high concentration is desired for the improvement in the process efficiency in other industry fields of pharmaceutical industry, etc. Therefore, it seems to be very useful to examine crystallization behavior in the high viscosity solution for not only sugar industry but also various crystallization process designs using concentrated solutions in the industry field. We have examined crystallization behavior in the batch crystallization until now [5]-[15] and in detail. The secondary nucleation is suppressed, if the seed crystal over some quantities is added, and it is clarified that the crystal that the seed crystal grew and that the crystal size was even is obtained. The effectiveness of seeding has been shown. However, it has not been proven on the existence of the seeding effect in the solution of high viscosity. Furthermore, there are few reports aimed at the application and quantitative investigation of seeded batch crystallization to other substances.

The effectiveness of seeding should be confirmed the solution of the high viscosity. In this study, we performed seeded batch cooling crystallization experiments for sucrose-water system. A mixing impeller (MR-210 of SATAKE) was used, which provides a general circulation flow in the stirring tank and exhibits good mixing action without stagnation. The effect of adding seed crystals would be effectively exhibited by using this mixing impeller.

2. Experimental

The experimental set-up used in this study is shown in Figure 1. A 2.3 L jacketed crystallizer made of glass and fitted with a thermocouple and probe of Focused Beam Reflectance Measurement (LASENTEC-FBRM^{TM}) was used. For the mixing impeller MR-210 of SATAKE that good mixing characteristic was shown even in high viscosity solution like this system was used. Typically, the solution of sucrose (76 wt%; saturation concentration at 70˚C) was cooled to constant temperature from a temperature above the saturation point by circulating a cooling water of constant temperature through the jacket. The temperature fell

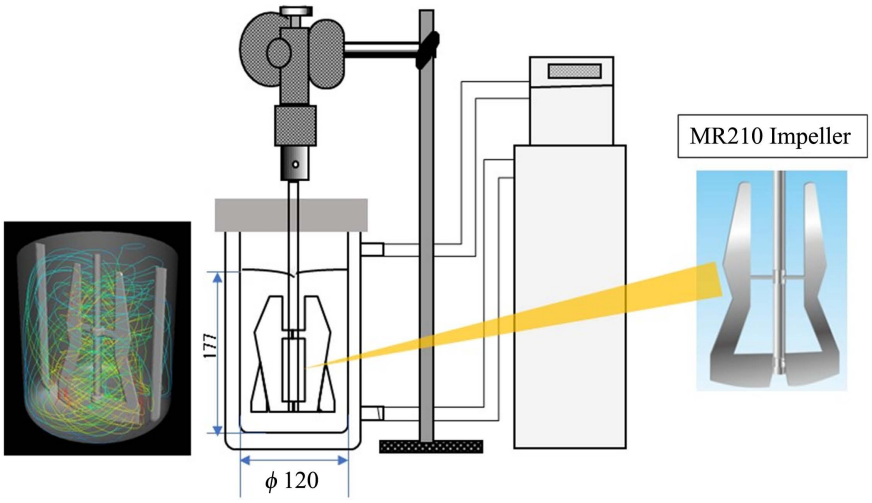

Figure 1. Experimental set-up.

down in an exponential manner. A known quantity of seed crystals was introduced just at the time when the solution temperature passed the saturation point. Just prior to the introduction, the seed crystals were washed with de-ionized water. At the end of a run, the product crystal was washed using ethanol, after the crystal was separated using a centrifuge. Crystals were dried over night in the air at room temperature. Crystal size distributions were determined by sieving and observed by an optical microscope.

3. Results and Discussion

3.1. Size Distribution of the Product Crystal

Figure 2 is crystal photographs got under the seed of 328 μm. At case of seed loading ratio C_s = 0.007, though the large crystals regarded as a growth of the seed crystal also existed, they were mostly small crystals. It is indicated that the nucleus has grown in crystallization. At seed loading ratio of C_s = 0.05, the small crystals decreased, and the large crystals in which seed crystals grew would occupy most. Further, at the larger seed loading ratio (C_s = 0.15), small crystals were almost perfectly nonexistent, and crystals of the uni-modal were obtained. Typical crystal size distributions are shown in mass basis in Figure 3. These distributions were obtained for the seeds of mean size of 328 μm. At low seed loading ratio of C_s = 0.007, the size of the product crystal is distributed over the wide range, in addition, there are many fine crystals. At high seed loading ratio of C_s = 0.05, small crystals are decreasing and large crystals are increasing. Furthermore, at high seed loading ratio of C_s = 0.15, the crystal size distribution becomes uni-modal without fines. These experiments were also performed at a seed crystal size of 90, 180, 463 μm. In each case, a uni-modal crystal size distribution was obtained by increasing the seed loading ratio. Figure 4 shows the transient crystal count number present in the crystallizer. At case of seed loading ratio C_s = 0.007,

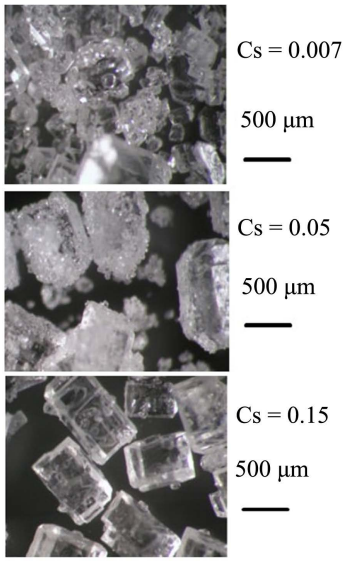

Figure 2. Photographs of product crystals obtained (Seed size = 328 μm).

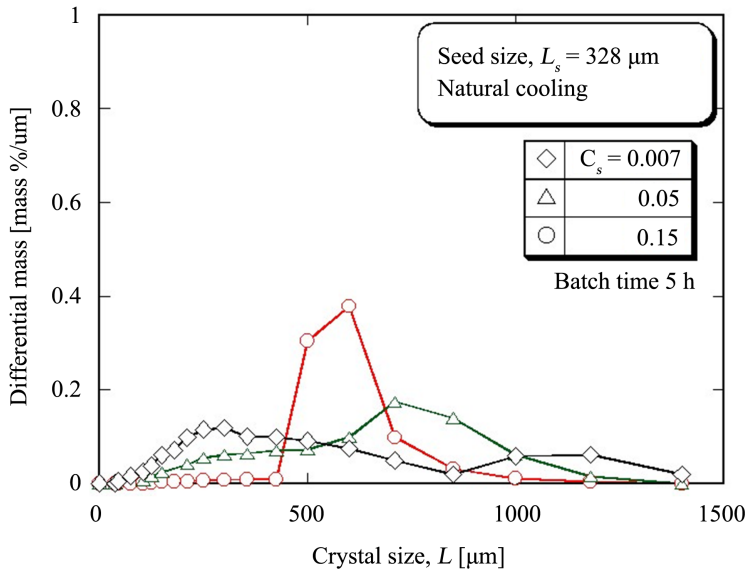

Figure 3. Effect of seed loading ratio on product crystal size distribution.

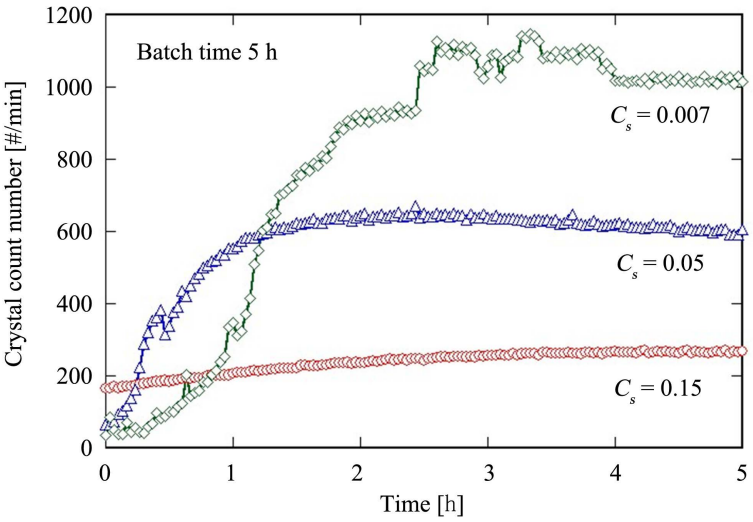

Figure 4. Transient crystal count number present in the crystallizer.

the number of crystals has increased sharply from around 1 hour later. And after 2.5 hours, it has been constant. At case of seed loading ratio C_s = 0.05, the number of crystals is gradually increasing from the beginning. And after 1 hour, it has been constant. The number of crystals is smaller for seed loading ratio C_s = 0.007. At case of seed loading ratio C_s = 0.15, the number of crystals has not changed much.

3.2. Seed Chart-Volume Mean Size of the Product vs. Seed-Loading Ratio

Figure 5 shows seed chart showing normalized volume mean size of product crystals of sucrose as a function of seed loading ratio. At high seed loadings, the volume mean size of product agreed with the theoretical volume mean size.

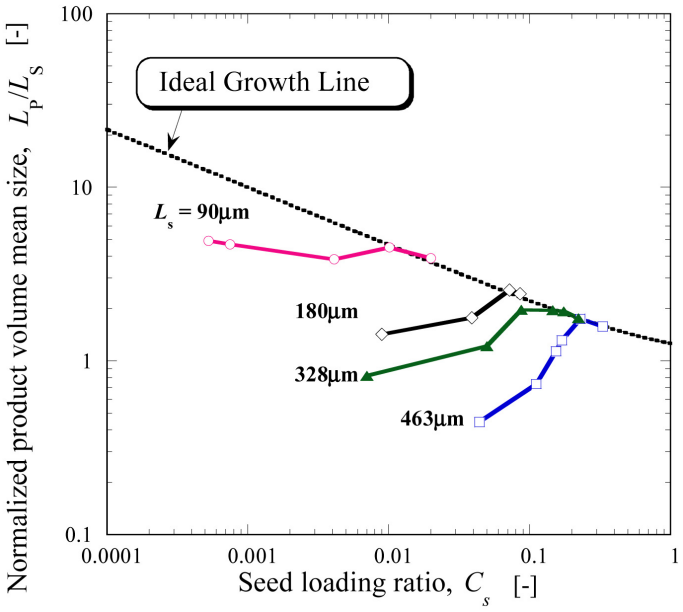

Figure 5. Seed chart showing normalized volume mean size of product crystals of sucrose as a function of seed loading ratio.

Therefore, the addition of sufficient seeds is concluded to be effective in producing the product with the size calculated by Equation (1) assuming no change in crystal number and shape [5] [9] [13].

$$\frac{L_p}{L_s} = \left(\frac{1+C_s}{C_s}\right)^{\frac{1}{3}} \tag{1}$$

where L_p and L_s are the volume mean sizes of product and seed crystals, respectively [5]-[13]. Even for the high-viscosity solution system similarly as observed for low-viscosity solution system. By increasing the seed loading ratio, the normalized product volume mean size is approaching ideal growth line (assuming no change in crystal number and shape). Results under $KAl(SO_4)_2$-water system were compared. By increasing the seed loading rate, the normalized product volume mean size approaches the ideal growth line, similar to the sucrose-water system. Therefore, we can produce the product crystals of sucrose with a controlled size.

3.3. Effects of Stirring Speed and Crystallization Temperature

Figure 6 shows effect of operating condition on product crystal size distribution. At an agitation speed of 250 min^{-1}, the particle size distribution shifted to the low particle size side at the low crystallization temperature 25℃. When the stirring speed was increased at the same crystallization temperature, the crystal size distribution did not change significantly. A study on the effect of agitation rate on crystal growth of saccharose was made by [1] van Hook (1944). Therefore, as far as this experiment is seen, although this system is a highly viscous system in the viscosity range of 50 mPa·s to 150 mPa·s, this suggests that the solute was

sufficiently supplied to the crystal surface under this stirring condition. Under natural cooling with no seeds, transient crystal count number obtained at various temperatures and agitated condition is shown in **Figure 7**. The theoretical crystal yield is same at all experiments. Induction time was short at high crystallization temperature 55℃ under same agitated condition. On the other hand, the induction time became shorter as the stirring speed increased. From these results, it was indicated that crystallization temperature and agitation speed strongly affected the primary nucleation. In the other, the increase of the crystal number with the increase in the agitation speed is because the secondary nucleation was accelerated. **Figure 8** shows effect of operating condition on product crystal size distribution. These product crystal size distribution shifts broadly toward the large particle size side in the following order: Low temperature (25℃: 550 min^{-1})→High temperature (55℃: 550 min^{-1})→Low temperature (25℃: 250 min^{-1})→High temperature (55℃: 250 min^{-1}).

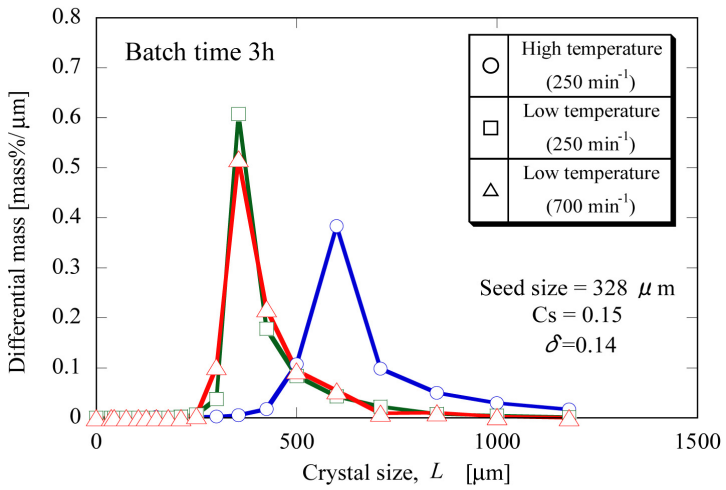

Figure 6. Effect of operating condition on product crystal size distribution.

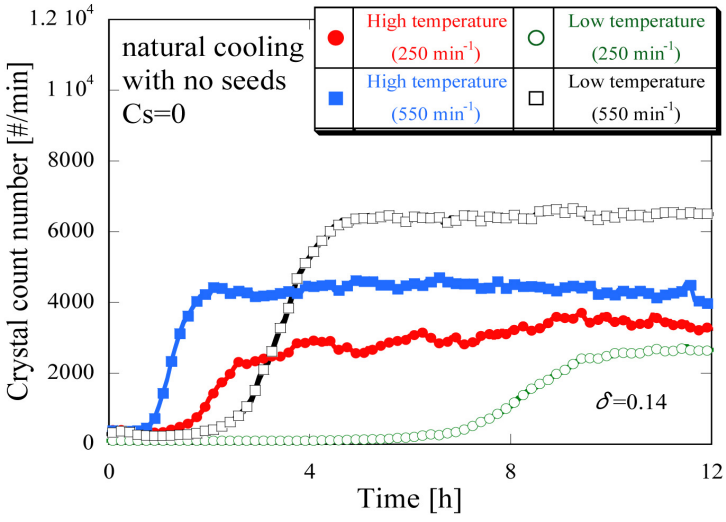

Figure 7. Transient crystal count number present in the crystallizer.

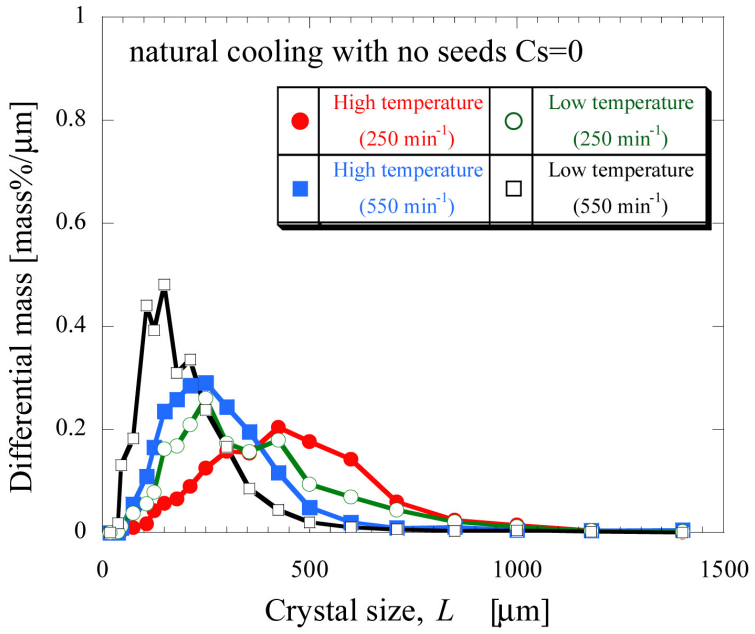

Figure 8. Effect of operating condition on product crystal size distribution.

4. Conclusion

Batch cooling crystallization of sucrose from high viscosity aqueous solution was conducted. A mixing impeller (MR-210 of SATAKE) was used, which provides a general circulation flow in the stirring tank and exhibits good mixing action without stagnation. The following conclusions were drawn. Sufficient seeding is effective in suppressing nucleation even in cooling crystallization in the high viscosity solution system examined, the same as in cooling crystallization in low viscosity solution systems.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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Nomenclature

C_s = seed loading ratio ($=W_s/W_{th}$) [-];
C_s^* = critical seed loading ratio [-];
L = crystal size obtained by sieving [μm];
L_s = mean size of seed crystals [μm];
L_p = volume mean size of product crystals [μm];
T = temperature [˚C];
W_s = mass of the seeds added [kg];
W_{th} = theoretical crystal yield calculated using solubilities [kg].